

Predicting NO, N₂O and CO₂ emission from
agricultural soil through related environmental
parameters

Ph.D. Dissertation

ABDUOSALAM A. A. ALGAIDI

**Gödöllő, Hungary
2009**

Name of Doctoral School: Environmental Science
Discipline: Environmental Chemistry
Acting Director: **Prof. Dr. György Füleky**

Name of Discipline Section: Soil Science, Agrochemistry and Environmental Chemistry

Leader: **Prof. Dr. György Füleky**
Professor,
Candidate of Agricultural Science
Director, Institute of Environmental Science

Supervisors: **Prof. Dr. György Heltai**
Professor,
Doctor of the Hungarian Academy of Sciences
Head, Department of Chemistry and Biochemistry,
Institute of Environmental Science

Prof. Dr. habil Dr. Hosam Bayoumi Hamuda
Professor,
Dr. habil of Environmental Science
Candidate of Biological Science
Institute of Environmental Science

Approval of School Leader

Approval of Supervisors

Contents

	Abbreviations	i	
1.	Introduction	1	
2.	Literature survey	1	
2.1.	Nitrogen use in agriculture	1	
2.2.	Environmental pollution by nitrogen from agricultural land use	1	
2.3.	Nitrogen cycle	2	
2.4.	Processes of N transformations	3	
2.4.1.	Mineralization	5	
2.4.2.	Nitrification	5	
2.4.3.	Denitrification	7	
2.4.4.	Chemodenitrification	9	
2.5.	Formation of nitrous oxide	10	
2.5.1.	Processes influencing nitrous oxides emission	11	
2.5.2.	Important factors controlling N ₂ O emissions	12	
2.6.	Processes involved in NO exchange	16	
2.6.1.	Factors influencing the NO exchange	17	
2.6.2.	NO emission rates from different ecosystems and land use types	21	
2.7.	Emission of CO ₂ gas	23	
2.7.1.	Meeting atmospheric CO ₂ concentration stabilization targets	26	
2.7.2.	Activities on the utilization of carbon dioxide	27	
2.8.	Impacts of heavy metals on emissions of trace gases	28	
2.8.1.	Cadmium influenced emission rates of trace gases	31	
2.8.2.	Effect of lead on emission rates of trace gases	31	
3.	Materials and methods	33	
3.1.	Materials	33	
3.1.1.	Field site and soil collection	33	
3.1.2.	Soil preparation and treatments	33	
3.1.3.	Chemicals used	35	
3.1.4.	Laboratory thermostat	35	
3.1.5.	Microcosm model	36	
3.1.6.	Instruments	37	
3.1.7.	Cultural medium	37	
3.2.	Methods	38	
3.2.1.	Determination of total available elements fraction	38	
3.2.2.	Determination of CO ₂ -production	38	
3.2.3.	Determination of total number of aerobic bacteria	38	
3.2.4.	Experimental conditions	38	
3.2.5.	The applied experiments	39	
3.2.6.	Soil incubations	39	
3.2.7.	Sampling and measurement of the trace gases		40
3.3.	Statistical analysis	41	
4.	Results	42	
4.1.	Bioavailability of heavy metals	42	
4.2.	Determination of CO ₂ -release	43	
4.3.	Population density of aerobe heterotrophic bacteria	43	
4.4.	Emissions of NO under the stresses of heavy metals	44	
4.4.1.	Experiment 1: at low temperature and low soil moisture content	44	
4.4.2.	Experiment 2: at low temperature and high soil moisture content	45	
4.4.3.	Experiment 3: at high temperature and high soil moisture content	46	
4.5.	Emissions of N ₂ O under the stresses of heavy metals	47	
4.5.1.	Experiment 4: at low temperature and high soil moisture content	47	
4.5.2.	Experiment 5: at high temperature and high soil moisture content	48	
4.6.	Emissions of CO ₂ under the stresses of heavy metals	49	
4.6.1.	Experiment 6: at low temperature and low soil moisture content	49	

4.6.2.	Experiment 7: at low temperature and high soil moisture content	50
4.6.3.	Experiment 8: at high temperature and high soil moisture content	51
5.	Discussion	52
5.1.	Effect of heavy metals on the soil respiration and microbial content	53
5.2.	Factors influencing trace gases emissions	55
5.2.1.	NO emissions	56
5.2.2.	N ₂ O emissions	58
5.2.3.	CO ₂ emissions	62
5.3.	Heavy metal influencing trace gases emissions	62
6.	Summary	66
7.	Összefoglalás	70
8.	New scientific results	72
9.	Proposals	73
10.	The Scientific Publications related to the Dissertation Work	75
11.	Further Task	78
12.	Acknowledgements	79
13.	References	80
14	Appendix	108

ABBREVIATIONS

A	Acre
AAFC	Agriculture and Agri-Food Canada
AAOB	autotrophic ammonia oxidizing bacteria
APOLLO	Application of Precision Agriculture for Field Management Optimization
APSIM	Agricultural Production Systems Simulator
ASW	Available Soil Water
CaCl ₂	Calcium chloride
C	Carbon
Cd	Cadmium
CERES	Crop Environment Resource Synthesis
CH ₄	Methane
CN SCS	Curve Number
Co	Cobalt
CO ₂	Carbon Dioxide
CP	Compensation Payment
Cr	Chromium
CUM	Current Uniform Management
Cu	Copper
CV	Coefficient of Variability
DCD	Dicyandiamide
DCP	Data Collection Points
dGPS	Differential Global Positioning System
DHP	Depth to the Hardpan or Restrictive Layer
DNDC	denitrification/decomposition
DSSAT	Decision Support System Agrotechnology Transfer
DR	Drainage Rate
EC	Electrical Conductivity
EC	European Community
EPIC	Environmental Policy Integrated Climate
ETDR	Effective Tile Drainage Rate
EU	European Union
FAO	Food and Agriculture Organization, United Nations
g	Gram
GDD	Growing Degree Days
Gg	Gigagram, 10 ⁹
GHGs	Greenhouse Gases
GWP	Global Warming Potential
h	Hour
HNO ₃	Nitric acid
HPF	Hardpan Factor or Restrictive Layer
IETC	International Environmental Technology Centre
IFA	International Fertilizer Industry Association, United Nations
IPCC	Intergovernmental Panel on Climate Change
K	Potassium
KAS	Kalkammonsalpeter
Kg	Kilogram
L	Liter
Lb	Pound
Lead	Pb
M	Million, 10 ⁶
M	Mole
MAB	methane assimilating bacteria
m	Meter
m ²	Square Meter

mg	Milligram
Mg	Magnesium
MNR	Marginal Net Return
mS	Milli Siemens
MOB	methane oxidizing bacteria
NH ₄ NO ₃	Ammonium nitrate
NH ₄ ⁺	Ammonium/Ammonium Ion
NH ₄	Ammonium
NH ₃	Ammonia
N/ N ₂	Nitrogen/Dinitrogen
NI	Nitrification Inhibitor
Ni	Nickel
N ₂ O	Nitrous Oxide
NO	Nitric Oxide
NO _x	Nitrogen Oxide
NO ₂	nitrogen Dioxide
NO ₃	Nitrate
NO ₂	Nitrite
NMF	Nitrogen Mineralization Factor
Nmin	Soil Available Mineral Nitrogen
NP	Ammonium phosphate and other NP fertilizers
Nt	Total Nitrogen
NUE	Nitrogen Use Efficiency
OC	Organic Carbon
OF	Organic fertilizers
OH	Hydroxyl Radical
O ₃	Ozone
OM	Organic Matter
OUM	Optimum Uniform Management
P	Phosphorus
PERFECT	Productivity Erosion Runoff Functions to Evaluate Conservation Techniques
PF	Precision Farming
ppb	Parts per Billion
R ²	Correlation
R ² or r ²	Coefficient of Determination
RDRF	Root Distribution Reduction Factor
R or r	Pearson's correlation coefficient
RMSE	Root Mean Square Error
SchALVO	Schutz- und Ausgleichs-Verordnung
SFF	Soil Fertility Factor
SHC	Saturated Hydraulic Conductivity of Deep Impermeable Layer
SIR	Substrate Induced Respiration
SOM	Soil Organic Matter
STICS	Simulateur Multidisciplinaire pour les Cultures Standard
T	Tonne
Tg	Tonne gram
Tg	Terragram, 10 ¹²
TI	Thallium
µg	microgram
UI	Urease Inhibitor
UN	United Nations
UNEP	United Nations Environment Programme
UNFCCC	United Nations Framework Convention on Climate Change
USDA-ARS	United States Department of Agriculture-Agricultural Research Service
US/USA	United States of America
VRM	Variable Uniform Management

WFPS	Water-Filled pore-Space
WHO	World Health Organization
WMO	World Meteorological Organization
yr	Year
yr ⁻¹	per year
Zn	Zinc

1. INTRODUCTION

Agriculture is both a source and sink for greenhouse gases (GHGs) and intensification of land use has increased the exchange of carbon (C) and nitrogen (N) between the land and the atmosphere. Concentrations of atmospheric GHGs, such as carbon dioxide (CO₂), methane (CH₄), and nitrous oxide (N₂O), and etc. which can alter the earth's climate have risen dramatically during the past century. This has resulted in an urgent need for process-based understanding of the main factors influencing the exchange of these gases between the land and atmosphere at a range of scales, as a route to developing effective mitigation technologies. Most of the nitrogen oxides (NO_x) are generated from mineral N originating from animal dung and urine, biologically fixed N₂, and mineralization of soil organic N.

The exchange of N containing gases between the atmosphere and terrestrial surfaces has been an important issue in agricultural and soil research for a long time. Prominent examples are the N₂-fixation by plants and microorganisms, denitrification loss of soil N in form of N₂, N₂O, and the emission of gaseous ammonia (NH₃) from fertilized soils. Unlike these processes, the exchange of nitric oxide (NO) between biosphere and atmosphere contributes only a minor part to the N budget of most terrestrial ecosystems. However, emissions from the soil-plant system are of enormous concern for the NO concentration in the troposphere.

A wide range of inorganic and organic compounds cause contamination, these include heavy metals, combustible and putrescible substances, hazardous wastes, explosives and petroleum products. Major component of inorganic contaminates are heavy metals they present a different problem than organic contaminants. Thus, metals render the land unsuitable for plant growth and destroy the soil biodiversity. There are three primary reasons for lack of knowledge about N₂ production: (1) it is difficult to measure due to the high atmospheric background concentrations; (2) N₂ production rates are very heterogeneous in space and time; and (3) there is a lack of synergy between the scientific communities that determine N₂ production rates.

In order to meet the necessity of reducing environmental impacts by excess N, political and technological measures have been taking at regional and country levels. Implementation of ***environmentally friendly technology and management***, such as use of controlled release fertilizers and pellets of animal wastes, is investigated and extended. Increasing attention is being paid to ***environmentally friendly*** N fertilization techniques/systems due to demands to maintain a cleaner environment and focus on sustainable agriculture. The effectiveness of such techniques strongly depends on their ability to synchronize nutrient demand by plants with its supply and the possibility to apply favored or optimal nutrient compositions.

During the last few decades, the introduction of reactive N into the biosphere by food and energy production has exceeded rates of N₂-fixation in native terrestrial ecosystems. Among the largest uncertainties about the human-dominated N cycle on all scales is the amount of reactive N that is converted back to N₂ during the last step of denitrification. Without this knowledge, it is impossible to determine the rate of accumulation of reactive N in most environmental reservoirs, and thus impossible to assess its long-term consequences. N interacts with C and other nutrient cycles and has numerous cascading effects on water and air quality and climate.

The bioavailability of Pb, Cd and Co and associated toxicity to soil biota vary with time, soil type, speciation, ageing, Pb, Cd and Co sources, organisms, and the other environmental factors. There appear to be no comparable reports in which the effects of heavy metals, singly or in combination, on soil microorganisms *in vivo* have been compared. Similarly, there is little information on the suppression of growth or tolerance developed by individual microorganism *in vivo* with respect to different combinations of metals. Soil microorganisms have various physical environmental requirements to grow and function. Soil porosity, aeration, water availability, substrate availability, temperature, and soil pH, influence the activity of soil microorganisms (TROEH & THOMPSON, 1993, SINGER & MUNNS, 1996). Soil porosity or the volume of soil that is not "earthen material" can be shared between soil moisture and air. Soil water content and air content can influence the rates of diffusion of various gasses and solute and substrate transport. Organic carbon (OC) and N substrate availability influences microbial activity. OC content significantly influences microbial growth by providing an energy source to

the microbes. Certain levels of organic N are required to maintain basic levels of biological activity. Soil microbial activity generally increases as soil temperature increases.

Soil temperature and atmospheric temperature can influence the rates of gaseous transfer and solute transport of N gases. Freeze thaw cycles affect annual N₂O emissions. NYBORG et al. (1997) established that in a normally well drained soil the spring thaw impeded drainage, and correspondingly the N₂O flux was higher during the spring thaw, compared to the rest of the year.

The pH of the soil environment can affect the type of organisms that are biologically active and the availability of nutrients in the soil. Management practices that influence the aforementioned variables will influence N₂O emissions from the soil microbial processes of nitrification and denitrification. It is possible that, upon soil drying, nitrification ceases and some microbes may die (KIEFT et al., 1987). Upon rewetting, surviving microbes may utilize dead microbial biomass or released organic solutes as substrate for their own growth and activity. In support of this idea, some authors have shown that NO_x emissions are correlated with an increase in soil concentrations of inorganic N after the first wetting of dry soil (ANDERSON & LEVINE, 1987, JOHANSSON & SANHUEZA, 1988). The microbial processes are essentially the same whether they take place in soils, wastewater treatment plants, sediments or water bodies. More than 35 years ago, it was proposed that some nitrifiers could not only nitrify, but denitrify as well (RITCHIE & NICHOLAS, 1972).

On a global scale, the primary source of tropospheric NO is anthropogenic emissions from combustion-related processes in industry and transport. According to present knowledge, however, NO is produced in soils nearly ubiquitously; and therefore soil emissions constitute a continuous (but not constant) background flux of NO to the atmosphere. Despite considerable uncertainties, there is substantial evidence that soil emissions make a significant contribution to the tropospheric NO burden even in industrialized regions of the globe (VALENTE & THORNTON, 1993; HALL et al., 1996; DAVIDSON & KINGERLEE, 1997). If current and future efforts to reduce NO_x emissions from vehicles and fossil fuel burning are successful, the importance of biogenic emissions will grow considerably in the near future. Many reports have shown that N₂O and NO are quickly emitted from the soil after N fertilizers is applied (McTAGGART et al., 1994; AKIYAMA et al., 2000; HOU et al., 2000; CHENG et al., 2002; 2004). The importance of other soil processes in the production of N₂O, including any role of dissimilatory nitrate (NO₃⁻) reduction to ammonium (NH₄⁺), heterotrophic nitrification by fungi and anaerobic oxidation of NH₄⁺, remains poorly known (WOLF & BRUMME, 2002; DALSGAARD et al., 2003). CHENG et al. (2004) suggested that pH is the most important factor in determining the kinetics of soil nitrification from NH₄⁺.

LUDWIG et al. (2001) mentioned that the net exchange between ecosystems and the atmosphere, however, is globally dominated by biogenic emissions of NO from soils. It is shown that interactions of environmental factors (e.g., N availability, soil water content, soil temperature, ambient NO concentration, etc.) are a major reasons for the broad range that exists in published data on NO fluxes. This variability makes it difficult to predict the magnitude of NO fluxes on relevant spatial and temporal scales.

Being a highly reactive trace gas, NO plays a crucial role in tropospheric chemistry (CRUTZEN, 1979; LOGAN et al., 1981; WARNECK, 1988). For the fast chemical interconversion with nitrogen dioxide (NO₂), which typically occurs within seconds to minutes, both species are commonly referred to as the single quantity NO_x (NO + NO₂). NO_x are precursors in the photochemical formation of gaseous nitric acid (HNO₃) and thus contribute to the acidity of clouds and precipitation (LIU et al., 1987; WARNECK, 1988). Probably even more severe is the impact of NO_x on the oxidative capacity of the troposphere. NO_x mediates the production and destruction of ozone (O₃) and influences the formation of the hydroxyl radical (OH), which in turn regulates the lifetime of numerous compounds in the atmosphere (LIU et al., 1987; CHAMEIDES et al., 1992). Sources and sinks of NO_x as well as their temporal and spatial distribution are therefore an essential prerequisite to understand and model atmospheric chemistry.

The N loss from agriculture through emissions is insignificant in terms of agronomy or economy, the emissions of N₂O has an enormous environmental impact. N₂O is a GHG, as well as CO₂, CH₄, halogenated fluorocarbon, and perfluorocarbon and sulfur hexafluoride. Investigations of the Intergovernmental Panel Climate Change (IPCC) have shown that the atmospheric concentration of GHGs, like CO₂, CH₄ and N₂O have increased by 31%, 151% and 17%, respectively (BOUWMANN et al., 2000) within less than 150 years (IPCC, 2001). The atmospheric concentration of N₂O has increased from 270 ppb at the preindustrial time to 314 ppb (IPCC, 2001), thus it causes between 5–6% of the global warming (LÆGREID, et al., 1999a; IPCC, 2001). Today, there is no doubt that the change in atmospheric composition is mainly caused by human activities (HOUGHTON, 1997). The increase of N₂O and other trace gases emissions is attributed to the increased N input in the biosphere (MOSIER et al., 1998; IFA & FAO, 2001).

It is widely known that the intense N fertilization in agriculture led to increased N leaching and to increased N emissions (HAAG & KAUPENJOHANN, 2001; LÆGREID et al., 1999b). Thus, the United Nation Framework Convention on Climate Change (UNFCCC) has called the attention to the effect of global warming, which is the result of human activities (UNFCCC, 2004b). At the conference in Kyoto, Japan (1997), 185 parties acknowledged the existence of the global warming (UNFCCC, 2004b). The Kyoto protocol, which was adopted at this conference, set the stage to reduce the emissions of GHGs worldwide (UNFCCC, 2004a).

N₂O and NO are both environmentally significant trace gases produced in soils by the processes of nitrification and denitrification (BREMNER & BLACKMER, 1978; FIRESTONE et al., 1980; ROBERTSON & TIEDJE, 1987; HOOPER et al., 1990; TORTOSO & HUTCHINSON, 1990; ROBERTSON et al., 1997).

Fertilization provides N substrates utilized in nitrification and denitrification and therefore can lead to increased N₂O and NO production in soils (HUTCHINSON & DAVIDSON, 1993; THORNTON & VALENTE, 1996). It is expected that the worldwide use of N-fertilizers will increase by 2.7 times to over 2.36x10⁸ metric tons yr⁻¹ over the next 50 years and therefore N₂O and NO emissions from soils will likely increase with time. However, as with fertilizers, the use of pesticides is expected to increase globally during the next 50 years by 2.7 times to 10.1x10⁶ metric tons yr⁻¹ (TILMAN et al., 2001). NO is an important pollutant involved in tropospheric photochemistry such as O₃ production and destruction (THOMPSON, 1992). The main sources of NO in the troposphere are fossil fuel combustion, biomass burning, lightning, soil biogenic emissions, and tropospheric oxidation of NH₃ by OH, stratospheric injection, and photolytic processes in oceans (DELMAS et al., 1997; VELDKAMP & KELLER, 1997). Modeling efforts have shown that soil NO emissions may have impacts on O₃ levels at the regional scale (STOHL et al., 1996) and in rural areas. Their contribution to the global NO_x budget is about 40%, ranging from 1.6 to 21 Tg N yr⁻¹ (YIENGER & LEVY, 1995; DAVIDSON & KINGERLEE, 1997; GALLOWAY et al. 2004; STEHFEST & BOUWMAN, 2006). More specifically, under cultivated conditions, agricultural soils are subject to heavy disturbances including tillage, fertilization, or irrigation; the use of synthetic N fertilizers is estimated to result in a 50% increase in NO emissions from terrestrial ecosystems (YIENGER & LEVY, 1995). Current inventories of NO emissions from agricultural soils have been primarily based on mean emission factors that express NO flux in terms of a fixed proportion of applied N fertilizer.

Reduced emissions could be accomplished through optimal application, timing and placement of fertilizer and through improved handling and storage of manure (AGRICULTURE & AGRIFOOD CANADA, 2000). The production of GHGs is associated with various environmental concerns such as a general warming of the earth, the melting of the polar ice cap, changes in ocean currents and extreme weather events (IPCC, 2001). N₂O emissions have high Global Warming Potential (GWP) and contribute to O₃ depletion. AGRICULTURE & AGRIFOOD CANADA (1998) report that N₂O emissions have 170 to 280 times more GWP than does CO₂ depending upon the time horizon, and N₂O released into the atmosphere breaks down O₃. N₂O can come from anthropogenic and non-anthropogenic sources. N₂O emissions from natural sources are about twice those from anthropogenic sources (KULSHRESHTHLA et al., 1999). Anthropogenic N₂O

sources include N-based fertilizers, soils, crop residues, industrial processes, biomass burning and animal production. Natural N₂O sources include oceans and tropical forest soils. AGRICULTURE & AGRI-FOOD CANADA (2002) reports primary agriculture is responsible for about 10% of Canada's GHGs which, does not include transportation input costs, or agri-food processing. Primary agriculture in Canada is responsible for 61% of the Nation's N₂O emissions, and less than 1% of the Nation's CO₂ emissions. The meeting in Kyoto Japan in 1997 is important to Canada. "Canada has committed to reduce its average annual emissions of GHGs for the 2008–2012 period to a level 6% below its GHG emissions in 1990. Identifying the sources of GHG emissions are important when developing policies to meet the GHG reduction commitments. On a national scale, N₂O contributions are a small portion of total GHG emissions, but agriculture is a significant source of Canadian N₂O emission.

Policies must be developed that economically and efficiently reduce GHG emissions. N₂O is a trace gas, which plays a central role in atmospheric chemistry. It is involved in O₃ decomposition in the stratosphere and exerts a significant GH effect with a GWP of 320 relative to CO₂ (KESTER et al., 1996). N₂O is mainly produced by nitrification, denitrification and nitrifier denitrification (WRAGE et al., 2001). Other biological processes contributing to N₂O production are dissimilatory reduction of NO₃⁻ to NH₄⁺ (BLEAKLY & TIEDJE, 1982), fungal denitrification (SCHOUN et al., 1992), NO₃⁻ assimilation (SATO et al., 1981) and production by green algae (Weathers, 1984). Each of these processes, and thus N₂O production, might be affected by heavy metals.

1.1. THE PURPOSE OF THE PRESENT STUDY

According to the above mentioned reasons, the main aim of the dissertation is to determine the effects of some environmental factors in a complex design on soil respiration, soil heterotrophic bacterial population and the emissions of trace gases such as NO, N₂O, and CO₂ which play an important role in global warming. *The objectives of my PhD research were:*

1. Determination the effects of heavy metals (Cd, Co and Pb) on soil respiration (CO₂-release) using the classical titration method and also, enumerate the bacterial population in cultivated and uncultivated soil samples activated by substrate induced respiration at different intervals. The study was carried out as following:

- To measure soil respiration (CO₂ evolution) as bioindicator parameter of soil contamination.
 - To study the effect of heavy metal on microbial survival and activity in heavy metal amended soil under laboratory incubations.
 - To detect the bioavailability of investigated metal in assayed soil.
2. Using the microcosms models to determine the impacts of various heavy metals (Cd and Pb) at different concentrations on the emission rates of trace gases (NO, N₂O and CO₂) from Ramann-type and clay loam brown forest soil types originated from Keszthely and Gödöllő, respectively, using chemiluminescent detector for measures the concentration of NO and gas chromatography to detect the amounts of N₂O and CO₂ emitted during 35 days.

The effects were detected under the interactions between different parameters of soil conditions such as:

- (1) Soil type and pH.
- (2) Soil incubation temperature (15, 37°C) and
- (3) Soil moisture (30, 60% WFPS)

The dissertation summarizes the modest knowledge in the field of emission of trace gases from different agricultural soils responses to cadmium and lead, as important environmental pollutants under different soil conditions.

2. LITERATURE SURVEY

2.1. NITROGEN USE IN AGRICULTURE

There are numerous sources available that discuss the N cycle and agriculture including e.g., TROEH & THOMPSON (1993), and SINGER & MUNNS (1996). Additions of N to the agriculture system come from four sources: electrical fixation, symbiotic N₂-fixation, non-symbiotic N₂-fixation, and industrial fixation. Electrical fixation occurs when lightning reacts with N₂ in the air. Free living bacteria in the soil carry out non-symbiotic fixation. Electrical and non-symbiotic fixation contribute relatively little N to agricultural systems. Symbiotic N₂-fixation and industrial fixation are significant N contributors to the soil system. Symbiotic N₂-fixation occurs when legume crops have been inoculated with the appropriate *Rhizobium* bacterial species. Industrial fixation is the application of commercial fertilizer, which requires significant amounts of energy to convert atmospheric N to NH₃. Losses of N from an agriculture system include harvesting of plant material, burning of straw, denitrification, volatile losses, and erosion and leaching. Harvesting of plant material involves the transport of N embodied in the plant tissue as protein to the market place. The burning of straw releases the N in straw to the atmosphere. Volatile loss occurs when NH₄⁺ based fertilizers are applied and the NH₃ embodied in the fertilizer evaporates. The type of fertilizer used, method and timing of application can influence Nitrogen Use Efficiency (NUE) and the profitability of the farm operation. NUE is a ratio of the amount of N taken up by the crop to the amount of N applied (GAUER et al. 1992). A high NUE value means the N applied is used for the growth of the crop. In general, spring fertilizer application results in higher NUE than fall application, and banding results in a higher NUE than broadcasting. Controlling, the rates of N transformations and the control over N supply offer solutions for increasing NUE and reducing environmental pollution by N fertilizer. This is a result of reducing excess mineral N in the rhizosphere, thus diminishing N gaseous and leaching losses. In addition, plant exposure to NH₄⁺ rich nutrition results in higher NUE and a reduction of rhizosphere pH, which in turn can increase availability of pH sensitive nutrients in arid and semi-arid soils. Control over NH₄⁺ and NO₃⁻ formation/consumption and release in soil can be achieved *via* several main application techniques or sophisticated fertilizers by: *a.* applying NH₄⁺ rich sources in nests, bands or super-granules thus inducing conditions that reduce the rate of nitrification; *b.* using bioamendments (nitrification inhibitors (NI), or urease inhibitors (UI)) incorporated in N fertilizers and by combining their application with the localized application; and, *c.* controlling the supply of N *via* fertigation or by applying controlled release N fertilizers. Denitrification is a biological process carried out under anaerobic conditions where nitrate is converted to N₂ gas. Leaching is the process of NO₃⁻ being washed below the plant rooting zone. The internal transformations of soil N include immobilization, mineralization and NH₄⁺ fixation. Immobilization describes the process during which, soil microbes feeding on N poor organic materials tie up the N, making it unavailable to plants. Mineralization is the biological process of converting organic N into inorganic N (ammonification, nitrification) for plant use. NH₄⁺ fixation involves the adsorption reactions between negatively charged clay particles and positively charged NH₄⁺ ions where the NH₄⁺ becomes fixed to the clay surface. The negative impact of overdose causes agricultural problems e.g. overturning the balance between pests and their parasites in soil ecosystem (NÁDASY & NÁDASY, 2006).

2.2. ENVIRONMENTAL POLLUTION BY NITROGEN FROM AGRICULTURAL LAND USE

It is well known that the current intense agricultural land use in the developed countries leads to environmental pollution. This is mainly caused by increased input of N fertilizer into farming systems (LÆGREID et al., 1999a). The input of nutrients and energy into the farming system is large compared to internal fluxes and cycling within the system (HAAG & KAUPENJOHANN, 2001). However, the nutrient balances in the developing countries are still negative (STOORVOGEL & SMALING, 1998), resulting in an imbalanced nutrient distribution on a global scale. N₂, which is essential for all life processes in plants and increases the plant growth and productivity, has been overused. In the developed countries where high crop yields are

achievable and commercial sources of N are readily available, fertilizer application rates per year reach levels of up to 200 kg N ha⁻¹ for cereals crops. Up to 400 kg N ha⁻¹ is used for fodder grass and for silage (HATCH et al., 2002). Studies of International Fertilization Industry Association (IFA) and Food and Agriculture Organization of the United Nations (IFA & FAO, 2001) showed that during the growing season plants often take up only 50% of the applied N, with the remaining N likely lost by emission or leaching. In 1985, the N surplus in Germany was calculated to be about 100 kg N ha⁻¹ (BACH, 1987), and in animal farms, the surplus was computed to be up to 253 kg N ha⁻¹. On a global scale, the surplus of N still continues to be high (BEHRENDT et al., 2002; KRAUSS, 1999). Any remaining N in the soil, which is not immobilized by microorganisms or utilized by the plants, is a potential source of N pollution (HATCH et al., 2002). Publications of the FAO (1996) showed that in parts of Europe, NO₃⁻ contamination of groundwater has grown to an extent that more than 10% of the population is exposed to levels that exceed the World Health Organization (WHO) guidelines for drinking water. To combat this problem, the European Union (EU) passed a law in 1991 designed to improve groundwater quality by providing incentives for producers to reduce N applications (EC-Council Directive, 1991).

2.3. NITROGEN CYCLE

Nitrogen is an incredibly versatile element, existing in both inorganic and organic forms, as well as many different oxidation states (MARSCHNER, 1986). The principal forms of N in soil are ammonium (NH₄⁺), nitrate (NO₃⁻) and organic substances. The movement of N between the atmosphere, biosphere, and geosphere in different forms is described by the N cycle as shown in Figure 1. N enters a farming system, which is defined as an integrated set of farm management practices used for crop and livestock production, by atmospheric deposition, as fertilizer, by irrigation water, livestock production, feed, and manures and by N₂-fixation. Current rates of atmospheric N decomposition achieve a level of 25–100 kg N ha⁻¹ yr⁻¹ in Europe and the USA, which is 5–20 times more than in the pre-industrial times (HATCH et al., 2002). KANWAR (1972) pointed out six basic reactions, which occur to N in soil. N could be utilized by crops in the form of ammonium (NH₄⁺) or NO₃⁻, incorporated into OM and thus be subject to immobilization, released from an unusable organic form into an inorganic form *via* mineralization, transformed into inert gas and lost through volatilization, lost out of the rooting zone of the plants by leaching or lost in surface runoff and soil erosion.

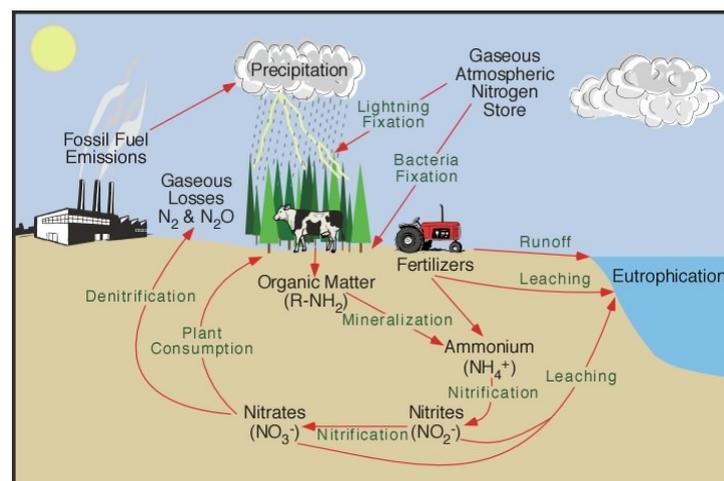


Figure 1. N cycle: Created by Michael Pidwirny, University of British Columbia Okanagan.

N₂O as well as NO_x are facultative by-products of the major microbiological N cycling processes in soils such as nitrification and denitrification (BUTTERBACH-BAHL et al., 1997; KNOWLES, 2000). Most plants are limited in their growth by the availability of N despite the fact that the atmosphere is 78% N₂ gas. The conversion of organic N to inorganic N within the soil is

a complex process that involves a number of organisms and chemical processes. Humans have also severely altered the nature of this nutrient cycle by generally making solid forms N more available. N is often the most limiting nutrient for plant growth. This problem occurs because most plants can only take up N in two solid forms: NH_4^+ and NO_3^- . Most plants obtain the N they need as inorganic NO_3^- from the **soil solution**. NH_4^+ is used less by plants for uptake because in large concentrations it is extremely toxic. In most ecosystems N is primarily stored in living and dead OM. This organic N is converted into inorganic forms when it re-enters the biogeochemical cycle *via* decomposition. Decomposers, found in the upper soil layer, chemically modify the N found in OM from NH_3 to NH_4^+ salts. This process is known as mineralization and it is carried out by a variety of bacteria, actinomycetes, and fungi.

Nitrogen in the form of NH_4^+ can be absorbed onto the surfaces of clay particles in the soil. The ion of NH_4^+ has a positive molecular charge is normally held by soil colloids. This process is sometimes called micelle fixation. NH_4^+ is released from the colloids by way of cation exchange. When released, most of the NH_4^+ is often chemically altered by a specific type of autotrophic bacteria (belong to the genus *Nitrosomonas*) into NO_2^- . Further modification by another type of bacteria (belonging to the genus *Nitrobacter*) converts the NO_2^- to NO_3^- . Both of these processes involve chemical oxidation and are known as nitrification. However, NO_3^- is very soluble and it is easily lost from the soil system by leaching. Denitrification is also common in anaerobic soils and is carried out by heterotrophic bacteria. The process of denitrification involves the metabolic reduction of NO_3^- into N_2 or N_2O gas. Both of these gases then diffuse into the atmosphere.

Almost the entire N found in any terrestrial ecosystem originally came from the atmosphere. Significant amounts enter the soil in rainfall or through the effects of lightning. The majority, however, is biochemical fixed within the soil by specialized microorganisms like bacteria, actinomycetes, and cyanobacteria. Members of the legumes and some other kinds of plants form mutualistic symbiotic relationships with N_2 -fixing bacteria. In exchange for some N, the bacteria receive from the plants carbohydrates and root nodules where they can exist in a moist environment. Scientists estimate that biological fixation globally adds approximately 140 million metric tons of N to ecosystems every year. The activities of humans have severely altered the N cycle. AMBUS et al. (2006) investigated the quantitative and qualitative relationships between N cycling and N_2O production in European forests in order to evaluate the importance of nitrification and denitrification for N_2O production. Increased nitrification in response to accelerated N inputs predicted for forest ecosystems in Europe may thus lead to increased greenhouse gas emissions from forest ecosystems.

2.4. PROCESSES OF N TRANSFORMATIONS

The emission of NO and N_2O from forest soils is mainly the result of simultaneously occurring production and consumption processes, most of which are directly linked to the microbial N turnover processes of nitrification and denitrification (CONRAD, 1996a,b, 2002). With regard to NO also the abiotic process of chemodenitrification, during which biologically produced NO_2^- is chemically decomposed to NO, has been shown to be an important production process in soils at pH values lower than 4.0 (VAN CLEEMPUT & BAERT, 1984). Like most other biological processes, microbial turnover processes vary largely on spatial and temporal scales, since they are significantly influenced by a number of environmental factors such as climate and meteorological conditions, soil and vegetation properties or human management of the land surface. Due to this also the emission of N trace gases from forest soils have been observed to vary over several orders of magnitudes between seasons, years or measuring sites (PAPEN & BUTTERBACH-BAHL, 1999; BRUMME et al., 1999; BUTTERBACH-BAHL et al., 2002). Furthermore gross and net rates of microbiological N turnover processes (N mineralization, nitrification) either directly or indirectly involved in N trace gas production were determined, and trace gas concentrations in different soil depths were measured. Microbial C and N turnover processes, including mineralization, nitrification, denitrification, and microbial immobilization are the main reason for N_2O production and consumption in soils (CONRAD, 2002). These processes is of

fundamental importance to understand the microbial mediated biosphere, atmosphere exchange of trace gases, and to build, parameterize and further improve process-oriented models. Such models constitute crucial tools in the up scaling of plot measurements in view of the large spatial and temporal variability of environmental conditions in forest ecosystems across Europe, and as tools to predict future N trace gas emissions from forest soils (BUTTERBACH-BAHL et al., 2004a). The exchange of N₂O between soils and the atmosphere depends specifically on the simultaneous, opposing processes of nitrification and denitrification (WRAGE et al., 2001). Nevertheless, both processes can take place simultaneously in the soil (ABBASI & ADAMS, 1998), since aerobic and anaerobic micro-sites can exist within the same soil aggregate (KUENEN & ROBERTSON, 1994). Nitrification is an oxidative process that requires the availability of molecular O₂ and during which NH₄⁺ is oxidised to NO₂⁻ and NO₃⁻. In contrast, denitrification is a reductive process, which mainly occurs in O₂-depleted soil zones. Under anaerobic conditions, some microbes use NO₃⁻ and NO₂⁻ as alternative electron acceptors, thereby reducing NO₃⁻/NO₂⁻ sequentially to NO, N₂O and finally to N₂ (CONRAD, 2002). Although nitrification and denitrification are characterised by different environmental controls and have optima under different environmental conditions, it is well known that both processes may occur simultaneously in the soil, thus giving rise to duplicate sources for N₂O (DAVIDSON et al., 2000). Chemical reactions seem to be important only for the production of NO, but not of N₂O (BREMNER et al., 1980; 1981a;b; NELSON, 1982), and NO production by chemodenitrification may only be significant under acidic conditions (VAN CLEEMPUT & BAERT, 1984). In both the nitrification and denitrification processes, NO is an intermediate which is not always emitted, since it can be further metabolized in soil. Although both nitrification (DUNFIELD & KNOWLES, 1999; GÖDDE & CONRAD, 2000) and denitrification (REMDE & CONRAD, 1991a; SCHAFER & CONRAD, 1993) processes can consume NO, relative consumption by denitrification seems to be higher (SKIBA et al., 1993). NO in soil is produced predominantly by nitrification and denitrification. Nitrification is the oxidation of NH₄⁺ to NO₃⁻ denitrification is the anaerobic reduction of NO₃⁻ to gaseous forms of N (BREMNER & BLACKMER 1978; PAYNE, 1981). Denitrification was shown to produce up to twice as much NO as nitrification (REMDE et al., 1989); however, the net release of NO from soil is greatly influenced by the gas phase diffusivity in soil and the rate of NO consumption by denitrifiers.

In principle NO and N₂O are formed by the microbial processes of nitrification and denitrification (FIRESTONE & DAVIDSON, 1989; CONRAD, 1996a,b). DAVIDSON et al. (1993) suggested that NO emissions may have resulted from low levels of nitrification in combination with biotic self-decomposition processes. HALL & MATSON (1996) established that NO is produced as a by-product of nitrification and denitrification, two microbial processes that occur in many natural and agricultural ecosystems. NO is also produced, although probably to a lesser extent, by a biotic chemical decomposition of HNO₂. Several recent papers have synthesized current understanding of biological NO_x production and emissions. Biogenic production in soils especially when fertilised with high levels of N, is one of the main sources of N₂O and may be a significant source of NO. NO and N₂O are formed by the microbial processes of nitrification and denitrification in soils. Biogenic production in soils, especially those fertilized with high levels of N, is one of the most important sources of N₂O (GRANLI & BÖCKMANN, 1994; MOSIER et al., 1996a,b; BÖCKMANN & OLFS, 1998; MOSIER et al., 1998) and may also be a significant source of NO (CONRAD, 1995; DAVIDSON & KINGERLEE, 1997; VELDKAMP & KELLER, 1997, RUSSOW et al., 2000).

KUENEN & ROBERTSON (1994) mentioned that nitrification and denitrification have traditionally been regarded as essentially separate phenomena, carried out by different bacteria in segregated areas of soil, sediments, water or reactors. Moreover, some bacteria are able to convert NH₃ and other reduced N-compounds to N₂ gas and the gaseous NO_x in combined nitrification/denitrification processes. Such organisms are of interest for water treatment for two opposing reasons. *Firstly*, the idea of single-stage N removal has obvious attractions for system design. *Secondly*, N₂O is a serious pollutant, implicated in virtually all current environmental problems (e.g. acid rain, greenhouse effect, O₃ depletion). KUENEN & ROBERTSON (1994) stated

that the increasing awareness of the need to control the emission of gaseous and dissolved N compounds, the possibility of single stage N removal has obvious attractions, and understanding of the combined processes is needed in order to be able to encourage the activity of bacteria capable of carrying it out. Nitrification and denitrification processes are linked by a “common” NO_3^- pool. In contrast the NO_3^- , an important intermediate of the two processes, evidently exists within two separate pools. NO is mainly produced by nitrification as a by-product of the oxidation of NH_4^+ to NO_2^- or directly by NO_2^- decomposition. If NH_4^+ contents are high under aerobic conditions NO emission can markedly exceed that of N_2O . N_2O is mainly formed by denitrification of NO_3^- . Therefore increasing water saturation promotes N_2O emission. NO could not be confirmed as a free precursor of N_2O formation *via* denitrification (RUSSOW et al., 2000). POTH & FOCHT (1985) and WEBSTER & HOPKINS (1996) suggested that this pathway of nitrification, called nitrifier denitrification, might contribute to a major part of the loss of NH_4^+ from soils in the form of NO or N_2O . LI et al., (1992a,b) mentioned that a DNDC model of N_2O emissions from agricultural soil that operates on the scale of an agricultural field and uses climate, soil, and agricultural practice data as input. N_2O evolution from soils, like NO_x , involves interactions among soil physical properties, microbial activity, and the decomposition/ transformation of organic substrates and inorganic N. In acid tropical soils, however, NO emission has frequently been linked with denitrification. NO emissions were stimulated by NO_3^- rather than NH_4^+ based fertilizers (SANHUEZA et al., 1990) and ^{15}N studies have also shown the dominance of the denitrification pathway (CARDENAS et al., 1993). REMDE & CONARD (1991a) suggested that the soil pH appears to be an important factor determining the mechanism of NO formation: in an alkaline loamy clay soil (pH 7.8), nitrification was the main source of NO; where as in an acid sandy clay loam (pH 4.7) denitrification dominated the NO production. It is difficult to quantify the overall global importance of nitrification and denitrification as sources of atmospheric NO_x (SKIBA et al., 1997).

2.4.1. MINERALIZATION

Once N is fixed, it is subject to several chemical reactions which can convert it to different organic or inorganic forms. Mineralization occurs in soil as microorganisms convert organic N to inorganic forms. The first step of mineralization is called aminization, in which microorganisms (primarily heterotrophs) break down complex proteins to simpler amino acids, amides, and amines. Heterotrophic microorganisms require preformed organic compounds as sources of C and energy. Autotrophic microorganisms can derive energy from the oxidation of inorganic elements or compounds such as Fe, S, NH_4^+ , NO_2^- , or from radiant energy; they derive their C from CO_2 . For example, urea is an amide added directly to soil either in urine or as commercial fertilizer.

Aminization: $\text{Proteins} \rightarrow \text{R-NH}_2 + \text{CO}_2$

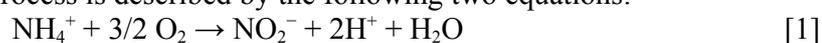
Ammonification is the second step of mineralization in which amino (NH_2) groups are converted to ammonium. Again, microorganisms (primarily autotrophic) accomplish this action.

Ammonification: $\text{R-NH}_2 + \text{H}_2\text{O} \rightarrow \text{NH}_3 + \text{R-OH}$ (BELOSO et al., 1993, COTE et al., 2000).

Mineralization of plant residues and thus the N_2O emission was found to be dependent on C:N ratio of the residues (EICHNER, 1990; AULAKH et al., 1991; NÉMETH et al., 1996). An earlier study conducted by PATTEN et al. (1980) demonstrated that the rate of denitrification was dependent on the quantity of OC readily utilized by denitrifying microorganisms, while the OC in various pools is not completely available to microorganisms.

2.4.2. NITRIFICATION

Nitrification is characterized as the process in which NH_4^+ is converted to NO_2^- and then NO_3^- . This process naturally occurs in the environment, where it is carried out by specialized bacteria. The process is described by the following two equations:



The process of creation, consumption and disposal of N_2O is described by FIRESTONE & DAVIDSON (1989) as the “hole-in-the-pipe” model (Figure 2.).

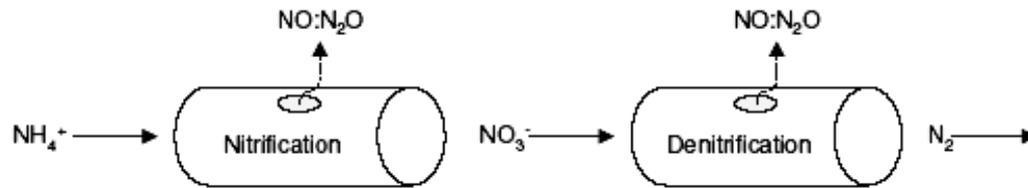


Figure 2. The “hole-in-the-pipe” model (modified from FIRESTONE & DAVIDSON, 1989).

In agricultural soils, the nitrification is mainly carried out by *Nitrosomonas*, *Nitrosospira* and *Nitrobacter* bacteria (ENQUÊTE-KOMMISSION SCHUTZ DER ERDATMOSPHÄRE DES DEUTSCHEN BUNDESTAGES, 1994; HAYNES, 1986). Soil water and O_2 content, as well as the macro pores, OM and pH in the soil mainly determine the development rate of N_2O . The optimum condition for the nitrification in soil is at a water content of 60%. When the water content is increased, nitrification is limited by O_2 , and vice versa. Between 1% and 4% of the N input is turned into NO during the nitrification process (ENQUÊTE-KOMMISSION SCHUTZ DER ERDATMOSPHÄRE DES DEUTSCHEN BUNDESTAGES, 1994), and about 0.5% is turned into N_2O (VELDKAMP & KELLER, 1997).

Nitrification is commonly defined as the biological oxidation of NH_4^+ to NO_3^- with NO_2^- as an intermediate (BREMNER, 1997). Although the capacity for nitrification is restricted to a few genera of strictly aerobic, mainly chemoautotrophic bacteria, this process is of major importance for the N cycling in most cultivated and many natural soils. The exact sequence of the nitrification pathway is still not clarified. Some evidence exists that NO is an intermediate in the oxidation step from NH_2OH to NO_2^- (HOOPER & TERRY, 1979). Other research groups (REMDE & CONRAD, 1990), however, suggested that NO formation during nitrification results from the reduction of NO_2^- (nitrifier denitrification), a mechanism also shown to be effective for the production of N_2O by nitrifying bacteria (POTH & FOCHT, 1985). The use of NO_2^- as an electron acceptor enables nitrifiers to sustain oxidation of NH_4^+ even at a low partial pressure of O_2 . Overall nitrification rates, however, will increase in well-aerated soils, provided that the soil is not very acidic ($pH > 4 - 5$). If these requirements are met, the nitrification rate is predominantly controlled by the availability of NH_4^+ (ROBERTSON, 1989).

Nitrification is therefore believed to be the main source of NO (ANDERSON & LEVINE, 1986). Regarding environmental considerations NO contributes to the formation of acid rain, while N_2O is involved in global warming and contributes to the destruction of parts of the O_3 layer; N_2O has great importance as a GHG because it has a mean atmospheric residence time of more than 100 yr (PRATHER et al., 2001). HALL & MATSON (1999) defined the nitrification as the oxidation process of NH_4^+ to NO_2^- and NO_3^- by a specialized group of bacteria that gain energy from the NH_4^+ oxidizing process. These bacteria gain C from CO_2 rather than from the consumption of organic compounds. Nitrifying bacteria may instead be limited by the availability of NH_4^+ in turn, is controlled by several factors, including mineralization; N uptake by microbiota (immobilization) or plants; retention of NH_4^+ by soil particles; factors governing diffusion, including temperature and water availability; and rates and types of fertilizer application. In addition, O_2 is critical for the NH_4^+ oxidation processes, so nitrification rates are often low in low O_2 environments. The concentration of NH_4^+ is generally low in agricultural soils, because the NH_4^+ produced by mineralisation of soil organic matter (SOM) is utilized by soil microorganisms and plants. Nitrification is severely limited under such soil conditions (NISHIO & FUJIMOTO, 1990).

WRAGE et al. (2001) concluded that nitrifier denitrification is the pathway of nitrification in which NH_3 is oxidised to nitrite (NO_2^-) followed by the reduction of NO_2^- to NO, N_2O and N_2 . The transformations are carried out by autotrophic nitrifiers. Thus, nitrifier denitrification differs from coupled nitrification–denitrification, where denitrifiers reduce NO_2^- or NO_3^- that was produced by nitrifiers. Nitrifier denitrification contributes to the development of the GH gas N_2O

and also causes losses of fertilizer N in agricultural soils. Low O₂ conditions coupled with low OC contents of soils favour this pathway as might low pH. As nitrifier denitrification can lead to substantial N₂O emissions, there is a need to quantify this pathway in different soils under different conditions. It has been suggested that this pathway of nitrification, called nitrifier denitrification, might contribute to a major part of the loss of NH₄⁺ from soils in the form of NO or N₂O (POTH & FOCHT, 1985; WEBSTER & HOPKINS, 1996). JULIASTUTI et al. (2003) found that Cu²⁺ has stronger inhibitory effects than Zn²⁺, and inhibits the nitrification process by 50% at 0.08 mg⁻¹, while the same concentration of Zn²⁺ establishes 12% inhibition only. At 50% WHC, nitrification as derived from the inhibition method is the process that most contributed to the production rate of N₂O. Nitrification is more dominant at higher O₂ concentrations (HWANG & HANAKI, 2000). Large amounts of O₂ (approximately 100 kPa) might suppress nitrification due to oxidative stress (WRAGE et al., 2004). The microbial activity as witnessed by the production of CO₂ was not affected by O₂, but it is still possible that autographs were affected. Production of N₂O by nitrification has often been reported (e.g. BOLLMANN & CONRAD, 1997). SKOPP et al. (1990) in theoretical calculations and LINN & DORAN (1984) in a field study showed that the rate of nitrification can be relatively high when the moisture content of the soil is at 50–60% WHC. BILLORE et al. (1996) reported more emission from fertilizer treated soil than from unfertilized soil at 50–60% water holding capacity (WHC) and suggested that nitrification plays a major role in N₂O production. The contribution of nitrification to the production of N₂O has been found to range between 61–98% (MUMMEY et al., 1994) and 60–80% (PARTON et al., 1988b).

2.4.3. DENITRIFICATION

Microbial denitrification requires an anaerobic environment, whereas aerobic conditions are necessary for nitrification (BREMNER & BLACKMER, 1979). NIEDER et al. (1989) stated that N losses by denitrification can be determined by three methods. The *first* is by estimating the non-recovery of ¹⁵N-labelled compounds. Using this method, denitrification losses are deduced from the balance of an N budget (¹⁵N-labeled fertilizer), having accounted for transformations in soil, plant uptake, and leaching losses. The evolution of gaseous N from native soil N is not taken into account by this procedure. Studies on arable land with annual crops in the temperate zone have shown that of the N fertilizer applied; about 20–50% (10–70 kg N ha⁻¹) is not recovered at the end of the growth period. The *second* method of determining denitrification N losses is by *in situ* field measurement of ¹⁵N₂ and ¹⁵N₂O productions. Under this procedure, ¹⁵N-enriched N is applied to a plot and the denitrification N losses are determined by covering the soil. The method allows a quantitative estimate of the relative contributions to the emitted gas by both the original enriched source and the native soil N. N-evolution rates measured on arable land under a temperate climate are approximately the same order of magnitude as the N losses estimated by the non-recovery of ¹⁵N method. The *third* measuring procedure is based on the acetylene inhibition phenomenon. This principle uses the inhibition of bacterial N₂O reduction to N₂ in the presence of acetylene (C₂H₂). The method determines the denitrification of all NO₃⁻-N irrespective of its source. Measurements on classical crop production systems show maximum N losses in the temperate climate of about 20–30 kg N ha⁻¹ during the growth period of annual crops.

Since 1850 denitrification is estimated to have increased from 270 to 310 Tg N yr⁻¹. Globally, hotspots for denitrification are estimated to occur in the same regions where anthropogenic N inputs are high. By 2050 denitrification rates are estimated to increase to 370 Tg N y⁻¹. However, the most effective solution to minimizing negative environmental effects of increased N mobilization is to decrease N use/emissions and N losses at the point of application/deposition (GALLOWAY et al., 2004). Denitrification is defined as the reduction of NO_x to molecular N₂ or NO_x with a lower oxidation state of N by bacterial activity. NO_x are used by bacteria as terminal electron acceptors in place of O₂ in anaerobic respiratory metabolism. Denitrification often occurs when the soil is wet or compacted or warm, because these are situations where O₂ is a limiting factor. The denitrification is described by the following equation:



The bacteria that carry out the denitrification process are mainly *Pseudomonas*, *Azospirillum* (ENQUÊTE-KOMMISSION SCHUTZ DER ERDATMOSPHÄRE DES DEUTSCHEN BUNDESTAGES, 1994) and *Alcaligenes* (HUTCHINSON & DAVIDSON, 1993), but also fungi and yeasts are involved. During denitrification, NO and NO_2 are formed (LÆGREID et al., 1999a,b). The rate of NO_2 can vary between 0 and 100 % in dependency of the availability of C and N, soil water and soil temperature (ARAH & SMITH, 1990). Decreasing O_2 content and increasing water content in the soil increases the process. The availability of OM and high temperature also speeds up the denitrification process (ENQUÊTE-KOMMISSION SCHUTZ DER ERDATMOSPHÄRE DES DEUTSCHEN BUNDESTAGES, 1994). Between 0.5% and 1.5% of the applied N to agricultural soil may be emitted as NO_2 (MCELROY & WOOFYSY, 1985).

Denitrification, defined as the dissimilatory reduction of NO_3 or NO_2 to N_2O and N_2 , has been considered a prokaryotic process for more than a century and has been extensively studied in several bacteria (ZUMFT, 1997). By the 1970s, it became clear that denitrification is a function of eukaryotes as well as bacteria. Yeasts (TSURUTA et al., 1998) and filamentous fungi (BOLLAG & TUNG, 1972) have been shown to be capable of denitrification. Fungi can use NO_3 as an alternate electron acceptor to O_2 for respiration and can perform aerobic respiration and denitrification simultaneously (ZHOU et al., 2001). The occurrence of fungal denitrification in soil could be of ecological significance if N_2O is the dominant gaseous end product, since N_2O is a radiatively active trace gas and N_2 is not. A few species of fungi can produce N_2 by a co-denitrification process where one N atom from NO_2 combines with one from a source other than NO_2 (TANIMOTO et al., 1992). The microbial biomass of temperate soils is often dominated by fungi (RUZICKA et al., 2000) and the proportion of fungi in the biomass can be affected by agricultural systems and land use. The potential for fungi to produce N_2O has been shown in two studies using woodland soils (CASTALDI & SMITH, 1998; LAVERMAN et al., 2000).

FIRESTONE & DAVIDSON (1989) defined denitrification as a group of processes during which NO_3^- or NO_2^- is reduced to the gaseous N species NO , NO_2 , or N_2 . Denitrifying bacteria survive under anaerobic conditions by using NO_x as their electron acceptors in place of O_2 . The general sequence of N species produced during denitrification is the following $\text{NO}_3^- \rightarrow \text{NO}_2^- \rightarrow \text{NO} \rightarrow \text{N}_2\text{O} \rightarrow \text{N}_2$. Where NO_3^- availability is high, OC compounds may limit denitrification. Although NO , N_2O and N_2 can all be produced in denitrification; numerous factors regulate the proportions of the gases that are actually produced, including soil pH, NO_3^- or NO_2^- concentration, O_2 content of the soil, C availability, and temperature. Denitrification has been considered a prokaryotic process for more than a century and has been extensively studied in several bacteria (ZUMFT, 1997). Denitrification activity has been reported in dried soils and in desert soils (PETERJOHN, 1991; SMITH & PARSONS, 1985), where it seems to depend on a complex interplay between soil moisture, C, N availability, pH, temperature and O_2 . Indeed, many soil denitrifying microorganisms have been found to be able to produce N_2O over a wide range of O_2 partial pressures (DAVIES et al., 1989; LLOYD et al., 1987; ROBERTSON & KUENEN, 1990). FRENEY (1997) stated that N may be lost by NH_3 volatilization, during nitrification (NO and N_2O), by biological denitrification (producing NO , N_2O and N_2), and by chemodenitrification as a result in emissions of NO , NO_2 , N_2O , N_2 and methyl nitrite. N emitted to the atmosphere as NH_3 may be returned to the biosphere and recycled thus adding to the N_2O and NO burden in the atmosphere. Thus NH_3 volatilization needs to be controlled as well as nitrification-denitrification to limit emission of NO_x .

CONRAD (1996a,b) established that one of mechanisms of NO consumption in soil is its utilization by denitrifying bacteria as an electron acceptor. Also, soil moisture may be an important negatively correlated regulator of NO consumption by other processes. Given the limited information on these processes, it is difficult to describe environmental conditions that regulate consumption. NO consumption by denitrifiers appears to be stimulated by OC compounds and by NO_3^- (BAUMGÄRTNER & CONRAD, 1992, SCHUSTER & CONRAD, 1992).

PATTEN et al. (1980) demonstrated that the rate of denitrification was dependent on the quantity of OC readily utilized by denitrifying microorganisms, while the OC in various pools is

not completely available to microorganisms. As a specific fraction of SOC, the dissolved OC (DOC) represents easily degradable and available to microorganisms (BOYER & GROFFMAN, 1996; YANO et al., 1998). Soil temperature depends on location, climate, weather, soil type, soil cover and soil bioactivity. Low rates of denitrification have been reported at -2°C (DORLAND & BEAUCHAMP, 1991) and -4°C (MALHI et al., 1990), but higher temperatures $> 5^{\circ}\text{C}$, are usually required for a significant denitrification rate (AULAKH et al. 1983; BENCKISER, et al., 1986). The effect of increasing soil temperature on denitrification rate has been investigated in many laboratory studies. Denitrification stops at temperatures of 75 to 85°C (KEENEY et al., 1979). However, such high temperatures are of little practical interest as soil temperatures will mostly be below 60°C , at least where water is present. The reported differences reflect to some extent bacterial adaptation to local conditions (MALHI et al., 1990).

Denitrification as derived from the inhibition method contributed 21% to the production rate of N_2O in soil incubated at 50% WHC. Denitrification is an anaerobic process and in the incubations at 60% WHC anaerobic conditions were limited so the reduction of NO_3^- and the production rate of N_2O were small. The total N_2O emission at 100% WHC was significantly larger than at 50% WHC (YOSHIDA & ALEXANDER, 1970; BLACKMER et al., 1980). The moisture regime of a soil is an important factor influencing N_2O emission by regulating oxidation and reduction reactions (KUMAR et al., 2000). Denitrification became the main process in the production of N_2O at 100% WHC. O_2 diffusion in soil decreases with increased water content (RENAULT & SIERRA, 1994). O_2 concentration in soil drops as consumption by microbial activity becomes larger than the O_2 that diffuses into the soil. Nitrifier denitrification is stimulated and as more micro-sites become anaerobic denitrification increases with increased production of N_2O (RUSSOW et al., 2000; WRAGE et al., 2004).

2.4.4. CHEMODENITRIFICATION

Although several chemical reactions can be characterized as chemodenitrification, the most significant in soils are reactions that involve the abiotic decomposition of HNO_2 to form NO (NELSON, 1982). These reactions can occur in acidic soils with high levels of OM and accumulation of NO_2^- from low levels of nitrification. Rapid soil processes such as freezing, wetting, and drying may concentrate nitrite in water films and accelerate its self-decomposition (FIRESTONE & DAVIDSON, 1989). DAVIDSON et al. (1993) mentioned that acidic soils might be expected to produce NO in this fashion, but chemodenitrification in neutral to alkaline soils is thought to be insignificant. However, processes that concentrate NO_2^- , such as wetting and drying events and micro-site acidification by nitrifying bacteria, may be more important than is indicated by bulk soil analyses of NO_2^- . It is possible that chemodenitrification may be important in the large pulse of NO emissions seen after wetting of dry soil in many seasonally dry ecosystems. At temperatures $> 50^{\circ}\text{C}$ chemodenitrification may be the major mechanism (KEENEY et al., 1979). The temperature increases, the $\text{N}_2\text{O}/\text{N}_2$ ratio declines. This inverse relationship has been demonstrated by several authors in laboratory incubations of soil (KEENEY et al., 1979). BREMNER (1996) concludes that there is no evidence to show that significant amounts of N_2O are produced by chemodenitrification.

The contribution of other processes as derived from the inhibition method to the N_2O production rate in soil incubated at 60% WHC was significant at 32%. The large contribution attributed to other processes may be an artifact of the method. Other sources may be overestimated, e.g. due to incomplete suppression of denitrification by O_2 or incomplete inhibition of NH_3 oxidation by C_2H_2 (WRAGE et al., 2004) or heterotrophic nitrification contributed to N_2O production. These heterotrophic nitrifiers are often able to denitrify under aerobic conditions (ROBERTSON et al., 1989). Chemodenitrification normally occurs at $\text{pH} < 5$ (CHALK & SMITH, 1983; VAN CLEEMPUT & BAERT, 1984), which is much lower than the pH measured in soil used in the experiment, so N_2O production by chemodenitrification was presumably low. ROBERTSON & TIEDJE (1987); WEBSTER & HOPKINS (1996) reported that non-biological N_2O production or chemodenitrification was not significant in their experiments.

Increases in the total concentration of Pb and Cd decreased the production rate of N₂O attributed to nitrification by the inhibition method. Some authors reported that increased Zn concentrations inhibited net nitrification rates (CELA & SUMNER, 2002a, 2003; SMOLDERS et al., 2003; STUCZYNSKI et al., 2003; RUSK et al., 2004). CELA & SUMNER (2002b) reported that Pb did not inhibit nitrification whereas Cu did. RUSK et al. (2004) also found that nitrification was not inhibited by Pb at 1960 or 3150 mg kg⁻¹. However, in the experiment, Pb (31–1845 mg kg⁻¹) did inhibit the production rate of N₂O attributed to nitrification by the inhibition method, whereas Cu (27–1620 mg kg⁻¹) did not. Differences in availability of those metals might explain the different effects of Pb and Cu (CHECKAI et al., 1987). STUCZYNSKI et al. (2003) found that Pb was strongly immobilized in soil, whereas immobilization of the Zn amendment was much weaker. The other processes as derived from the inhibition method that contributed to the production rate of N₂O in soil incubated at 60% WHC were not affected by heavy metal concentrations. It has to be stated that the production of N₂O might have been affected by other soil characteristics, such as total N, pH and clay content, as they are different between the locations sampled.

Denitrification as derived from the inhibition method was the most important process in N₂O production rate at 60% WHC and it was decreased by heavy metals. BARDGETT et al. (1994) found a gradual decline in N₂O production from NO₃⁻ along a gradient of increasing concentrations of Cu, Cr, and As. GUMEALIUS et al. (1996) found a 50% inhibition of NO₂⁻ reduction in pure cultures of denitrifying bacteria amended with 12 mg Cd l⁻¹. SAKADEVAN et al. (1999) in a study of the effects of heavy metal addition on surface wetland sediments receiving wastewater found that the addition of 500 and 1000 mg Cd, Cu or Zn (kg⁻¹ sediment) significantly inhibited denitrification. Application of 100 mg Cu and Zn kg⁻¹, however, stimulated N₂O denitrification, but Cd did not. HOLTAN-HARTWIG et al. (2002) reported a general reduction of the denitrification rate after heavy metal addition. However, N₂O production had partly recovered 8 days after heavy metal addition and was completely restored after 2 months. BOLLAG & BARABASZ (1979) observed an increased accumulation of NO₂⁻ and N₂O in an anaerobic incubation, although transiently, when metal concentration (Cd, Cu, Zn, Pb) increased in soil slurries, indicating a greater inhibition of the last enzymes in the denitrification enzyme cascade.

2.5. FORMATION OF NO

Nitrous oxide is generated by nitrification and denitrification when microbes transform inorganic N, including NH₃ and NO₃ (FIRESTONE & DAVIDSON, 1989; GRANLI & BØCKMAN, 1994; HUTCHINSON & DAVIDSON, 1993). Both processes are governed by the soil water content. Nitrification mainly occurs when 30–60% of the pore space is water-filled, and denitrification mainly occurs when 50–80% or 60–90% of the pore space is filled with water, depending on the soil properties (BOUWMAN, 1998). The faculty to reduce NO_x, when O₂ becomes limiting, enables denitrifying bacteria to grow in anaerobic environments. As a broad diversity of bacterial groups is capable of this metabolic pathway (FOCHT & VERSTRAETE, 1978; CONRAD, 1996a,b), denitrifiers are present almost ubiquitously in natural and cultivated soils. It is generally accepted that NO constitutes an obligatory intermediate in the denitrification sequence (PAYNE, 1981). This involvement as an intermediate provides good reason to assume that denitrifiers can not only produce but also consume NO. Such a dual behaviour has indeed been demonstrated in studies on bacteria cultures and soil samples (JOHANSSON & GALBALLY, 1984; REMDE & CONRAD, 1991a). The rate of NO production (or consumption) not only depends on the overall denitrification rate but is also strongly affected by parameters that influence the proportion of NO relative to the terminal products N₂O and N₂ (FIRESTONE & DAVIDSON, 1989). Hence, environmental control of NO production and consumption by denitrification is accomplished through complex interactions of numerous relevant parameters (ROBERTSON, 1989). O₂ availability, for instance, which strongly controls the total turnover rate of the denitrification process as well as the relative rate of NO production, is in turn regulated by various other factors (e.g., soil water content, soil texture, activity of plant roots, and microbial respiration).

Despite the fact that most field studies have not explicitly separated nitrification from denitrification contributions to the observed NO flux, there is some evidence that only a small fraction of the N oxidized by nitrifiers may be released in form of NO. In well-aerated soils the yield of NO is typically 1% to 4% of the NH_4^+ oxidized (JOHANSSON & GALBALLY, 1984, HUTCHINSON & BRAMS, 1992). Further studies, however, have demonstrated that the relative NO yield can range from 0.1% (DAVIDSON et al., 1993) to 10% (SHEPHERD et al., 1991; VELDKAMP & KELLER, 1997). To assess the importance of nitrification vs denitrification for the exchange of NO is a difficult task. By application of specific inhibitors or by examination of the response to NH_4^+ and NO_3^- based fertilizers, several investigators were able to identify the dominating process for an individual soil; but the results are contradictory. Prevalence of the nitrification pathway has been observed in many soils, including those from temperate (VOS et al., 1994; YAMULKI et al., 1995) as well as subtropical (HUTCHINSON & BRAMS, 1992) and tropical (DAVIDSON et al., 1993) ecosystems.

2.5.1. PROCESSES INFLUENCING NITROUS OXIDES EMISSION

Soil microbial processes are primarily responsible for soil N_2O emissions. BEAUCHAMP (1997) reported that climate, soil characteristics, cropping practices and their interactions affect the nitrification and denitrification processes (Figure 3.) and hence the production and emission of N_2O . HUTCHINSON (1995) mentioned that nitrifiers produce most of the NO and denitrifiers produce most of the N_2O .

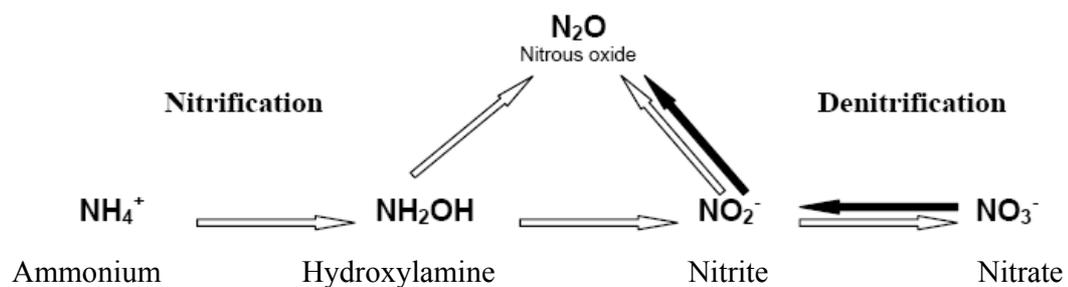
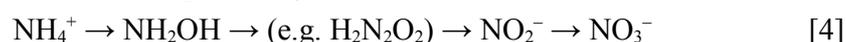


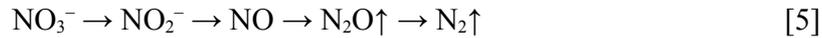
Figure 3. Conceptual model indicating the major pathways for N_2O formation regarded in this study. Nitrification is indicated with open arrows and denitrification is indicated with bold arrows. Adapted from WRAGE et al. (2001).

The N_2O emission into the atmosphere was measured in closed chambers at the soil surface (RETH et al., 2008). Concurrently the soil temperature and soil water content were recorded in order to quantify their effects on the fate of N_2O in the soil. The highest N_2O concentration was recorded after 'special events' like snowmelt, heavy rain, fertilization, and grubbing. The combination of fertilization and heavy rain led to an increase of up to 2,700 ppb in the subsoil. COLBOURN & DOWDELL (1984) measured 0–20% and 0–7% N loss on field soils and grass land, respectively. Besides NO_2 , other N gases can also contribute to the N emission from N fertilizers as products of their transformation processes (ammonification, nitrification and denitrification) in the soil and through NH_3 volatilisation. RUSSOW et al (2000) formed a conceptual model of coupled nitrification and denitrification describes the formation of NO and N_2O . Under the quasi-semiarid conditions in the dry belt of Central Germany Mollisols have a high potential for NO emission which clearly exceeds N_2O emission if high NH_4^+ contents are present in the soil. BEAUCHAMP (1997) reported that climate, soil characteristics, cropping practices and their interactions affect the nitrification and denitrification processes and hence the production and emission of N_2O . Nitrification is the process of converting atmospheric N_2 into NO_3^- . Equation 4. shows the oxidative nitrification chemical process. Soil Nitrification is accomplished by genera of aerobic chemoautotrophic bacteria (*Nitrosomonas* and *Nitrosospira*: $\text{NH}_4^+ \rightarrow \text{NO}_2^-$, *Nitrobacter*: $\text{NO}_2^- \rightarrow \text{NO}_3^-$).





Denitrification is the process of converting plant available NO_3^- into N_2 gas. Certain aerobic bacteria carry out denitrification when O_2 becomes limiting. These bacteria have the ability to reduce NO_x depending upon the availability of a suitable reductant (usually OC), and the presence of NO_x (NO_3^- , NO_2^- , NO, or N_2O) (HUTCHINSON, 1995). The microbial conversion of reductive denitrification is displayed in Equation 5.



The amount of N_2O emission is mainly influenced by the N fertilization (GRANLI & BØCKMAN, 1994) as shown in studies of SCHMIDT & BOCK (1998), who determined a strong correlation between N content in the soil and N_2O emissions. The positive correlation between increased N input and increased N emissions (BOUWMAN, 1990; EICHNER, 1990) provides the basis for estimating the impact of agriculture on N_2O emissions on a global scale (IPCC, 1997). The emission factor is based on studies of BOUWMAN (1996) and is calculated by the following function:

$$\text{EF} = \text{NI} * 1.25 (+/-1) \% + \text{BE} \quad [6]$$

Where EF = emission factor (kg N ha^{-1}), NI = N input (kg N ha^{-1}), and BE = background emission ($\text{kg NO}_2\text{-N ha}^{-1}$), which are normally set to 1. N that remains in the soil after harvest is the major source for N pollution of the groundwater (VAN DER PLOEG et al., 1995). At the same time, a substantial part of agricultural emissions is believed to be derived from N lost from agricultural land after leaching and run-off into drainage waters (DOWDELL et al., 1979). This means reducing NO_3^- leaching would also reduce N_2O emissions.

2.5.2. IMPORTANT FACTORS CONTROLLING N_2O EMISSIONS

Empirical up-scaling of the global source strength of tropical ecosystems is thus based on a very limited database that is unable to take account of the spatial and temporal variability of the soil-atmosphere exchange of trace gases (SERÇA et al., 1994; BREUER et al., 2000; KIESE et al., 2003, 2005). The high variability in trace gas flux rates is generally caused by the underlying biogeochemical processes (e.g., mineralization, nitrification and denitrification), which are controlled by environmental factors such as soil moisture, soil temperature and nutrient availability (DAVIDSON, 1992; CONRAD, 1996a,b; SMITH et al., 2003). As these environmental factors vary in time and space, site specific estimates of annual trace gas exchange are likely to contain large uncertainties.

Soil temperature and soil moisture were the most important factors controlling N_2O emissions. Those parameters affect microorganisms and their metabolism and, hence, the production and consumption of N trace gases in soils (CONRAD, 1996a,b). The air-filled porosity controls the movement of the gases towards and away from the atmosphere; it also affects soil aeration, and, thus, indirectly controls the capacity of the soil for producing or consuming soil-produced trace gases (SMITH et al., 2003; DAVIDSON et al., 2000).

MOISTURE REGIME

There are various parameters that might have contributed to the N_2O emissions. Soil water can directly/indirectly influence denitrification through: provision for suitable conditions for microbial growth and activity; restricting supply of O_2 to micro-sites by filling soil pores; release of available C and N substrates through wetting and drying cycles; and providing a diffusion medium through which substrates and products are moved to and away from soil microorganisms. However, 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 an anaerobic condition (DAVIDSON, 1992).

In a laboratory parameterization study, SCHINDLBACHER et al. (2004) found that a N₂O emission maximum at a soil moisture range of 60%–90% water field pore space (WFPS) which corresponds to a water content of 53–80%. In the field authors found that maximum N₂O emissions occurred at soil moisture values in the range of 50%–65%. High precipitation and low air temperature showed a significant effect on N₂O emissions with a lag of 8 days. In a microcosm experiment SHARMA et al. (2006) found that maximum N₂O emissions occurred 8 days after thawing. After a rainfall event soil moisture increased again and may have caused an increase in microbial activity. On the other hand, the actual level of N-deposition and the NO₃⁻ pool in the soil might have played an important role in the sudden release of N₂O (DAVIDSON et al., 2000). Highest amounts in NO₃⁻ and NH₄⁺ *via* through-fall reached the forest floor in August. Although, throughout the study bulk N-deposition accounted for up to only 31% of the variation in N₂O emission, a strong relationship was apparent between the two factors. This high N₂O peak coincided with significant larger available soil N concentrations, in particular soil NO₃⁻. It has been observed that N in microbes may have a turnover rate of 3 months (TIETEMA & VAN DAM, 1996). According to the theories of microbial stoichiometry (SCHIMEL & WEINTRAUB, 2003) microbes tend to immobilize N from the soil solution and use it for cell growth at times when it is the limiting nutrient. This could be the case during favourable growth conditions of soil moisture and high temperatures but little N-input. After 3 months microbial death may occur, which may lead to enhanced N-release and N₂O emissions as observed in beech forests (ZECHMEISTER-BOLTENSTERN et al., 2002). Measurements provide the first set of simultaneously measured soil N₂O and CO₂ fluxes for three different forest cover types in continental, tropical Southeast Asia. So far, only measurements of C and N trace gas fluxes for tropical forest ecosystem in Indonesia and Borneo have been published (HALL et al. 2004; ISHIZUKA et al. 2002, 2005a,b). After prolonged dry periods, it has been shown that re-wetting of the soil can be accompanied by high emissions of N trace gases (DAVIDSON et al. 1993; GARCIA-MONTIEL et al. 2003; BUTTERBACH-BAHL et al. 2004b). Such pulse fluxes are associated with the rapid microbial consumption of NH₄⁺ or NO₂⁻ accumulated during the dry period (DAVIDSON et al. 1993), which are in turn partly oxidized NH₄⁺ or reduced NO₂⁻ to N₂O by nitrifying bacteria (POTH & FOCHT 1985). Authors detected significant N₂O pulse emissions due to re-wetting not only in the watered chambers but also in the control ones. However, it has to be stressed that for further improvement and validation of mechanistic models it is of utmost importance to provide detailed data such as daily or sub-daily trace gas fluxes in order to test our process understanding and to develop suitable algorithms describing processes involved in trace gas production, consumption and emission. Such detailed data were e.g., used to test the anaerobic balloon concept of the Forest-DNDC model for predicting simultaneously production (consumption) of N₂O by anaerobic (denitrification) and aerobic (nitrification) microbial processes (LI et al. 2000). In earlier studies, soil moisture changes are the main driver for temporal variations of N₂O emissions in tropical forest ecosystems (DAVIDSON 1993; STEUDLER et al. 1996; BREUER et al. 2000; KIESE & BUTTERBACH-BAHL 2002). Changes in soil moisture ultimately control soil aeration and effect nutrient availability. This finally feeds back into the spatial and temporal differences in the occurrence and magnitude of the oxidative nitrification and reductive denitrification processes and associated N trace gas emissions (SMITH, 1980; CONRAD 1996a,b). Authors found that in unsaturated soil, higher moisture values are generally expected to support higher N₂O emissions. N₂O emissions were only stimulated for a few days. But after the end of the artificial watering, the enhanced N₂O emissions of the watered chambers diminished and even dropped below those of the control chambers. This means that simulating rainfall during the transition from dry to wet season influenced the timing of N₂O emissions, but not the total amount of N₂O released over the entire observation period. This may be attributed to the fact that after the rapid mineralization of easily decomposable organics litter and/or rapid microbial consumption of NH₄⁺ and NO₂⁻ accumulated during the dry period (DAVIDSON et al. 1993), microbial N turnover processes, such as mineralization, nitrification and denitrification, and associated N₂O emissions decreased due to substrate limitations regardless of the suitable soil moisture condition. SHARMA et al. (2006) observed a linear relationship between WFPS (range from 15% to 85%) and N₂O

emission fluxes. BUTTERBACH-BAHL et al. (2004b) also found a positive linear correlation between WFPS (ranging from 10% to 50%) and N₂O emissions for tropical forest soils in Northern Queensland, Australia, while KELLER & REINERS (1994) described an exponential correlation in primary and secondary forests of Costa Rica for a WFPS range of 50–90%. KIESE et al. (2002) reported a linear correlation between N₂O emissions and WFPS less than 60%, but noted a decline in N₂O emissions at higher moisture levels, which is most likely due to the increasing formation of N₂, rather than N₂O, as the denitrification process begins to dominate, as has been shown elsewhere (BUTTERBACH-Bahl et al. 2002).

Recent studies (SAGGAR et al. 2005) showed emissions from effluent irrigation were most strongly influenced by soil WFPS and excretal inputs through grazing. These studies suggest strategic application of dairy effluent during a dry summer and autumn could significantly reduce N₂O emissions from grazed pastures, and delaying effluent-irrigation after a grazing event could reduce emissions by reducing the levels of surplus mineral N. Freeze thaw cycles affect annual N₂O emissions. KIESE & BUTTERBACH-BAHL (2002) established that N₂O emissions were positively correlated to changes in WFPS up to a threshold of 50% WFPS at the Bellenden Ker and Kauri Creek sites and up to a threshold of 60% WFPS at the Pin Gin Hill site. The temporal variability of N₂O emissions was pronounced in the study. SHARMA et al. (2006) found the coefficients of variation (CV) for N₂O emissions of the entire measurement period ranged from 35% to 62%. The observed variations in N₂O emissions this study are within the CV range of 14–125% reported for tropical rainforests soils in Queensland, Australia (BREUER et al. 2000; BUTTERBACH-BAHL et al. 2004a,b), but lower than the range of 94–195% reported for tropical rain forest soils in Amazonia (VITOUSEK et al. 1989; VERCHOT et al. 1999). This supports the explanation of ISHIZUKA et al. (2002) that the relatively low N trace gas emissions of rubber sites is due to the loss of labile C and N stocks following land-use conversion, which is supposed to feed back on reduced mineralization and nitrification activities (NEILL et al. 1995). DEBRECZENI & BERECZ (1998) mentioned that the composition of the N gases changed during vegetation depending on the applied N fertilizer form. The proportion of N₂O increased within the total amount of N gases in the field traps with all N fertilizer forms. It decreased. However, in the traps of the pots, where the soil had a higher moisture level. FLESSA et al. (1996) measured an increased N₂O emission with increased soil moisture. DEBRECZENI et al (1997) mentioned that the rate of transformation of the mineral forms of N depends on the C:N ratio.

TEMPERATURE

Nitrous oxide in the atmosphere is involved in the destruction of the O₃ layer (CICERONE, 1987) and as a GHG it makes an important contribution to the global GH effect (DUXBURY, 1994). Soil temperature, soil water content, and plant growth are known to affect N₂O and N₂ losses, and their ratio. The N₂/N₂O ratio was found to increase with soil temperature (BAILEY, 1976; McKEENEY et al., 1979), whereas others observed no relationship with temperature (FOCHT, 1974; LENSİ & CHALAMET, 1979). Under constant laboratory conditions the N₂/N₂O ratio increased exponentially with soil temperature (MAAG & VINTHER, 1996). However, the ratio was strongly influenced by soil type. In contrast, the N₂/N₂O ratio increases with increasing soil water content (COLBOURN & DOWDELL, 1984; VINTHER, 1984). The influence of the plant on denitrification is not clear. Positive effects of roots were found in soils at low soil moisture content (BAKKEN, 1988), or at high NO₃⁻ concentrations (SMITH & TIEDJE, 1979), and advanced maturity of the plant (BECK & CHRISTENSEN, 1987; KLEMEDTSSON et al., 1987). This may result from denitrification because of an enhancement of available C from decaying roots, and the subsequent decrease in the availability of O₂ resulting from increased biological activity. This is supported by the observed increase in N₂O loss after grass cutting in pot experiments (BECK & CHRISTENSEN, 1987). CHRISTENSEN et al. (1990) also observed a strong stimulation of N₂O production resulting from a modest increase in soil water around field capacity. Tropical rainforest soils have been identified as a major source of the radiatively active trace gases N₂O and CO₂ (MOSIER et al., 1998, 2004; KROEZE et al., 1999; PRATHER & EHHALT, 2001; POTTER et al., 1996a,b; RAICH et al., 2002). In order to quantify the source strength, empirical equations are now commonly used to up-scale flux

measurements to regional or global trace gas budgets (PRATHER & EHHALT, 2001), but, being a generic approach, do not account for regional variations and controlling factors. Recently, approaches which link detailed geographic information systems to mechanistic biochemical models like CASA (POTTER et al. 1993), CENTURY (PARTON et al. 1988a,b) or PnET-N-DNDC (LI et al. 2000; STANGE et al., 2000) to calculate regional or global emission inventories (POTTER et al., 1996a,b; KIESE et al., 2003, 2005) are seen as a promising option to improve the current estimates and reduce the associated uncertainties (DAVIDSON et al., 1998; LI et al., 2000; BUTTERBACH-BAHL et al., 2001, 2004a). These models operate in daily time, to adequately calibrate and validate them trace gas flux measurements of a high temporal resolution, from a variety of ecosystems are required (KIESE et al., 2005). Diurnal variation in N₂O emissions from agricultural and forest soils have been observed in temperate regions (BLACKMER et al., 1982; BRUMME & BEESE, 1992; SKIBA et al., 1996; BALL et al., 1999; LAVILLE et al., 1999; SMITH et al., 1998). However, no daily variation was seen in tropical agricultural soils with high N₂O fluxes and minor diurnal variations in temperature (CRILL et al., 2000). MARJA et al. (2002) measured the short-term variation in the fluxes of N₂O in boreal organic soils with different cultivation practices (grass or forestry) using an automatic chamber system *in situ*. The diurnal variation in the fluxes of N₂O was compared to that of CO₂ production, which is known to be associated closely to the fluctuation in air temperature (SILVOLA et al., 1985; BENSTEAD & LLOYD, 1996). Abiotic production of NO was demonstrated in a sterilised soil (pH 5.6) from an oak woodland/grassland site in California after wetting (DAVIDSON, 1992). Abiotic production of NO requires accumulation of NO₂⁻. High nitrification rates at high temperatures in acid tropical soils may lead to NO₂⁻ accumulation and the chemical decomposition of NO₂⁻ may be an important pathway of NO loss (LAUDELOUT et al., 1977).

OTHER FACTORS

MERINO et al. (2004) established that soil also plays a major role in contributing to the atmospheric concentrations of other GHG, such as N₂O. The fluxes of these gases are influenced by soil variables that influence microbial activity, such as pH and concentrations of NO₃⁻, NH₄⁺, and O₂, which, in turn, are controlled by a combination of soil properties (soil moisture, texture, structure) and soil management practices. Intensive soil management has therefore led to a considerable increase in the exchange of N₂O between soils and the atmosphere (BOUWMAN, 1990). A high pH value is also one of the factors that provide favourable conditions for denitrification at the site. Furthermore, close C/N-ratios (16–18) suggest favourable conditions for N mineralization and nitrification (HERMAN et al., 2002). BUTTERBACH-BAHL et al. (2002) detected negative N₂O fluxes in pine forests with moderate N deposition whereas a pine forest with high N loads exclusively functioned as a source of N₂O during winter. On the other hand winter emissions, comparable to the ones during the year. These large emissions were either a result of enhanced denitrification activity or could be due to the physical release of accumulated N₂O in the snow or in the soil (TEEPE et al., 2001).

SCHINDLBACHER et al. (2004) concluded that the GARCH model is better than a conventional regression analysis, because soil N emissions can be modeled with a higher r². It reflects lagged effects of soil moisture, soil temperature, precipitation, air temperature and N deposition on NO emissions. NO emissions were three times smaller compared to N₂O emissions and total emissions of N were small compared to N inputs. This may be attributed to the fact that in the limestone Alps soil pH is high, a large microbial biomass can be found and N is mainly emitted in the form of N₂. Alone in Austria, about a third of forests is on calcareous bedrock and this is the first report on processes determining NO_x fluxes in these ecosystems.

WERNER et al. (2006) evaluated the effects of soil moisture and temperature on temporal variation of N₂O and CO₂ soil–atmosphere exchange at a primary seasonal tropical rainforest (PF) site in Southwest China and to compare these fluxes with fluxes from a secondary forest (SF) and a rubber plantation (RP) site. Agroforestry systems, such as RP, are increasingly replacing PR and SR forest systems in tropical Southwest China and thus effect the N₂O emission in these regions on a landscape level. The dependency of N₂O fluxes on soil moisture

levels was demonstrated in a watering experiment; however, artificial rainfall only influenced the timing of N₂O emission peaks, not the total amount of N₂O emitted. For all sites, significant positive correlations existed between N₂O emissions and both soil moisture and soil temperature. A dependency of soil CO₂ emissions on changes in soil water content could be demonstrated for all sites, thus, the watering experiment revealed significantly higher CO₂ emissions as compared to control chambers. Correlation of CO₂ emissions with soil temperature was significant at the PF site, but weak at the SF and not evident at the RP site. Even though we demonstrated that N and C trace gas fluxes significantly varied on sub-daily and daily scales, weekly measurements would be sufficient if only the sink/source strength of non-managed tropical forest sites needs to be identified. TEEPE et al. (2000) mentioned that the dynamics of the N₂O winter emissions were influenced by the changes in soil temperatures. Also differences in the winter emissions among the three sites could not be explained by means of nitrate concentration but rather by WFPS. However, the average WFPS in the top 0–5 cm of soil was positively correlated with the total N₂O winter emissions indicating the importance of O₂ diffusion as a regulator for N₂O emissions in winter which is in agreement with GROFFMAN & TIEDJE (1991). They showed that the denitrification rate in a loamy soil was negatively correlated to the air filled porosity. In order to reduce the loss of N fertilizer in the form of N₂O and N₂ by adjusting grassland management, it is important to understand the relationship between the emission of these gasses after fertilization and the conditions in the soil–plant system. This relationship was studied by determining the seasonal patterns of N₂O and N₂ fluxes, soil temperature, and soil water content based on weekly measurements. Highest N fluxes were measured from wet soil after plant cutting, and after N fertilizer application. Also the magnitude of the fluxes of N₂O and N₂ were not directly correlated with soil temperature, but increased with increasing soil water content (RUDAZ et al., 1999).

2.6. PROCESSES INVOLVED IN NO EXCHANGE

Several biotic and abiotic processes in soils and plants are mechanisms for production and consumption of NO (CONRAD, 1996a,b). Although uptake of NO by plants is a common phenomenon, this process is rarely considered to be a major pathway for the NO surface exchange, as the characteristic deposition velocity is extremely low (well below 10⁻³ m/s, c.f. JOHANSSON, 1989; MEIXNER, 1994). Abiotic formation of NO in soils may only be of importance in acid soils with high NO₂⁻ concentrations. However, on a global scale, it seems to be likewise unimportant (GALBALLY, 1989). Among microbial processes, all those that involve oxidative or reductive transformation of N through the +2 valence state carry the potential to act as source or sink for NO (CONRAD, 1990). Nevertheless it is widely accepted that microbial nitrification and denitrification constitute the principal processes (WILLIAMS et al., 1992b).

Some evidence exists that NO is an intermediate in the oxidation step from NH₂OH to NO₂⁻ (HOOPER & TERRY, 1979). Other research groups (REMDE & CONRAD, 1990), however, suggested that NO formation during nitrification results from the reduction of NO₂⁻ (nitrifier denitrification), a mechanism also shown to be effective for the production of N₂O by nitrifying bacteria (POTH & FOCHT, 1985). The use of NO₂⁻ as an electron acceptor enables nitrifiers to sustain oxidation of NH₄⁺ even at a low partial pressure of O₂. Overall nitrification rates will increase in well-aerated soils, provided that the soil is not very acidic (pH > 4 – 5). If these requirements are met, the nitrification rate is predominantly controlled by the availability of NH₄⁺ (ROBERTSON, 1989).

On the other hand, production of NO was attributed to denitrifiers in the experiments of REMDE et al. (1993), CARDENAS et al. (1993), and SANHUEZA et al. (1990). Some indication that the dominant mechanism for the formation of NO is influenced by the soil pH can be taken from a laboratory study of REMDE & CONRAD (1991b). They found that nitrifiers were responsible for NO production in an alkaline soil (pH 7.8), whereas denitrification was the dominant process in an acidic soil (pH 4.7). In many field situations, however, it is difficult to ascribe NO production to one of both processes as nitrifying and denitrifying bacteria might act simultaneously owing to micro-site heterogeneities within the same soil profile. Up to now little attention has been given

to the role of transport processes for soil–air exchange of NO. Commonly, molecular diffusion is considered the driving mechanism for gas transport in soil pores (GALBALLY & JOHANSSON, 1989). Laboratory studies, however, have pointed out that convective transfer may not be ignored (RUDOLPH et al., 1996; RUDOLPH & CONRAD, 1996). Since the NO diffusion coefficient in water is about five orders of magnitude lower than in air, it is obvious that water-filled pores create a strong barrier to the emission of NO into the atmosphere (GALBALLY, 1989). Soil water content also has a strong impact on the diffusion of O₂ into the soil and consequently on the microbial activity (SKOPP et al., 1990). Thus high soil water content favours denitrifiers but restricts NO transport. This creates a situation where the probability of NO being reconsumed by denitrifiers is largely enhanced; and as a consequence, emission of NO to the atmosphere might deviate significantly from the production of NO in soil. Illustrative for this fact is a laboratory experiment of SKIBA et al. (1997), who reported that only 13% of the amount of NO produced in an anaerobic soil was actually emitted from the soil surface.

Emission of NO from plants or plant material has been observed only in a few studies (KLEPPER, 1979; DEAN & HARPER, 1986). Thus the general capability of plants to emit NO remains rather uncertain (JOHANSSON, 1989). However, biogenic NO emission from a variety of plant species was recently observed by WILDT et al. (1996) during laboratory fumigation experiments at low ambient NO concentrations. Plants primarily act as a sink for atmospheric NO, but the uptake rate is limited by low solubility of NO (HILL, 1971). Deposition velocities observed for different plant species and under various physiological conditions are generally less than 10⁻³ m s⁻¹ (HANSON & LINDBERG, 1991; MEIXNER, 1994). This implies that only at exceptionally high ambient NO concentration, direct deposition to plants might constitute a significant removal mechanism for atmospheric NO. Major relevance of plant uptake for the net flux of NO, however, results from the close coupling with the surface exchange of NO₂. Once emitted, NO is oxidized rapidly to NO₂ owing to the presence of O₃, and the uptake by plants is much more effective for NO₂ than for NO (HANSON & LINDBERG, 1991; MEIXNER, 1994). Therefore, NO, once emitted from vegetated soils and converted to NO₂ within the plant canopy, may be immediately deposited to the vegetation elements (in form of NO₂), which will then reduce the amount of NO that escapes from the plant canopy. This internal cycling of NO_x likely occurs in all ecosystems (especially in forests), but adequate quantitative information is currently lacking. On the basis of rough simplifications, YIENGER & LEVY (1995) and JACOB & BAKWIN (1991) have computed a global “canopy reduction factor” of about 50%. The “zero-order” approach of YIENGER & LEVY (1995), however, should be taken as an indication that in-canopy processes affect the NO exchange substantially rather than as an accurate assessment of this effect. Better understanding and quantification of canopy reduction remains an imperative task for future research on NO (and NO₂) exchange (e.g., ANDREAEE et al. 2000).

2.6.1. FACTORS INFLUENCING THE NO EXCHANGE

Basically, the complete set of environmental factors that regulate the underlying processes of NO production and consumption in soils has the potential to affect the exchange of NO between soil and the atmosphere significantly. The following section will be restricted to the discussion of some factors, which have been encountered as major controllers over a wide range of field situations. Further chemical (soil pH, concentration and composition of OC), physical (soil texture), and biological (plant cover) variables as well as some cultivation practices (tillage, burning) might be of importance under more specific environmental conditions (WILLIAMS et al., 1992b; MEIXNER, 1994). When reviewing the influence of soil properties on the NO exchange, it has to be noted that there is no common agreement with regard to the appropriate depth of soil where these properties should be determined. It is obvious that the correlation of soil parameters with observed NO fluxes depend on the vertical distribution of the relevant processes within the soil. Although the zone of maximum NO productivity most likely varies from soil to soil, there is broad evidence that the primary production zone is located within a very shallow layer at the soil surface (JOHANSSON & GRANAT, 1984, LUDWIG et al., 1992; RUDOLPH et al., 1996; RUDOLPH & CONRAD, 1996; YANG & MEIXNER, 1997).

REMDE et al. (1993) observed NO fluxes in a marsh soil could be explained by model calculations when applying an effective depth (0.002 m). Soil parameters are typically measured at depths of 0.01 to 0.1 m and thus may, in many cases, only inaccurately reflect the conditions in the shallow topsoil layer, where NO production (or consumption) predominantly occurs. The production of NO is strongly dependent on climate and varies considerably with soil temperature and soil moisture (DAVIDSON et al., 2000; LUDWIG et al., 2001). The optimum soil temperature (20°C), as detected in laboratory studies by SCHINDLBACHER et al. (2004), could not be confirmed in the field experiment, where largest NO emissions were measured at 8–10°C soil temperature; maximum soil temperature in the field was 16°C. Optimum WFPS in the field for NO emission was found to be at 30–45% WFPS (water_c 27–40%) and was higher than in laboratory studies (SCHINDLBACHER et al., 2004). In the field largest NO emissions were found in autumn and in spring, when soil water content was between 45–50%. Large spring emissions were detected in May, when soil was moistened and soil temperature increased.

NITROGEN AVAILABILITY AND FERTILIZATION

It has been shown by a large number of studies that availability of soil N has a strong impact on NO emission rates. Special interest in this respect is given to the pool size of soil NH₄⁺ and NO₃⁻, since these compounds serve as substrate for nitrifying and denitrifying bacteria. By examining results from various natural and cultivated sites in North America (WILLIAMS & FEHSENFELD, 1991) were able to show that differences in the NO₃⁻ content of the soils accounted for much of the variance in the observed NO emission levels. Similar trends were reported for several European ecosystems (SKIBA et al., 1994; LUDWIG & MEIXNER, 1994). Therefore it has been argued that the NO₃⁻ concentration in soils might serve as a useful variable to predict NO emission rates across ecosystems. Further studies, however, have indicated that the relation between soil N and NO flux is more complex than it appears from these results. A stronger correlation of NO fluxes with soil NH₄⁺ than with NO₃⁻ concentrations have been reported by LEVINE et al. (1988), ANDERSON et al. (1988), and HUTCHINSON et al. (1993). It is worth to note that typically the spatial variability of NO fluxes within a given field site is not explained by the spatial distribution of soil NO₃⁻ concentrations (WILLIAMS & FEHSENFELD, 1991; LUDWIG, 1994).

One has to keep in mind that observed relationships between NO emission and soil NO₃⁻ or soil NH₄⁺ do not allow drawing simple conclusions concerning the mechanisms of NO production. As pointed out by WILLIAMS et al. (1992b), the correlation of soil NO₃⁻ concentrations and NO emission rates may reflect (a) the status of NO₃⁻ as a substrate for denitrification, (b) the status of NO₃⁻ as a product of nitrification, or (c) the fact that accumulation of NO₃⁻ tends to be a general characteristic of soils that exhibit leaky N cycles. Overall, pool size of available N may be seen as a rough indicator for the N turnover rate in a soil, and thus it also provides some indication for microbial production of NO. There are, however, exceptions to this general picture as it is the case in soils where high and rapid turnover rates of nitrifying or denitrifying bacteria lead to low soil NO₃⁻ or soil NH₄⁺ pool sizes (DAVIDSON et al., 1990). Given the importance of N availability, it appears logical that application of N fertilizers has a profound effect on the exchange of NO. A strong stimulation of NO emission by addition of N fertilizers has been noticed at uncultivated (JOHANSSON, 1984; JOHANSSON et al., 1988; CARDENAS et al., 1993) as well as agricultural sites (SLEMR & SEILER, 1984; ANDERSON & LEVINE, 1987; SHEPHERD et al., 1991; LUDWIG, 1994; VERMOESEN et al., 1996; MCKENNY & DRURY, 1997). Likewise, input of N by the excreta of grazing animal's results in enhanced levels of the NO release over grasslands (COLBOURN et al., 1987; THORNTON et al., 1998). Independent of fertilizer type and land use, a rapid increase of NO emissions following fertilizer addition is commonly observed. Maximum emission rates are typically approached within one or two days after fertilization. The period until emission rates drop to pre-fertilization levels can last for a few days or for several weeks. Similar observations were made by HUTCHINSON & BRAMS (1992), who suggested that the enhancement in post-harvest emissions results from temperature effects and from microbial transformation of N contained in plant residues. Although numerous observations of elevated NO emissions subsequent to N fertilizer application have been reported

in literature, quantification of this effect is difficult. Substantial variability in data prevails with respect to the absolute as well as the relative increase of NO emissions immediately after fertilizer addition. Similar scatter can be found with respect to the persistence of enhanced emissions. For comparison purposes, the fraction of applied N lost as NO is commonly employed. Reported values of fractional losses range from 0.003% (SLEMR & SEILER, 1991) to 11% (SHEPHERD et al., 1991), but a consistent explanation for this wide divergence is lacking. VELDKAMP & KELLER (1997) noted that some discrepancy in previous results may be due to the fact that in several studies the fertilizer was applied in dissolved form and thus an additional effect due to water could not be excluded. Their careful evaluation of previous measurements covering a variety of fertilizer types, soils, and climatic conditions indicated that on average approximately 0.5% of applied fertilizer N is released as NO. This is in reasonable agreement with the mean value (0.3%) postulated by SKIBA et al. (1997) but a factor of five lower than that derived by YIENGER & LEVY (1995). There is clearly a need for systematic investigations to verify and to narrow the range of the fraction of N fertilizer lost as NO.

SOIL MOISTURE CONTENT

It is widely accepted that soil moisture strongly affects the exchange of NO. Much of the current knowledge originates from observations of the change in NO emission rates subsequent to precipitation events or artificial watering of the soil. Addition of water to very dry soils typically produces a distinct increase of NO emission rates ('pulsing'). It seems, that 'pulsing' is caused by a 'dormant' water-stressed microbial community which consequently 'wakes up', feeding of accumulated nutrients as soon as the first water drops are supplied to the desiccated soil. As noted by WILLIAMS et al. (1992b), even a slight rain event (0.3 mm) might enhance the emission of NO by a factor of almost 10 compared to that under dry conditions. Commonly the increase of NO fluxes becomes visible within a few minutes after wetting and persists during one or more days. This is of special importance in tropical and subtropical climates with distinct dry and wet seasons, where large bursts of NO emissions at the onset of the rainy season have been encountered (DAVIDSON et al., 1991; HARRIS et al., 1996; MEIXNER et al., 1997; OTTER et al., 1999). The magnitude of this stimulatory effect appears to be related to the length of the dry period preceding a rain or irrigation event. This was indicated by experiments of SLEMR & SEILER (1984), JOHANSSON et al. (1988), and DAVIDSON et al. (1991), who reported that the irrigation-induced stimulation of NO emissions decreased with repeated watering of the soil. It seems that NO emissions decreasing with successive irrigation are due to the gradual depletion of soil nutrients which have once accumulated prior to the very first watering of the very dry soils. However, several early investigators had to conclude that no clear relation between soil moisture and NO fluxes could be established in their experiments (WILLIAMS et al., 1988). VALENTE & THORNTON (1993) reported a tenfold increase of NO emissions subsequent to a light rainfall event, whereas heavy rains eliminated nearly all emissions from the same corn field. Further experiments (ANDERSON & LEVINE, 1987; SHEPHERD et al., 1991; YAMULKI et al., 1995) have demonstrated that NO emissions decrease drastically as soil moisture approaches saturation. Clearly, the differences in the observations reflect the multiple regulatory role of soil moisture for many processes controlling the NO exchange.

Soil moisture governs whether nitrification or denitrification is the dominant process in a given soil and strongly influences the corresponding turnover as well as the ratio of NO production over NO consumption rates. Soil moisture, moreover, controls transport of microbial substrates and products of microbes. Thus a simple relationship between the flux of NO and the soil water content may not be expected (DAVIDSON, 1991, 1993). Surprisingly few workers (CARDENAS et al., 1993; YANG & MEIXNER, 1997; OTTER et al., 1999) have yet attempted a systematic investigation of this relationship by examining NO emissions as a function of either gravimetric water content or water-filled pore space (WFPS). The uniformity in their findings is, however, encouraging. It indicates the existence of an optimum soil water content (approximately 20% WFPS) for emission of NO and a strong decrease of NO emissions towards extreme values of WFPS (i.e., <10% and > 40% WFPS for very dry and fully saturated soils,

respectively). Such a response function is in accordance with conceptual considerations that propose a substrate diffusion limit at low and a gas diffusion limit at high moisture contents (SKOPP et al., 1990). An optimal WFPS of about 60% has been noticed for a number of microbial processes (LINN & DORAN, 1984). The results of POTTER et al. (1996a,b), YANG & MEIXNER (1997), and OTTER et al. (1999), however, suggest that this value is not applicable with respect to the emission of NO.

SOIL TEMPERATURE

Considering the dominance of soil microbial processes for the production of NO, one has to expect an influence of soil temperature on NO emission rates. Indeed, the bulk of existing studies (SLEMR & SEILER, 1984; ANDERSON & LEVINE, 1987; WILLIAMS et al., 1987; WILLIAMS et al., 1988; WILLIAMS & FEHSENFELD, 1991; LUDWIG et al., 1992; VALENTE & THORNTON, 1993; YANG & MEIXNER, 1997; OTTER et al., 1999) has shown an increase of NO emissions with increasing soil temperatures. The response of NO emission is due to increasing soil temperature. This response is due to the fact that rates of enzymatic processes generally increase exponentially with temperature, as long as other factors (substrate or moisture availability) are not limiting. Then, a typical diurnal variation of the NO release, correlating closely with soil temperature, is observed. Based on observations at eight North American locations WILLIAMS & FEHSENFELD (1991) concluded that in a temperature range between 15°C and 35°C the response of NO emission to soil temperature will be rather uniform, regardless of the absolute magnitude of emitted NO. According to their finding, each 10°C rise in temperature results in an approximate doubling of NO emission rates. The general applicability of this relationship appears to be questionable, as can be seen from the results of VALENTE & THORNTON (1993), who reported on average an almost five-fold increase of NO emissions per each 10°C temperature rise with a considerable variation between different ecosystems. Further restrictions to the validity of a uniform temperature response concern the emission of NO at more extreme temperatures and soil water contents. Some experiments have shown that the relationship between NO emission and soil temperature changes at temperatures higher than about 35°C and 50°C, respectively (VALENTE & THORNTON, 1993; YANG & MEIXNER, 1997). Other observations even indicate a decline of NO release rates as temperature increases above this value (WILLIAMS & FEHSENFELD, 1991). No (or only a very weak) relationship between NO flux and temperature could be established in a number of measurements performed over very dry soils (CARDENAS et al., 1993; MEIXNER et al., 1997). Obviously, primary control over the NO flux is accomplished by factors other than soil temperature under dry conditions. Frequently a pronounced positive temperature response becomes visible when moisture is added to these soils (JOHANSSON et al., 1988; MEIXNER et al., 1997). It should be noted that soil temperature often fails as a variable to account for seasonal variations of NO fluxes (SHEPHERD et al., 1991; LUDWIG, 1994). It seems therefore appropriate to regard soil temperature as a factor that mainly modulates short-term variations of the NO exchange, whereas the magnitude of NO emission is predominantly controlled by other factors (OTTER et al., 1999).

ATMOSPHERIC CONCENTRATION OF NO

An influence of ambient NO concentration on the exchange of NO was noticed first by a number of investigators, who used the static (closed) chamber method (JOHANSSON, 1984; SLEMR & SEILER, 1984). When applying this technique, an enclosure is placed over the surface of interest and the NO emission rate is derived from the increase of NO concentration in the headspace with time. However, in these experiments, NO mixing ratios increased only until a particular (equilibrium) level was approached. Adjusting the initial NO concentration in the headspace air to a value beyond this level resulted in a concentration decrease to reach the same equilibrium concentration. Evidently, the ambient (headspace) NO concentration determined whether a given soil acted as source or as sink for NO. Such a concentration controlled bi-directional exchange has meanwhile been established for a number of trace gases (CONRAD, 1994, 1996a,b). The equilibrium concentration at which the rate of NO production equals the rate of

NO consumption is commonly termed NO compensation concentration or 'compensation point'. More detailed information about the effect of ambient NO concentrations on direction and the magnitude of the rates of the NO exchange has been gained primarily in controlled laboratory experiments. Using dynamic (flow through) systems, the net NO flux can be determined while the NO concentration in the gas stream that flushes the enclosure is varied systematically. Positive fluxes at low mixing ratios change to negative fluxes (net deposition) at high NO mixing ratios. A similar behaviour was observed in a study with soil columns by JOHANSSON & GALBALLY (1984). On the basis of their observations, they proposed a model that treats NO production and NO consumption as two autonomous processes that occur simultaneously (GALBALLY & JOHANSSON, 1989). When plotting NO flux as a function of the NO concentration, the NO emission term is represented by the intercept with the y-axis; and the proportionality coefficient between NO uptake and NO concentration is given by the slope of the fitted regression line. The results obtained under four different soil temperature conditions in the course of a (simulated) day (LUDWIG et al., 1992; LUDWIG, 1994). NO emission rate (y-axis intercept) changed strongly with temperature while the uptake coefficient remained rather constant. Evidently, environmental control of NO production differs from that of NO consumption. It remains rather unclear whether the capability of soils to act as a sink for atmospheric NO is of major importance for the exchange of NO on a larger scale. Systematic investigations concerning the uptake of NO and its regulation are scarce and the range of previously observed compensation concentrations is extremely wide. Compensation concentrations of less than 1 ppb have been documented as well as values that exceed several hundred ppb (SLEMR & SEILER, 1984; REMDE et al., 1989; SLEMR & SEILER, 1991; KIM et al., 1994). Some of this data indicate that low compensation concentrations are associated with situations that are unfavourable for NO production processes. For example, compensation concentrations as low as 0.2–2 ppb were measured over unfertilized forest soils in Sweden, whereas values up to 170 ppb were found over fertilized soils at the same site (JOHANSSON, 1984). In all previous studies, average concentration of NO in the ambient air was found to be less than the compensation concentration; and consequently the mean net flux was directed from the surface to the atmosphere (mean net emission). However, a detailed inspection of published results reveals that a considerable number of field studies have encountered occasional events of net deposition (e.g., SLEMR & SEILER, 1984; JOHANSSON, 1984; DELANY et al., 1986; SLEMR & SEILER, 1991; LUDWIG & MEIXNER, 1994). This appears plausible considering that both ambient NO concentrations and compensation points may fluctuate strongly at a given site. It has to be stressed that, even at ambient mixing ratios below the compensation point, the consumption of NO will counterbalance the production to some extent and reduce the actual release of total biogenic NO into the atmosphere. In this context it is important to note that a lot of research on NO exchange has involved the use of a technique where NO is removed from the ambient air stream that flushes a dynamic enclosure ('zero-air' application; WILLIAMS et al., 1987; SHEPHERD et al., 1991; YAMULKI et al., 1995). Application of this technique definitely excludes any uptake of NO and thus may yield the potential (maximal) emission, but never the actual net flux of NO.

2.6.2. NO EMISSION RATES FROM DIFFERENT ECOSYSTEMS AND LAND USE TYPES

A recent, comprehensive compilation of available data was provided in tabular form by DAVIDSON & KINGERLEE (1997). DAVIDSON & KINGERLEE's basic (in 1997) classification scheme of ecosystems was cultivated land, forest, grassland/woodland, others. High emission fluxes of NO have also been reported from cultivated land and from tropical and subtropical grassland woodland. In contrast, forest soils may be regarded as minor sources of NO, except those forest soils in temperate regions which receive considerable N inputs (NH_3 , HNO_3 , NH_4^+ , NO_3^-) by wet and dry deposition. Other natural ecosystems, like wetlands and marshes, appear to be negligible with respect to the emission of NO. Some of the patterns in the emission data from different ecosystem classes can be related to characteristic differences in regulatory factors. Thus, the rough ranking of NO emission levels (fertilized agricultural fields > grasslands > forests > other natural systems) is in broad accordance with the N status of the corresponding soils (WILLIAMS et

al., 1992b). Soil water ('pulsing' effect) is a major parameter to explain the high NO emission flux that is indicated for savanna ecosystems. To some extent, this difference mirrors the influence of soil temperature, soil moisture and N availability on NO emission rates.

The general patterns outlined above have to be viewed in consideration of the broad range of variation of the data. Average NO fluxes reported in the literature for similar surfaces deviate by up to two orders of magnitude. For example, the mean value for rainy season emissions at different sites of the Venezuelan savanna region amounted to $0.64 \text{ ng N m}^{-2} \text{ s}^{-1}$ in one study (SANHUEZA et al., 1990) but to $56 \text{ ng N m}^{-2} \text{ s}^{-1}$ in another (JOHANSSON & SANHUEZA, 1988). The span between minimum and maximum values is even much larger and can range for a given ecosystem type from negative NO fluxes to emission rates higher than $100 \text{ ng N m}^{-2} \text{ s}^{-1}$. Some of this variation may be due to discrepancies in the techniques that were applied for determination of the NO exchange (FOWLER & DUYZER, 1989; MOSIER, 1989; MEIXNER, 1994). However, to a major part, the observed variability in NO flux rates is a consequence of spatial heterogeneities and temporal changes in the underlying processes and the environmental factors that control those processes. Even within a few meters of a seemingly uniform field site, the NO emission can differ by as much as a factor of 50 (WILLIAMS et al., 1988). However, micrometeorological techniques, capable to integrate NO net fluxes from a whole ecosystem, are in favour over small-scale enclosure techniques (MEIXNER, 1994).

The high level of NO emissions that is associated with the application of N fertilizers to cultivated lands demands some further consideration. WILLIAMS et al. (1988) pointed out soil emissions of NO from heavily fertilized areas can reach the same magnitude as the anthropogenic NO release in urban areas. This is primarily the case for a short period following fertilizer application; otherwise NO emissions are markedly lower during the major part of the season. Only few investigators have attempted to yield long-term information about the emission of NO from agricultural systems. The annual loss of NO derived from such studies was $0.7 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ for a fertilized ($218 \text{ kg N ha}^{-1} \text{ yr}^{-1}$) wheat field in Germany (LUDWIG, 1994) and $0.6 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ for fertilized ($200 \text{ kg N ha}^{-1} \text{ yr}^{-1}$) arable land in Sweden (JOHANSSON & GRANAT, 1984). The good agreement may be somewhat fortuitous, and one might conclude that those emissions of NO are of little agronomic importance. Recently, JAMBERT et al. (1997) published NO emissions of $12\text{--}52 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ for fertilized ($280 \text{ kg N ha}^{-1} \text{ yr}^{-1}$) and irrigated maize fields in southwestern France. There, the NO emissions correspond to 11.3% of the N input from fertilizer. In any case, emissions from agricultural sites cannot be ignored as a significant source of atmospheric NO. WILLIAMS et al. (1992a) estimated that agricultural land accounts for about 66% of the annual emission of NO from soils in the United States. Authors emphasized that NO emissions resulting from agricultural activities are commonly at a maximum when photochemical activity in the troposphere is also at a maximum 'ozone episodes'. Further concern about fertilizer induced emissions from agricultural soils arises from the fact that a continuous increase of this NO source has to be expected for the future (MATTHEWS, 1994). While use of N fertilizer has stabilized in Europe and Northern America, largely increasing consumption rates are reported from Asia, South America, and Africa. However, experimental data from some of the regions, which are of primary interest in this respect (e.g., the huge agricultural areas of China and the former U.S.S.R) are inadequate or completely lacking (YIENGER & LEVY, 1995).

The production of NO by soil microflora originates from two processes: nitrification, which is the oxidation of NH_4^+ to NO_2^- and NO_3^- , and denitrification, which is the anaerobic reduction of NO_3^- to gaseous forms of N (N_2O , N_2). The nitrification pathway predominates in temperate zones, accounting for 60–90% of total NO emissions (GÖDDE & CONRAD, 2000). NO is also produced by denitrification, but its diffusion to the soil surface is greatly reduced by the low gas diffusivity usually prevailing during denitrification episodes. It is thus likely to be reduced to N_2 under such anaerobic conditions. It was reported that topsoil WFPS was mostly below the threshold triggering denitrification (HÉNAULT et al., 2005), and the denitrification pathway was not taken into account. The production of NO depends on environmental and agronomic factors, including cropping practices, soil characteristics and climate sequence. The former determines

the dynamics of soil NH_4^+ content and thereby nitrification activity, while the latter influences soil temperature and WFPS, which is a proximate for soil O_2 concentration and a driver for gaseous diffusivity (DAVIDSON, 1993; THORNTON & VALENTE, 1996; ANEJA et al., 2001). The typical yield of NO in well aerated soil ranges from 0.29 to 4% of the NH_4^+ oxidized (HUTCHINSON & BRAMS, 1992; YIENGER & LEVY, 1995; GARRIDO et al., 2002; YAN et al., 2003; LAVILLE et al., 2005; STEHFEST & BOUWMAN, 2006). The vertical gradients and time course of water and N content may be abrupt in the topmost centimeters of soil, unlike in the deeper soil layers. Emissions may be therefore irregular too: large ‘pulses’ of NO fluxes, up to 10–100 times higher than background emissions, have been found (DAVIDSON et al., 1991; DAVIDSON, 1992, 1993; YIENGER & LEVY, 1995; LUDWIG et al., 2001). This implies that to simulate NO emissions, a finer modeling of the soil surface is necessary, such as in the case of the ISBA model for the prediction of evaporation affecting the crop growth after rainfall events, in mesoscale atmospheric transport models (NOILHAN & MAHFOUF, 1996).

Early models focused on the prediction of crop yields (JONES & KINIRY, 1986), but had a limited capability to predict soil processes. Several biogeochemical models have recently been introduced to simulate trace gas emissions from soils, such as DAYCENT (PARTON, et al. 2001), CASA Biosphere (POTTER, et al. 1996a,b), HIP (DAVIDSON et al., 2000), and DNDC (LI, 2000). Some of them were used to carry out NO inventories in Europe (LI, 2000; BUTTERBACH-BAHL et al., 2001; KESIK et al., 2005) and Australia (KIESE et al., 2005), where the PnET-NDNDC model was used with GIS databases. However, their simulation of crop yield and its relation to management practices is rather empirical. The crop and environmental model CERES-EGC (GABRIELLE et al., 2006a) offers a more balanced approach to the prediction of N gas emissions (N_2O , CO_2 , and NH_3), crop growth, and yields under a range of European agricultural conditions (GABRIELLE et al., 2002). It has also been used for regional inventories (GABRIELLE et al., 2006b).

2.7. EMISSION OF CO_2

JOLÁNKAI & BIRKAS (2005) mentioned that the climate change phenomena may be related to the rise in atmospheric CO_2 . Long-term rise in atmospheric CO_2 highlights crop production regarding both adaptation and mitigation (JOLÁNKAI et al., 2005). The gradual increase in atmospheric CO_2 concentration and potential climatic changes are likely to affect plant, soil and ecosystem processes, including carbon flux from plants to soil and from soil to atmosphere (PAJARI, 1995). In a typical forest ecosystem, the components of soil CO_2 efflux include respiration due to litter decomposition, root respiration, rhizo-microbial respiration, and microbial respiration utilizing native SOM (CHENG, 1999). Some researchers and planners argue (IPCC, 2000; LAL, 2004) that land use and soil management technologies are feasible options of reducing the net rate of increase of CO_2 abundance. For example, COX et al. (2000) observed that the biosphere will act as an overall C sink until about 2050, and will become a source thereafter when ocean will become a bigger sink at about 5 Pg C yr^{-1} . PACALA & SOCOLOW (2004) proposed 16 technological interventions to stabilize CO_2 abundance over the 50 year period between 2004 and 2054, each with a CO_2 -C sink capacity of 1 Pg C yr^{-1} . Three of the 16 options include: producing biomass feedstock for fossil fuel based on establishing biofuel plantations on 250 Mha to produce ethanol from lingo-cellulosic feedstock, reducing tropical deforestation to zero, and establishing 300 Mha of new tree plantations, and converting 1500 Mha of cropland soils from plow tillage to no-till farming. Despite the promise of stabilizing CO_2 concentration at less than doubling of the pre-industrial loads, there remain numerous uncertainties in biotic strategies of C sequestration. Uncertainties are due to the complexity of the climate system (LUMP, 2002) and numerous feedback mechanisms (COX et al., 2000).

BAYOUMI HAMUDA & KECSKÉS (2003) mentioned that the biological activity in a soil is usually evaluated by measuring CO_2 evolution. In sewage sludge amended soil with high level of Pb, Cd and Zn the CO_2 evolution was increased. Soil respiration and microbial biomass can be useful indicators of soil contamination, combining the two measurements to give amounts of CO_2 evaluated per unit of biomass ($\mu\text{g CO}_2\text{-C/g soil}$). GRÖNLUND et al. (2008) reported that drainage and cultivation of peat soils stimulates SOM mineralization, which substantially

increases CO₂ emissions from soils. Large uncertainties are associated with this CO₂ flux, and little data are available, especially in Norway. Subsidence of cultivated peat soils averaged about 2.5 cm² yr⁻¹. Authors estimated that peat loss and compaction were respectively responsible for 38% and 62% of the total subsidence during a 25 year period after drainage. Based on this estimate the corresponding C loss equals 0.80 kg C m⁻² yr⁻¹. The observed increase in mineral concentration of the topsoil of cultivated peat is proportional to their C loss, providing no mineral particles other than lime and fertilizers are added to the soil. Using this novel approach across 11 sites, authors estimated a mean C loss of 0.86 kg C m⁻² yr⁻¹. Soil CO₂ flux measurements, corrected for autotrophic respiration, yielded a C loss estimate from cultivated peat soils of 0.60 kg C m⁻² yr⁻¹. The three methods yielded fairly similar estimates of C losses from Norwegian cultivated peat lands. Cultivated peat lands in Norway cover an estimated 63,000 ha. Total annual C losses from peat degradation were estimated to range between 1.8 and 2 million tons CO₂ yr⁻¹, which equals about 3–4% of total anthropogenic GHG emissions.

LAL (2008) and SMITH (2008) mentioned that there is an urgent need to identify strategies of stabilizing atmospheric concentration of CO₂, responsible for 62% of the radiative forcing of Earth by long-lived GHG, at less than doubling of the pre-industrial concentration of 280 ppm. For about 10,000 years before 1750, CO₂ concentration was about 280 ppm. Since the late 1700s, the CO₂ abundance has increased progressively and reached 377 ppm in 2004 with an overall increase of about 35% (WMO, 2006). The CO₂ concentration is currently increasing at the rate of 1.9 ppm yr⁻¹ or 0.47% yr⁻¹ (WMO, 2006). This increase is attributed to two principal sources: land use conversion and deforestation, and fossil fuel combustion. The impact of land use conversion and agricultural activities on CO₂ abundance began with the onset of settled agriculture about 10,000 years ago (RUDDIMAN, 2003). CO₂ emissions due to land use conversion and deforestation intensified with the clearance of Northern Hemisphere forests in the 19th century. Emissions were exacerbated by deforestation of tropical rainforests (TRF) during the 20th century. It is estimated that 350 Mha of TRF were deforested and another 500 Mha of secondary and primary tropical forests were degraded (LAMB et al., 2005) with substantial CO₂ emission to the atmosphere. Rapid expansion of agriculture during the 20th century, to meet the food demands of increase in world's population, also accentuated the release of CH₄ from rice paddies and livestock, and N₂O from fertilized croplands. Consequently, abundance of CH₄ increased from a pre-industrial level of 700 ppb to 1783 ppb in 2004, and is currently increasing at the rate of about 5 ppb yr⁻¹ or 0.28% yr⁻¹. N₂O abundance increased from a pre-industrial level of 270 ppb to 319 ppb in 2004, and is currently increasing at the rate of 0.8 ppb yr⁻¹ or 0.22% yr⁻¹ (WMO, 2006). Deforestation and land use conversion presently contribute 0.6 to 2.5 Pg C yr⁻¹. In contrast, fossil fuel combustion emits ~7 Pg C yr⁻¹ (WMO, 2006).

LAL (2008) stated that world soils and terrestrial ecosystems have been a source of atmospheric abundance of CO₂ ever since settled agriculture began about 10–13 millennia ago. The amount of CO₂-C emitted into the atmosphere is estimated at 136 ± 55 Pg from terrestrial ecosystems, of which emission from world soils is estimated at 78 ± 12 Pg. Conversion of natural to agricultural ecosystems decreases SOC pool by 30–50% over 50–100 years in temperate regions, and 50–75% over 20–50 years in tropical climates. The projected global warming, with estimated increase in mean annual temperature of 4–6°C by 2100, may have a profound impact on the total soil C pool and its dynamics. The SOC pool may increase due to increase in biomass production and accretion into the soil due to the so-called CO₂ fertilization effect, which may also enhance production of the root biomass. Increase in weathering of silicates due to increase in temperature, and that of the formation of secondary carbonates due to increase in partial pressure of CO₂ in soil air may also increase the total C pool.

In contrast, however, SOC pool may decrease because of: increase in rate of respiration and mineralization, increase in losses by soil erosion, and decrease in protective effects of stable aggregates which encapsulate OM. Furthermore, the relative increase in temperature projected to be more in arctic and boreal regions, will render Cryosols under permafrost from a net sink to a net source of CO₂ if and when permafrost thaws. Thus, SOC pool of world soils may decrease with increase in mean global temperature. In contrast, the biotic pool may increase primarily

because of the CO₂ fertilization effect. The magnitude of CO₂ fertilization effect may be constrained by lack of essential nutrients (e.g., N, P) and water. The potential of SOC sequestration in agricultural soils of Europe is 70–190 Tg C yr⁻¹. This potential is realizable through adoption of recommended land use and management, and restoration of degraded soils and ecosystems including wetlands (LAL, 2008). Aerobic soils may act as a sink for atmospheric CH₄ through oxidation by methanotrophic bacteria (TOPP & PATTEY, 1997; LE MER & ROGER, 2001). This oxidation has been estimated to be 30 ± 15 Tg CH₄ yr⁻¹ of the total atmospheric loading of 598 Tg CH₄ yr⁻¹ (IPCC, 2001a,b). Whilst much is known about aboveground plant responses to increasing atmospheric concentrations of CO₂, comparatively little information is available on soil process responses. There is uncertainty about the effect of elevated pCO₂ on the processes of nitrification and resulting emissions of N₂O from soils.

As a practical manner to improve soil fertility, amendment of local organic residues has been gaining worldwide support. Incorporation of crop residues provides a source of readily available C and N in the soil, and subsequently influences the CO₂ and N₂O emissions (FLESSA & BEESE, 1995; COCHRAN et al., 1997; LEMKE et al., 1999). ROBERSON et al. (2008) found that an increased CO₂ release from soils resulting from agricultural practices such as tillage has generated concerns about contributions to global warming. Maintaining current levels of soil C and/or sequestering additional C in soils are important mechanisms to reduce CO₂ in the atmosphere through production agriculture. The authors conducted a study in northern Alabama from 2003 to 2006 to measure CO₂ efflux and C storage in long-term tilled and non-tilled cotton plots receiving poultry litter or NH₄NO₃. Treatments were established in 1996 on a Decatur silt loam and consisted of conventional-tillage (CT), mulch-tillage (MT), and no-tillage (NT) systems with winter rye cover cropping and NH₄NO₃ and poultry litter (PL) as N sources. Cotton was planted in 2003, 2004, and 2006. Corn was planted in 2005 as a rotation crop using a no-till planter in all plots, and no fertilizer was applied. Poultry litter application resulted in higher CO₂ emission from soil compared with NH₄NO₃ application regardless of tillage system. In 2003 and 2006, CT (4.39 and 3.40 μmol m⁻² s⁻¹, respectively) and MT (4.17 and 3.39 μmol m⁻² s⁻¹, respectively) with PL at 100 kg N ha⁻¹ (100 PLN) recorded significantly higher CO₂ efflux compared with NT with 100 PLN (2.84 and 2.47 μmol m⁻²s⁻¹, respectively). In general, cotton produced with NT conservation tillage in conjunction with PL and winter rye cover cropping reduced CO₂ emissions and sequestered more soil C compared with control treatments. It is involved in O₃ decomposition in the stratosphere and exerts a significant greenhouse effect with a global warming potential 320 relative to CO₂ (KESTER et al., 1996).

AL-KAISI et al. (2008) mentioned that N application can have a significant effect on soil C pools, plant biomass production, and microbial biomass C processing. In the corn year, season-long cumulative soil CO₂ emission was greatest with the zero N application. There was no effect of N applied in the prior year on CO₂ emission in the soybean year, except at one of three sites, where greater applied N decreased CO₂ emission. Soil CO₂ emission from aerobically incubated soil showed a more consistent declining trend with increase in N rate than found in the field. N fertilization of corn reduced the soil CO₂ emission rate and seasonal cumulative loss in two out of three sites, and increased microbial biomass carbon (MBC) at only one site with the highest N rate. N application resulted in a reduction of both emission rate and season-long cumulative emission of CO₂-C from soil.

UPENDRA et al. (2008) stated that the management practices can influence soil CO₂ emission and C content in cropland, which can effect global warming. Authors mentioned that irrigation increased CO₂ flux by 13% compared with non-irrigation by increasing soil water content in North Dakota. Tillage increased CO₂ flux by 62 to 118% compared with no-tillage places. The flux was 1.5- to 2.5-fold greater with tilled than with non-tilled treatments following heavy rain or irrigation in North Dakota and 1.5- to 2.0-fold greater with crops than with fallow following substantial rain in Montana. N fertilization increased CO₂ flux by 14% compared with no N fertilization in North Dakota and cropping increased the flux by 79% compared with fallow in no-till and 0 kg N ha⁻¹ in Montana. Although soil C content was not altered, management practices influenced CO₂ flux within a short period due to changes in soil temperature, water,

and nutrient contents. LEMKE et al. (2007) mentioned that agricultural activities are an important source of anthropogenic GHGs, contributing ~20% of the annual atmospheric increase. Management choices largely determine if agricultural soils will be a source, a sink, or will be neutral with respect to GHG net flux. The proportion of agricultural land that is seeded to pulse crops in the Northern Great Plains (NGP) region of North America has been increasing rapidly over the past decade. Introducing pulses into cereal-based cropping systems could influence the net GHG balance of those systems because pulse crops are thought to stimulate soil-emitted N₂O, have different pesticide and fertilizer requirements, and the quality and quantity of their residues vary substantially compared with cereal crops. The authors briefly review the available literature, and discuss the potential impact of pulse crops on the net flux of CO₂ and N₂O from soils, and the CO₂ emissions associated with energy inputs for cropping systems in the NGP. Authors calculated the net GHG balances for two example sites. Estimating the final GHG outcome of introducing pulses into cereal-based cropping systems is still uncertain, but current information suggests that replacing a cereal with a pulse crop will likely result in no change or a small but positive net GHG benefit for crop rotations in the NGP region.

KERR (2005) mentioned that concentrations of atmospheric GHG, such as CO₂, and N₂O, which can alter the earth's climate, have risen dramatically during the past century. This has resulted in an urgent need for process-based understanding of the main factors influencing the exchange of these gases between the land and atmosphere at a range of scales as a route to developing effective mitigation technologies. Natural boreal peat lands usually act as sink for CO₂. In general, they are small sink for N₂O. Drainage of these soils can lead to major changes in the gas fluxes. After drainage, decomposition of OM increases and the sites may turn into net sources of CO₂ emissions. Cultivated peat soils are major sources of N₂O (KASIMIR-KLEMEDTSSON et al., 1997).

GESTEL et al. (1991) from the magnitude of the flushes of CO₂ and ¹⁴CO₂ after the various combinations of treatments, and from their specific activities, authors have deduced that microbial cells killed by soil desiccation had made only a minor contribution to the C and N mineralization flushes after soil rewetting and incubation. The larger contribution had come from other sources, the relative importance of which appears to be influenced by soil characteristics, possibly CEC, and microporosity. MARJA et al. (2002) measured the short-term changes in flux of N₂O with an automatic opaque chamber method in boreal organic soils growing barley, grass or birch and on bare agricultural organic soil. The diurnal variation in these gas fluxes was compared with that of CO₂ production which is known to be highly temperature-dependent. Here, the mean daytime (10:00–16:00) CO₂ production rates was 14-23% higher than the mean daily fluxes. The Q₁₀ (air temperature range 15–25°C) for the CO₂ production was 1.5 in the agricultural soils and 1.3 in the forest. The N₂O fluxes followed the changes in the temperature of the surface soil (depth of 3 cm) in the agricultural soils. The maximum emission occurred in the afternoon, a few hours later than the maximum air temperature and CO₂ production. MERINO et al. (2004) revealed that soil respiration has received considerable attention in recent years because of the release of large quantities of CO₂ from the soils to the atmosphere. Changes in land use and soil management practices (tillage, use of fertilizers, organic residues, pesticides) induce changes in soil OC, and are largely responsible for increases in atmospheric CO₂ from terrestrial ecosystems (BOUWMAN, 1990). Less intensive management improves biological properties (EMMERLING et al., 2001) and conversion of agricultural land to forest usually results in considerable gains in SOC and reductions in CO₂ fluxes (PAUL et al., 2002, MERINO et al., 2004).

AUSMUS et al. (2004) studied the smelter emissions and contaminated litter were applied to intact forest microcosms to determine effects of heavy metals on soil C metabolism. It was found that heavy metals increased daily CO₂ efflux rates and cumulative gaseous C loss. In addition, seasonal patterns of CO₂ efflux rates were altered. Soil bacterial density was significantly increased at the expense of soil fungal biomass. Non-destructive monitoring of CO₂ efflux provided an early indicator of smelter emission effects on soil biota. Effects on C metabolism may be detected prior to effects on communities or populations within chemically

contaminated ecosystems. On a global scale, CO₂ is the most important greenhouse gas contributing to global warming (LAL *et al.* 1995). Despite the fact that soils are an important source of CO₂, only a few studies have determined NI effects on soil CO₂ emissions. WEISKE *et al.* (2001) suggested that 3,4-dimethylpyrazole phosphate (DMPP) may reduce soil CO₂ emissions.

2.7.1. MEETING ATMOSPHERIC CO₂ CONCENTRATION STABILIZATION TARGETS

KITZLER *et al.* (2006) mentioned that CO₂ emissions, a measure for general microbial activity, followed a typical seasonal trend, with highest rates in summer, when mineralization of OM occurs. Lowest rates were measured in winter. OC is converted to CO₂ during mineralization. This process is strongly dependent on soil temperature and soil moisture. Soil temperature at a soil depth of 3 and 10 cm was mostly responsible for temporal variation in soil respiration. This finding is in good agreement with results from other studies (EPRON *et al.*, 1999; MERINO *et al.*, 2004). Soil moisture also showed a significant effect on soil respiration rates. CO₂ release was reduced during periods of heavy rain (summer 2002), when the water content was between 50–65%, probably as a consequence of O₂ deficiency in soil due to diffusion restrictions (HOWARD & HOWARD, 1993). The cumulative soil respiration rates at investigated site are lower than values for temperate coniferous forests reported by RAICH & SCHLESINGER (1992).

KÁTAI *et al.* (2005) realized that the maximum amount of CO₂ production was found in the meadow chernozem, marshy meadow and brown forest soil, while the maximum amount of microbial biomass C was recorded in the meadow solonetz soil. VAGÓ *et al.* (2005) found that the total number of microbes and the CO₂ production slightly increased in both investigated soils compared to the control. The treatments significantly increased the microbial biomass values. The total number of bacteria in the typical meadow soil was 1.5–2 times higher than that in the calcareous chernozem soil.

GRÖNLUND *et al.* (2008) mentioned that C loss from cultivated peat-land is a significant source for GHG emission in Norway. Cultivation of peat soils stimulates SOM mineralization, which substantially increases CO₂ emissions from soils. SMITH (2008) mentioned that since soils contain more than twice the C found in the atmosphere, loss of C from soils can have a significant effect of atmospheric CO₂ concentration, and thereby on climate. Halting land-use conversion would be an effective mechanism to reduce soil C losses, but with a growing population and changing dietary preferences in the developing world, more land is likely to be required for agriculture. The current annual emission of CO₂-C to the atmosphere is $6.3 \pm 1.3 \text{ Pg C y}^{-1}$ ($1 \text{ Pg} = 1 \text{ Gt} = 10^{15} \text{ g}$). C emission gaps by 2100 could be as high as 25 Pg C y^{-1} meaning that the C emission problem could be up to four times greater than at present. The maximum annual global C sequestration potential is about $0.4\text{--}0.7 \text{ Pg C y}^{-1}$ (SMITH *et al.*, 2007) meaning that even if these rates could be maintained until 2100, soil C sequestration would contribute a maximum of about 1–3% towards reducing the C emission gap under the highest emission scenarios. The limited duration of C sequestration options in removing C from the atmosphere. C sequestration could play only a minor role in closing the emission gap by 2100. It is clear that if authors wish to stabilize atmospheric CO₂ concentrations by 2100, the increased global population and its increased energy demand can only be supported if there is a large-scale switch to non-C emitting technologies in the energy, transport, building, industry, agriculture, forestry and waste sectors (IPCC WGIII, 2007). This demonstrates that soil C sequestration alone can play only a minor role in closing the C emission gap by 2100. Nevertheless, if atmospheric CO₂ levels are to be stabilized at reasonable concentrations by 2100 (e.g. 450–750 ppm), drastic reductions in emissions are required over the next 20–30 years (IPCC, 2000b; IPCC WGIII, 2007). During this critical period, all measures to reduce net C emissions to the atmosphere would play an important role—there will be no single solution (IPCC WGIII, 2007). IPCC WGIII (2007) showed that there is significant potential for GHG mitigation at low cost across a range of sectors, but for stabilization at low atmospheric CO₂/GHG concentrations, strong action needs to be taken in the very near future, echoing the findings of the Stern Review (STERN, 2006). Given that C sequestration is likely to be most effective in its first 20 years of implementation, it should form a central role in any portfolio of measures to reduce atmospheric

CO₂ concentrations over the next 20–30 years whilst new technologies, particularly in the energy sector, are developed and implemented (SMITH, 2004). KIESE & BUTTERBACH-BAHL (2002) established that CO₂ emission rates were positively correlated to changes in WFPS at dry to moderate soil water contents during the dry season, but were negatively correlated to changes in WFPS during the wet season.

2.7.2. ACTIVITIES ON THE UTILIZATION OF CARBON DIOXIDE

SHARMA et al. (2006) found that CO₂ emission fluxes ranged from 18.1 mg C m⁻² h⁻¹ to 131.6 mg C m⁻² h⁻¹. The peak flux was up to 217.7 mg C m⁻² h⁻¹ in a watered chamber. The lower CO₂ emissions at the investigated soil site may be explained by a smaller contribution of plant root autotrophic respiration and a shift in C quality towards more resistant C pools as a consequence of human management, e.g., logging and burning (inert C). The magnitude of soil CO₂ emissions is in good agreement with previous measurements for other tropical rainforest soils. LA SCALA et al. (2000), KIESE & BUTTERBACH-BAHL (2002), ISHIZUKA et al. (2002) and RAICH (1998) reported CO₂ emissions from tropical forest floors as 54.4–107.2, 24.0–247.7, 51.3–93.7 and 41.7–125.0 mg C m⁻² h⁻¹, respectively. ISHIZUKA et al. (2002) found no clear relationship between CO₂ emissions and soil moisture. Many researchers have proven the anthropogenic effect of CO₂ in the atmosphere. The concentration of CO₂ is more than 64% (CHOI & CHO, 2008) effective among the global warming gases and the most responsible for global climate change. This global warming will possibly induce many tragic catastrophes such as depletion of the O₃ layer, and changing ocean currents. After considering the increasing scientific evidence, many researchers and politicians have realized the serious nature of the global warming problem and suggested many counter-measurements. Nevertheless, many countries still use large amounts of fossil fuels, and therefore, inevitably emit 6 GtC yr⁻¹. It has been proven that the concentration of CO₂ in the atmosphere per year is continuously increasing. Therefore, the role of most organizations relating to the energy and environmental issue now is to significantly highlight various kinds of policy and technical strategies for mitigation of global warming gases emitted from fossil-fuel energy based industries worldwide are encourage discussion in order to adopt some of each nation's national policies. CO₂ is known to have the highest global warming potential among global warming gases, in view of large amounts of its emission from the agricultural lands, industry, fossil fuel power plants and petrochemical industry worldwide. Thus, three kinds of mitigation technology are undergoing significant consideration: Reduction of fossil fuel energy consumption from related industries. Replacement of fossil fuel energy by renewable energy sources. Efficient utilization of CO₂ as a clean carbon raw material for C market products. CO₂ is thermodynamically stable with very low energy levels since it is formed from fossil-fuel derived C market products. However, CO₂ can be converted to some hydrocarbons with the aid of a proper agent such as H₂. The separation technologies for the recovery of CO₂ from emission sources include its absorption, adsorption, membrane and hybrid technologies, which combined with absorption and membrane or pressure swing adsorption, provide powerful recovery methods. During this period, the catalytic chemical conversion of CO₂ was also carried out fundamentally in order to produce methanol, dimethyl ether (DME) and hydrocarbons with a target of producing synthetic fuels. In addition, biological fixation and utilization were also carried out for the production of useful materials such as micro-algae derived animal food ingredients, in view of the utilization or mitigation of CO₂ emitted. Electrochemical and photochemical fixation and utilization also were accomplished under a program of separation and utilization of CO₂, funded by a government scientific plan. Technological trials in sequestration and storage of CO₂ in forests and sea dumping were also accomplished with the development of detection technologies for climate changes including defense strategies against global climate change and related technologies all over the world. Technological characteristics for various chemicals *via* efficient utilization of CO₂: Synthesis of methanol and DME from CO₂, synthesis of hydrocarbons to be utilized as α -olefins and heavy fractions such as wax from CO₂, formation of carbonate from CO₂, technology for application

of CO₂ as an oxidizing agent, utilization and conversion of CO₂ by photo-catalysts, and bioconversion technology with biomass.

2.8. IMPACTS OF HEAVY METALS ON TRACE GASES EMISSIONS

Heavy metals are elements having atomic weight between 63.54 and 200.59, and a specific gravity greater than 4 (KENNISH, 1992). Trace amount of some heavy metals are required by living organisms, however any excess amount of these metals can be detrimental to the organisms (BERTI & JACOBS, 1996). Non-essential heavy metals include arsenic, antimony, cadmium, chromium, mercury, lead, etc; these metals are of particular concern to surface water and soil pollution (KENNISH, 1992). Heavy metals exist in colloidal, ionic, particulate and dissolved phase. These metals also have a high affinity for humic acids, organo-clays, and oxides coated with OM (ELLIOT et al., 1986, CONNELL & MILLER, 1984). The soluble forms are generally ions or unionized organo-metallic chelates or complexes. The solubility of metals in soil and groundwater is predominantly controlled by pH (HENRY, 2000, BAKER & WALKER, 1990, McNEIL & WARING, 1992), amount of metal (GAREIA, 1984), cation exchange capacity (MARTINEZ & MOTTO, 2000), OC content (ELLIOT et al., 1986), the oxidation state of the mineral components, and the redox potential of the system (CONNELL & MILLER, 1984). In general, soil pH seems to have the greatest effect of any single factor on the solubility or retention of metals in soils. With a greater retention and lower solubility of metal cations occurring at, high soil pH (BASTA et al., 1993). Under the neutral to basic conditions typical of most soils, cationic metals are strongly adsorbed on the clay fractions and can be adsorbed by hydrous oxides of iron, aluminium, or manganese present in soil minerals. Elevated salt concentration creates increased competition between cations and metals for binding sites. Also competitive adsorption between various metals has been observed in experiments involving various solids with oxide surfaces, in several experiments, Cd adsorption was decreased by the addition of Pb or Cu (BENJAMIN & LECKIE, 1980).

Heavy metals are released into the environment from a wide range of natural and anthropogenic sources. The rate of influx of these heavy metals into the environment exceeds their removal by natural processes. Therefore there is attendance of heavy metals accumulating in the environment. KAKAREKA et al. (2004) evaluated the Cd and Pb emission into the atmosphere in ambient air over vast parts of Eurasia-territories of the former Soviet Union now called New Independent States (NIS). Total Cd emissions into the atmosphere from determined source categories were estimated as 388.4 tons in 1990 for the whole domain with reduction by up to 207.0 tons yr⁻¹ for 1997. Pb emission amounted to 24903 tons in 1990 and 9652.5 tons in 1997. It was mentioned that the obtained results can be used for global and regional air pollution modeling activity as well as for integrated assessment and projection of emissions in the territory of the former Soviet Union.

BENAVIDES et al. (2005) mentioned that heavy metals are important environmental pollutants and their toxicity is a problem of increasing significance for ecological, evolutionary, nutritional, and environmental reasons. Environmental pollution by metals became extensive as mining and industrial activities increased in the late 19th, 20th and 21st century. The current worldwide mine production of Cu, Cd, Pb, and Hg is considerable (PINTO et al., 2004). These pollutants, ultimately derived from a growing number of diverse anthropogenic sources (industrial effluents and wastes, urban runoff, sewage treatment plants, boating activities, agricultural fungicides runoff, domestic garbage dumps, and mining operations), have progressively affected more and more different ecosystems (MACFARLANE & BURCHETT, 2001). Metal toxicity and tolerance in plants is a subject that has been broadly reviewed on several occasions over the last 30 years (BROWN & JONES, 1975; FOY et al., 1978; ERNST et al., 1992; DAS et al., 1997; SANITÁ DI TOPPI & GABRIELLI, 1999; HALL, 2002; CLEMENS et al., 2002). Fifty-three of the ninety naturally occurring elements are heavy metals (WEST, 1984). Among these metals, Fe, Mo and Mn are important as micro-nutrients, while Zn, Ni, Cu, Co, Va and Cr are toxic elements, with high or low importance as trace elements. Ag, As, Hg, Cd, Pb and Sb have no known function as nutrients and seem to be more or less toxic to plants and microorganisms

(NIESS, 1999). The presence of both essential and non-essential heavy metals in the atmosphere, soil and water, in excessive amounts, can cause serious problems to all organisms. Knowledge of metal-plant interactions is important for the safety of the environment, but also for reducing the risks associated with the introduction of trace metals into the food chain.

The toxicity produced by transition metals generally involves neurotoxicity, hepatotoxicity and nephrotoxicity (STOHS & BAGCHI, 1995). Differences in solubility, absorbability, transport and chemical reactivity in these metals will lead to specific differences in toxicity within the body (STOHS & BAGCHI, 1995). The chemical form of heavy metals in soil solution is dependent of the concentration, pH and the presence of other ions (DAS et al., 1997). The bioavailability of some metals is limited because of low solubility in oxygenated water and strong binding to soil particles. Both the acidification of the rhizosphere and the exudation of carboxylates are considered potential targets for enhancing metal accumulation (CLEMENS et al., 2002). The degree to which higher plants are able to take up Cd depends on its concentration in the soil and its bioavailability, modulated by the presence of OM, pH, redox potential, temperature and concentrations of other elements. With exception of Fe, which is solubilized by either reduction to Fe (II) or extrusion of Fe(III)-chelating phytosiderophores (HIRSCH et al., 1998).

Heavy metals are known to influence the activity of soil microbial communities, altering the conformation of enzymes, blocking essential functional groups or by exchanging with essential metal ions (TYLER, 1981). Numerous studies have demonstrated that heavy metals affect soil respiration, soil biomass, N mineralization and nitrification (BÄATH, 1989; GILLER et al., 1998). Studies focussing on denitrification and the production of N₂O have indicated that denitrification might be inhibited by heavy metals (BARDGETT et al., 1994; GUMEALIUS et al., 1996; SAKADEVAN et al., 1999; HOLTAN-HARTWIG et al., 2002). A general inhibition of denitrification may be conceived as a minor problem, as seen from an agronomic point of view. However, the different steps in the reduction of NO₃⁻ to N₂ appear to differ in their heavy metal tolerance (HOLTAN-HARTWIG et al., 2002). A selective inhibition of nitrite reductase could result in the accumulation of NO₂⁻ to toxic concentrations. A selective inhibition of N₂O reductase would enhance N₂O emission from soils.

VÁSQUEZ-MURRIETA et al. (2006) found a significant negative correlation between production rates of CO₂ and concentrations of As, Pb, Cu and Zn, and there was a significant positive correlation with pH, WHC, total N and SOC. There was a significant negative correlation between production rate of N₂O attributed to nitrification by the inhibition method in soil incubated at 50% WHC and total concentrations of Pb and Zn, and there was a significant positive correlation with pH and total N content. There was a significant negative correlation between the production rate of N₂O attributed to denitrification by the inhibition method in soil incubated at 100% WHC and total concentrations of Pb, Cu and Zn, and a significant positive correlation with pH; there was a significant positive correlation between the production of N₂O attributed to other processes by the inhibition method and WHC, inorganic C and clay content. A negative value for production rate of N₂O attributed to nitrifier denitrification by the inhibition method was obtained at 100% WHC. The large concentrations of heavy metals in soil inhibited microbial activity and the production rate of N₂O attributed to nitrification by the inhibition method when soil was incubated at 50% WHC and denitrification when soil was incubated at 100% WHC. BARTHA et al. (2005) found that in plants, NO has multiple roles in defense reactions under abiotic stresses, including heavy metal load. Literature data suggest that there is a causal relationship between NO and Fe metabolism but the effects of essential micronutrients/toxic heavy metals on NO production have not been investigated. Authors indicated that NO production was measured in the root tips, using 4,5 diamino fluorescein diacetate, a specific dye to NO. Also, they obtained different NO levels with the different heavy metal load: the most effective metal were Cu and Cd, in this case the NO production became double after one week treatment. In case of Cu load, two-phase kinetics was found: a fast NO burst in the first six hours was followed by a slower, gradual increase. After long-term treatment, NO levels were inversely related to the NO₂⁻ concentrations originated from NO₃ reductase activity suggesting the conversion of NO₂⁻ to NO by the known enzymatic ways.

DEVANEY et al. (2008) described an investigation into the bioavailability and fate of trace metals and their subsequent impact on important soil microbiological functions such as nitrification, denitrification and methane oxidation in low and high Cu containing soils in the presence and absence of residual OM from sewage sludge additions made 10 years earlier. The soils being studied are part of a long term sewage sludge trials and include a low Cu soil (13.3 mg Cu/kg soil), left un-amended to serve as a control soil, soil amended with a high Cu sewage sludge (278.3 mg Cu/kg soil) and soil amended with a low Cu sewage sludge (46.3 mg Cu/kg soil). Low soil Cu levels may stimulate an increase in the emission of N_2O to the atmosphere as the conversion of N_2O to N_2 is catalyzed by the enzyme N_2O reductase. This enzyme is a Cu-enzyme and its activity is dependent on the availability of Cu (GODLEY, 2003). Under Cu limiting conditions, the amount of the enzyme produced and its activity may become reduced, thus the reduction of N_2O to N_2 may become affected releasing more N_2O to the atmosphere. The uptake of CH_4 by soils from the atmosphere by CH_4 oxidizing bacteria may also be compromised in soils with low available Cu. Certain methanotrophic bacteria produce the enzyme CH_4 mono-oxygenase (MMO), allowing them to use CH_4 as an energy source. STANLEY et al. (1983) have shown that methanotrophic bacteria do not produce pMMO when grown in the absence of Cu. Although the overall impact of most parameters affecting these processes is largely known, the fine details, for example how the heavy metals affects denitrification, nitrification and emission rates are still insufficiently understood. Soils are major sources for the production of N_2O and NO , which are by-products or intermediate products of microbial nitrification and denitrification processes (BREMNER & BLACKMER, 1981; YIENGER & LEVY, 1995; MOSIER & KROEZE, 2000). N_2O mainly produced by nitrification, denitrification and nitrifier denitrification (WRAGE et al., 2001, 2004). Also, other biological processes involved in the N_2O emission. Each of these processes, and N_2O emission might affected by heavy metals.

Little information is currently available concerning the impact of increased heavy metal concentrations on the generation of trace gases (SAKADEVAN et al., 1999; HOLTAN, et al., 2002). VÁSQUEZ-MURRIETA et al. (2006) mentioned that there was a significant negative correlation between production rates of CO_2 and concentrations of Pb. The fertilizer and manure substituting employment of sewage sludge and compost amended sewage sludge means new opportunities in agriculture. Heavy metals known to influence the activity of soil microbial communities, that, affecting the soil respiration, soil biomass, N mineralization and nitrification (GILLER et al., 1998).

PROBANZA et al. (1996): studied the toxicity of Cd, Zn and Cu, in a Mediterranean soil. The soil was incubated (108 h) with mixed solutions of those metals before evaluating denitrification and CO_2 production, both by gas chromatography. These activities were used as biological indicators of heavy metal toxicity, and compared to non-treated control soil samples. Statistical analyses showed no significant differences in CO_2 production between treated and non-treated control soils. The lowest levels of respiration were observed in soils treated with the largest amounts of Zn and Cd. Denitrification increased significantly in soils treated with solutions containing 100 micrograms/ml of Cu and 1000 micrograms/ml of Cd or Zn.

2.8.1. CADMIUM INFLUENCED EMISSION RATES OF TRACE GASES

In general, Cd is non-essential element that negatively affects plant growth and development. Cd has been interfering with the uptake, transport and use of several elements (Ca, Mg, P and K) and water by plants (DAS et al., 1997). Cd also reduced the absorption of NO_3^- and its transport from roots to shoots, by inhibiting the nitrate reductase activity in the shoots (HERNANDEZ et al., 1996). Several studies have suggested that an oxidative stress could be involved in Cd toxicity, by either inducing O free radical production, or by decreasing enzymatic and non-enzymatic antioxidants (STOHS & BAGCHI, 1995; CHO & SEO, 2004). Cd is released into the environment by power stations, heating systems, metal-working industries or urban traffic. It is widely used in electroplating, pigments, plastic stabilizers and Ni-Cd batteries (SANITÁ DI TOPPI & GABRIELLI, 1999). Cd can alter the uptake of minerals from the soil, or through a reduction in

the population of soil microbes (MORENO et al., 1999). Cd is adsorbed to soil but to a much lesser extent than most other heavy metals. Soil pH is the principal factor governing the concentration of Cd in the soil solution. Cd adsorption to soil particles is greater in neutral or alkaline soils than in acidic ones and this leads to increased Cd levels in the soil solution.

2.8.2. EFFECT OF LEAD ON EMISSION RATES OF TRACE GASES

Lead (Pb) has been used worldwide since ancient time for its malleability, resistance to corrosion, and low melting point. The background concentrations of Pb in uncontaminated soil lie within the range of 10-50 ppm; however, in the soil with low-level contamination, Pb concentration can be expected to range from 30 to 100 mg/kg (McLAUGHLIN et al., 1999, DAVIES, 1990). With rapid development in industry all around the world since the 20th century, the inputs of Pb to agricultural soils have been occurring through the combustion of gasoline containing Pb additives, the fugitive emissions from nonferrous metal, the widespread uses of fertilizers, herbicides, and pesticides, and the additions of sewage sludge to the soil, etc. (MERRY et al., 1983, STEFFENS, 1990). Pb is one of the most abundant hazardous heavy metal pollutants of the environment that originates from various sources like mining and smelting of lead-ores, burning of coal, effluents from storage battery industries, automobile exhausts, metal plating and finishing operations, fertilizers, pesticides and from additives in pigments and gasoline (EICK et al., 1999). Its increasing levels in soil environment inhibit germination of seeds and exert a wide range of adverse effects on growth and metabolism of plants (GODBOLD & KETTNER, 1991, MOUSTAKAS et al., 1994, KASTORI et al., 1992).

According to National Academy of Sciences of the United States, in the US alone, nearly 200 000 tones of Pb were consumed annually as a gasoline anti-knock agent in the mid-1970s (NATIONAL ACADEMY OF SCIENCES, 1972). As a result, the Pb concentrations in agricultural soil increased rapidly in many areas around the world, and the accumulations of Pb in surface soils exposed to various pollution sources at some sites have already reached values of about 2% of dry soil material (KABATA-PENDIAS & PENDIAS, 1984, CHEN et al., 1999).

Owing to industrial development and population expansion, the concentrations of heavy metals in agricultural soils have also become increasingly serious in China (LI et al., 2000, JI et al., 2000). Average Pb concentrations of agricultural soils of the Pearl River Delta, South China, show more than 20% higher than that in natural soils and two times higher in some sites (WONG et al., 2000). In Shenyang, the heavily industrialized city, North China, the Pb concentration in soil had doubled in 1987 than in 1960s (BOYLE et al., 1999).

Pb is toxic to many organ systems of human body, such as the central and peripheral nervous system, the red blood cells, the kidneys, the cardiovascular systems, and the male and female reproduction organs (TODD et al., 1996). Pb can decrease sperm counts and increase prevalence of morphologically abnormal sperm in male, and increase risk of miscarriage in female (ASSENNATO et al., 1986). Prenatal and early postnatal exposure to Pb at the level 10-20 mg/dl (in blood) would result in damage to the central nervous systems (BELLINGER et al., 1987, WASSERMAN et al., 1997). The damage is characterized by diminished intelligence, shortened attention span, and slowed reaction time. The effects are irreversible, untreatable, and lifelong (NEEDLEMAN et al., 1990). VERMA & DUBEY (2003) concluded that a $Pb(NO_3)_2$ levels of 500 mM is moderately toxic and 1000 mM is highly toxic. Pb is a proven animal carcinogen on the basis of 'sufficient' animal data. It is currently considered by the International Agency for Research on Cancer (IARC) to be a possible human carcinogen (group 2B) on 'inadequate' evidence (SILBERGELD et al., 2000).

The Pb concentrations in soil that are toxic to vital plant processes vary greatly in different research, due to the interaction of Pb with plant species and many environmental factors. The levels of Pb in soils that are toxic to plant are not easy to evaluate. However, it is generally agreed that soil Pb concentration ranging from 100 to 500 ppm are considered to be excessive (KABATA-PENDIAS & PENDIAS, 1984). For its toxic to plant, animal, and human being, Pb has recently received much attention as a major chemical pollutant of environment. The absorption and transport of Pb by crops are of great concern, especially its accumulation in the edible part

(LIU et al., 2003). Although there is no evidence that Pb is essential for the growth of any plant species, there are many reports on the stimulating effects of Pb on plant growth at low concentration. It was reported that 100 ppm of Pb in soil increased the biomass weight and grain yield of rice (WANG & WU, 1997), and the plant fresh weight and seed production of sunflower was improved by 96.9 ppm of Pb in soil (MURILLO et al., 1999). LIU et al., (2003) exhibited that the effect of Pb on the growth and development of rice differed greatly with rice cultivars at 800 ppm of Pb in soil. Some cultivars were greatly inhibited, some were significantly improved, and others showed no significant changes. So the sensitivity and tolerance of rice to soil Pb pollution are cultivar-dependent. The mechanism has not yet been fully understood.

The main objectives of the this study were to investigate the impacts of temperature, humidity and soil type on emission rates of NO, N₂O and CO₂ under the stress of Cd and Pb at different concentrations, and hence to better understand the contribution of ecological factors incorporation to N₂O, NO and CO₂ emissions.

3. MATERIALS AND METHODS

KOPONEN et al. (2004) studied in laboratory microcosms N₂O and CO₂ emissions from four different agricultural soil types at low temperatures with or without freezing–thawing events. According to the LAVILLE et al. (2005) sub-model, its input variables include surface soil moisture content, soil temperature and the contamination of soil sub-samples with different concentrations of heavy metals. Because the nitrification rate is controlled by soil NH₄⁺ content (VELDKAMP & KELLER, 1997), water content (DAVIDSON, 1993), temperature (WILLIAMS & FEHSENFELD, 1991) and other ecological factors.

The water-filled pore space (WFPS) defined as the ratio of volumetric soil water content to total porosity of the soil, has proved to be the most suitable among various expressions of soil

water, since WFPS is largely comparable among soils of different texture. Such a response function is in accordance with conceptual considerations that propose a substrate diffusion limit at low and a gas diffusion limit at high moisture contents (SKOPP et al., 1990). An optimal WFPS of about 60% has been noticed for a number of microbial processes (LINN & DORAN, 1984). WFPS response function was originally based on results from (GARRIDO et al., 2002), who found nitrification to vary linearly with volumetric soil water content, over a range of 0.09–0.27 m³m⁻³.

The responses were established under controlled conditions in the laboratory, at a temperature of 15 and 37°C, and without N supply. Moreover, nitrification was thus assumed to increase linearly from a minimum WFPS of 10% to a maximum of 60%, and to decrease thereafter until 80%. However, we decided to substitute this linear function with that of LINN & DORAN (1984), based on WFPS and not w_c (water content), because it appeared more universally applicable to different soils (LINN & DORAN 1984).

Before the incubation, the microcosms were allowed to stabilize for 4 h and then gas flux was measured. This procedure ensured homogenous temperature throughout the soil profiles, and that the measured flux reflected gas production from soil at the set temperature. Without this stabilization period, the flux would show merely the diffusion of the stored N₂O without a close association to the actual gas production.

In the laboratory, trace gases concentrations in each microcosm (by the help of needle of the syringes) were determined from sampling with a gas chromatograph equipped with thermal conductivity detector for CO₂ and electron capture detector for N₂O. Peak areas were integrated with the computer program as described in MALJANEN et al. (2001). The gas flux rates were calculated from the linear increase in the gas concentrations in the chamber with time (NYKÄNEN et al., 1995).

3.1. MATERIALS

3.1.1. SOIL COLLECTION SITES AND TYPES

The field sites that soils were collected from a native forest land or uncultivated and wheat cultivated areas located at the experimental region of the Faculty of Agricultural and Environmental Science at Szent István University, Gödöllő (approximately 30 km north east of Budapest). The second soil samples were collected from the maize cultivated field experimental station of Georgikon Faculty of Agriculture, University of Pannon, Keszthely (approximately 240 km south east of Budapest).

Soils from the Gödöllő region have previously been characterized as a brown forest clay loam (ALGAIDI et al., 2007, 2008), while the soil samples collected from Keszthely were characterized as Ramann's brown forest soil type.

3.1.2. SOIL PREPARATION AND TREATMENTS

The soil samples were collected from the upper 200 – 250 mm layer after removing the first top 20 – 30 mm from a sample site. Soil samples were ground and sieved (2 mm) and stored in plastic bags at cold room temperature (less than 4±2°C) for further investigation. Prior to incubation, soils were homogenized and brought to room temperature (~21±2°C).

PART (A): Determination of bioavailability of heavy metals (Pb, Cd, and Co) and their effects on CO₂-release and density of the aerobic heterotrophic bacterial population density in control and heavy metal contaminated soil samples.

A variety of methods exists to estimate the size of the microbial biomass in soil. The most simple and rapid is substrate induced respiration (SIR), which stimulates a maximal respiratory response from the soil biomass, measured conductimetrically as CO₂ evolution, and methods currently available are those involving direct counting in which microorganisms can be variously stained, and relates this respiration to biomass C (ANDERSON & DOMSCH, 1978).

The supply of mineralized C, N, and P from SOM, the decomposition of plant and animal residues and the maintenance of soil structure are all-dependent upon the correct functioning of the soil microbial ecosystem (De HAAN et al. 1989). Therefore, it is important to determine and predict the adverse effects of heavy metals and other pollutants on soil microorganisms (BAATH, 1989).

The physical and chemical properties of the investigated room temperature air-dried uncultivated and wheat cultivated acidic sandy brown forest soil samples which were collected from Gödöllő, Hungary are:

1. Uncultivated soil sample:

pH_(KCl) 5.33, humus content 1.22%, C:N ratio 10.7, and the following properties are in mg kg⁻¹: NH₄⁺-N (1.69), NO₃⁻-N (3.08), SO₄⁻² (3.9), K₂O (107), P₂O₃ (121.3), Cu (2.7), Mg (203), Mn (136), Cd (0.11), Co (2.05), Pb (19.59), and Zn (9.85).

2. Wheat cultivated soil sample:

pH_(KCl) 4.67, humus content 1.21%, C:N ratio 12.4, and the following properties are in mg kg⁻¹: NH₄⁺-N (3.2), NO₃⁻-N (4.5), SO₄⁻² (4.6), K₂O (123), P₂O₃ (209), Cu (1.86), Mg (206), Mn (195), Cd (0.065), Co (1.57), Pb (8.48), and Zn (7.22).

The soil samples were activated by substrate induced respiration (SIR) materials which were in the form of:

- 170 mg kg⁻¹ soil sodium nitrate,
- 50 mg kg⁻¹ soil potassium phosphate, and
- 3 mg kg⁻¹ soil glucose.

The substrate induced respiration (SIR) materials were the sources of N, P, and C, respectively.

All activated and non-activated (control) of cultivated and uncultivated soil samples were contaminated with three concentrations of each heavy metal:

- 1.5, 3, and 6 mg Cd kg⁻¹ soil in form of CdCl₂·2.5H₂O,
- 4, 8, and 16 mg Co kg⁻¹ soil in form of CoCl₂ and
- 40, 80, and 160 mg Pb kg⁻¹ soil in form of PbCl₂.
- The control microcosms were heavy metals free.

The heavy metal amended soil samples were incubated for six weeks at 28°C. The population density of aerobic heterotrophic bacteria and the amount of CO₂-release in each soil sample were investigated after first, third and six weeks of incubation.

PART (B): Predict the ecological factors influencing the NO, N₂O and CO₂ emissions

The soil samples collected in the upper 200 – 250 mm layer after removing the first top 20 – 30 mm from a sample site. The soil is a sandy-loam texture in the upper (200 –250 mm) horizon.

A 200 g per microcosm was homogenised (2 mm) soil samples of the brown forest soil obtained from Keszthely and Gödöllő, Hungary) were placed into the microcosm of 1200 cm³. The main physico-chemical properties of the (200 –250 mm) soil obtained from Keszthely and Gödöllő were:

1. Keszthely soil samples:

pH_(KCl) 7.55, total salt content 0.054%, humus 1.48%, total organic C 1.08%, total N 0.08%, NH₄⁺-N 0.53 mg 100 g⁻¹ soil, NO₃⁻-N 0.18 mg 100 g⁻¹ soil, K₂O 136 mg 100 g⁻¹ soil, P₂O₅ 130 mg 100 g⁻¹ soil, soil density 2.45 g cm⁻³ and C:N ratio 13.5.

2. Gödöllő soil samples:

pH_(KCl) 5.56, total salt content 0.037%, humus 3.51%, NH₄⁺-N 0.40 mg 100 g⁻¹ soil, NO₃⁻-N 0.28 mg 100 g⁻¹ soil, K₂O 82 mg 100 g⁻¹ soil, P₂O₅ 34 mg 100 g⁻¹ soil, and soil density 2.52 g cm⁻³.

The physical and chemical characteristics of the investigated soil samples were determined according to the applied methods for soil analysis in the Environmental Science Institute, Department of Soil Science and Agrochemistry, at Szent István University, Gödöllő.

The soil samples were contaminated with the heavy metal by the addition of different doses as followings:

- 40, 80 and 160 mg Pb kg⁻¹ soil of Pb(CH₃COO)₂·3H₂O or
- 6, 12 and 24 mg Cd kg⁻¹ soil of CdCl₂·2.5H₂O.
- The control microcosms are heavy metal free.

The water filled pore space (WFPS) of soil samples was adjusted to be 30 and 60%. The gravimetric moisture content was determined from the collection sample (from the upper 200 – 250 mm soil layer, five replicates from each field, 50 g fresh weight) by drying the soil samples for 24 h at 65°C. Bulk density was determined according to BLAKE (1965). Soil moisture was adjusted to the desired content (30 and 60% WFSP) for each set of microcosms by addition of equivalent amount of distilled water.

3.1.3. CHEMICALS USED

The heavy metals used for soil contamination were represented by:

1. Cadmium Chloride (CdCl₂·2.5H₂O)
2. Cobalt chloride (CoCl₂)
3. Lead chloride (PbCl₂) and
4. Lead acetate Pb(CH₃COO)₂·3H₂O.

The chemicals for substrate induced respiration are:

- Sodium nitrate (NaNO₃)
- Potassium phosphate (K₂HPO₄), and
- Glucose (C₆H₁₂O₆).
- Nitric acid (HNO₃)
- Hydrogen peroxide (H₂O₂)

The chemicals were obtained from Reanal Company for the production of Chemicals, Budapest.

3.1.4. LABORATORY THERMOSTAT

The vessels (microcosms) containing soil samples treated in different ways were placed into an incubator (thermostat) at 15°C or 37°C.



3.1.5. MICROCOSM MODEL

This version of the CO₂, N₂O, NO, nitrification and denitrification sub-model was developed to enable a finer simulation of the climate soil conditions interaction in the top few centimeters of soil. We thus reduced the thickness of the topsoil layer from 5 to 15 cm, and assigned a particular functioning to this 'microcosm-layer'. For this version trace gases emissions are calculated in the 0–5 cm layer. The nitrification is evaluated in the 0–5 cm from soil temperature and soil moisture content for these layer thicknesses under the stress of different Cd and Pb concentrations.

Static chambers (microcosms) are the most commonly used tools in the World (RUZ-JEREZ et al., 1994; CARRAN, et al. 1995; SAGGAR et al., 2004a, 2007a,b; DE KLEIN et al., 2003; HEDLEY et al., 2006; BHANDRAL et al., 2007a,b; LUO et al., 2007a,b; TATE et al., 2007). Chambers are cylinders or boxes. Alternatively, for experiments where there is a need to tightly control environmental variables, intact soil cores (10 cm dia., 0–10 cm depth) are collected in metal liners and are placed in robust PVC chambers (SAGGAR et al., 2004a) glued to a PVC base (HEDLEY et al. 2002). Gas fluxes are monitored at regular intervals after temporarily sealing the chambers with a gas-tight seal using self-locking lids and a greased O-ring. Chamber techniques are based on the increase in gas concentration within the enclosed headspace to a concentration that is then precisely determined by gas chromatography (HEDLEY et al., 2006). Gas fluxes are then calculated (MOSIER & MACK, 1980) using linear regression and the ideal gas law.

Chambers are portable, compact, easy to install, and can be readily adapted for taking measurements. Chamber techniques have contributed most to our current understanding of the magnitude and spatiotemporal variability of trace gases fluxes (HEDLEY et al., 2002; SAGGAR et al., 2004a,c,d, 2005a, 2007a,b; BHANDRAL et al., 2007a,b; SINGH et al., 2004; LUO et al., 2007a,b; TATE et al., 2006). Despite their low cost and ease of use under a wide range of conditions, however, these static chambers can only cover a small area of the soil surface.

The small chambers are simple, adaptable and easy to operate. Recently, GANZ et al. (2006) compared N₂O and CO₂ gas fluxes measured from a dairy-grazed pasture using both conventional small chambers (Ø250 mm, 300 mm high) (described in SAGGAR et al., 2004a) and large chambers (1 m×0.5 m, 300 mm high) (described in TATE et al., 2006). The results from two intensive 6 week measurement campaigns using 20 small and 8 large chambers showed no significant differences in gaseous fluxes between the two types of chambers but the spatial variability was higher from small chambers than large chambers.

For the present investigations, similar devices were designed to measure the emissions of the trace gases from controlled and treated soil sub-samples during the experimental incubation time intervals under different soil conditions. The designed chamber was characterized by dark brown glass bottle with round neck and sealed open of volume approximately 1200 ml. The used chamber (8 x 8 x 20 cm with sealed neck (Ø 40 mm, 40 mm high) in our experimental model is named "microcosm". The microcosm of experiment conducted in glass vessels covered tightly by silicone septa. The water-filled pore-space (WFPS), soil temperature, and heavy metal contaminated soil control the rate of denitrification according to FROLKING et al. (1998). The model has reasonable data requirements.

The soil sub-sample was mixed with different concentrations of Cd or Pb and was homogenized and the WFPS was adjusted to 30 or 60% in order to promote N mineralization as well as trace gases emissions originating from nitrification and denitrification processes (MERINO et al. 2001). A WFPS around 60% favours nitrification because the diffusion of substrates and O₂ is not restricted (PARTON et al. 1996).

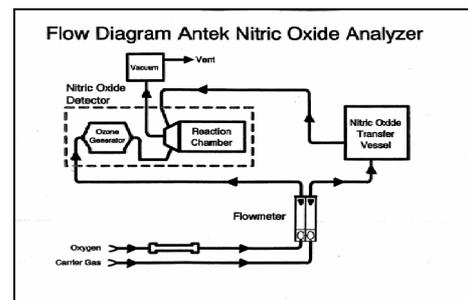
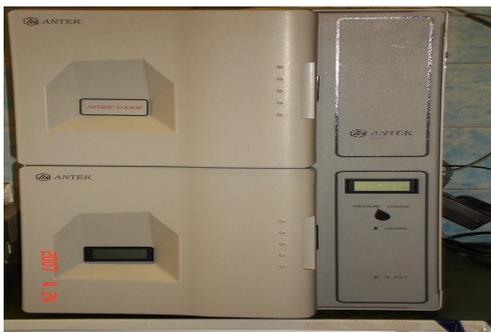
The photolysis rate of NO, NO₂ and CO₂ inside the dark chambers was estimated to be zero.

3.1.6. INSTRUMENTS

- The bioavailability of the soil contaminated heavy metals was performed by jobin-Yvon 24 type ICP atomic emission spectrometer.
- The trace gases (N_2O and CO_2) were detected by gas chromatography which controlled by software named HP PEAK-96 and the first evaluation of data was executed by an HP 3390 Ser. II integrator.
- Chemiluminescence Model 7050 analyzer of ANTEK Instruments L.P., USA was used for NO detection



Accumulations of N_2O and CO_2 were measured by a gas chromatography .



Chemiluminescence Model 7050 analyzer of ANTEK Instruments



Injection needle

3.1.7. CULTURAL MEDIUM

For counting the population density of the aerobic heterotrophic bacteria the Nutrient agar medium was used with the following composition (SHARMA & JOHRI, 2003) in $g\ l^{-1}$: 5 peptone, 3 beef extract, 18 agar-agar, and pH 7.

3.2. METHODS

3.2.1. Determination of soluble fraction of heavy metals (Pb, Cd, and Co) and their effects on CO_2 -release and density of the aerobic heterotrophic bacterial population density.

A SAMPLE PREPARATION FOR DETERMINATION OF SOLUBLE FRACTION OF HEAVY METALS

MI-08-1735-1990 is the Hungarian technical directive method which was used to detect Pb, Cd and Co content in the soil samples. Five gram of air-dry and fine ground soil sample was weighed and shaken with 25 ml of 1.5 M nitric acid at 20°C for two hours. The element analysis of the filtrate was performed by Jobin-Yvon 24 type ICP atomic emission spectrometer.

B. ELEMENT ANALYSIS BY ICP-AES:

In the extracts made by the Hungarian standard procedures the following elements (Pb, Cd, Co) were determined with Jobin-Yvon JY-24 of sequential ICP-AES instrument as described in its operating manual.

3.2.2. DETERMINATION OF CO₂-PRODUCTION

For measurement of CO₂-production, a 0.5 kg of the heavy metal treated soil was filled in about 1500 ml glass vessels and in the middle of the soil a fixed plastic tube, containing 50 ml of 10 M NaOH solution for trapping the evolution of CO₂ and vessel was closed tightly. The NaOH was titrated with HCl (1M) to calculate the volume of CO₂ released as soil respiration, which represented the (1) respiration due to litter decomposition, (2) root respiration, (3) microbial respiration (i.e. microbial respiration utilizing C directly derived from living roots), and (4) microbial respiration utilizing native soil organic matter. Applied method of WARDLE & PARKINSON (1991) was used for simultaneous determination of NaOH and Na₂CO₃ content in our experimental soil samples.

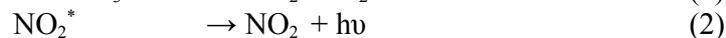
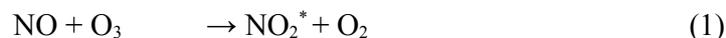
3.2.3. DETERMINATION OF TOTAL NUMBER OF AEROBIC BACTERIA

Under sterile conditions, a 10 g of fresh soil sample was suspended with 90-cm³ water. The soil suspension was diluted gradually to 10⁻³ and 10⁻⁶ and from the diluted suspensions 1 cm³ was pipetted in (Petri dish, and mixed thoroughly with Nutrient agar). The plates were incubated on 27°C for 48 hours. After that, the developed bacterial colonies were counted.

PART (B): Predict the ecological factors influencing the NO, N₂O and CO₂ emissions

3.2.4. EXPERIMENTAL CONDITIONS

- ◆ The principle of operation for the NO detection begins with the complete, high temperature oxidation of the entire sample matrix as illustrated in equation (1). The conversion of NO to NO₂* (meta-stable NO₂) is quantitative. The NO is passed through the reaction chamber where they react with O₃ to form NO₂*



As the excited species decays to the ground state, a quantum of light is emitted and detected, at a specific wavelength by the photomultiplier tube (2). This chemiluminescent emission is specific for N and is proportional to the amount of NO in the original sample. Calibration standards containing NO may be analysed to produce calibration curves. External data systems may be interfaced to ANTEK 7050 for calculations and documentation.

- ◆ During the experiment N₂O and CO₂ concentrations of gas samples from each microcosm were measured at different time intervals. ECD and TCD detectors were used in gas chromatograph HP 5980 Series II type and packed columns (Porapak Q). The gas chromatograph was controlled by software named HP PEAK-96 and the first evaluation of data was executed by an HP 3390 Ser. II integrator.

3.2.5. THE APPLIED SOIL INCUBATIONS EXPERIMENTS

Independent incubations were also performed in order to determine CO₂, N₂O and NO emissions. Static system incubations were carried out in microcosm (~1200 ml) with a gas-tight septum fitting in the lid according to BOLLMANN et al. (1999). Heavy metal contaminated soil subsamples with various soil moisture (30 or 60% WFPS) were incubated at different temperatures (15, 37°C) in the dark thermostatic incubator. Changes in the concentration of N₂O, NO and CO₂ in the headspace of the microcosms were determined by periodic sampling of the headspace with gas tight syringes and subsequent trace gas analysis throughout 35 incubation days.

Mainly, three experiments were conducted. In addition, the NO, N₂O and CO₂ emissions were measured during time intervals of incubation under different ecological parameters.

Experiment 1: Effects of temperature

The hypothesis for this experiment was that the emissions of NO, N₂O and CO₂ will decrease when the incubation temperature was at low, and higher when the temperature was close to 30°C. We determined if there is any difference in the trace gases emissions at low and high soil temperatures. There were 3 replicate soil microcosms for each soil type per each treatment with different soil water content (30 and 60% WFPS).

Gas samples (0.250 ml) were taken through the septa by injection needles.

Experiment 2: Effects of soil moisture

Here, we ran this experiment at low and high soil moisture (30% and 60% of the WFPS). Three replicate microcosms per each treatment per for two soil types (Keszthely and Gödöllő) were used. Soil was moistened, and to omit a possible major N₂O pulse (DAVIDSON, 1992; MUMMEY et al., 1994; JØRGENSEN & JØRGENSEN, 1997), the soil microcosms were stabilized for 4 h before incubation. The fluxes of the trace gases were measured at the various temperatures (15°C and 37°C). During the incubation time intervals, the development of gases concentrations in the microcosms were followed by the gas samples (0.250 ml) were taken through the septa by injection needles.

Experiment 3: Effects of heavy metals

In this experiment, the effects of different concentrations of Cd and Pb on the release of NO, N₂O and CO₂ from different soil types, with different water content and incubated at different soil incubation temperatures were studied, using three replicate microcosms per treatment. The microcosms with their two different water content (30 and 60% WFPS) were incubated at 15°C and 37°C for 35 days as incubation time intervals. The fluxes of NO, N₂O and CO₂ were measured throughout 35 days as the incubation period with time intervals. Gas samples (0.250 ml) were taken through the septa by injection needles.

3.2.6. SAMPLING AND MEASUREMENT OF THE TRACE GASES

Measurements of NO, CO₂ and N₂O were made in triplicate for each microcosm by the help of injection needle. Also, triplicate microcosms incubations were set up and measured for the 30 and 60% WFPS soil moistures at different concentrations of heavy metals and temperatures. The relative contribution of nitrification and denitrification to the production of N₂O and NO as well as CO₂ in the various incubations with and without heavy metals was determined by comparison of replicate incubations at different soil moistures and incubation temperatures. The moisture represents the upper limit of normal field conditions at the sites from where the soil samples were collected. Although there have been recent concerns about the effectiveness of nitrification (WRAGE, 2003).

The microcosms were independently incubated in a laboratory thermostat at 15 or 37°C for 35 days.

During the run of the experiments and during incubation time intervals, NO, N₂O, and CO₂ gas samples were taken from the headspace of each microcosm and determined regularly by chemiluminescent detector (for NO) and gas chromatographic method (for N₂O and CO₂).

A 250 µl gas sample in the closed atmospheric condition in each microcosm containing the specific treated soil sub-sample of the incubation headspace were used for each analysis of N₂O, NO and CO₂ was taken by gas tight Hamilton syringes and injected to the HP 5890 gas chromatography. Packed columns (Porapak Q) used to separate the different constituents of gas samples. Electron Capture Detector (ECD) and Thermal Conductivity Detector (TCD) detected N₂O and CO₂ concentrations, respectively.

The most important properties of gas chromatography measurements are mentioned in Table 1.

Table 1. The most important characteristics of gas chromatography for N₂O and CO₂ measurements

GC analysis of gas samples	HP 5980 Series II type gas chromatography	
Analysed gases	N₂O	CO₂
Carrier gases (types and flow rates):	N ₂ : 23 ml/min	He: 27 ml/min
Temperature of Injector	70°C	
Columns (oven temperature is 50°C)	Porapak Q (80/100 mesh, 6 ft)	
Detectors (temperature, detection limit)	ECD (250°C, >5-10 ppm)	TCD (150°C, >100 ppm)
Retention time	1.0-1.2 min	1.1 – 1.3 min
Duration of a run	3.5 min	2.5 min
Calibration	external standard	
Calibration gas mixture contains	7.9 vpm N ₂ O	9.7 v/v% CO ₂
Evaluation of chromatograms	HP 3390 Ser. II integrator, HP CHEM	

The separated gas content was analysed three times per day whenever measurements carried out using external standard and one point linear calibration.

The NO gas emission detected by chemiluminescent detector (Model 7050 analyzer of ANTEK Instruments L.P., USA) which is specifically designed for the analysis of NO in samples.

3.3. STATISTICAL ANALYSIS

All microcosms were incubated under the same controlled environmental conditions used for the main incubation experiment. NO, N₂O and CO₂ fluxes were measured during 35 days.

After subtracting ambient concentrations of CO₂, NO and N₂O, production of NO, N₂O and CO₂, was regressed on elapsed time using a linear regression model which was forced to pass through the origin but allowed different slopes (emission rates) for each treatment. CO₂, NO and N₂O emission rates were subjected to a one-way analysis of variance according to VÁSQUEZ-MURRIETA et al. (2006).

All experimental investigations in three replicates, and the results were represented by the means of the replicates. Group differences across metric dependent variables based on set of categorical (non-metric) variables were assessed by multiple analyses of variance (MANOVA). Differences in means were evaluated by F-probe according to S_VAB (1981). Excel 5.0 statistical functions were used for calculations and graphic presentation of data. Standard deviation (SD) and Least Significant Difference at 5% level (LSD_{0.05}) were calculated as well.

Linear regression models and correlation (R^2) were used to assess the additive effects of ecological parameters and soil characteristics on trace gases emissions. Pearson's correlation coefficients (r) and the coefficients of variability or variation (CV%) were calculated. CV was defined as standard deviation/mean \times 100. Analysis of variance was performed for emission at all parameters to examine differences in emission between and within the experimental conditions. The non-systematic error (coefficient of variability or variation) of sampling and analysis with repeated sampling performed on each gas sampling from each soil treatment and for each soil types.

4. RESULTS

CRUTZEN et al. (2008) stated that the relationship, on a global basis, between the amount of N fixed by chemical, biological or atmospheric processes entering the terrestrial biosphere, and the total emission of N_2O , has been re-examined, using known global atmospheric removal rates and concentration growth of N_2O as a proxy for overall emissions. For both the pre-industrial period and in the large-scale changes in synthetic N fertilizer production, an overall conversion factor of 3–5% from newly fixed N to N_2O -N was found. Rapid expansion of agriculture during the 20th and 21st century, to meet the food demands of increase in world's population, also accentuated the release of CH_4 from rice paddies and livestock, and N_2O from fertilized croplands. Consequently, N_2O abundance increased from a pre-industrial level of 270 ppb to 319 ppb in 2004, and is currently increasing at the rate of 0.8 ppb yr^{-1} or 0.22% yr^{-1} (WMO, 2006). Deforestation and land use conversion presently contribute 0.6 to 2.5 Pg C yr^{-1} . In contrast, fossil fuel combustion emits about 7 Pg C yr^{-1} (WMO, 2006). The urgency to optimize N

fertilization strategies and reducing the emissions of trace gases is strengthened by the fact that the N uptake within a field is not necessarily homogenous.

The results of this study is concerned with determination the bioavailability of Pb, Cd and Co, the impacts of the different concentrations of Pb, Cd and Co on CO₂-release as well as enumeration of aerobic heterotrophic bacterial populations in wheat cultivated and uncultivated brown forest soil. Results were collected and analyzed after one, three and six weeks of incubation in greenhouse and under laboratory conditions at 28°C. The second investigation of the present study provides information concerning the results of the microcosm models. These models described the influences of various concentrations of Cd and Pb on the emissions of NO, N₂O and CO₂ under the impacts of soil moisture regimes and incubation temperatures of two soil samples Ramann-type brown forest soil originated from Keszthely and clay loam brown forest soil originated from Gödöllő.

4.1. BIOAVAILABILITY OF HEAVY METAL

Data presented in (Figures 1, 2 and 3) shows that the addition of inorganic forms of Pb, Cd, and Co respectively, to wheat cultivated and uncultivated brown forest soil samples significantly increases the mobile (HNO₃ soluble) fraction of the investigated metals but after one week incubation, their concentration does not reach the 100% recovery. Taking in the consideration that time can be an ecological factors, it was found that the amount of Pb recovery (Figure 1) was increased by increasing the incubation time to reach a maximum recovery at the 6th week of incubation. Also, there were no differences between the metal recovery of the control soils and those activated with SIR and the soil samples incubated for one week. However, the results indicated significant differences between the metal recoveries at the third week of incubation with the metal recovery detected after one week of incubation and six weeks of incubation. Here, the observations demonstrated the variance between the metal recoveries in wheat cultivated and uncultivated brown forest soil samples contaminated by Pb. Higher significant differences were detected between the Pb recovery after six weeks of incubation and the metal detection after one and three weeks of incubation. However, results did not show differences between the cultivated and cultivated soils.

Similar results were found in the soil samples treated with Cd (Figure 2), which indicated that the recovery of Cd in uncultivated soils was more than those of cultivated soils as it is shown in the case of Pb. But the Cd recovery in the uncultivated soil sample was more than the metal detected in the cultivated soil samples after six weeks of incubation.

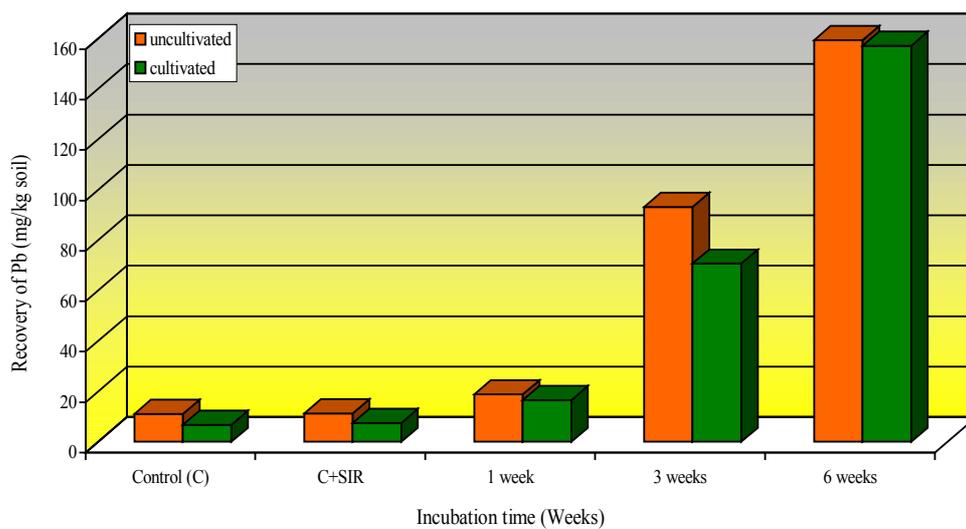


Fig. 1. Time as the ecological factor for recovery of Pb in cultivated and uncultivated brown forest soil (Gödöllő) contaminated soil with 160 mg Pb/kg soil

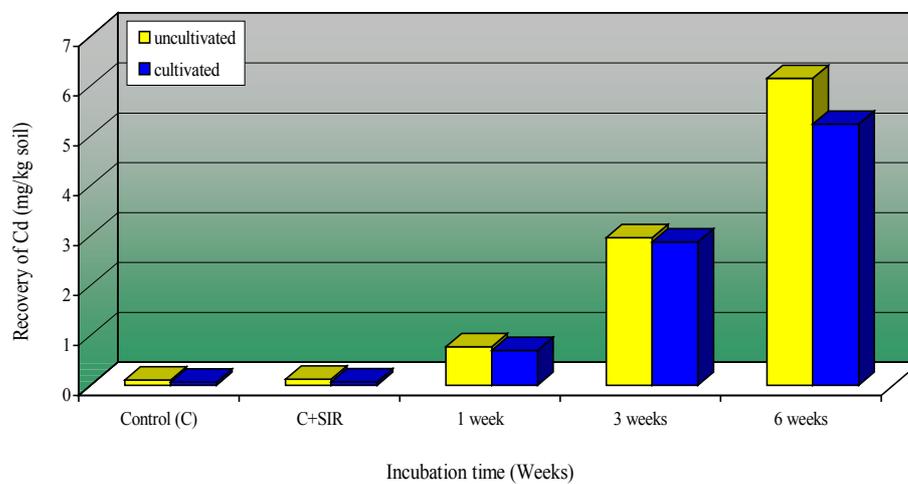


Fig. 2. Time as the ecological factor for recovery of Cd in cultivated and uncultivated brown forest soil (Gödöllő) contaminated soil with 6 mg Cd/kg soil

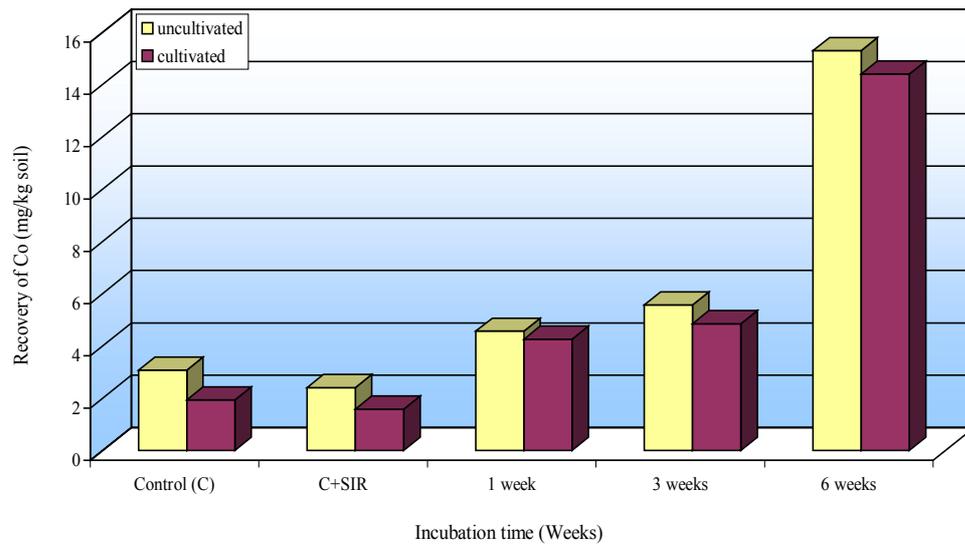


Fig. 3. Time as the ecological factor for recovery of Co in cultivated and uncultivated brown forest soil (Gödöllő) contaminated soil with 16 mg Co/kg soil

(Figure 3) illustrates that when the soil samples contaminated with Co and incubated for six weeks were more significantly different than those incubated for three or one week comparing with the control or activated control soils.

Linear regression, correlation (R^2), correlation coefficient (r), standard deviation (SD) and coefficients of variability (CV%) were calculated to describe the differences in the recoveries of Pb (Figure A-1), Cd (Figure A-2) and Co (Figure A-3) in cultivated and uncultivated soil samples. It was found that the values of R^2 and r in cultivated soil samples higher than those of uncultivated soil samples in all cases. But the value of "a" and the value of "b" variables in the regression equation of the uncultivated soil samples contaminated by Cd was higher than those found in cultivated soil samples. The value of CV% was higher only in the uncultivated (129.8805) than the cultivated (126.3873) soil samples contaminated by Cd. In the other cases of soil samples contaminated by Pb and Co, the CV% values were higher in cultivated than uncultivated soil samples.

4.2. DETERMINATION OF CO₂-RELEASE

(Figure 4) and Figure 5 represented the results of the effects of heavy metals on the CO₂-released from uncultivated and wheat cultivated brown forest soil samples (Gödöllő), respectively, which were amended with various concentrations of Pb, Cd and Co. It is clear that activated soil samples by SIR showed higher rate of CO₂-production than the control and heavy metals contaminated soil samples even by increasing the incubation time (Figures 4 and 5). It was found that by increasing the concentration of contaminated metal, the rate of CO₂-production throughout the incubation time intervals decreased. Throughout the contaminated metals, Pb had the lowest effect on CO₂-production in both uncultivated and cultivated soil samples (Figure 4 and Figure 5, respectively). While CO₂-production, was more inhibited by Cd than Co during incubation period between the third and sixth weeks. Comparatively, the increasing the incubation time decreased the CO₂-production and significant depressions in CO₂-production in soils contaminated with all metals especially Cd and followed by Co at different concentrations.

Linear regression, correlation (R^2), correlation coefficient (r), standard deviation (SD) and coefficients of variability (CV%) were calculated to describe the differences in the CO₂-

production in uncultivated (Figure A-4) and cultivated (Figure A-5) soil samples contaminated by different concentrations of Pb, Cd and Co. It can be shown from such data that the statistical values increased by the increasing incubation time and are higher in the case of cultivated than in uncultivated soil samples contaminated by the Pb, Cd and Co. In both soil samples, the lowest statistical values were obtained after the first week of incubation (e.g., R^2 was 0.0008 and CV% was 18.5275 for uncultivated while for cultivated were 0.0277 and 18.5594, respectively).

4.3. POPULATION DENSITY OF AEROBE HETEROTROPHIC BACTERIA

The presented results indicated that there were no significant effects of the Pb concentrations applied to the uncultivated soil samples, on the density of aerobic heterotrophic bacterial population. Moreover, the results showed that no significant differences between the populations densities of bacteria under the stresses of Cd and Co, too. The increasing Co concentrations applied to the same soil caused more inhibition to the population density of aerobic heterotrophic bacteria more than caused by Cd (Figure 6) at one week of incubation. Statistically, (Figure A-6) shows that there are no significant differences between the bacterial populations throughout the incubation period. (Figure 7) demonstrates the \log_{10} of the density of aerobic heterotrophic bacterial population in cultivated soil samples contaminated by different concentrations of Pb, Cd and Co. It was found that by increasing the incubation time the population density of the aerobic heterotrophic bacteria in the control as well as in the activated soil increased. Also, it was found that by increasing the Cd concentrations and incubation time, the \log_{10} of the population densities decreased significantly in comparison with those grown under the stresses of Co and Pb. (Figure A-7) indicated that values of R^2 for the data obtained after one (0.0242), three (0.2728) and six (0.3369) weeks incubation were lower than those of uncultivated (0.5610, 0.8453 and 0.7806, respectively) soil samples. While, the values of CV% in the cultivated (6.9807, 9.9300 and 13.2179) soil samples were higher than the values obtained in uncultivated (5.6804, 8.4063 and 11.2578) soil samples. It can be concluded that Cd was the most toxic metal to the density of bacterial population occurred in uncultivated and wheat cultivated soils.

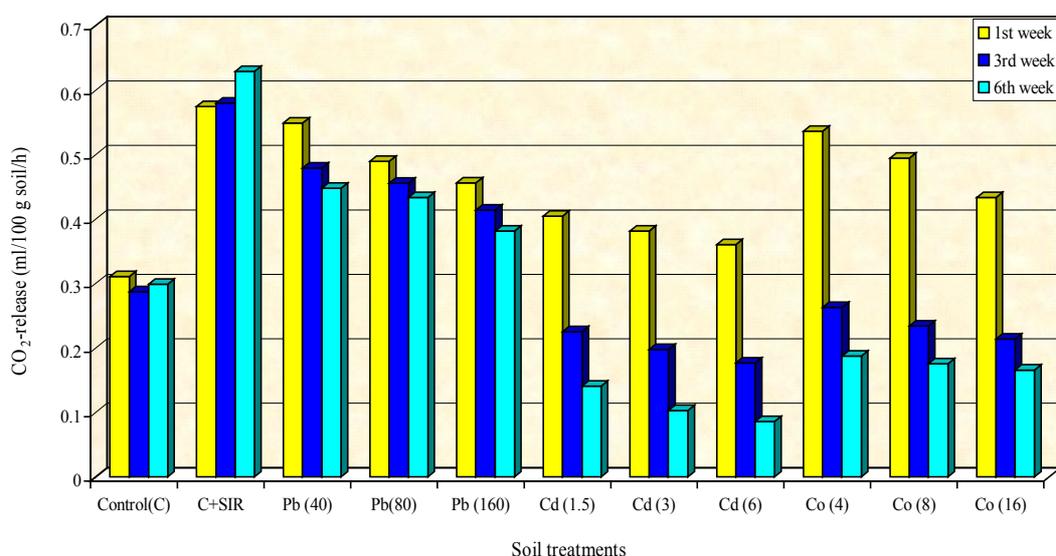


Fig. 4. CO_2 - release from uncultivated brown forest soil (Gödöllő) contaminated by different concentrations (mg/kg soil) of Pb, Cd, and Co

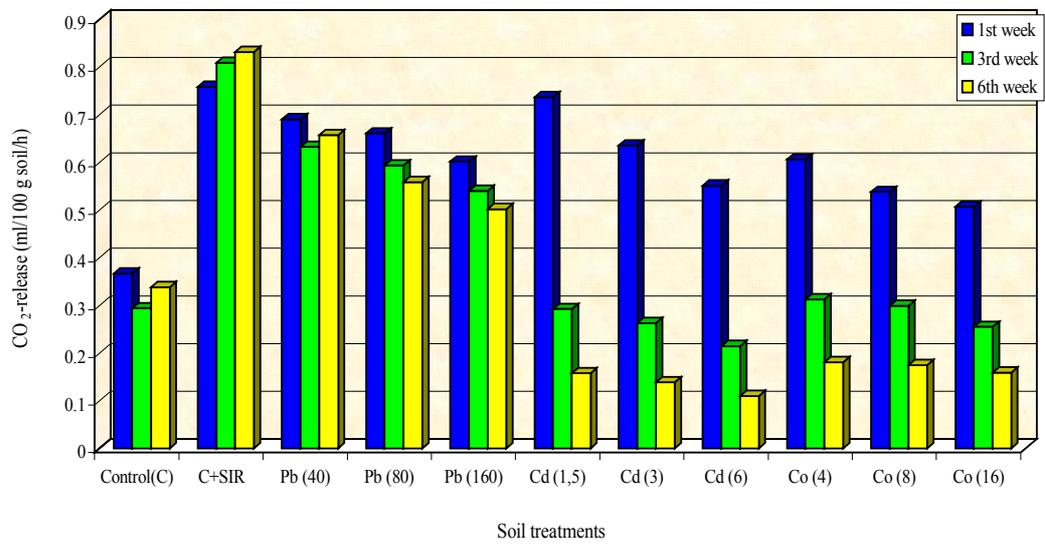


Fig. 5. CO₂- release from cultivated brown forest soil (Gödöllő) contaminated by different concentrations (mg/kg soil) of Pb, Cd, and Co

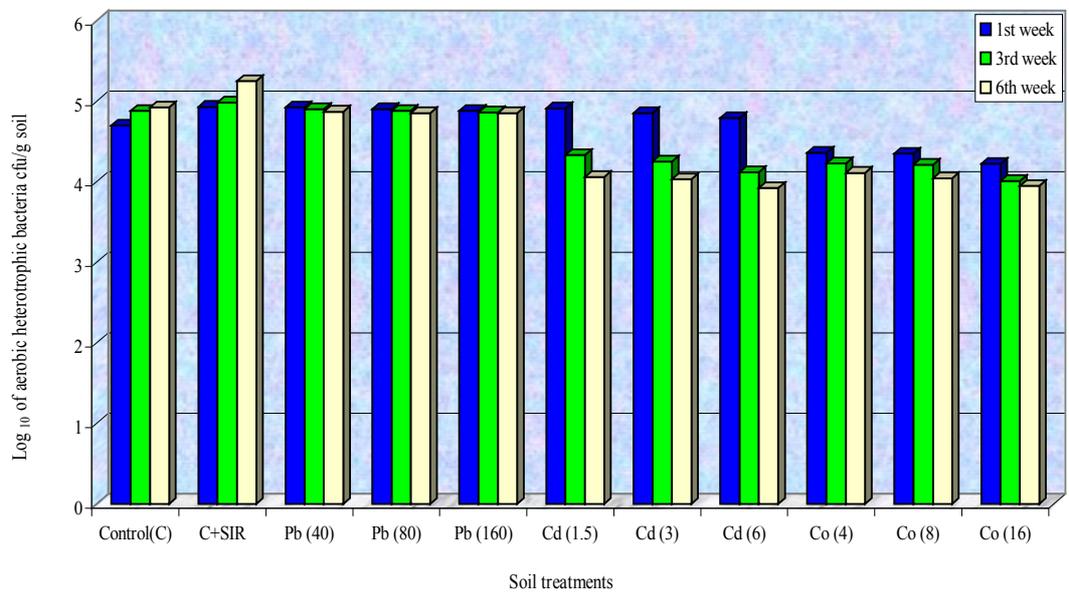


Fig.6. Log₁₀ of aerobic heterotrophic bacterial count (cfu/g soil) from uncultivated brown forest soil (Gödöllő) contaminated by different concentrations (mg/kg soil) of Pb, Cd, and Co

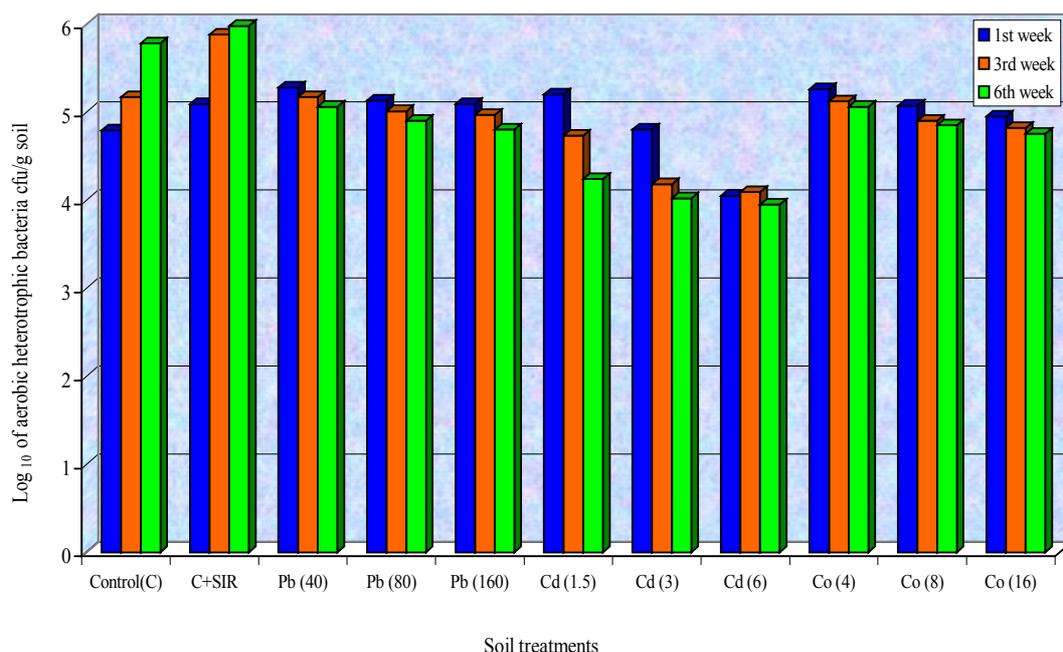


Fig. 7. Log₁₀ of aerobic heterotrophic bacterial count (cfu/g soil) from cultivated brown forest soil (Gödöllő) contaminated by different concentrations (mg/kg soil) of Pb, Cd, and Co

4.4. EMISSIONS OF NO UNDER THE STRESSES OF HEAVY METALS

In well-controlled laboratory experiments we studied the predicting environmental factors on the emissions of trace gases NO, N₂O and CO₂ production in brown forest soil from Keszthely previously cultivated by maize and native uncultivated brown forest agricultural soil originated from Gödöllő at two soil moisture regimes (30 and 60% WFPS) and incubated at low temperature (15°C) and high temperature (37°C) both without and with heavy metal contamination (Cd and Pb).

4.4.1. EXPERIMENT 1: AT LOW TEMPERATURE AND LOW SOIL MOISTURE CONTENT

The experiment was carried out in microcosms to detect the NO emissions under the stresses of different concentrations of two heavy metals, cadmium and lead in two brown forest soils one originated from Keszthely and the second from Gödöllő. The experiment was conducted at low incubation temperature (15°C) and low soil moisture regime (30% WFPS).

When soil samples of Keszthely contaminated with 6, 12 and 24 mg Cd kg⁻¹ soil, (Figure 8) illustrates that the amount (emission rate) of NO in heavy metal free (control) soil microcosms was increased up to the 6th day of incubation, and then gradually significantly decreased by increasing the incubation time. Also, it was observed that the rate of NO emissions was inversely proportional with the Cd concentration applied to the soil samples. The maximum emission of the NO was at the 4th day and then significantly decreased by increasing the incubation time up to 32nd day. The emission of gas at lowest Cd concentration was significant differences with the emission of the gas at the other two concentrations. At 32nd day of incubation, the amount of gas emissions were reduced by 73, 82, 88 and 95%, respectively with the soil contaminated doses (0, 6, 12 and 24 mg Cd kg⁻¹).

(Figure A-8) gives the statistical information about the gas emission during the incubation time by means of the linear regression, correlation (R²), correlation coefficient (r), standard deviation (SD) and coefficients of variability (CV%). For example, it was found that the values of CV% were increased by increasing the concentrations of the metal contaminant. Table 1 demonstrates the calculations of ANOVA, statistical analysis and the interaction between the

investigated factors and the detected amounts of gas and it was found that the $LSD_{0.05}$ of the experiment under these conditions was 0.7719. Comparing with the control, the result of ANOVA test indicated negative significant differences between the emissions of the gas within the incubation time intervals from the 9th to 24th at 6 mg Cd kg⁻¹ soil compared with the control, and from 6th day of incubation to 27th day at 12 mg Cd kg⁻¹ and from 4th day to 32nd day of incubation time.

Nevertheless, when the microcosms of native brown forest soil (30% WFPS moisture regime) originated from Gödöllő and contaminated by Cd were incubated at 15°C (Figure 9), the trace gas production rate at the 2nd incubation day was increased approximately two times of those produced from Keszthely soil under similar incubation conditions. To some extent, there was no differences between the emissions of the gas at the 2nd and 4th incubation days except at 6 mg dose. But, by increasing the incubation time intervals the amounts of detected gas were decreased significantly with the control soil microcosms which showed increases in the amounts of gas from the 7th incubation day up to the 32nd day. These increases of gas detection were very high positive significant differences compared with the amounts of detected gas in the Cd contaminated soil samples. The linear regression gave up the only positive regression of the gas detection in the case of control. (Figure A-9) shows the linear regression, correlation (R^2), correlation coefficient (r), standard deviation (SD) and coefficients of variability (CV%). For example, it was found that the values of CV% were increased by increasing the concentrations of the contaminant metal. Table 2 demonstrates the calculations of ANOVA, statistical analysis and the interaction between the investigated factors and the detected amounts of gas and the calculated value of the $LSD_{0.05}$ was 0.8981. Comparing with the control, the result of ANOVA test indicated negative significant differences between the emissions of the gas within the incubation period from the 2nd to 32nd day of incubation at 24 mg Cd kg⁻¹ and at 12 mg Cd kg⁻¹ was at 2nd, and from 9th to 21st day. While, at 6 mg Cd kg⁻¹ the negative significant difference laid within the period between 9th to 21st days.

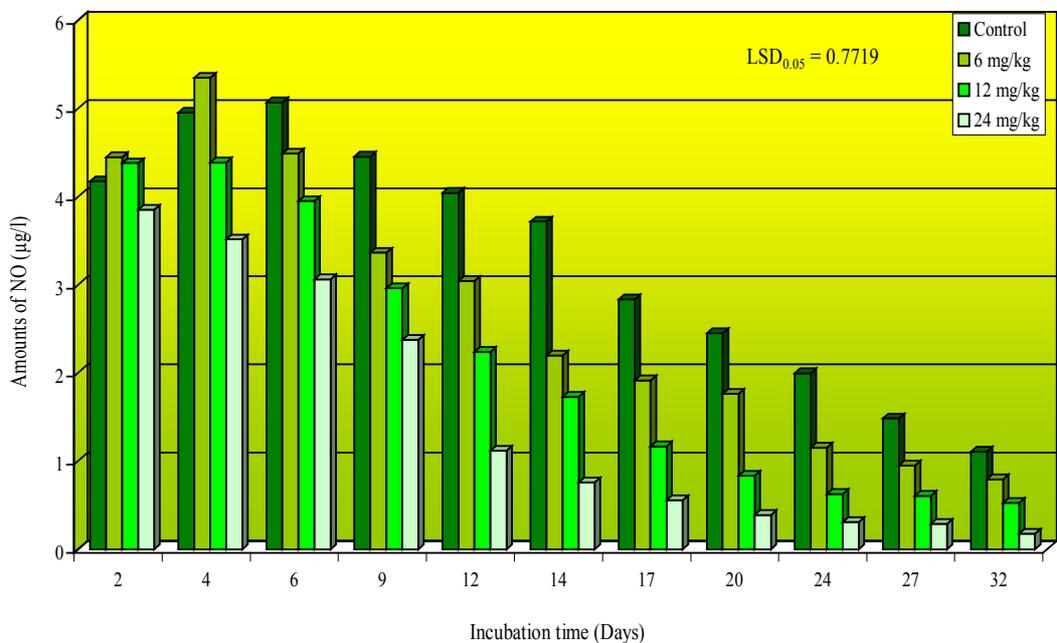


Fig. 8. Nitric oxide amounts detected in microcosm containing Ramann's brown forest soil (Keszthely) of 30% WFPS treated with different concentrations of Cd and incubated at 15°C

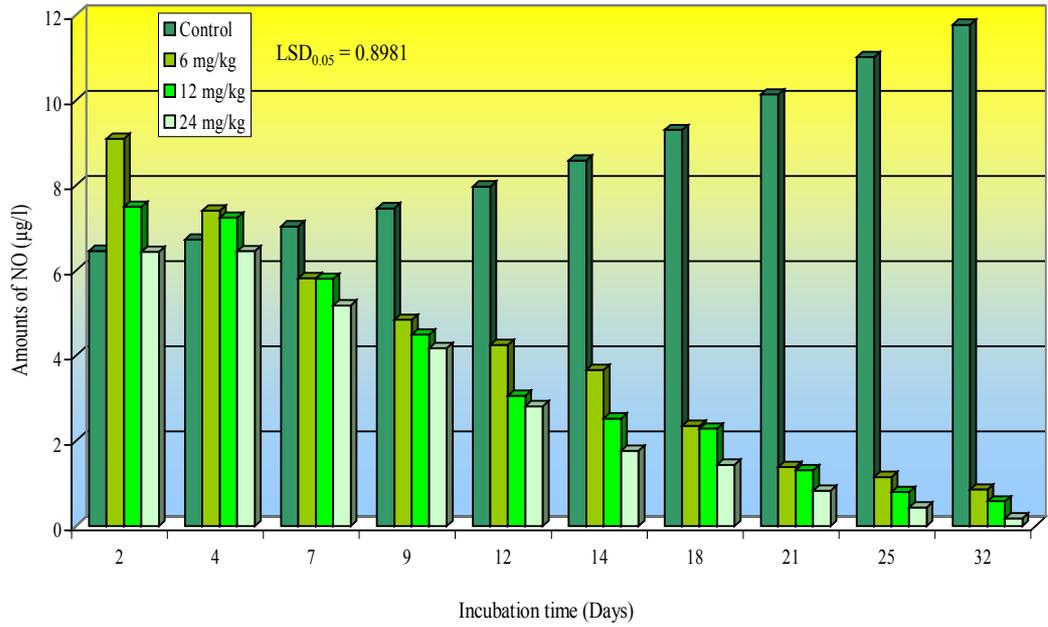


Fig. 9. Nitric oxide amounts detected in microcosm containing brown forest clay loam soil (Gödöllő) of 30% WFPS treated with different concentrations of Cd and incubated at 15°C

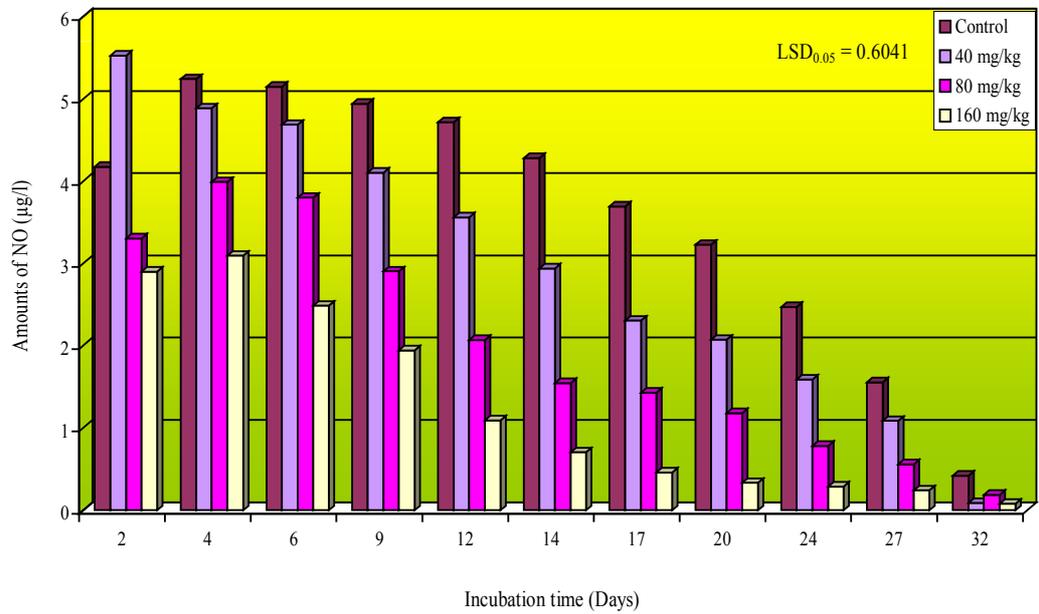


Fig. 10 Nitric oxide amounts detected in microcosm containing Ramann's brown forest soil (Keszthely) of 30% WFPS treated with different concentrations of Pb and incubated at 15°C

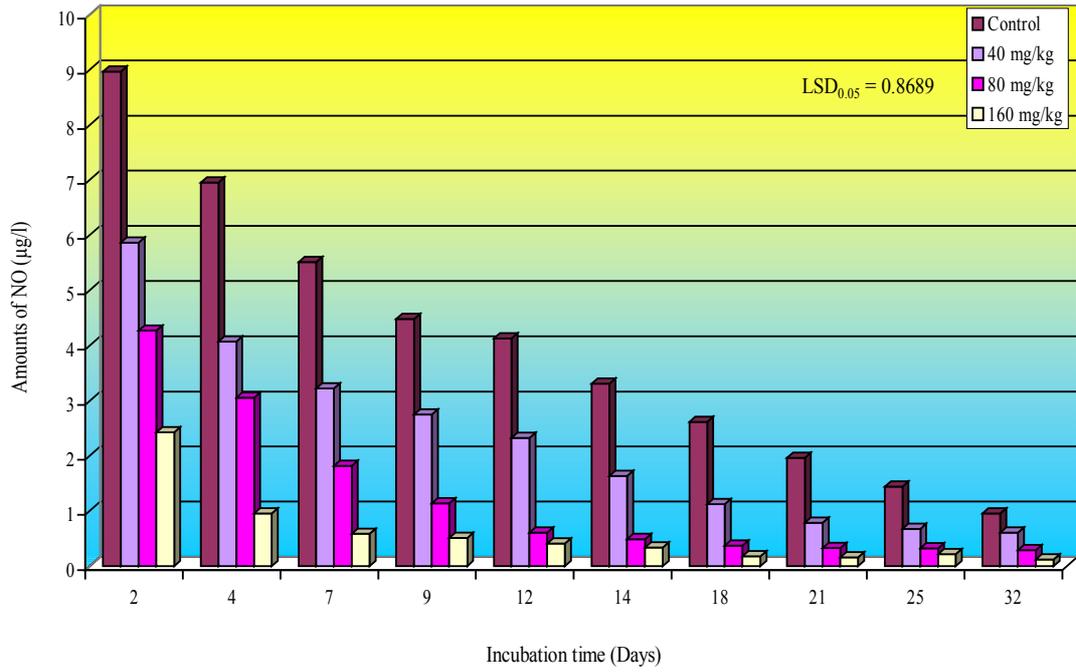


Fig. 11. Nitric oxide amounts detected in microcosm containing brown forest clay loam soil (Gödöllő) of 30% WFPS treated with different concentrations of Pb and incubated at 15°C

Table (1) Calculations of the variance analysis of NO emission from Cd treated Keszthely soil with 30% WFPS at incubation temperature 15°C

Table of Variation						F Interaction	
Source of Variation	n	FG	SQ	MQ	F	SD _{0.05}	LSD _{0.05}
Total	132	131	334.5271	2.5536			
Replications	3	2	0.1536	0.0768	0.6564	0.1429	0.2015
Treatment	44	43	324.3111	7.5421	64.4596	0.5474	0.7719
Time (A)	11	10	251.8663	25.1866	215.2605	0.2737	0.3859
Concentration (B)	4	3	58.9744	19.6581	168.0104	0.1651	0.2327
Cadmium (C)	1					0.1651	0.2327
A×B		30	13.4704	0.4490	3.8376	0.5474	0.7719
A×C						0.2737	0.3859
B×C						0.1651	0.2327
A×B×C		0	2.27374E-13			0.5474	0.7719
Error		86	10.0625	0.1170			
Accuracy of the experiment = 85.7431 %, t _{0.05} = 1.96							

Calculations of statistical analysis of NO emission from Cd treated Keszthely soil with 30% WFPS at incubation temperature 15°C

Time (Days)	Control	6 mg/kg	12 mg/kg	24 mg/kg	LSD _{0.05}	F		
2	4.1753	4.4490	4.3797	3.8535	0.3859	0		
4	4.9530	5.3498	4.3871	3.5155				
6	5.0697	4.4886	3.9502	3.0613				
9	4.4520	3.3637	2.9620	2.3748				
12	4.0458	3.0435	2.2393	1.1164				
14	3.7175	2.2007	1.7295	0.7570				
17	2.8355	1.9158	1.1683	0.5541				
20	2.4517	1.7650	0.8342	0.3904				
24	1.9966	1.1537	0.6281	0.3078				
27	1.4833	0.9493	0.6077	0.2883				
32	1.1075	0.7942	0.5251	0.1763				
LSD _{0.05}	0.2327						0.7719	
F	168.0104							64.4596

The shadow numbers are significantly negative with the controls

Table (2) Calculations of the variance analysis of emission of NO emission from Cd treated Gödöllő soil with 30% WFPS at incubation temperature 15°C

Table of Variation						F Interaction	
Source of Variation	n	FG	SQ	MQ	F	SD _{0.05}	LSD _{0.05}
Total	120	119	820.4839	6.8948	3.3744		
Replications	3	2	1.0690	0.5345	130.6421	0.1744	0.2460
Treatment	40	39	807.0596	20.6938	515.9571	0.6369	0.8981
Time (A)	10	9	735.5532	81.7281	121.6793	0.3185	0.4490
Concentration (B)	4	3	57.8224	19.2741		0.2014	0.2840
Cadmium (C)	1	0	0		3.1996	0.2014	0.2840
A×B		27	13.6841	0.5068		0.6369	0.8981
A×C		0	0			0.3185	0.4490
B×C		0	-4.5E-13			0.2014	0.2840
A×B×C		0	4.55E-13			0.6369	0.8981
Error		78	12.3553	0.1584			
Accuracy of the experiment = 89.7084 %, t _{0.05} = 1.96							

Calculations of statistical analysis of emission of NO emission from Cd treated Keszthely soil with 30% WFPS at incubation temperature 15°C

Time (Days)	Control	6 mg/kg	12 mg/kg	24 mg/kg	LSD _{0.05}	F
2	9.4044	9.0944	7.4983	6.4345	0.4490	0
4	7.9586	7.4088	7.2432	6.4543		
7	6.4606	5.8194	5.8027	5.1758		
9	6.1097	4.8445	4.4984	4.1775		
12	5.5066	4.2532	3.0545	2.8083		
14	4.5234	3.6616	2.5232	1.7681		
18	3.5472	2.3541	2.2838	1.4378		
21	2.4963	1.3807	1.3112	0.8279		
25	1.4577	1.1482	0.8002	0.4326		
32	1.1115	0.8556	0.5791	0.1795		
LSD _{0.05}	0.2840					
F	121.6793					130.6421

The shadow numbers are significantly negative with the controls

When the soil was contaminated with Pb and after two days of incubation, the detection NO amounts in the microcosms of control soil samples of Keszthely (Figure 10) was 4.1753 $\mu\text{g l}^{-1}$, while the detected amounts from Gödöllő (Figure 11) was 8.9696 $\mu\text{g l}^{-1}$. (Figure 10) demonstrates that the amount of detected NO in control microcosms was increased by increasing the incubation time up to the 14th day and it started to decrease gradually to be at the minimum (0.4210 $\mu\text{g l}^{-1}$) at the 32nd day of incubation. The results showed that the amount of NO in the soil contaminated with 40 mg Pb kg⁻¹ soil was at the maximum (5.5274 $\mu\text{g l}^{-1}$) in the 2nd day of incubation and followed by gradual reduction in the emissions to be at minimum in the 32nd day of incubation (0.0904 $\mu\text{g l}^{-1}$). Also, the amounts of gas detected in the microcosms contaminated by 80 mg Pb kg⁻¹ soil were higher than those detected in microcosms of soil contaminated by 160 mg Pb kg⁻¹ soil and lesser than those contaminated by 40 mg Pb kg⁻¹ soil. Similar tendency of results were obtained from the microcosms of Gödöllő (Figure 11).

(Figures A-10 and A-11) illustrate the linear regression, correlation (R^2), correlation coefficient (r), standard deviation (SD) and coefficients of variability (CV%) for the gas detection in Keszthely and Gödöllő, respectively. Similarly, it was found that the values of CV% were

increased by increasing the concentrations of soil contaminant metal. Table 3 demonstrates the calculations of statistical analysis and the interaction between the investigated factors and the detected amounts of NO from the microcosms of soil samples of Keszthely and the calculated value of the $LSD_{0.05}$ was 0.6041. The relationship between the amounts of NO in control and the microcosms of soil contaminated with 40 mg Pb has positive significant difference at the 2nd day of incubation, but it was negative between the 9th and 32nd day of incubation. While the relationship between the amounts of NO under the stresses of 80 and 160 mg Pb kg⁻¹ soil was negatively significant.

Table 4 demonstrates the calculations of ANOVA, statistical analysis and the interaction between the investigated factors and the detected amounts of NO from the microcosms of soil samples of Gödöllő and the calculated value of the $LSD_{0.05}$ was 0.8689. Negative significant differences between the amounts of NO in control and in Pb contaminated soil microcosms were recognized.

Comparatively, according to the results the experimental observations of the amounts of NO detected from the two (Keszthely and Gödöllő) soils, it is necessary to mention that the soil characteristics (e.g., soil pH, organic and inorganic contents, etc.) may be the main factors for gas emissions under the investigated ecological factors. These soil conditions and other ecological factors are suitable for the NO production, consumption and emission. The amount of NO detected is the net amount of the above mentioned processes. The emissions of gas in Gödöllő microcosms were more than emitted from Keszthely microcosms. Also heavy metal acted as inhibitors of gas emission. From Keszthely and Gödöllő microcosms, Pb is more inhibit NO emission than Cd.

4.4.2. EXPERIMENT 2: AT LOW TEMPERATURE AND HIGH SOIL MOISTURE CONTENT

The experiment was set up with the microcosms of two soils (Keszthely and Gödöllő) with 60% WFPS incubated at 15°C for 33 days under the stresses of different concentrations of cadmium and lead. (Figure 12) shows that the amounts of NO detected under the effect of Cd were decreased since the first detection at 2nd day of incubation and the reduction in the gas emissions was reversely proportional with the increasing the Cd concentrations and time of incubation. From the (Figure 12) the amount of NO detected in the microcosms of 24 mg Cd contaminated soil decreased from 5.4178 at 5th incubation day to 1.2729 at 19th day of incubation and 0.0124 $\mu\text{g l}^{-1}$ at the 33rd day of incubation. Similar tendencies were demonstrated in the microcosms containing Gödöllő soil samples (Figure 13). The results indicated that the amounts of NO at Gödöllő soil samples contaminated with 24 mg Cd kg soil⁻¹ were sharply decreased from 4.5939 $\mu\text{g l}^{-1}$ at the 3rd day of incubation to 1.6757 $\mu\text{g l}^{-1}$ at the 4th day of incubation and gradually decreased to 0.6350 $\mu\text{g l}^{-1}$ at the 13th day of incubation to reach 0.2186 $\mu\text{g l}^{-1}$ at the 33rd day of incubation. (Figures A-12 and A-13) illustrate the linear regression, correlation (R^2), correlation coefficient (r), standard deviation (SD) and coefficients of variability (CV%) for the gas detection in Keszthely and Gödöllő, respectively. For example, it was found that the values of CV% were increased by increasing the concentrations of the soil metal contaminant. Table 5 demonstrates the calculations of ANOVA, statistical analysis and the interaction between the investigated factors and the detected amounts of NO from the microcosms of soil samples of Keszthely and the calculated value of the $LSD_{0.05}$ was 0.5285. The Table 5 also shows the detected amounts of NO in microcosms contaminated with 12 and 24 mg Cd were significantly negative with the controls. This conclusion was found with soil contaminated by 6 mg Cd, but the negative significant differences were found during the period of incubation between the 5th and 29th days of incubations. Table 6 illustrates the ANOVA and the statistical analysis of NO detection from Gödöllő soil samples contaminated with Cd under the low temperature and high soil moisture content. It was found that the amounts of NO detected in Cd contaminated soil samples were negatively significant differences with the control samples during the whole period of incubation. The calculated value of the $LSD_{0.05}$ was 0.4069. Similar tendencies were found in the detections amounts of NO in Keszthely (Figures 14) and Gödöllő (Figures 15) soil samples were obtained under the impacts of Pb concentrations. From (Figures 14 and 15), it was found that Pb causes

more inhibition in Gödöllő (Figure 15) than in Keszthely (Figure 14) soil samples. (Figures A-14 and A-15) illustrate the linear regression, correlation (R^2), correlation coefficient (r), standard deviation (SD) and coefficients of variability (CV%) for the gas detection in Keszthely and Gödöllő, respectively. For example, it was found that the values of CV% were increased by increasing the heavy metal concentrations. Table 7 demonstrates the calculations of statistical analysis and the interaction between the investigated factors and the detected amounts of NO from the microcosms of soil samples of Keszthely and the calculated value of the $LSD_{0.05}$ was 1.2274, while the $LSD_{0.05}$ of Gödöllő microcosms was 0.2902 (Table 8). Table 7 illustrates the ANOVA Table shows negative significant differences between the microcosms of control and the microcosms of the 80 and 160 mg Pb during the incubation period from 3rd to 33rd incubation day, and during 8th day to 19th day of incubation. However, the Table 8 illustrates the significant differences between the microcosms of control and the microcosms of the 40, 80 and 160 mg Pb during the incubation period.

Table (3) Calculations of the variance analysis of NO emission from Pb treated Keszthely soil with 30% WFPS at incubation temperature 15°C

Table of Variation						F Interaction	
Source of Variation	n	FG	SQ	MQ	F	SD _{0.05}	LSD _{0.05}
Total	132	131	373.5069	2.8512			
Replications	3	2	0.1033	0.0516	0.72061	0.1119	0.1577
Treatment	44	43	367.2408	8.5405	119.1790	0.4284	0.6041
Time (A)	11	10	231.0404	23.1040	322.4076	0.2142	0.3020
Concentration (B)	4	3	110.8753	36.9584	515.7400	0.1292	0.1821
Lead (C)	1					0.1292	0.1821
A×B		30	25.3251	0.8442	11.7801	0.4284	0.6041
A×C			0			0.2142	0.3020
B×C			0			0.1292	0.1821
A×B×C		0	-4.5E-13			0.4284	0.6041
Error		86	6.1628	0.0717			
Accuracy of the experiment = 89.1041 %, $t_{0.05} = 1.96$							

Calculations of statistical analysis of NO emission from Cd treated Keszthely soil with 30% WFPS at incubation temperature 15°C

Time (Days)	Control	40 mg/kg	80 mg/kg	160 mg/kg	LSD _{0.05}	F		
2	4.1753	5.5274	3.3041	2.9015	0.3020	0		
4	5.2429	4.8887	3.9920	3.0946				
6	5.1497	4.6855	3.7996	2.4850				
9	4.9417	4.1067	2.9053	1.9420				
12	4.7184	3.5598	2.0699	1.0947				
14	4.2801	2.9380	1.5451	0.7038				
17	3.6923	2.3057	1.4279	0.4572				
20	3.2288	2.0714	1.1790	0.3343				
24	2.4718	1.5906	0.7810	0.2887				
27	1.5551	1.0872	0.5575	0.2432				
32	0.4210	0.0904	0.1868	0.0795				
LSD _{0.05}	0.182127102						0.6041	
F	515.7498							119.1790

The bold numbers are significantly positive with the controls

The shadow numbers are significantly negative with the controls

Table (4) Calculations of the variance analysis of emission of NO from Pb treated Gödöllő soil with 30% WFPS at incubation temperature 15°C

Table of Variation						F Interaction	
Source of Variation	n	FG	SQ	MQ	F	SD _{0.05}	LSD _{0.05}
Total	120	119	532.5224	4.4750	0.0396		
Replications	3	2	0.0117	0.0059	90.0840	0.1688	0.2380
Treatment	40	39	520.9449	13.3576	196.4808	0.6162	0.8689
Time (A)	10	9	262.2057	29.1340	454.3304	0.3081	0.4345
Concentration (B)	4	3	202.1029	67.3676		0.1949	0.2748
Lead (C)	1	0	0		14.1466	0.1949	0.2748
A×B		27	56.6363	2.0976	0.0396	0.6162	0.8689
A×C		0	0			0.3081	0.4345
B×C		0	-1.1E-13			0.1949	0.2748
A×B×C		0	1.14E-13			0.6162	0.8689
Error		78	11.5658	0.14828			
Accuracy of the experiment = 81.2111 %, t _{0.05} = 1.96							

Calculations of statistical analysis of emission of NO from Pb treated Gödöllő soil with 30% WFPS at incubation temperature 15°C

Time (Days)	Control	40 mg/kg	80 mg/kg	160 mg/kg	LSD _{0.05}	F
2	8.9696	5.8694	4.2713	2.4296	0.4345	0
4	6.9543	4.0698	3.0547	0.9500		
7	5.5091	3.2184	1.8226	0.5867		
9	4.4775	2.7499	1.1397	0.5142		
12	4.1255	2.3278	0.6089	0.4095		
14	3.3094	1.6386	0.4874	0.3371		
18	2.6150	1.1198	0.3722	0.1803		
21	1.9640	0.7850	0.3264	0.1623		
25	1.4452	0.6716	0.3174	0.2152		
32	0.9558	0.6096	0.2913	0.1168		
LSD _{0.05}	0.27477					
F	454.3304					90.0840

The shadow numbers are significantly negative with the controls

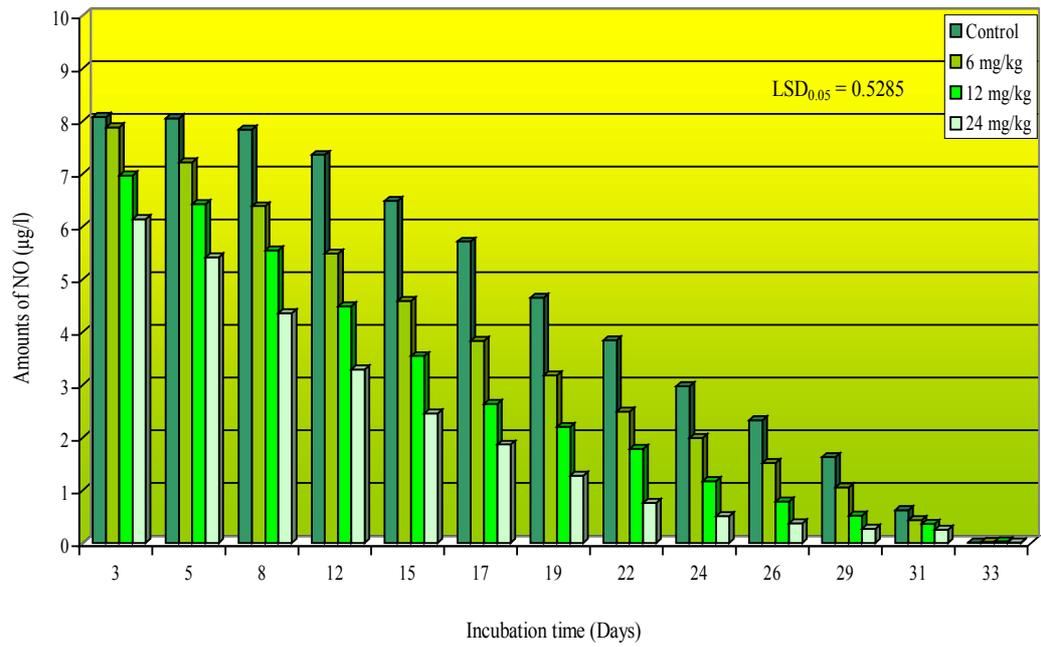


Fig. 12. Nitric oxide amounts detected in microcosm containing Ramann's brown forest soil (Keszthely) of 60% WFPS treated with different concentrations of Cd and incubated at 15°C

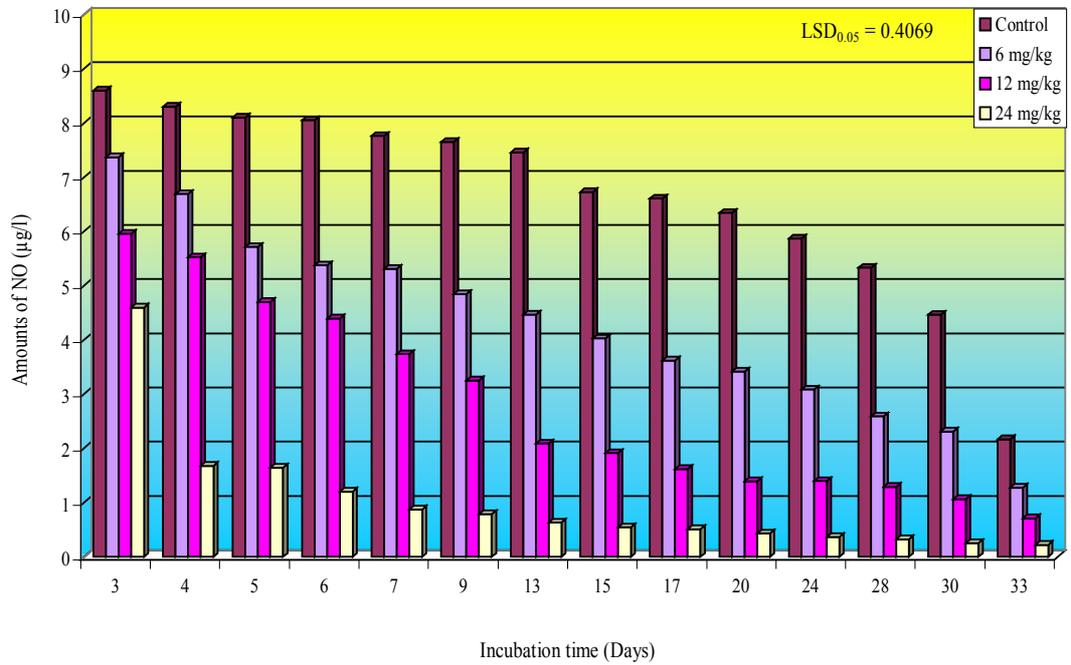


Fig. 13. Nitric oxide amounts detected in microcosm containing brown forest clay loam soil (Gödöllő) of 60% WFPS treated with different concentrations of Cd and incubated at 15°C

Table (5) Calculations of the variance analysis of emission of NO from Cd treated Keszthely soil with 60% WFPS at incubation temperature 15°C

Table of Variation						F Interaction	
Source of Variation	n	FG	SQ	MQ	F	SD _{0.05}	LSD _{0.05}
Total	156	155	1051.430	6.7834			
Replications	3	2	0.0210	0.0105	0.1914	0.0900	0.1270
Treatment	52	51	1045.813	20.5062	373.7856	0.3748	0.5285
Time (A)	13	12	875.3882	72.9490	1329.713	0.1874	0.2643
Concentration (B)	4	3	134.3197	44.7732	816.1257	0.1040	0.1466
Cadmium (C)	1	0	0			0.1040	0.1466
A×B		36	36.1055	1.0029	18.2814	0.3748	0.5286
A×C		0	0			0.1874	0.2643
B×C		0	-4.5E-13			0.1040	0.1466
A×B×C		0	-9.1E-13			0.3748	0.5285
Error		102	5.5958	0.0549			
Accuracy of the experiment = 92.7980 %, t _{0.05} = 1.96							

Calculations of statistical analysis of emission of NO from Cd treated Keszthely soil with 60% WFPS at incubation temperature 15°C

Time (Days)	Control	6 mg/kg	12 mg/kg	24 mg/kg	LSD _{0.05}	F
3	8.0810	7.8777	6.9696	6.1375	0.2643	0
5	8.0546	7.2170	6.4218	5.4178		
8	7.8337	6.3858	5.5438	4.3603		
12	7.3588	5.4898	4.4841	3.2935		
15	6.4856	4.5940	3.5453	2.4596		
17	5.7146	3.8324	2.6331	1.8667		
19	4.6522	3.1789	2.2025	1.2729		
22	3.8418	2.4890	1.7812	0.7571		
24	2.9749	1.9936	1.1730	0.5147		
26	2.3277	1.5169	0.7889	0.3767		
29	1.6336	1.0543	0.5177	0.2672		
31	0.6219	0.4354	0.3629	0.2486		
33	0.0126	0.0169	0.0315	0.0124		
LSD _{0.05}	0.1466					
F	816.1257					373.7856

The shadow numbers are significantly negative with the controls

Table (6) Calculations of the variance analysis of emission of NO from Cd treated Gödöllő soil with 60% WFPS at incubation temperature 15°C

Table of Variation						F Interaction	
Source of Variation	n	FG	SQ	MQ	F	SD _{0.05}	LSD _{0.05}
Total	168	167	1140.34	6.8284			
Replications	3	2	0.0507	0.0254	0.7804	0.0668	0.0942
Treatment	56	55	1136.713	20.6675	635.6854	0.2886	0.4069
Time (A)	14	13	349.9473	26.9190	827.968	0.1443	0.2034
Concentration (B)	4	3	725.8932	241.9644	7442.275	0.0771	0.1087
Cadmium (C)	1	0	0			0.0771	0.1087
A×B		39	60.8721	1.5608	48.0074	0.2886	0.4069
A×C		0	0			0.1443	0.2034
B×C		0	4.55E-13			0.0771	0.1087
A×B×C		0	-2.3E-12			0.2886	0.4069
Error		110	3.5763	0.0325			
Accuracy of the experiment = 95.1121 %, t _{0.05} = 1.96							

Calculations of statistical analysis of emission of NO from Cd treated Gödöllő soil with 60% WFPS at incubation temperature 15°C

Time (Days)	Control	6 mg/kg	12 mg/kg	24 mg/kg	LSD _{0.05}	F
3	8.5964	7.3678	5.9559	4.5939	0.2034	0
4	8.2993	6.6871	5.5213	1.6757		
5	8.1004	5.7173	4.6994	1.6417		
6	8.0484	5.3778	4.3911	1.2011		
7	7.7562	5.3077	3.7367	0.8708		
9	7.6485	4.8418	3.2495	0.7879		
13	7.4555	4.4638	2.0887	0.6350		
15	6.7267	4.0289	1.9110	0.5451		
17	6.6075	3.6232	1.6186	0.5107		
20	6.3439	3.4175	1.3955	0.4346		
24	5.8676	3.0852	1.3979	0.3628		
28	5.3308	2.5891	1.2890	0.3257		
30	4.4617	2.3101	1.0659	0.2513		
33	2.1635	1.2735	0.7085	0.2186		
LSD _{0.05}	0.1087				0.4069	
F	7442.2750					635.6854

The shadow numbers are significantly negative with the control

4.4.3. EXPERIMENT 3: AT HIGH TEMPERATURE AND HIGH SOIL MOISTURE CONTENT

The microcosms of Keszthely soil samples with 60% WFPS incubated at 37°C for 32 days under the stresses of different concentrations of cadmium (Figure 16) and lead (Figure 17).

The rate of NO emissions due to the impacts of two heavy metals was decreased gradually throughout the incubation time. Comparatively, similar results obtained in Cd or Pb contaminated soils at different concentrations. However, the rate of the trace gas emission was higher from soil contaminated with Pb than from soil contaminated by Cd. The results of the present study indicated that increasing the concentrations decreases the amounts of NO at 37°C. Also, Cd showed lower toxicity than Pb regarding to the rate of NO emission. From (Figures 16 and 17) we can found that the magnitude of NO emission from soil depends on the rates of nitrification and denitrification and the diffusion properties of the soil. This tendency becomes as the basis of the results obtained under different ecological factors. (Figures A-16 and A-17) show the regression lines and some statistical information of cadmium and lead, respectively. Correlation (R^2), correlation coefficient (r), standard deviation (SD) and coefficients of variability (CV%) for the gas detection in Keszthely and Gödöllő, respectively. For example, it was found that the values of CV% were increased by increasing the incubation time intervals. Tables 9 and 10 Table 7 demonstrate the calculations of statistical analysis and the interaction between the investigated factors and the detected amounts of NO from the microcosms of soil samples contaminated with cadmium ($LSD_{0.05}$ was 0.8695), and lead ($LSD_{0.05}$ was 0.6348). The ANOVA Tables in Tables 9 and 10 demonstrate negative significant differences between the microcosms of control and the microcosms of the cadmium and lead concentrations, respectively during the incubation period from 2nd to 32nd incubation day.

However, the net release of NO from soil is greatly influenced by the gas phase diffusivity in soil and the rate of NO consumption by denitrifiers. Taking in the consideration that soil WFPS was 60%, in this situation anaerobic condition is created, and the probability of NO being reconsumed by the denitrifiers is greatly enhanced. When plotting NO flux as a function of the NO concentration, the NO emission term is represented by the intercept with the y-axis; and the proportionality coefficient between NO uptake and NO concentration is given by the slope of the fitted regression line.

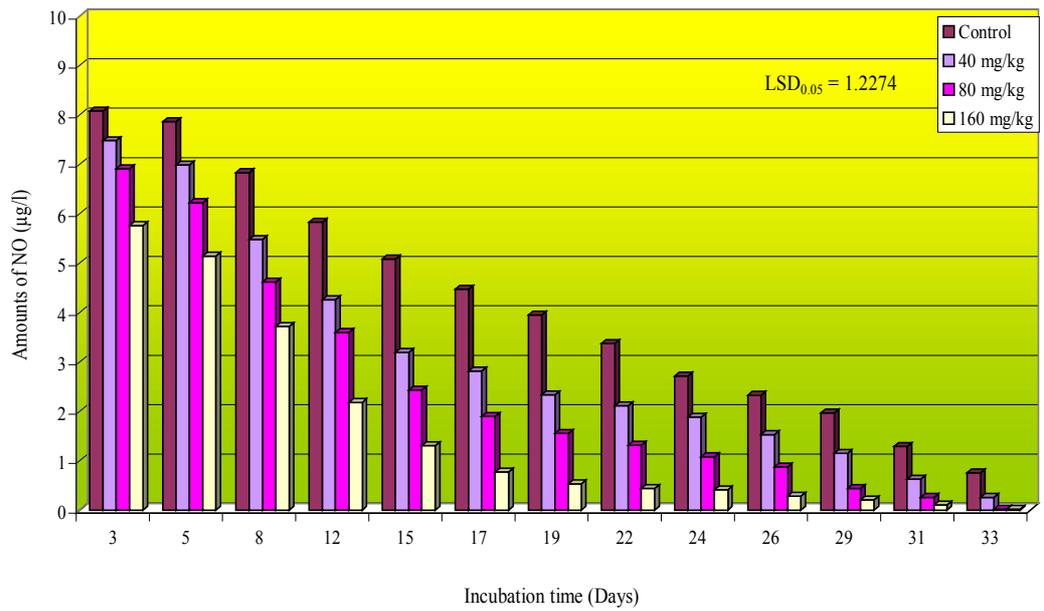


Fig. 14. Nitric oxide amounts detected in microcosm containing Ramann's brown forest soil (Keszthely) of 60% WFPS treated with different concentrations of Pb and incubated at 15°C

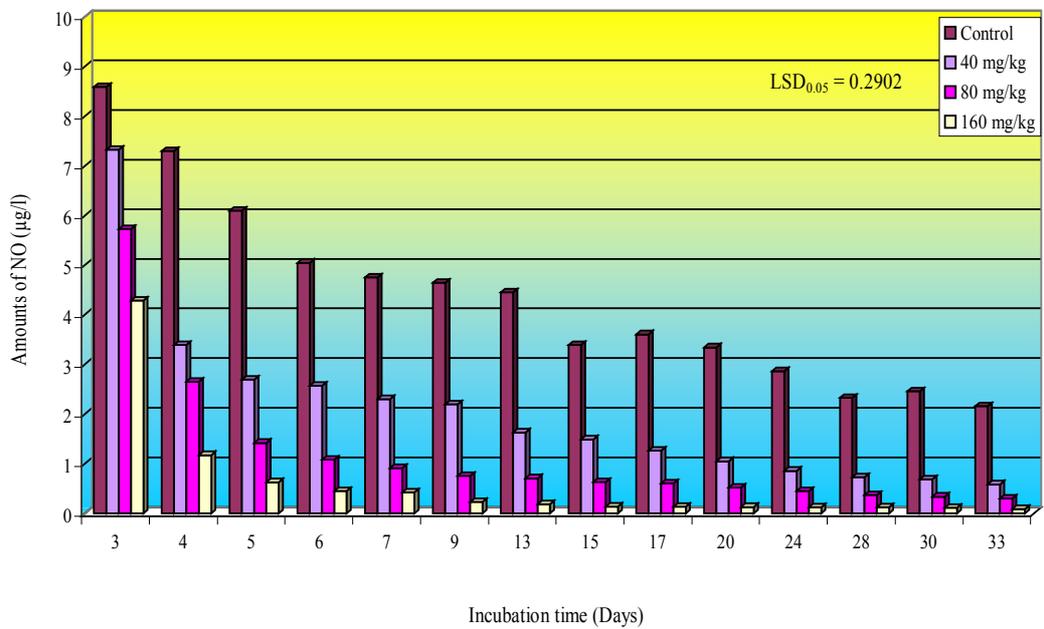


Fig. 15. Nitric oxide amounts detected in microcosm containing brown forest clay loam soil (Gödöllő) of 60% WFPS treated with different concentrations of Pb and incubated at 15°C

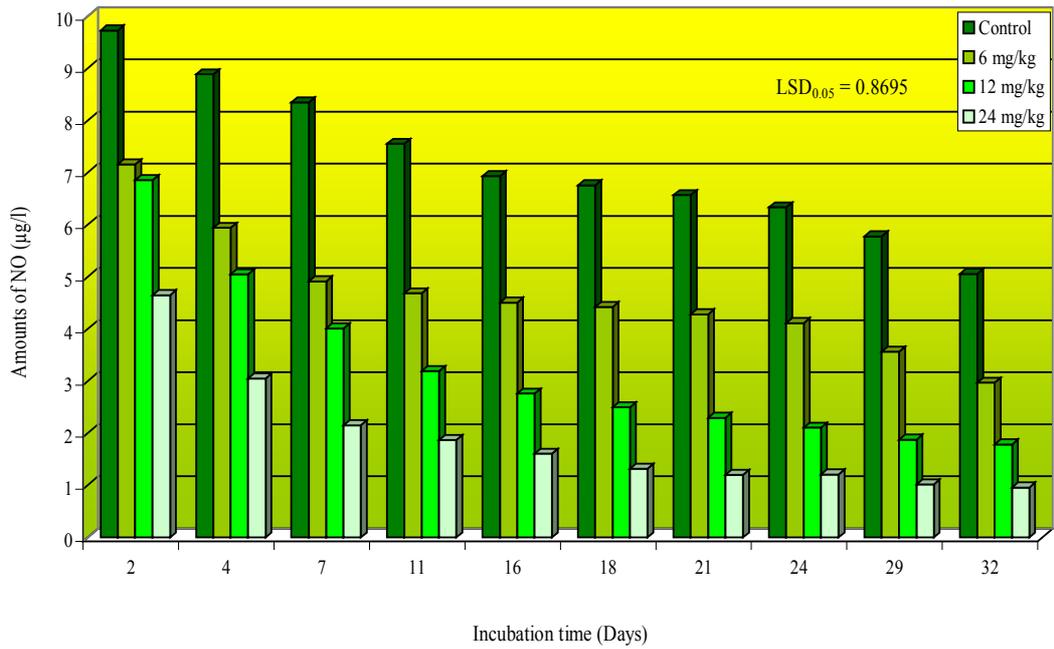


Fig. 16. Nitric oxide amounts detected in microcosm containing Ramann's brown forest soil (Keszthely) of 60% WFPS treated with different concentrations of Cd and incubated at 37°C

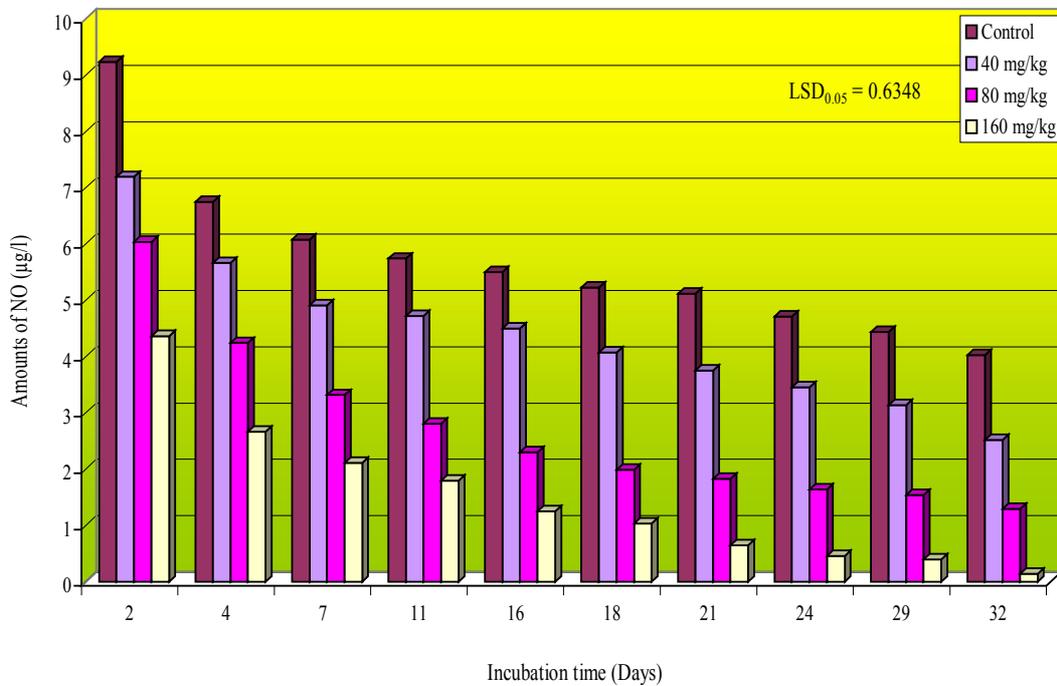


Fig. 17. Nitric oxide amounts detected in microcosm containing Ramann's brown forest soil (Keszthely) of 60% WFPS treated with different concentrations of Pb and incubated at 37°C

Table (7) Calculations of the variance analysis of emission of NO from Pb treated Keszthely soil with 60% WFPS at incubation temperature 15°C

Table of Variation						F Interaction	
Source of Variation	n	FG	SQ	MQ	F	SD _{0.05}	LSD _{0.05}
Total	156	155	908.1813	5.8592			
Replications	3	2	2.0076	1.0038	3.3928	0.2091	0.2948
Treatment	52	51	875.9955	17.1764	58.0549	0.8705	1.2274
Time (A)	13	12	716.0082	59.6674	201.6714	0.4352	0.6137
Concentration (B)	4	3	141.0574	47.0191	158.9213	0.2414	0.3404
Lead (C)	1	0	0			0.2414	0.3404
A×B		36	18.9299	0.5258	1.7773	0.8705	1.2274
A×C		0	0			0.4352	0.6137
B×C		0	0			0.2414	0.3404
A×B×C		0	-4.5E-13			0.8705	1.2274
Error		102	30.1782	0.2959			
Accuracy of the experiment = 92.7980 %, t _{0.05} = 1.96							

Calculations of statistical analysis of emission of NO from Pb treated Keszthely soil with 60% WFPS at incubation temperature 15°C

Time (Days)	Control	40 mg/kg	80 mg/kg	160 mg/kg	LSD _{0.05}	F
3	8.0810	7.4818	6.9127	5.7603	0.6137	0
5	7.8595	6.9861	6.2211	5.1396		
8	6.8337	5.4786	4.6174	3.7132		
12	5.8254	4.2592	3.5970	2.1760		
15	5.0851	3.1930	2.4295	1.3064		
17	4.4715	2.8121	1.8978	0.7711		
19	3.9502	2.3360	1.5510	0.5321		
22	3.3752	2.1122	1.3082	0.4363		
24	2.7139	1.8805	1.0814	0.4134		
26	2.3277	1.5298	0.8779	0.2804		
29	1.9669	1.1450	0.4375	0.2025		
31	1.2886	0.6265	0.2575	0.0980		
33	0.7582	0.2601	0.0194	0.0158		
LSD _{0.05}	0.3404					
F	158.9213					58.0549

The shadow numbers are significantly negative with the controls

Table (8) Calculations of the variance analysis of emission of NO from Pb treated Gödöllő soil with 60% WFPS at incubation temperature 15°C

Table of Variation						F Interaction	
Source of Variation	n	FG	SQ	MQ	F	SD _{0.05}	LSD _{0.05}
Total	168	167	739.4888	4.4281			
Replications	3	2	0.0345	0.0172	1.0415	0.0476	0.0672
Treatment	56	55	737.6355	13.4116	811.0815	0.2058	0.2902
Time (A)	14	13	353.3668	27.1821	1643.871	0.1029	0.1452
Concentration (B)	4	3	346.3516	115.4505	6982.023	0.0550	0.0776
Lead (C)	1	0	0			0.0550	0.0776
A×B		39	37.9172	0.9722	58.7972	0.2058	0.2902
A×C		0	0			0.1029	0.1451
B×C		0	6.82E-13			0.0550	0.0776
A×B×C		0	0			0.2058	0.2902
Error		110	1.8189	0.0165			
Accuracy of the experiment = 93.7148 %, t _{0.05} = 1.96							

Calculations of statistical analysis of emission of NO from Pb treated Gödöllő soil with 60% WFPS at incubation temperature 15°C

Time (Days)	Control	40 mg/kg	80 mg/kg	160 mg/kg	LSD _{0.05}	F
3	8.5964	7.3295	5.7275	4.2913	0.1451	0
4	7.2993	3.3911	2.6549	1.1751		
5	6.1004	2.6959	1.4196	0.6280		
6	5.0484	2.5779	1.0823	0.4475		
7	4.7562	2.3014	0.9168	0.4232		
9	4.6485	2.1963	0.7581	0.2319		
13	4.4555	1.6314	0.7077	0.1848		
15	3.3934	1.4891	0.6364	0.1365		
17	3.6075	1.2643	0.6068	0.1315		
20	3.3439	1.0514	0.5169	0.1289		
24	2.8676	0.8564	0.4495	0.1254		
28	2.3308	0.7281	0.3706	0.1236		
30	2.4617	0.6872	0.3386	0.1142		
33	2.1635	0.5859	0.2994	0.0866		
LSD _{0.05}	0.0776					
F	6982.023					811.0815

The shadow numbers are significantly negative with the controls

Table (9) Calculations of the variance analysis of emission of NO from Cd treated Keszthely soil with 60% WFPS at incubation temperature 37°C

Table of Variation						F Interaction	
Source of Variation	n	FG	SQ	MQ	F	SD _{0.05}	LSD _{0.05}
Total	120	119	674.0555	5.6643			
Replications	3	2	0.1388	0.0694	0.4676	0.1689	0.2381
Treatment	40	39	662.3362	16.9830	114.3885	0.6166	0.8695
Time (A)	10	9	191.6484	21.2943	143.4271	0.3083	0.4347
Concentration (B)	4	3	460.8592	153.6197	1034.7030	0.1950	0.2750
Cadmium (C)	1	0	0			0.1950	0.2750
A×B		27	9.8286	0.3640	2.4519	0.6166	0.8695
A×C		0	0			0.3083	0.4347
B×C		0	-4.5E-13			0.1950	0.2750
A×B×C		0	0			0.6166	0.8695
Error		78	11.5805	0.1485			
Accuracy of the experiment = 90.9322 %, t _{0.05} = 1.96							

Calculations of statistical analysis of emission of NO from Cd treated Keszthely soil with 60% WFPS at incubation temperature 37°C

Time (Days)	Control	6 mg/kg	12 mg/kg	24 mg/kg	LSD _{0.05}	F
2	9.7300	7.1595	6.8588	4.6487	0.4347	0
4	8.8877	5.9412	5.0502	3.0521		
7	8.3471	4.9152	4.0108	2.1527		
11	7.5572	4.6864	3.1893	1.8721		
16	6.9318	4.5072	2.7615	1.6061		
18	6.7560	4.4216	2.4947	1.3160		
21	6.5693	4.2807	2.2977	1.2002		
24	6.3344	4.1144	2.1086	1.2067		
29	5.7775	3.5650	1.8771	1.0146		
32	5.0597	2.9707	1.7838	0.9572		
LSD _{0.05}	0.2750					
F	1034.7030					114.3885

The shadow numbers are significantly negative with the controls

Table (10) Calculations of the variance analysis of emission of NO from Pb treated Keszthely soil with 60% WFPS at incubation temperature 37°C

Table of Variation						F Interaction	
Source of Variation	n	FG	SQ	MQ	F	SD _{0.05}	LSD _{0.05}
Total	120	119	526.5112	4.4245			
Replications	3	2	0.0281	0.0140	0.1775	0.1233	0.1739
Treatment	40	39	520.3097	13.3413	168.5654	0.4502	0.6348
Time (A)	10	9	209.8483	23.3165	294.6009	0.2251	0.3174
Concentration (B)	4	3	307.1758	102.3919	1293.7100	0.1424	0.2008
Lead (C)	1	0	0			0.1424	0.2008
A×B		27	3.2856	0.12169	1.5375	0.4502	0.6348
A×C		0	0			0.2251	0.3175
B×C		0	6.82E-13			0.1424	0.2008
A×B×C		0	-9.1E-13			0.4502	0.6348
Error		78	6.1734	0.0792			
Accuracy of the experiment = 92.1045 %, t _{0.05} = 1.96							

Calculations of statistical analysis of emission of NO from Pb treated Keszthely soil with 60% WFPS at incubation temperature 37°C

Time (Days)	Control	40 mg/kg	80 mg/kg	160 mg/kg	LSD _{0.05}	F
2	9.2351	7.1903	6.0348	4.3621	0.3174	0
4	6.7477	5.6660	4.2416	2.6643		
7	6.0742	4.9109	3.3141	2.1076		
11	5.7411	4.7173	2.8084	1.7972		
16	5.5002	4.4968	2.2999	1.2517		
18	5.2206	4.0699	1.9822	1.0321		
21	5.1159	3.7476	1.8262	0.6426		
24	4.7133	3.4539	1.6347	0.4547		
29	4.4339	3.1353	1.5363	0.3965		
32	4.0242	2.5181	1.2901	0.1373		
LSD _{0.05}	0.2008					
F	1293.7100					168.5654

The shadow numbers are significantly negative with the controls

4.5. EMISSIONS OF N₂O UNDER THE STRESSES OF HEAVY METALS

Denitrification was the main process responsible for total N₂O emissions from soil. N₂O emissions were influenced by the contamination of soil by Cd or Pb and several peaks were registered for each treatment during the experimental period at low (15°C) and high (37°C) incubation temperatures. For 5 cm soil layer, the total rate of N₂O production decreased as the concentration of Cd or Pb increased. These results are consistent with a previous study at the same origin site where the soil cores for this study were collected. In this study, N₂O emissions were suppressed for several weeks from test microcosms amended with a single application of different concentrations of Cd or Pb. Production of N₂O by either net nitrification or net denitrification decreased with increasing concentration of the heavy metal that contaminated soil samples. However, the relative importance of nitrification for N₂O production decreased as the concentration of Cd or Pb increased. Therefore, the total inhibitory effect of the heavy metals on nitrification was greater than that for denitrification in terms of N₂O production. The degree of inhibition was depended on the degree of the contamination with Cd and Pb.

4.5.1. EXPERIMENT 4: AT LOW TEMPERATURE AND HIGH SOIL MOISTURE CONTENT

The N₂O emissions under soil conditions of incubation temperature at 15°C and moisture regime of 60% WFPS, were detected in the two soil samples originated from two field sites under the impacts of different concentrations of Cd and Pb. In both soil samples, heavy metal free soil samples had the maximum detected amounts of N₂O emissions throughout the incubation period. When the soil microcosms incubated at low temperature (15°C), the microcosms of Keszthely soil (Figure 18) contaminated by Cd showed decrease in N₂O detected and the emission was more rapidly decreased than those obtained from the microcosms of Gödöllő soil (Figure 19) contaminated by Cd.

In the Keszthely soil contaminated by Cd, the maximum N₂O emission was 4.948 µg l⁻¹ at the 3rd day of incubation in the microcosms of soil contaminated by 6 mg Cd, while the minimum amount (0.6661 µg l⁻¹) of N₂O was detected at 33rd day of incubation at 24 mg Cd. The microcosms of soil samples originated from Gödöllő had higher N₂O amounts than those detected in the microcosms of Keszthely soil samples and their maximum N₂O emissions at 6 mg Cd was 8.1076 µg l⁻¹ at the 3rd day of incubation. The minimum amount (0.3945) of the N₂O emissions was detected at 32nd day of incubation at 24 mg Cd. In both soil samples (Keszthely and Gödöllő), similar rates of emissions were recognized after the 15th day of incubation and at the end of incubation time interval, the microcosms of Gödöllő soil samples showed that N₂O emission rates were more sensitive property of the degree of contamination with Cd than those microcosms of Keszthely. (Figures A-18 and A-19) indicated the some statistical determinations (ccorrelation (R²), correlation coefficient (r), standard deviation (SD) and coefficients of variability (CV%) and the mode of regression lines of detected amounts of N₂O in the microcosms of Keszthely and Gödöllő soil samples, respectively. Also, it was found that the values of CV% were increased by increasing the metal concentrations. These decreases in N₂O were statistically negatively significant in Keszthely soil samples (Table 11) at 24 mg Cd throughout the incubation time intervals, and at the 12 mg Cd contamination dose except the detected amount between the 17th and 22nd incubation days. But in soil samples contaminated by 6 mg Cd, the results were not significant at all time intervals except at 3rd, 12th, and 26th incubation days were negatively significant. Table 12 shows that in the microcosms of Gödöllő soil samples, there was no significant difference between the N₂O detected amounts at the 6 mg Cd throughout the incubation period except at the 7th day. While the ANOVA Table indicated negative significant differences when the contamination doses of Cd were 12 mg (except at the 4th, 24th, 28th, 30th, and 32nd day) and 24 mg (except at 28th, 30th, and 32nd days). The LSD_{0.05} values of the observations of the microcosms from Gödöllő and Keszthely soil samples were 0.7237 and 0.5224, respectively. In case of contaminating the soil samples with different doses of Pb, the microcosms of Keszthely soil samples (Figure 20) illustrates much lower N₂O emissions than those emitted from Gödöllő soil samples (Figure 21). The minimum detected amounts of N₂O were 0.5802 (Keszthely soil

sample) and 1.1124 (Gödöllő soil samples) at 160 mg Pb. The maximum amounts of N₂O were detected was 5.821 μg l⁻¹ at the 3rd day of incubation in Keszthely soil samples where it was 13.7579 μg l⁻¹ at the 3rd day of incubation in the microcosms of Gödöllő soil samples when contaminated by 40 mg Pb. It can be noted that approximately double amounts of gas emissions were detected in the microcosms of Gödöllő soil samples. (Figures A-20 and A-21) demonstrate some statistical determinations and the modes of regression lines of the amounts of N₂O detected in Keszthely (Figure A-20) and in Gödöllő (Figure A-21) soil samples. Also, it was found that the values of CV% increased with the increasing applied doses of the heavy metals. However, Table 13 and Table 14 illustrate the ANOVA and some statistical interactions between the investigated parameters in the microcosms of soil samples contaminated by different concentrations of Pb of Keszthely and Gödöllő, respectively. The LSD_{0.05} for the emissions of N₂O from the two soil samples were 0.5647 and 1.2039, respectively. It was found that no significant differences between the control Keszthely (Table 13) soil samples and the contaminated soil with 40 mg, also with 80 mg Pb except those detected at 3rd, 4th, 15th and at 33rd day of incubation. However, it was negatively significant differences under the stresses of 160 mg Pb throughout the incubation intervals except those detected at 24th, 26th and 29th day. While in the case of the microcosms of soil samples from Gödöllő, the results showed negative significant differences under the effect of 80 and 160 mg Pb. Under the effect of 40 mg Pb contamination, the emissions of N₂O were not significant differences except at 22nd, 28th, 30th, and 32nd incubation day.

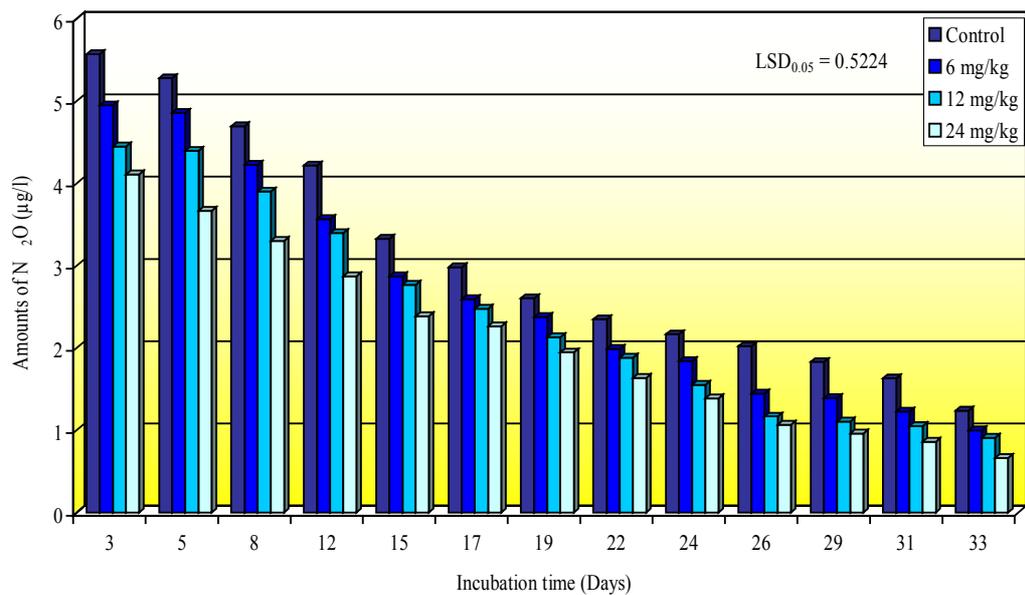


Fig. 18. Nitrous oxide amounts detected in microcosm containing Ramann's brown forest soil (Keszthely) of 60% WFPS treated with different concentrations of Cd and incubated at 15°C

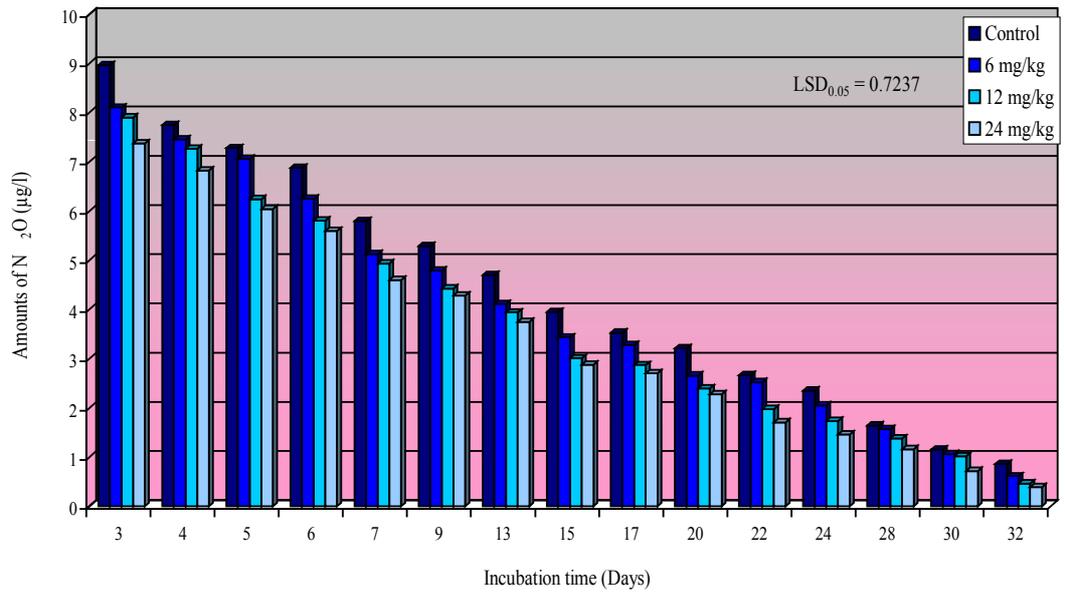


Fig. 19. Nitrous oxide amounts detected in microcosm containing brown forest clay loam soil (Gödöllő) of 60% WFPS treated with different concentrations of Cd and incubated at 15°C

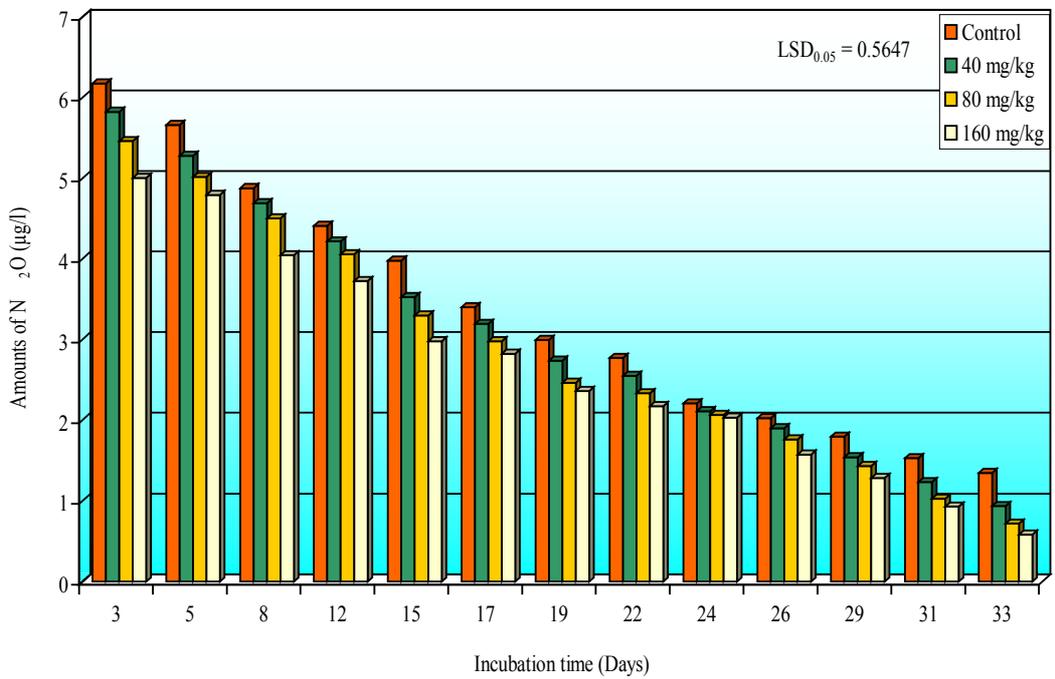


Fig. 20. Nitrous oxide amounts detected in microcosm containing Ramann's brown forest soil (Keszthely) of 60% WFPS treated with different concentrations of Pb and incubated at 15°C

Table (11) Calculations of the variance analysis of emission of N₂O from Cd treated Keszthely soil with 60% WFPS at incubation temperature 15°C

Table of Variation						F Interaction	
Source of Variation	n	FG	SQ	MQ	F	SD _{0.05}	LSD _{0.05}
Total	156	155	273.2996	1.7632			
Replications	3	2	0.3620	0.1810	3.3771	0.0890	0.1255
Treatment	52	51	267.4702	5.2445	97.8417	0.3705	0.5224
Time (A)	13	12	244.4963	20.3747	380.1104	0.1853	0.2612
Concentration (B)	4	3	20.1366	6.7122	125.2229	0.1028	0.1449
Cadmium (C)	1	0	0			0.1028	0.1449
A×B		36	2.8373	0.0788	1.4704	0.3705	0.5224
A×C		0	0			0.1853	0.2612
B×C		0	0			0.1028	0.1449
A×B×C		0	2.27E-13			0.3705	0.5224
Error		102	5.4674	0.0536			
Accuracy of the experiment = 90.9164 %, t _{0.05} = 1.96							

Calculations of statistical analysis of emission of N₂O from Cd treated Keszthely soil with 60% WFPS at incubation temperature 15°C

Time (Days)	Control	6 mg/kg	12 mg/kg	24 mg/kg	LSD _{0.05}	F
3	5.5721	4.9486	4.4472	4.1098	0.26121	0
5	5.2764	4.8575	4.3937	3.6689		
8	4.6922	4.2269	3.9004	3.3009		
12	4.2175	3.5663	3.3952	2.8700		
15	3.3269	2.8693	2.7711	2.3839		
17	2.9793	2.5932	2.4747	2.2637		
19	2.6056	2.3736	2.1304	1.9476		
22	2.3510	1.9866	1.8804	1.6388		
24	2.1658	1.8410	1.5521	1.3853		
26	2.0221	1.4443	1.1659	1.0681		
29	1.8306	1.3916	1.1039	0.9638		
31	1.6320	1.2256	1.0504	0.8609		
33	1.2394	0.9991	0.9093	0.6661		
LSD _{0.05}	0.1449					
F	125.2229					97.8417

The shadow numbers are significantly negative with the controls

Table (12) Calculations of the variance analysis of emission of N₂O from Cd treated Gödöllő soil with 60% WFPS at incubation temperature 15°C

Table of Variation						F Interaction	
Source of Variation	n	FG	SQ	MQ	F	SD _{0.05}	LSD _{0.05}
Total	180	179	986.3628	5.5104			
Replications	3	2	0.3170	0.1585	1.5410	0.1148	0.1618
Treatment	60	59	973.9074	16.5069	160.4681	0.5133	0.7237
Time (A)	15	14	947.5656	67.6833	657.9671	0.2566	0.3619
Concentration (B)	4	3	22.8196	7.6065	73.9451	0.1325	0.1869
Cadmium (C)	1	0	0			0.1325	0.1869
A×B		42	3.5222	0.0839	0.8153	0.5133	0.7237
A×C		0	0			0.2566	0.3619
B×C		0	-4.5E-13			0.1325	0.1869
A×B×C		0	9.09E-13			0.5133	0.7237
Error		118	12.1383	0.1029			
Accuracy of the experiment = 91.7513 %, t _{0.05} = 1.96							

Calculations of statistical analysis of emission of N₂O from Cd treated Gödöllő soil with 60% WFPS at incubation temperature 15°C

Time (Days)	Control	6 mg/kg	12 mg/kg	24 mg/kg	LSD _{0.05}	F
3	8.9641	8.1076	7.9036	7.3743	0.3619	0
4	7.7479	7.4610	7.2678	6.8232		
5	7.2810	7.0635	6.2417	6.0461		
6	6.8759	6.2547	5.8059	5.5979		
7	5.7951	5.1244	4.9375	4.6028		
9	5.2886	4.7919	4.4266	4.2807		
13	4.6985	4.1157	3.9434	3.7487		
15	3.9515	3.4354	3.0090	2.8757		
17	3.5333	3.2817	2.8734	2.7047		
20	3.2147	2.6602	2.3931	2.2767		
22	2.6667	2.5272	1.9758	1.7103		
24	2.3482	2.0489	1.7317	1.4585		
28	1.6402	1.5727	1.3832	1.1598		
30	1.1531	1.0667	1.0142	0.7220		
32	0.8623	0.6144	0.4631	0.3945		
LSD _{0.05}	0.18673				0.7237	
F	73.9451					160.4681

The shadow numbers are significantly negative with the controls

4.5.2. EXPERIMENT 5: AT HIGH TEMPERATURE AND HIGH SOIL MOISTURE CONTENT

The effect of Cd on the N₂O emissions in Keszthely soil samples when the water content was elevated to 60% WFPS and incubated at 37°C is illustrated in (Figure 22) shows increases in the emissions of N₂O in the comparison with the emissions at 15°C (Figure 18) at the same moisture regime. Maximum emission of the gas in soil contaminated with 6 mg Cd at the 4th day of incubation was 5.9250 µg l⁻¹ at the 4th day of incubation while the lowest value of emission was 0.0817 µg l⁻¹ at the at 31st day of incubation under the effect of 24 mg Cd. (Figure A-22) shows some statistical determinations and the linear regression model of the emissions of N₂O under the conditions studied. It was found that the CV% increased by increasing the concentrations of Cd contaminations. Table 15 demonstrates the interaction relationship between the N₂O emissions at the study parameters. The ANOVA test shows the LSD_{0.05} for the emissions of N₂O was 0.9748, and also no significant difference between the emission of N₂O at control microcosms and in microcosms of treated soil samples, except the emissions of the gas at 4th and 7th day of incubation under the effect of 12 mg and 24 mg Cd and 10th day of incubation in soil samples contaminated by 24 mg Cd. (Figure 23) indicates that under the similar incubation conditions, the emission rate of the gas under Pb stress at 37°C was little higher than those emitted at 15°C (Figure 20). The maximum emission rate at 37°C was 6.2861 µg l⁻¹ at the 4th day of incubation while at 15°C was 5.8231 µg l⁻¹ at the 3rd day of incubation. It was found that at 15th day of incubation, the emission rates of the gas were 3.4944, 2.9097, 1.5153 µg l⁻¹ when the incubation temperature was 37°C, and they were 3.5269, 3.2990 and 2.9758 µg l⁻¹ when the microcosms incubated at 15°C. Meanwhile, at 31st day of incubation, the emission rates of the gas were 1.2320, 1.0260, 0.9270 µg l⁻¹ at 15°C, but at 37°C were 0.6129, 0.4175, and 0.0594 µg l⁻¹. This means that the emission rate of the gas is limited by two factors the temperature and the heavy metal.

(Figure A-23) illustrates some useful statistical determinations and the linear regression model of the emissions of N₂O under the conditions studied. It was found that the CV% increased by increasing Cd concentrations applied to the soil samples. Table 16 indicates the LSD_{0.05} for the emissions of N₂O was 0.9341 under the effect of Pb. The ANOVA Table demonstrates that no significant differences between the investigated parameters and the emission rates of the gas under the impacts of the 40 and 80 (except at 4th day of incubation) mg Pb concentrations. But it was negatively significant differences between the emission rates and other investigated parameters under the effects of 160 mg Pb except at the 31st day of incubation.

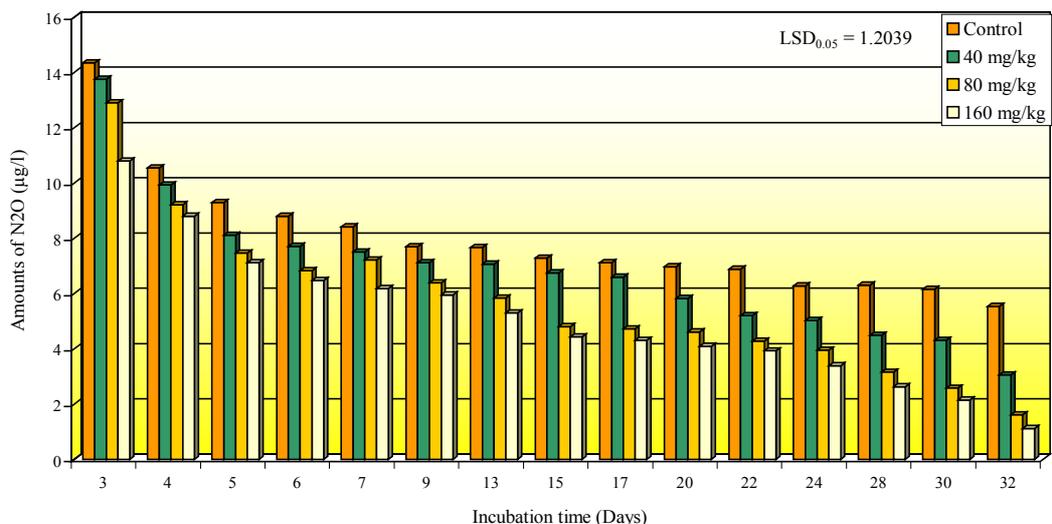


Fig. 21. Nitrous oxide amounts detected in microcosm containing brown forest clay loam soil (Gödöllő) of 60% WFPS treated with different concentrations of Pb and incubated at 15°C

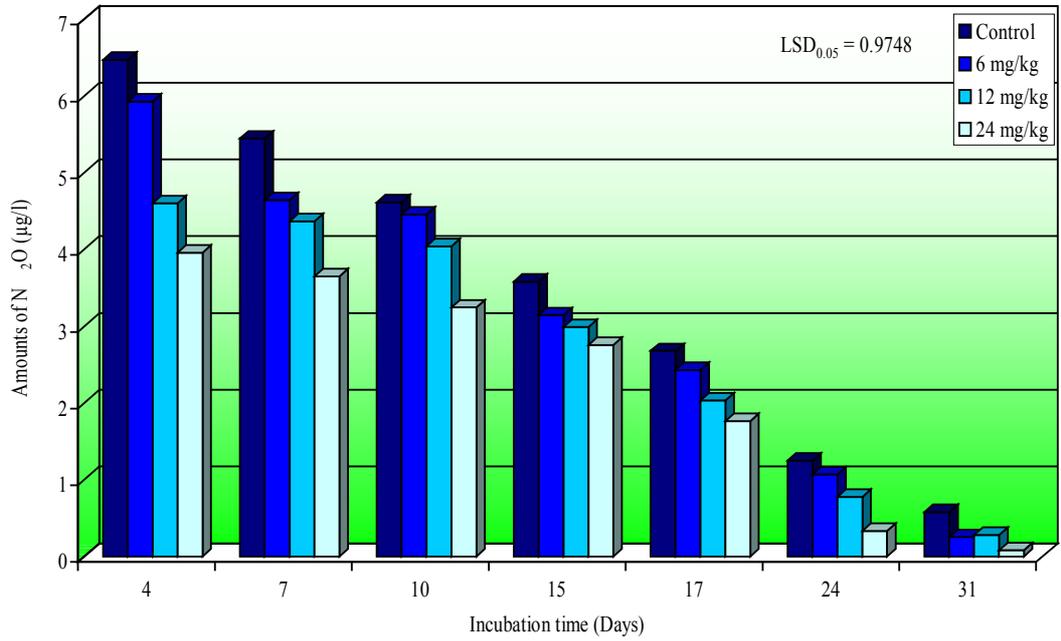


Fig. 22. Nitrous oxide amounts detected in microcosm containing Ramann's brown forest soil (Keszthely) of 60% WFPS treated with different concentrations of Cd and incubated at 37°C

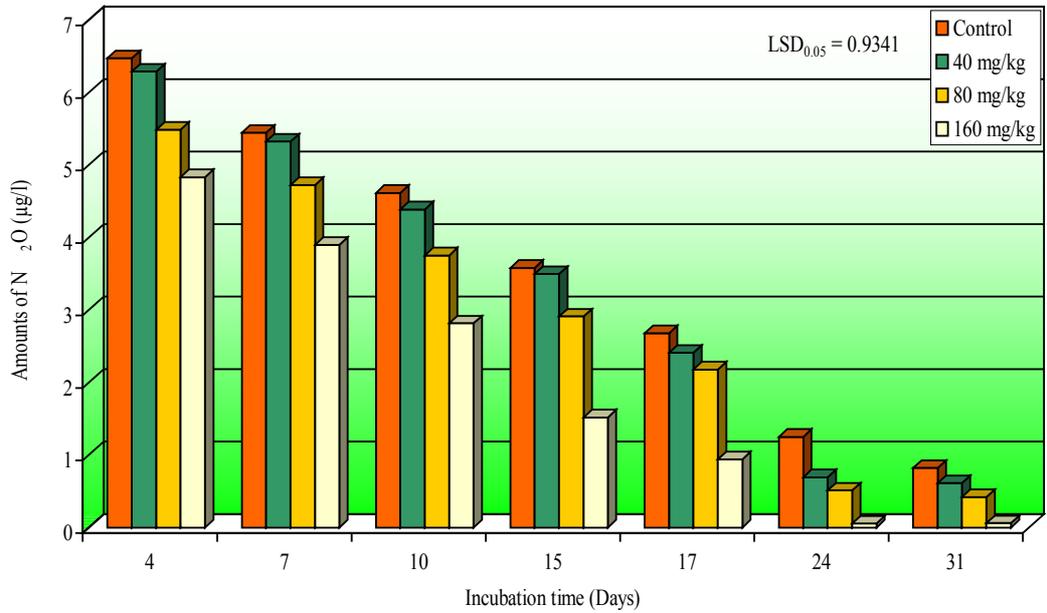


Fig. 23. Nitrous oxide amounts detected in microcosm containing Ramann's brown forest soil (Gödöllő) of 60% WFPS treated with different concentrations of Pb and incubated at 37°C

Table (13) Calculations of the variance analysis of emission of N₂O from Pb treated Keszthely soil with 60% WFPS at incubation temperature 15°C

Table of Variation						F Interaction	
Source of Variation	n	FG	SQ	MQ	F	SD _{0.05}	LSD _{0.05}
Total	156	155	353.3783	2.27986			
Replications	3	2	0.0324	0.016214	0.2589	0.0962	0.1356
Treatment	52	51	346.9581	6.8031	108.633	0.4005	0.5645
Time (A)	13	12	335.5691	27.96409	446.5353	0.2002	0.2823
Concentration (B)	4	3	9.9065	3.302152	52.7293	0.1111	0.1566
Lead (C)	1	0	0			0.1111	0.1566
A×B		36	1.4826	0.0412	0.6576	0.4005	0.5647
A×C		0	0			0.2002	0.2823
B×C		0	-4.5E-13			0.1111	0.1566
A×B×C		0	1.36E-12			0.4005	0.5647
Error		102	6.3877	0.0626			
Accuracy of the experiment = 90.9164 %, t _{0.05} = 1.96							

Calculations of statistical analysis of emission of N₂O from Pb treated Keszthely soil with 60% WFPS at incubation temperature 15°C

Time (Days)	Control	40 mg/kg	80 mg/kg	160 mg/kg	LSD _{0.05}	F
3	6.1736	5.8231	5.4627	5.0030	0.2823	0
5	5.6629	5.2765	5.0152	4.7943		
8	4.8756	4.6922	4.4998	4.0435		
12	4.4116	4.2175	4.0568	3.7277		
15	3.9766	3.5269	3.2990	2.9758		
17	3.3993	3.1953	2.9793	2.8235		
19	2.9949	2.7390	2.4638	2.3622		
22	2.7735	2.5510	2.3350	2.1706		
24	2.2055	2.1125	2.0633	2.0329		
26	2.0221	1.9005	1.7627	1.5726		
29	1.7972	1.5399	1.4331	1.2823		
31	1.5302	1.2320	1.0260	0.9270		
33	1.3466	0.9361	0.7152	0.5802		
LSD _{0.05}	0.1566					
F	52.7293					108.6330

The shadow numbers are significantly negative with the controls

Table (14) Calculations of the variance analysis of emission of N₂O from Pb treated Gödöllő soil with 60% WFPS at incubation temperature 15°C

Table of Variation						F Interaction	
Source of Variation	n	FG	SQ	MQ	F	SD _{0.05}	LSD _{0.05}
Total	180	179	1342.886	7.5022			
Replications	3	2	0.2349	0.1175	0.4127	0.1909	0.2692
Treatment	60	59	1309.063	22.1875	77.9479	0.8538	1.2039
Time (A)	15	14	1070.55	76.4679	268.6425	0.4269	0.6019
Concentration (B)	4	3	213.4362	71.1454	249.9439	0.2205	0.3108
Lead (C)	1	0	0			0.2205	0.3108
A×B		42	25.0772	0.5971	2.0976	0.8538	1.2039
A×C		0	0			0.4269	0.6019
B×C		0	1.82E-12			0.2205	0.3108
A×B×C		0	-1.8E-12			0.8538	1.2039
Error		118	33.5882	0.2847			
Accuracy of the experiment = 91.7513 %, t _{0.05} = 1.96							

Calculations of statistical analysis of emission of N₂O from Pb treated Gödöllő soil with 60% WFPS at incubation temperature 15°C

Time (Days)	Control	40 mg/kg	80 mg/kg	160 mg/kg	LSD _{0.05}	F
3	14.3482	13.7579	12.8976	10.8003	0.60194	0
4	10.5425	9.9235	9.2068	8.7990		
5	9.2974	8.1146	7.4623	7.1201		
6	8.7951	7.7081	6.8311	6.4658		
7	8.4146	7.5028	7.2129	6.1871		
9	7.6985	7.1181	6.3909	5.9505		
13	7.6667	7.0588	5.8354	5.3010		
15	7.2886	6.7462	4.8125	4.4293		
17	7.1144	6.5927	4.7172	4.3110		
20	6.9735	5.8269	4.6085	4.0927		
22	6.8814	5.2024	4.2847	3.9317		
24	6.2849	5.0285	3.9578	3.3826		
28	6.3019	4.4954	3.1611	2.6285		
30	6.1531	4.3162	2.5824	2.1430		
32	5.5333	3.0599	1.6122	1.1124		
LSD _{0.05}	0.3109				1.2039	
F	249.9439					77.9479

The shadow numbers are significantly negative with the controls

Table (15) Calculations of the variance analysis of emission of N₂O from Cd treated Keszthely soil with 60% WFPS at incubation temperature 37°C

Table of Variation						F Interaction	
Source of Variation	n	FG	SQ	MQ	F	SD _{0.05}	LSD _{0.05}
Total	84	83	287.7203	3.4665			
Replications	3	2	1.2269	0.6135	3.2873	0.2263	0.3191
Treatment	28	27	276.4161	10.2376	54.8595	0.6913	0.9748
Time (A)	7	6	251.5627	41.9271	224.6711	0.3457	0.4874
Concentration (B)	4	3	18.4796	6.1599	33.0084	0.2613	0.3684
Cadmium (C)	1	0	0			0.2613	0.3684
A×B		18	6.3738	0.3541	1.8975	0.6913	0.9748
A×C		0	0			0.3457	0.4874
B×C		0	-2.3E-13			0.2613	0.3684
A×B×C		0	3.41E-13			0.6913	0.9748
Error		54	10.0772	0.1866			
Accuracy of the experiment = 85.1400 %, t _{0.05} = 1.96							

Calculations of statistical analysis of emission of N₂O from Cd treated Keszthely soil with 60% WFPS at incubation temperature 37°C

Time (Days)	Control	6 mg/kg	12 mg/kg	24 mg/kg	LSD _{0.05}	F
4	6.4698	5.9250	4.6000	3.9573	0.4874	0
7	5.4435	4.6404	4.3684	3.6487		
10	4.6138	4.4563	4.03995	3.2432		
15	3.5801	3.1441	2.9899	2.7557		
17	2.6769	2.4309	2.0298	1.7636		
24	1.2511	1.0665	0.7750	0.3310		
31	0.5794	0.2544	0.2819	0.0817		
LSD _{0.05}	0.3684				0.9748	
F	33.0084					54.8595

The shadow numbers are significantly negative with the controls

Table (16) Calculations of the variance analysis of emission of N₂O from Pb treated Keszthely soil with 60% WFPS at incubation temperature 37°C

Table of Variation						F Interaction	
Source of Variation	n	FG	SQ	MQ	F	SD _{0.05}	LSD _{0.05}
Total	84	83	341.3736	4.1129			
Replications	3	2	3.0699	1.5350	8.9569	0.2169	0.3058
Treatment	28	27	329.0495	12.1870	71.1140	0.6625	0.9341
Time (A)	7	6	296.8838	49.4806	288.7308	0.3313	0.4671
Concentration (B)	4	3	28.8890	9.6297	56.1912	0.2501	0.3531
Lead (C)	1	0	0			0.2504	0.3531
A×B		18	3.2768	0.1820	1.0623	0.6625	0.9341
A×C		0	0			0.3313	0.4671
B×C		0	0			0.2504	0.3531
A×B×C		0	2.27E-13			0.6625	0.9341
Error		54	9.254137	0.1714			
Accuracy of the experiment = 85.1400 %, t _{0.05} = 1.96							

Calculations of statistical analysis of emission of N₂O from Pb treated Keszthely soil with 60% WFPS at incubation temperature 37°C

Time (Days)	Control	40 mg/kg	80 mg/kg	160 mg/kg	LSD _{0.05}	F
4	6.4698	6.2861	5.4846	4.8300	0.4671	0
7	5.4435	5.3217	4.7207	3.8977		
10	4.6138	4.3838	3.7511	2.8128		
15	3.5801	3.4944	2.9097	1.5153		
17	2.6769	2.4080	2.1760	0.9382		
24	1.2511	0.6903	0.5106	0.0541		
31	0.8229	0.6129	0.4175	0.0594		
LSD _{0.05}	0.3531				0.9341	
F	56.1912					71.1140

The shadow numbers are significantly negative with the controls

4.6. EMISSIONS OF CO₂ UNDER THE STRESSES OF HEAVY METALS

4.6.1. EXPERIMENT 6: AT LOW TEMPERATURE AND LOW SOIL MOISTURE CONTENT

The experiment was carried out to detect the amount of CO₂ emission from two heavy metals contaminated soil samples with different concentrations of Cd and Pb in microcosms of low moisture regime (30% WFPS) and incubated at low temperature (15°C). In case of Cd contamination, (Figure 24) shows that the amount of CO₂ emitted from the microcosms of Keszthely soil samples contaminated by 6, 12 and 24 mg Cd kg⁻¹ soil. It was found that the maximum emission rate (97440.74 µg l⁻¹) of the gas was detected at 20th day of incubation from heavy metal free soil (control soil). While it was 98197.78 µg l⁻¹ at 6 mg Cd contaminated soil samples and 100183.3 µg l⁻¹ at 12 mg Cd and 67667.9452 µg l⁻¹ in soil samples contaminated by 24 mg Cd kg⁻¹ soil. The Figure illustrates the gradual increases in the emission rates up to the 20th day of incubation and then started to decrease to the end of the detection time at 32nd day of the incubation. Also, it was found that the emission rates of the gas were increased by increasing the contamination doses up to 12 mg Cd and decreased in microcosms of contaminated soil samples with 24 mg Cd. (Figure A-24) shows the positions of the linear regressions at different Cd concentrations in comparison with the control soil of Keszthely as well as other statistical determinants which gave the interactions between the amounts of gas emission and the ecological factors that influence the gas emission. One of these determinants is CV% which shows an increasing with the increases the concentrations of Cd. Table 17 demonstrates the ANOVA test and the important statistical values e.g., LSD_{0.05} (40862.29) from ANOVA Table. This Table shows that no significant differences between the amounts of gas detection at the different incubation time intervals under the effects of Cd concentrations. Similar conclusion was drawn by the Table 18 which shows the statistical analysis carried out on the Gödöllő soil samples of 30% WFPS and contaminated with different concentrations of Cd and incubated at 15°C. The LSD_{0.05} was 14493.66. Other statistical determinants were found in the (Figure A-25), e.g., the CV% values show an increasing with the increasing the concentrations of Cd. (Figure 25) illustrates the impacts of Cd doses on the emission rates of CO₂ from Gödöllő soil samples. It was found that the amounts of gas emissions were increased up to the 16th day of the incubation in Cd free soil microcosms and in 6 mg Cd contaminated soil samples in the microcosms and then decreased. While at 12 and 24 mg Cd contaminated soil samples the maximum emission rates were found at 9th day of incubation and then the gas flux started to decrease. Also, it can be seen that by increasing the Cd contamination in the soil samples the rate of emission decreased. Generally, under similar conditions it was found that the amounts of gas emissions from Keszthely were lower than emitted from Gödöllő. But in case of Pb contaminations, it was found that the gas emissions increased with incubation time in Keszthely (Figure 26) contaminated soil samples and gave maximum emission rates of CO₂ at 20th day of incubation and then decreased. The emission rates were depended on the doses of Pb contaminated the soil samples. (Figure A-26) indicates the linear regressions of the gas emitted during the incubation time under different contaminated concentrations of Pb and also some statistical calculations to distinguish between the ecological factors influencing the gas emissions. Table 19 demonstrates the ANOVA test and gave the LSD_{0.05} (14811.26). However, the Table indicates that gas emission rates had positive significant differences between the Pb free soil samples and the Pb contaminated soil samples. However, the results of the microcosms of Gödöllő soil samples are shown in (Figure 27) which demonstrates the detected amounts of CO₂ detected during 32 days of incubation. It was found that maximum emission rates were 147338.9 µg l⁻¹ at 9th day of incubation in Pb free control microcosms and 146862.4 µg l⁻¹, 148249.9 µg l⁻¹ at 16th day of incubation under the effects of 40 and 80 mg Pb, but it was 158428.4 µg l⁻¹ at 21st day under the impacts of 160 mg Pb. (Figure A-27) indicates the linear regressions of the gas emitted during the incubation time under different contaminated concentrations of Pb and also some statistical calculations to distinguish between the ecological factors influencing the gas emissions. Table 20 demonstrates the ANOVA test and gave the LSD_{0.05} (3006.36). The Table indicates only positive significant differences at 21st, 26th and 32nd day of incubation under the impacts of 160 mg of Pb, and negative significant differences at 9th

under the effect of 80 and 160 mg Pb and 12th day under the stress of 160 mg of Pb. The amounts of gas emitted from Gödöllő soil samples were higher than those emitted from Keszthely soil samples.

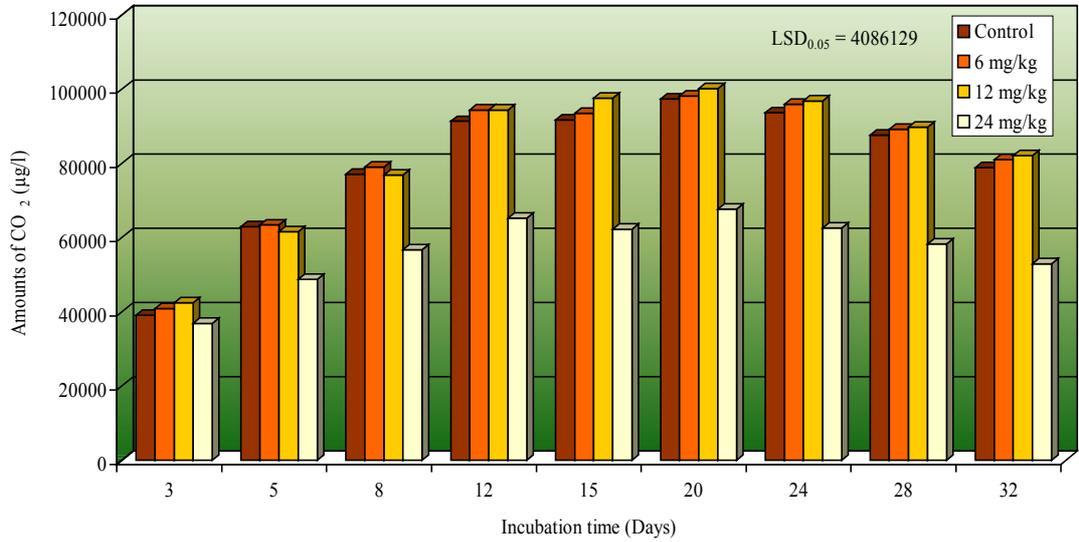


Fig. 24 Carbon dioxide amounts detected in microcosm containing Ramann's brown forest soil (Keszthely) of 30% WFPS treated with different concentrations of Cd and incubated at 15°C

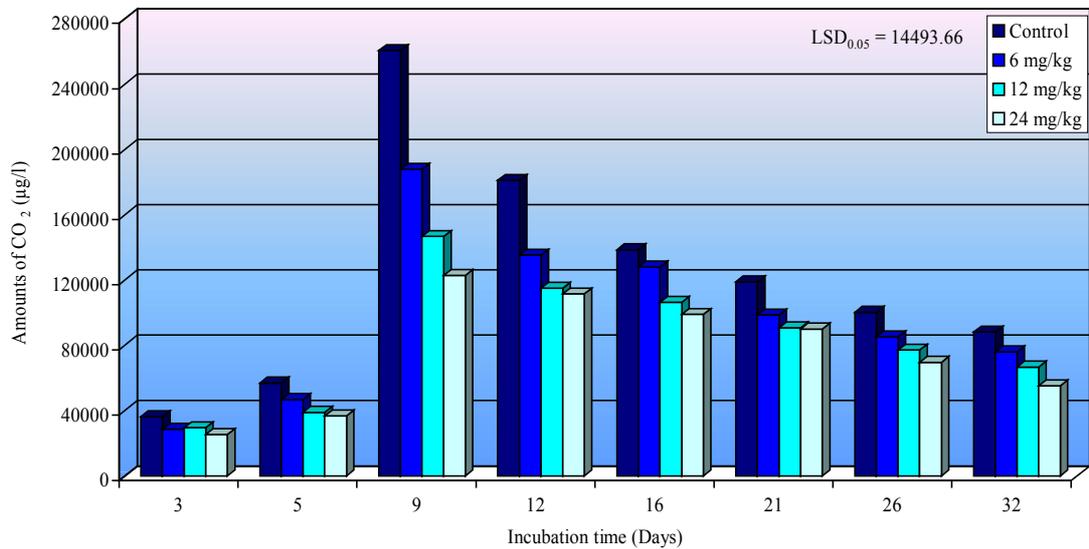


Fig. 25. Carbon dioxide amounts detected in microcosm containing brown forest clay loam soil (Gödöllő) of 30% WFPS treated with different concentrations of Cd and incubated at 15°C

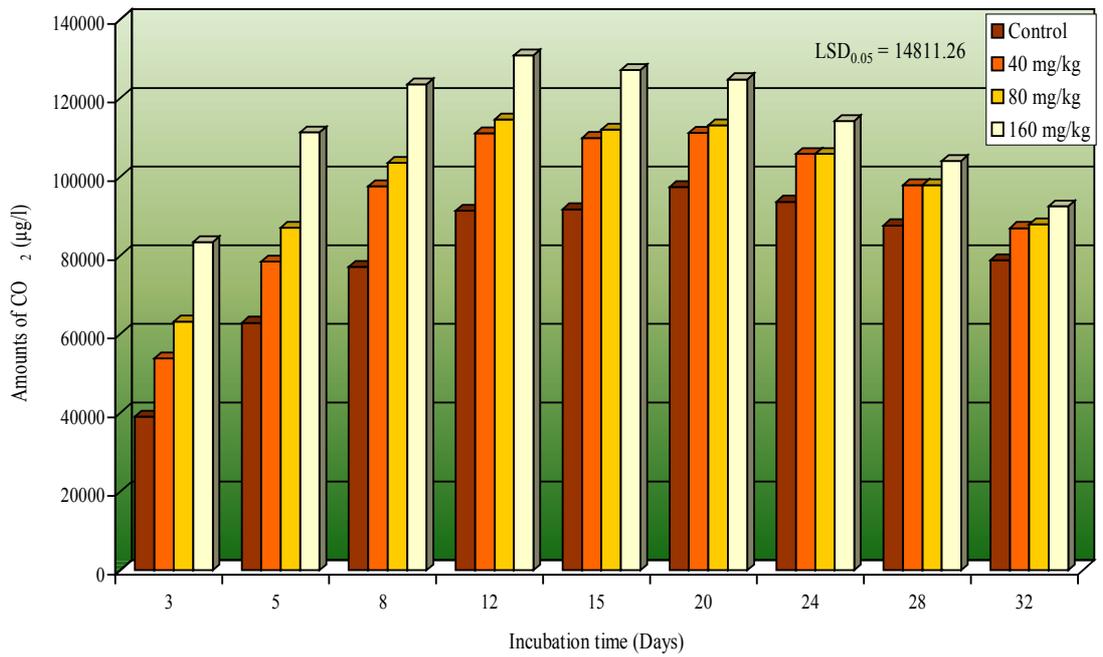


Fig. 26. Carbon dioxide amounts detected in microcosm containing Ramann's brown forest soil (Keszthely) of 30% WFPS treated with different concentrations of Pb and incubated at 15°C

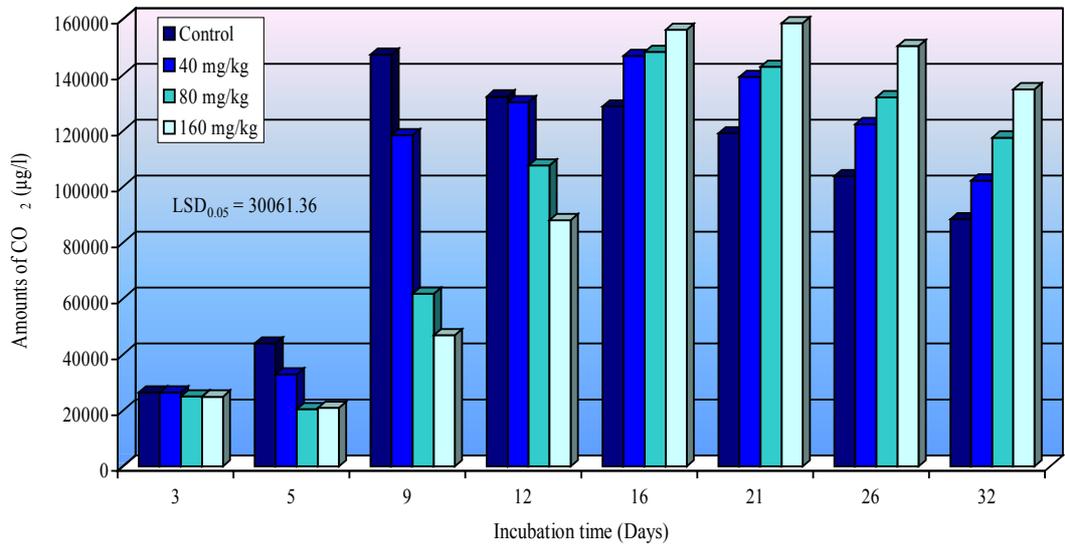


Fig. 27. Carbon dioxide amounts detected in microcosm containing brown forest clay loam soil (Gödöllő) of 30% WFPS treated with different concentrations of Pb and incubated at 15°C

Table (17) Calculations of the variance analysis of emission of CO₂ from Cd treated Keszthely soil with 30% WFPS at incubation temperature 15°C

Table of Variation						F Interaction	
Source of Variation	n	FG	SQ	MQ	F	SD _{0.05}	LSD _{0.05}
Total	108	107	68925768968	644166065.1			
Replications	3	2	5545272063	2772636032	8.455275	8365.702	11795.64
Treatment	36	35	40426243600	1155035531	3.522331	28979.64	40861.29
Time (A)	9	8	26327658863	3290957358	10.03592	14489.82	20430.65
Concentration (B)	4	3	12277443715	4092481238	12.48020	9659.880	13620.43
Cadmium (C)	1	0	0			9659.880	13620.43
A×B		24	1821141022	75880875.91	0.231402	28979.64	40861.29
A×C		0	0			14489.82	20430.65
B×C		0	0			9659.880	13620.43
A×B×C		0	-0.00012207			28979.64	40861.29
Error		70	22954253305	327917904.4			
Accuracy of the experiment = 75.9355 %, t _{0.05} = 1.96							

Calculations of statistical analysis of emission of CO₂ from Cd treated Keszthely soil with 30% WFPS at incubation temperature 15°C

Time (Days)	Control	6 mg/kg	12 mg/kg	24 mg/kg	LSD _{0.05}	F
3	39069.09	40886.84	42448.98	36878.2865	20430.65	0
5	62941.05	63436.12	61583.14	48798.7320		
8	77093.29	79053.21	76858.78	56772.5069		
12	91367.11	94386.39	94421.95	65297.4463		
15	91750.44	93524.65	97673.01	62239.7472		
20	97440.74	98197.78	100183.3	67667.9452		
24	93691.52	96009.46	96849.29	62639.5892		
28	87659.00	89159.42	89777.44	58328.5030		
32	78876.88	80966.34	82069.77	53001.2685		
LSD _{0.05}	13620.43					
F	12.4802					3.5223

No significant differences

Table (18) Calculations of the variance analysis of emission of CO₂ from Cd treated Gödöllő soil with 30% WFPS at incubation temperature 15°C

Table of Variation						F Interaction	
Source of Variation	n	FG	SQ	MQ	F	SD _{0.05}	LSD _{0.05}
Total	96	95	2.55E+11	2.69E+09			
Replications	3	2	648318.70	324159.4	0.007857	3147.347	4437.760
Treatment	32	31	2.53E+11	8.15E+09	197.4431	10279.19	14493.66
Time (A)	8	7	2.02E+11	2.88E+10	697.9163	5139.597	7246.832
Concentration (B)	4	3	2.99E+10	9.98E+09	241.9461	3634.244	5124.284
Cadmium (C)	1	0	0			3634.244	5124.284
A×B		21	2.1E+10	1E+09	24.26107	10279.19	14493.66
A×C		0	0			5139.597	7246.832
B×C		0	0			3634.244	5124.284
A×B×C		0	-0.0002			10279.19	14493.66
Error		62	2.56E+09	41256959			
Accuracy of the experiment = 93.2651 %, t _{0.05} = 1.96							

Calculations of statistical analysis of emission of CO₂ from Cd treated Gödöllő soil with 30% WFPS at incubation temperature 15°C

Time (Days)	Control	6 mg/kg	12 mg/kg	24 mg/kg	LSD _{0.05}	F
3	36371.66	28698.32	29582.94	25436.55	7246.832	0
5	56911.12	46922.09	39058.68	36870.41		
9	260672.2	187918.2	146871.0	122994.4		
12	181234.2	135378.2	115174.5	111511.7		
16	138682.0	128163.6	106550.4	99066.57		
21	119076.0	98783.24	90779.13	90030.91		
26	100444.5	85340.41	77229.23	69709.48		
32	88296.66	76145.85	66756.63	55203.60		
LSD _{0.05}	5124.284				14493.66	
F	241.9461					197.4431

No significant differences

Table (19) Calculations of the variance analysis of emission of CO₂ from Pb treated Keszthely soil with 30% WFPS at incubation temperature 15°C

Table of Variation						F Interaction	
Source of Variation	n	FG	SQ	MQ	F	SD _{0.05}	LSD _{0.05}
Total	108	107	4.8E+10	4.49E+08			
Replications	3	2	4.5E+08	2.25E+08	5.216791	3032.371	4275.643
Treatment	36	35	4.45E+10	1.27E+09	29.53026	10504.44	14811.26
Time (A)	9	8	2.78E+10	3.47E+09	80.52536	5252.220	7405.630
Concentration (B)	4	3	1.44E+10	4.78E+09	111.0355	3501.480	4937.087
Lead (C)	1	0	0			3501.480	4937.087
A×B		24	2.42E+09	1.01E+08	2.343736	10504.44	14811.26
A×C		0	0			5252.220	7405.630
B×C		0	0			3501.480	4937.087
A×B×C		0	-0.00024			10504.44	14811.26
Error		70	3.02E+09	43084883			
Accuracy of the experiment = 93.1888 %, t _{0.05} = 1.96							

Calculations of statistical analysis of emission of CO₂ from Pb treated Keszthely soil with 30% WFPS at incubation temperature 15°C

Time (Days)	Control	40 mg/kg	80 mg/kg	160 mg/kg	LSD _{0.05}	F
3	39069.09	53878.19	63253.57	83390.39	7405.63	0
5	62941.05	78446.08	87074.66	111278.1		
8	77093.29	97631.69	103537.1	123455.7		
12	91367.11	111066.3	114578.1	130891.6		
15	91750.44	109864.1	112005.7	127071.7		
20	97440.74	111148.7	113145.6	124783.5		
24	93691.52	105813.2	105848.2	114165.1		
28	87659.00	97818.48	97857.49	103970.5		
32	78876.88	86978.91	87968.61	92473.64		
LSD _{0.05}	4937.0870					
F	111.0355					29.5303

The bold numbers are significantly positive with the controls

4.6.2. EXPERIMENT 7: AT LOW TEMPERATURE AND HIGH SOIL MOISTURE CONTENT

The experiment was conducted to measure the amount of CO₂ emission from two heavy metals contaminated soil samples with different concentrations of Cd and Pb in microcosms of high moisture regime (60% WFPS) and incubated at low temperature (15°C).

In case of Cd contamination, (Figure 28) shows the detected amount of CO₂ emitted from the microcosms of Keszthely soil samples contaminated by 6, 12 and 24 mg Cd kg⁻¹ soil. It was found that the maximum emission rate (84469.68 µg l⁻¹) of the gas was detected at Cd free soil samples (control) at the 8th day of incubation, and on the same day, the maximum emission rate (130010.3245 µg l⁻¹) of the gas was detected under the effect of 24 mg Cd. While the maximum emission rates under the effects of 6 and 12 mg Cd were 103082.3 and 116200.6 µg l⁻¹, respectively at the 15th day of incubation. (Figure 28) illustrates that the rates of emissions were increased by increasing the dose of Cd contamination up to 29th day of incubation then decreased. It should be noted that the control soil samples did not emit CO₂ with significant differences throughout the incubation period.

(Figure A-28) illustrates the linear regressions of the detected amounts of CO₂ during the incubation time and some statistical determinants e.g., CV% values which increased with the increases of the doses of heavy metal contamination. Table 21 shows the ANOVA test and statistical analysis of the experiment, e.g., the LSD_{0.05} value (33504.49) and the positive significant differences of the detected amounts of gas at 24 mg Cd during the incubation time except at the 3rd day. Also the result showed the positive significant differences of the detected amounts of gas at 12 mg Cd during the incubation time except at the 3rd, 5th and 29th day. While under the stress of 6 mg Cd, the result indicated no significant differences during the incubation except negative significant differences at the 31st and 33rd day.

Table 22 shows the statistical analysis of the emission of CO₂ from Cd treated soil sample of Gödöllő with 60% WFPS contaminated with different concentrations of Cd. The Table indicated no significant differences between the emission rates of gas emitted from control and microcosms of contaminated soil. The LSD_{0.05} was 107486.8.

(Figure 29) illustrates that maximum emission rates were found at the 15th day of incubation. The emission rates were increased with increasing the dose of Cd contamination. (Figure 29) illustrates the statistical calculations and linear regressions of the detected amounts of gas at different concentration of Cd that contaminate the Gödöllő soil samples. Table 22 indicate that the LSD_{0.05} was 107486.8 and no significant differences between the emission rates of gas emitted from control and microcosms of contaminated soil. In conclusion, the emission rates of gas emitted from Gödöllő soil samples were more than those emitted from Keszthely Cd contaminated soil samples.

In the case of Pb contamination, it was observed that the gas emissions increased with increasing dose of contamination in Keszthely (Figure 30) with Pb. The Figure shows the maximum emission rates of CO₂ at 15th day of incubation at metal free soil. The maximum emission rates of contaminated soil were found at 19th day of incubation. The lowest emission rates were detected at 33rd of incubation time interval of Pb contamination. (Figure A-30) indicates the linear regressions of the gas emitted during the incubation time under different contaminated concentrations of Pb and also some statistical calculations to distinguish between the ecological factors influencing the gas emissions. Table 23 demonstrates the ANOVA test and gave the LSD_{0.05} (6226.215). However, the Table indicates that gas emission rates had positive significant differences between the Pb free soil samples and the 160 mg Pb contaminated soil samples during the incubation intervals except at 3rd day. Under the effects of 80 mg of Pb, the emissions were positive significant differences during the incubation intervals except at 3rd, 5th, 8th and 15th day. At 6 mg Pb contamination, there was no significant differences throughout the incubation time except positive significant differences were detected at 19th, 26th, 29th, 31st, and 33rd day.

But in case of microcosms of Pb contaminated Gödöllő soil samples, (Figure 31) demonstrates the amounts of CO₂ detected during 32 days of incubation. It was found that the CO₂ emissions were increased to reach maximum emission rates 234779.7, 240059.8, 261109.7 and

277424 $\mu\text{g l}^{-1}$ at 17th day of incubation in Pb free control microcosms and 40, 80 mg and 160 mg Pb contaminated doses, respectively. (Figure A-31) indicates the linear regressions of the gas emitted during the incubation time under different contaminated concentrations of Pb and also some statistical calculations to distinguish between the ecological factors influencing the gas emissions. Table 24 demonstrates the ANOVA test and gave the $\text{LSD}_{0.05}$ (16694.49). The Table indicates only positive significant differences under the effect of 160 mg Pb during the incubation period except at 3rd and 4th day of incubation and under the impacts of 80 mg of Pb, except at 3rd, 4th, 5th and 9th day. Under the impacts of 40 mg Pb, no significant differences except at 20th day which had positive significant difference. The amounts of gas emitted from Gödöllő soil samples were higher than those emitted from Keszthely soil samples.

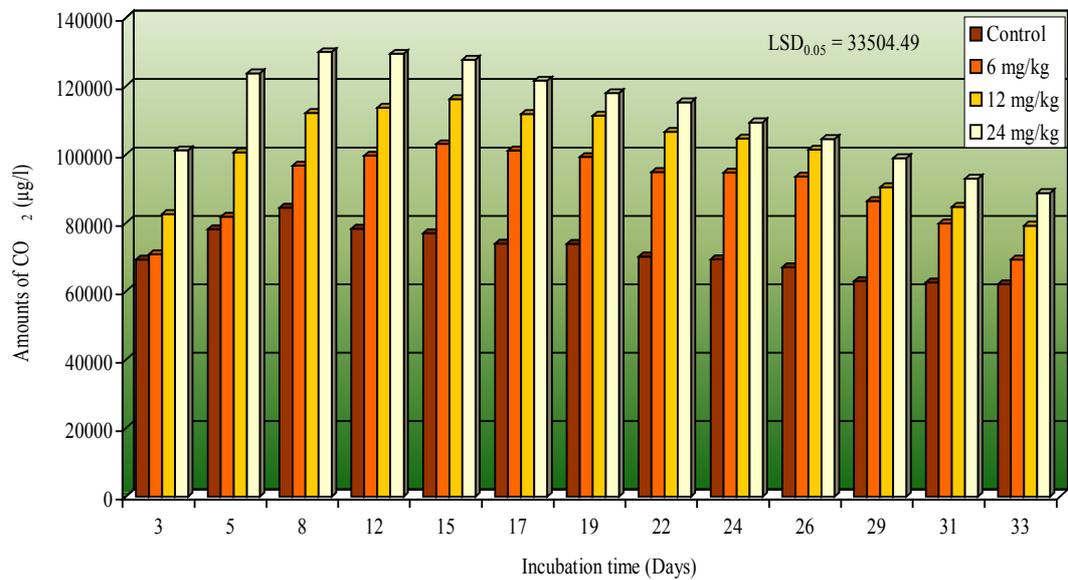


Fig. 28. Carbon dioxide amounts detected in microcosm containing Ramann's brown forest soil (Keszthely) of 60% WFPS treated with different concentrations of Cd and incubated at 15°C

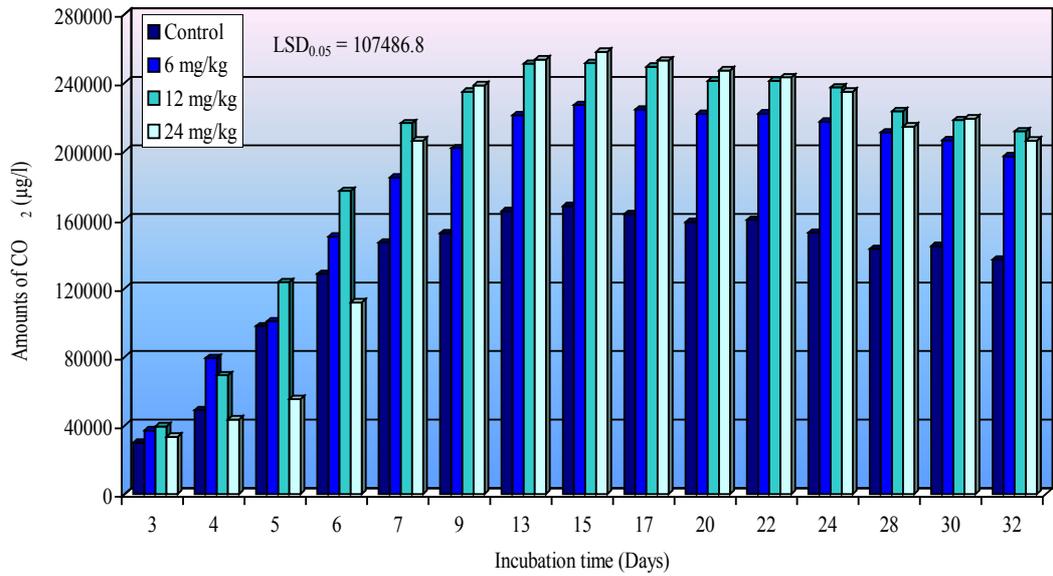


Fig. 29. Carbon dioxide amounts detected in microcosm containing brown forest clay loam soil (Gödöllő) of 60% WFPS treated with different concentrations of Cd and incubated at 15°C

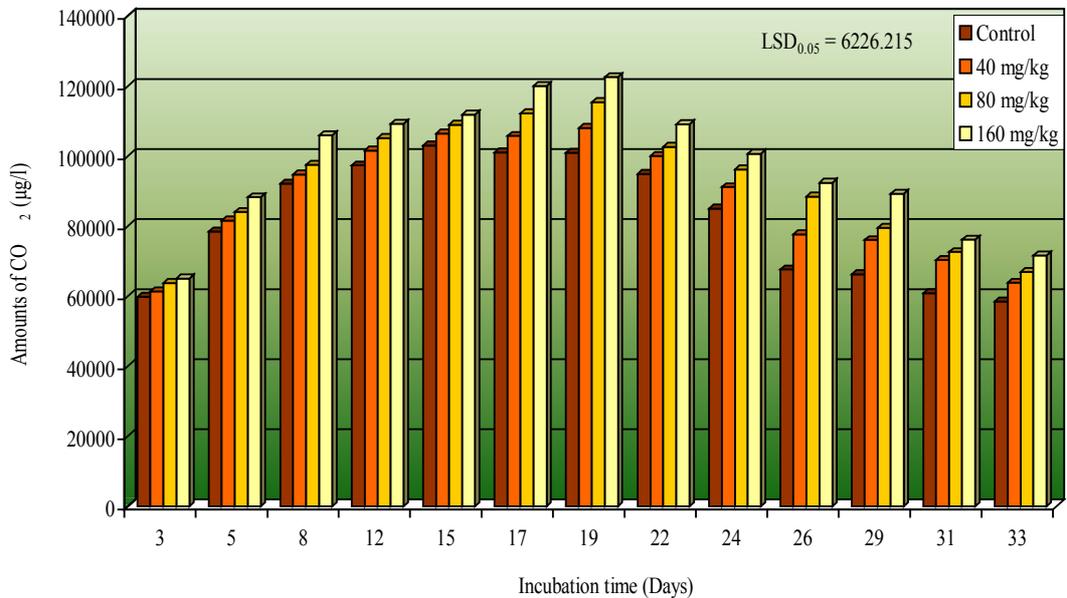


Fig. 30. Carbon dioxide amounts detected in microcosm containing Ramann's brown forest soil (Keszthely) of 60% WFPS treated with different concentrations of Pb and incubated at 15°C

Table (20) Calculations of the variance analysis of emission of CO₂ from Pb treated Gödöllő soil with 30% WFPS at incubation temperature 15°C

Table of Variation						F Interaction	
Source of Variation	n	FG	SQ	MQ	F	SD _{0.05}	LSD _{0.05}
Total	96	95	2.29E+11	2.41E+09			
Replications	3	2	65338238	32669119	0.184068	6527.926	9204.375
Treatment	32	31	2.18E+11	7.03E+09	39.60273	21320.12	30061.36
Time (A)	8	7	1.82E+11	2.6E+10	146.631	10660.06	15030.68
Concentration (B)	4	3	7.69E+08	2.56E+08	1.443575	7537.799	10628.30
Lead (C)	1	0	0			7537.799	10628.30
A×B		21	3.5E+10	1.66E+09	9.377934	21320.12	30061.36
A×C		0	0			10660.06	15030.68
B×C		0	0			7537.799	10628.30
A×B×C		0	-0.00024			21320.12	30061.36
Error		62	1.1E+10	1.77E+08			
Accuracy of the experiment = 86.4418 %, t _{0.05} = 1.96							

Calculations of statistical analysis of emission of CO₂ from Pb treated Gödöllő soil with 30% WFPS at incubation temperature 15°C

Time (Days)	Control	40 mg/kg	80 mg/kg	160 mg/kg	LSD _{0.05}	F
3	26371.66	26482.24	25036.24	24942.73	15030.68	0
5	43911.12	32844.79	20432.72	20884.24		
9	147338.9	118435.9	61727.66	46940.2		
12	132234.2	130210.7	107517.6	88002.28		
16	128682.0	146862.4	148249.9	156143.1		
21	119076.0	139281.3	142913.4	158428.4		
26	103777.8	122374.1	131996.2	150260.9		
32	88296.66	102256.9	117588.8	134819.8		
LSD _{0.05}	10628.3				30061.36	
F	1.4436					39.6027

The shadow numbers are significantly negative with the controls

The bold numbers are significantly positive with the controls

Table (21) Calculations of the variance analysis of emission of CO₂ from Cd treated Keszthely soil with 60% WFPS at incubation temperature 15°C

Table of Variation						F Interaction	
Source of Variation	n	FG	SQ	MQ	F	SD _{0.05}	LSD _{0.05}
Total	156	155	82156681278	530043105			
Replications	3	2	4475863757	2237931878	10.15079	5707.460	8047.519
Treatment	52	51	55193006574	1082215815	4.908704	23762.05	33504.49
Time (A)	13	12	16293059064	1357754922	6.158492	11881.03	16752.25
Concentration (B)	4	3	35643963993	11881321331	53.89118	6590.408	9292.475
Cadmium (C)	1	0	0			6590.408	9292.475
A×B		36	3255983517	90443986.58	0.410235	23762.05	33504.49
A×C		0	0			11881.03	16752.25
B×C		0	0			6590.408	9292.475
A×B×C		0	0			23762.05	33504.49
Error		102	22487810947	220468734.8			

Accuracy of the experiment = 84.1723 %, t_{0.05} = 1.96

Calculations of statistical analysis of emission of CO₂ from Cd treated Keszthely soil with 60% WFPS at incubation temperature 15°C

Time (Days)	Control	6 mg/kg	12 mg/kg	24 mg/kg	LSD _{0.05}	F
3	69331.50	70813.25	82626.78	101234.4957	16752.25	0
5	78145.45	81829.88	100621.5	123774.5693		
8	84469.68	96766.35	112186.6	130010.3245		
12	78253.47	99672.64	113703.3	129487.8122		
15	76970.76	103082.3	116200.6	127725.9451		
17	73957.49	101125.8	111875.7	121631.1606		
19	73833.50	99275.24	111423.6	117972.2758		
22	70159.99	94942.41	106687.0	115251.9348		
24	69420.22	94736.69	104708.9	109382.7604		
26	67100.90	93640.70	101413.1	104540.7114		
29	62963.28	86455.41	90416.98	98998.7443		
31	62579.01	79840.56	84758.08	92899.2380		
33	62091.27	69247.40	79219.3	88736.7138		
LSD _{0.05}	9292.475					
F	53.89118					4.9087

The bold numbers are significantly positive with the controls

Table (22) Calculations of the variance analysis of emission of CO₂ from Cd treated Gödöllő soil with 60% WFPS at incubation temperature 15°C

Table of Variation						F Interaction	
Source of Variation	n	FG	SQ	MQ	F	SD _{0.05}	LSD _{0.05}
Total	180	179	1.16501E+12	6508432235			
Replications	3	2	77570398219	38785199109	17.09288	17045.93	24034.77
Treatment	60	59	8.19687E+11	13892999095	6.122732	76231.74	107486.8
Time (A)	15	14	6.56669E+11	46904893902	20.67128	38115.87	53743.38
Concentration (B)	4	3	1.13758E+11	37919287268	16.71127	19682.95	27752.96
Cadmium (C)	1	0	0			19682.95	27752.96
A×B		42	49260570178	1172870719	0.5169	76231.74	107486.8
A×C		0	0			38115.87	53743.38
B×C		0	0			19682.95	27752.96
A×B×C		0	0			76231.74	107486.8
Error		118	2.67752E+11	2269084960			
Accuracy of the experiment = 72.8004 %, t _{0.05} = 1.96							

Calculations of statistical analysis of emission of CO₂ from Cd treated Gödöllő soil with 60% WFPS at incubation temperature 15°C

Time (Days)	Control	6 mg/kg	12 mg/kg	24 mg/kg	LSD _{0.05}	F
3	29956.55	37101.83	39491.47	33386.2608	53743.38	0
4	48989.33	79471.72	69337.18	43491.5080		
5	97973.67	100912.1	123676.6	55369.1600		
6	128448.0	150312.9	176994.8	111854.7768		
7	146793.4	184798.4	216500.9	206214.7484		
9	152337.8	201857.4	234860.9	238621.7045		
13	165219.5	221150.9	251219.4	253779.8302		
15	168115.7	227130.0	251660.1	258244.5774		
17	163492.9	224443.0	249452.2	253069.8246		
20	158870.6	221949.7	241260.8	247393.2812		
22	160007.7	222243.4	241320.8	243218.3348		
24	152596.0	217464.8	237390.7	234974.5614		
28	143047.2	211205.1	223583.0	214493.3200		
30	144723.5	206594.7	218391.1	219284.8049		
32	136916.4	197254.7	211690.6	206253.2267		
LSD _{0.05}	27752.96				107486.8	
F	16.7113					6.1227

No significant differences

Table (23) Calculations of the variance analysis of emission of CO₂ from Pb treated Keszthely soil with 60% WFPS at incubation temperature 15°C

Table of Variation						F Interaction	
Source of Variation	n	FG	SQ	MQ	F	SD _{0.05}	LSD _{0.05}
Total	156	155	4.95E+10	3.2E+08			
Replications	3	2	24956910	12478455	1.638973	1060.630	1495.488
Treatment	52	51	4.87E+10	9.55E+08	125.4915	4415.755	6226.215
Time (A)	13	12	4.31E+10	3.59E+09	472.0991	2207.878	3113.107
Concentration (B)	4	3	4.79E+09	1.6E+09	209.8623	1224.710	1726.841
Lead (C)	1	0	0			1224.710	1726.841
A×B		36	8.02E+08	22268220	2.924802	4415.755	6226.215
A×C		0	0			2207.878	3113.107
B×C		0	0			1224.710	1726.841
A×B×C		0	0.000244			4415.755	6226.215
Error		102	7.77E+08	7613583			
Accuracy of the experiment = 96.9214 %, t _{0.05} = 1.96							

Calculations of statistical analysis of emission of CO₂ from Pb treated Keszthely soil with 60% WFPS at incubation temperature 15°C

Time (Days)	Control	40 mg/kg	80 mg/kg	160 mg/kg	LSD _{0.05}	F
3	59813.25	61416.12	63715.24	65051.50	3113.107	0
5	78496.55	81603.61	84069.93	88279.92		
8	92099.69	94732.22	97526.58	105954.1		
12	97339.31	101649.0	105185.9	109272.6		
15	103082.3	106444.6	108923.7	111854.1		
17	101125.8	105757.9	112280.6	120060.5		
19	100941.9	108021.9	115391.9	122568.2		
22	94942.41	100017.6	102693.6	109088.3		
24	85070.03	91148.61	96184.56	100708.5		
26	67640.70	77735.81	88432.31	92430.31		
29	66247.40	76037.76	79519.04	89297.08		
31	60840.56	70280.49	72621.35	76190.93		
33	58455.41	63833.22	66924.33	71640.60		
LSD _{0.05}	1726.841					
F	209.8623					125.4915

The bold numbers are significantly positive with the controls

4.6.3. EXPERIMENT 8: AT HIGH TEMPERATURE AND HIGH SOIL MOISTURE CONTENT

The experiment was designed to determine the amount of CO₂ emission from two heavy metals contaminated Keszthely soil samples with different concentrations of Cd and Pb in microcosms of low moisture regime (60% WFPS) and incubated at low temperature (37°C).

(Figure 32) illustrates the effects of Cd concentrations on the emission of CO₂ from Keszthely soil samples. It was found that the emission of the gas was increased by increases the doses of soil contamination. Maximum emission rates were 306224.2 µg l⁻¹ from soil free metal at 15th day of incubation, while in Cd contaminated soil, the emissions were 328704.6, 380801.5 and 388406.2154 µg l⁻¹ at 17th day of incubation. (Figure A-32) shows the linear regressions of the gas emitted during the incubation time under different contaminated concentrations of Pb and also some statistical calculations to distinguish between the ecological factors influencing the gas emissions. Table 25 demonstrates the ANOVA table and gave the LSD_{0.05} (38878.62). Also, it shows positive significant differences during the incubation time under the effects of 24 mg Cd contamination. But under the effect of 12 mg Cd treated soil, the emissions at 2nd and 7th day had no significant differences and the rest of time intervals had the positive significant differences.

(Figure 33) demonstrates the effects of Pb on the emissions of CO₂ from Keszthely soil samples. It was found that at 17th day of incubation, maximum rates of emissions were detected. The gas fluxes increased by increases the dose of contamination. (Figure A-33) shows the linear regressions of the gas emitted during the incubation time under different contaminated concentrations of Pb and also some statistical calculations to distinguish between the ecological factors influencing the gas emissions. Table 26 demonstrates the ANOVA table and gave the LSD_{0.05} (39495.83). Also, it shows positive significant differences during the incubation time under the effects of 160 mg Pb contamination. While no significant differences under the effect of 40mg Pb. It was concluded that gas emissions from Keszthely soil samples contaminated Pb were higher than emitted from soil samples contaminated with Cd.

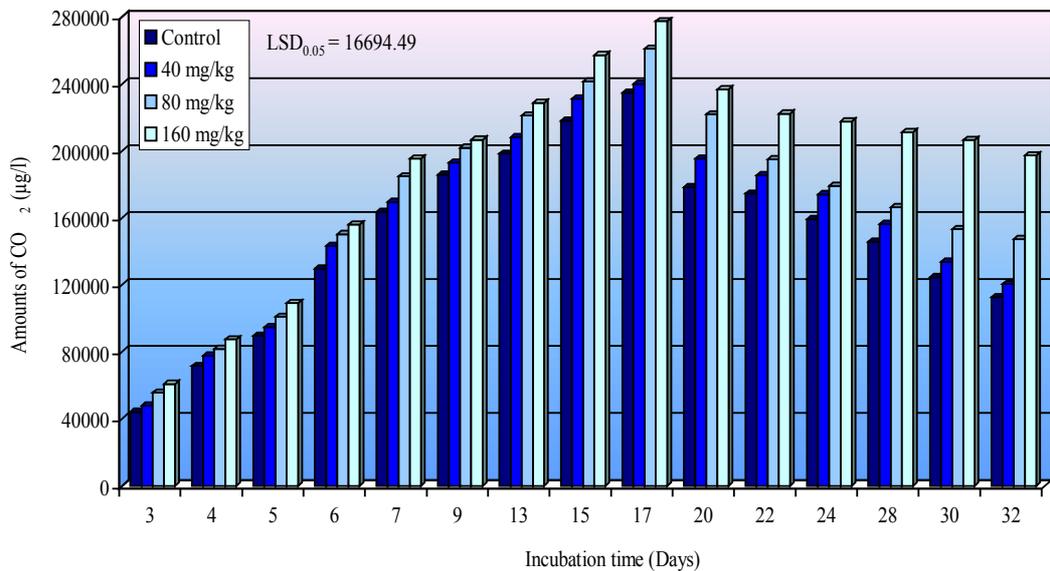


Fig. 31. Carbon dioxide amounts detected in microcosm containing brown forest clay loam soil (Gödöllő) of 60% WFPS treated with different concentrations of Pb and incubated at 15°C

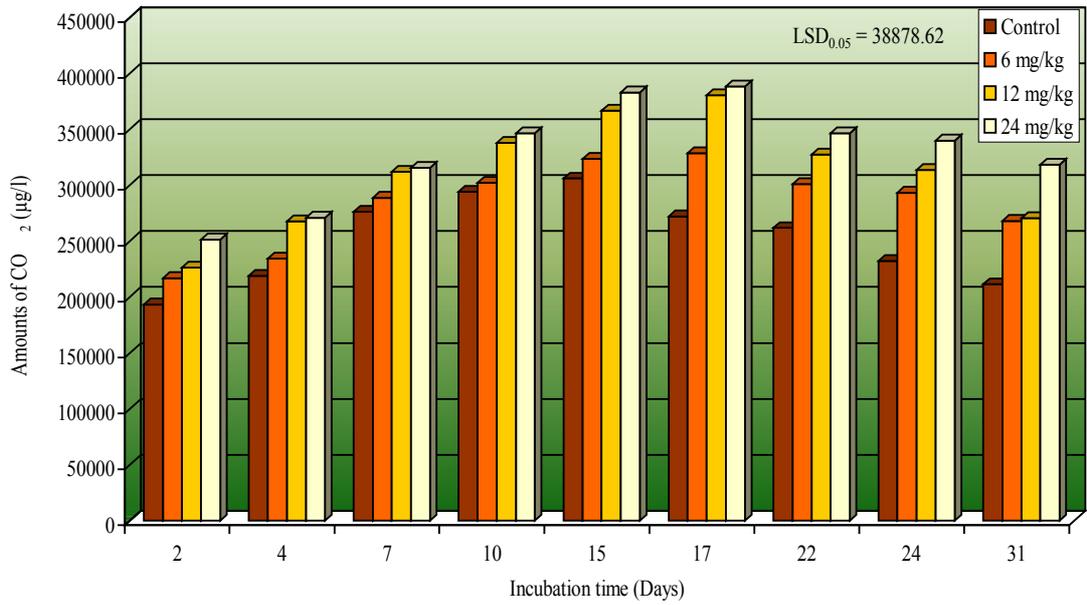


Fig. 32. Carbon dioxide amounts detected in microcosm containing Ramann's brown forest soil (Keszthely) of 60% WFPS treated with different concentrations of Cd and incubated at 37°C

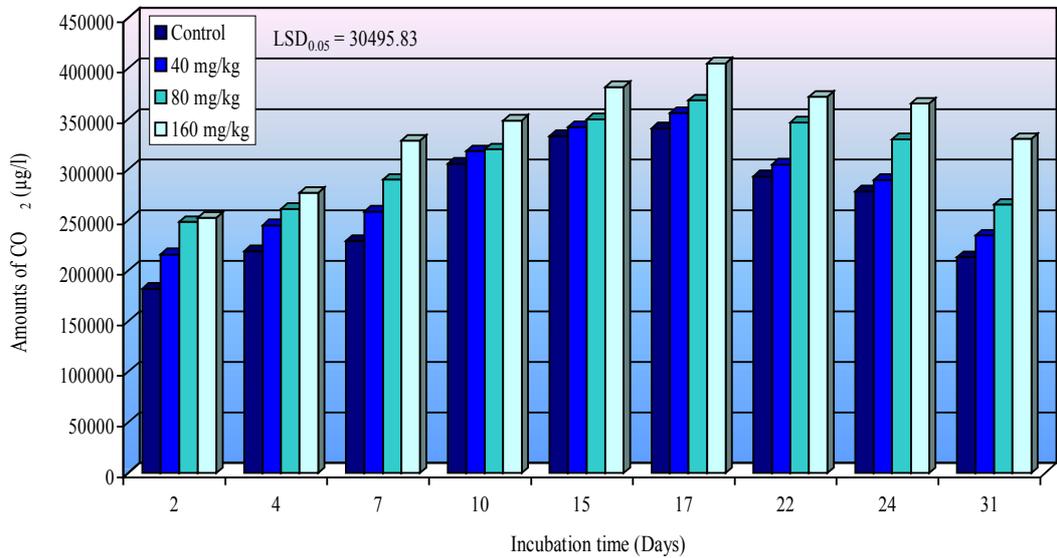


Fig. 33. Carbon dioxide amounts detected in microcosm containing Ramann's brown forest soil (Keszthely) of 60% WFPS treated with different concentrations of Pb and incubated at 37°C

Table (24) Calculations of the variance analysis of emission of CO₂ from Pb treated Gödöllő soil with 60% WFPS at incubation temperature 15°C

Table of Variation						F Interaction	
Source of Variation	n	FG	SQ	MQ	F	SD _{0.05}	LSD _{0.05}
Total	180	179	6.07E+11	3.39E+09			
Replications	3	2	1.84E+08	92106514	1.682686	2647.519	3733.001
Treatment	60	59	6E+11	1.02E+10	185.8021	11840.06	16694.49
Time (A)	15	14	5.39E+11	3.85E+10	703.3157	5920.032	8347.244
Concentration (B)	4	3	4.59E+10	1.53E+10	279.7753	3057.091	4310.499
Lead (C)	1	0	0			3057.091	4310.499
A×B		42	1.51E+10	3.6E+08	6.585219	11840.06	16694.49
A×C		0	0			5920.032	8347.244
B×C		0	0			3057.091	4310.499
A×B×C		0	0			11840.06	16694.49
Error		118	6.46E+09	54737776			

Accuracy of the experiment = 95.5769 %, $t_{0.05} = 1.96$

Calculations of statistical analysis of emission of CO₂ from Pb treated Gödöllő soil with 60% WFPS at incubation temperature 15°C

Time (Days)	Control	40 mg/kg	80 mg/kg	160 mg/kg	LSD _{0.05}	F
3	44231.86	47924.17	55768.50	60911.34	8347.244	0
4	71559.48	77809.04	81805.05	87526.1		
5	89588.51	94817.61	100912.1	109164.8		
6	129669.2	143329.6	150312.9	155983.1		
7	163519.8	169612.7	184798.4	195476.5		
9	185814.8	193033.9	201857.4	206660.0		
13	198302.2	208210.2	221150.9	228589.2		
15	218095.8	231332.5	241463.4	257252.9		
17	234779.7	240059.8	261109.7	277424.0		
20	178390.4	195499.3	221949.7	236872.9		
22	174590.5	185459.0	195000.8	222243.4		
24	159256.4	174123.8	179098.6	217464.8		
28	145843.7	156350.1	166520.2	211205.1		
30	124642.6	133926.9	153341.7	206594.7		
32	112652.4	120569.0	147488.0	197254.7		
LSD _{0.05}	4310.499					
F	279.7753					185.8021

The bold numbers are significantly positive with the controls

Table (25) Calculations of the variance analysis of emission of CO₂ from Cd treated Keszthely soil with 60% WFPS at incubation temperature 37°C

Table of Variation						F Interaction	
Source of Variation	n	FG	SQ	MQ	F	SD _{0.05}	LSD _{0.05}
Total	108	107	2.93698E+11	2.74E+09			
Replications	3	2	309881798.7	1.55E+08	0.5219	7959.780	11223.29
Treatment	36	35	2.72608E+11	7.79E+09	26.2366	27573.49	38878.62
Time (A)	9	8	1.66497E+11	2.08E+10	70.1057	13786.74	19439.31
Concentration (B)	4	3	91787198704	3.06E+10	103.0619	9191.163	12959.54
Cadmium (C)	1	0	0			9191.163	12959.54
A×B		24	14323670694	5.97E+08	2.0104	27573.49	38878.62
A×C		0	0			13786.74	19439.31
B×C		0	0			9191.163	12959.54
A×B×C		0	0			27573.49	38878.62
Error		70	20780718898	2.97E+08			
Accuracy of the experiment = 94.1444 %, t _{0.05} = 1.96							

Calculations of statistical analysis of emission of CO₂ from Cd treated Keszthely soil with 60% WFPS at incubation temperature 37°C

Time (Days)	Control	6 mg/kg	12 mg/kg	24 mg/kg	LSD _{0.05}	F
2	193590.1	217172.5	226478.3	251571.4000	19439.31	0
4	219045.9	234530.0	267991.4	271151.4943		
7	276315.5	289085.8	312105.7	315726.6417		
10	294288.1	302276.2	337961.8	346641.0197		
15	306224.2	323965.4	366805.4	383097.1163		
17	272326.8	328704.6	380801.5	388406.2154		
22	261991.8	301341.0	327563.7	346710.3424		
24	232668.6	293296.3	313677.4	340069.1878		
31	211606.9	268243.0	270745.8	318695.3148		
LSD _{0.05}	12959.54					
F	103.0619					26.2366

The bold numbers are significantly positive with the controls

Table (26) Calculations of the variance analysis of emission of CO₂ from Pb treated Keszthely soil with 60% WFPS at incubation temperature 37°C

Table of Variation						F Interaction	
Source of Variation	n	FG	SQ	MQ	F	SD _{0.05}	LSD _{0.05}
Total	108	107	3.45E+11	3.22E+09			
Replications	3	2	1.4E+08	69973126	0.228396	8086.144	11401.46
Treatment	36	35	3.23E+11	9.24E+09	30.15351	28011.23	39495.83
Time (A)	9	8	2.29E+11	2.86E+10	93.38738	14005.61	19747.91
Concentration (B)	4	3	8.22E+10	2.74E+10	89.40284	9337.075	13165.28
Lead (C)	1	0	0			9337.075	13165.28
A×B		24	1.23E+10	5.11E+08	1.6694	28011.23	39495.83
A×C		0	0			14005.61	19747.91
B×C		0	0			9337.075	13165.28
A×B×C		0	0			28011.23	39495.83
Error		70	2.14E+10	3.06E+08			
Accuracy of the experiment = 94.1668 %, t _{0.05} = 1.96							

Calculations of statistical analysis of emission of CO₂ from Pb treated Keszthely soil with 60% WFPS at incubation temperature 37°C

Time (Days)	Control	40 mg/kg	80 mg/kg	160 mg/kg	LSD _{0.05}	F
2	182172.2	216191.0	248238.1	252241.7	19747.91	0
4	219317.8	245055.7	261151.5	276917.9		
7	229450.7	258296.4	290060.0	328487.0		
10	306023.3	318274.7	319974.4	348533.7		
15	333175.1	342117.1	349763.8	381800.7		
17	340987.7	355918.5	368406.2	404947.9		
22	293436.0	305096.7	346710.3	372114.1		
24	278669.7	289745.4	330069.2	365223.5		
31	213247.8	234922.8	265362.0	330250.4		
LSD _{0.05}	13165.28					
F	89.40284					30.1535

The bold numbers are significantly positive with the controls

5. DISCUSSION

Because of the harmful impact on the environment, there was an international agreement that the emissions of GHGs, including CO₂, CH₄ and NO_x must be limited (UN, 1997). The Intergovernmental Panel on Climate Change (IPCC) has been established by the World Meteorological Organization (WMO) and the United Nations Environment Programme (UNEP) *to assess scientific, technical and socio-economic information relevant for the understanding of climate change, its potential impacts and options for adaptation and mitigation* (IPCC, 2004). The United Nations Framework Convention on Climate Change (UNFCCC) was negotiated in 1992 (UNFCCC, 1992). The UNFCCC postulated the stabilization of the GHG concentration in the atmosphere *at a level that would prevent dangerous anthropogenic interference with the climate systems* (UNFCCC, 1992). At the Conference of the Parties to the UNFCCC in Kyoto in 1997, the basis was established to pass a law. In the Kyoto Protocol, the developed countries committed to reduce the overall emissions of the main GHGs in the period from 2008 to 2012 under the level of the 1990 (UNFCCC, 2004a). The government in Germany plans a reduction of emissions of about 21% compared to the 1990, while a reduction of 19% was achieved in 2004 (BUNDESREGIERUNG, 2004b). This equals a reduction of overall N emissions from about 1100000 t⁻¹ yr⁻¹ in 1985 to about 700000 t⁻¹ yr⁻¹ in 2000 (BUNDESREGIERUNG, 2004a). The entry into force of the Kyoto Protocol was discussed at the 10th Session of the Conference of the Parties to the UNFCCC in Buenos Aires (2004). The Kyoto Protocol is scheduled to enter into force on February 16, 2005 (BUNDESREGIERUNG, 2004c).

Agriculture accounts for approximately half of the anthropogenic N₂O emission in the EU (UNFCCC, 1998). On a global scale, 47% of N₂O emissions (IPCC, 2001) come from anthropogenic sources, particularly from the agricultural N cycle (MOSIER et al., 1998). The N₂O emissions caused by human activities are mainly due to tillage (44%) and fertilization (22%) on agricultural soils, followed by burning of biomass (9%) and fossil fuels (10%). The chemical production contributes 15% to the N₂O emissions. The high emissions from agricultural soils are mainly caused by the application of N fertilizer, which is transformed by nitrification and denitrification into N₂O.

In the last 150 years, the atmospheric CO₂ concentration has increased by approximately 33% due to human activity, and is predicted to continue to rise by 0.4% per year (ALLEY et al., 2007). A continued rise in CO₂ may stimulate plant biomass production as well as root growth when sufficient mineral nutrients are available (CURTIS & WANG, 1998; GHANNOUM et al., 2000). This could result in greater C inputs into the soil due to higher rates of plant litter-fall, root turnover and rhizo-deposition (ROGERS et al., 1994; COTRUFO & GORISSEN, 1997; SADOWSKY & SCHORTEMAYER, 1997; DELUCIA et al., 1999) as well as alterations in the chemical composition of plant tissues (e.g. higher C/N ratio) and root exudates (COTRUFO et al., 1994; JONGEN et al., 1995; SCHORTEMAYER et al., 1996).

Amendments of plant residue enhanced both N₂O and CO₂ emissions, which is in accordance with the results from AULAKH et al. (1991) and FLESSA & BEESE (1995). Most soil microorganisms get their energy and substance from organic materials. N mineralization and the following transformation, i.e. nitrification and denitrification whereby N₂O is produced as an immediate product, are intimately linked to the organic carbon decomposition. Since the responsible microorganisms operate under various optimum conditions it is generally assumed that nitrification is the predominant N₂O producing process under moderately moist and that denitrification is the predominant process under wet conditions when NH₄⁺ and NO₃⁻ are available in soil (CONRAD, 1996a; BOUWMAN, 1998). In our study there were conditions that should have been favorable for nitrification: moderately moist soil samples (water content of 30% WFPS). However, the relationships between emissions of N₂O and CO₂, as well as between N₂O emissions and DOC implied that denitrification might be a candidate for the active mechanism. GROFFMAN & CRAWFORD (2003) reported that denitrification enzyme activity was highly correlated with soil respiration.

Nitrous Oxide is potentially agriculture's greatest contributor to the GHG Problem. N₂O is a serious pollutant, implicated in virtually all current environmental problems (e.g. acid rain, GH effect, O₃ depletion). N₂O causes global warming and stratospheric O₃ depletion. Model calculations suggest that atmospheric N₂O may approach a value ranging from 354 to 460 ppb by 2100, compared with the present concentration of 316 ppb (IPCC, 2001a). Annual anthropogenic N₂O emissions to the atmosphere are estimated to be 3–8 Tg N and recent estimates suggest that agricultural systems impart a large portion of anthropogenic emissions (MOSIER & KROEZE, 1998).

There are numerous agricultural practices that can influence the rate of CO₂, N₂O and NO fluxes from agricultural soils (KINNEY, 2002), however, only some of these influences can be investigated with soil incubation experiments. The gas emission depends on factors such as type of fertilizer and soil moisture (PATHAK & NEDWELL, 2001). The range of N₂O production rates observed in this study is similar to those observed by others in fertilized soil incubation experiments (PARTON et al., 1988a,b; PATHAK & NEDWELL, 2001).

5.1. EFFECT OF HEAVY METALS ON THE SOIL RESPIRATION AND MICROBIAL CONTENT

Sludge application increased soil metal concentrations up to current limits with the exception of Cd which was three to five times the maximum limit. However, in other studies with the same soils there were no effects of metal concentration on respiration rate. Therefore, the respiration rate per unit weight of biomass was considerably greater in the metal-contaminated soil. The gradual increase in atmospheric CO₂ concentration and potential climatic changes are likely to affect plant, soil and ecosystem processes, including C flux from plants to soil and from soil to atmosphere.

Soil microorganisms are the key processors of SOM and heavily rely on organic carbon supply for their growth. Any change in the amount and/or composition of plant material input into the soil in response to elevated CO₂ is therefore likely to affect soil microbial growth and metabolism of plant-derived substrates, and consequently C and N cycling in soils (ZAK et al., 1993).

Heavy metal pollution in agricultural land has a major influence on soil microbial processes. The soil pollution causes a decrease in microbial populations and increases the soil respiration rate, and there was also a remarkable change in microbial community structure of the heavy metal amended soil. Soil microorganisms, the living component of SOM, are responsible for mineralization of nutrients, decomposition, and degradation or transformation of toxic compounds. Being a labile fraction of SOM, the microbial biomass can be a useful early indicator of change and future trends and can reflect organic matter changes and soil development. In contrast, an increase in CO₂-production after adding Pb and Cd to the soil was observed. These observations were confirmed by CHANDER & BROOKES (1991) who found that more CO₂-production was evolved per unit biomass C in soils amended with contaminated sewage sludge.

In the present study, it was found that an increase in soil respiration rate in cultivated and uncultivated brown forest soil samples contaminated with Cd, Co and Pb. These increases in the respiration rates were unspecifically in all contaminated soil samples in the first week of incubation. One reason for large increase in the soil respiration rate in these contaminated soil samples may be the need of living organisms to consume more energy to survive. This result is confirmed by CHANDER & BROOKES (1993) and BAYOUMI HAMUDA & KECSKÉS (2003).

However, there are some positive and negative interactions between metals upon their toxic effects on soil microorganisms *in vitro*. (BAYOUMI HAMUDA et al., 1996). One particular uncertainty is whether the toxic effects of combinations of metals are synergistic, additive, or antagonistic. There have been numerous reviews on the effect of metals on microorganisms (e.g., TREVORS et al., 1986, BAYOUMI HAMUDA et al., 1995) that have dealt mainly with *in vitro* studies of the biochemical and physiological mechanisms whereby metals exert their effects on microorganisms.

COOK & ORCHARD (2008) studied the interaction of soil microbes with their physical environment affects their abilities to respire, grow and divide. One of these environmental factors is the amount of soil moisture. The results showed that microbial respiration was linearly related to soil-water content and log-linearly related to water potential. The initial peak is due to the application of the work to studies on microbial processes. The second peak is associated with the rise of simulation modelling and the third with the relevance of the findings to climate change research.

The available fraction or soil solution containing Pb, Cd and Co and not the total concentration of the elements seem to be correlated well with the toxicity parameters (VIG et al., 2003). Different aspects of heavy metal toxicity towards microorganisms and microbial mediated processes in soil have been reviewed previously (e.g., BÄATH, 1989). These previous results are in accordance with the results found by DE HAAN et al. (1989) who reported that the supply of the mineralized C, N and P sources to soil SOM, the decomposition of the residues animals and plants and maintenance of soil structure all are depended upon the activities of microbial content in each ecosystem. Our results are also in agreement with investigation of HOSSAIN et al. (1995). It was reported that P and N treatments significantly affected soil microbial biomass C content. The N and P treatment increased biomass C content. Microbial specific respiratory activity was higher in the unfertilized treatments. NANNIPIERI et al. (1990) stated that the changes in CO₂-release were related to glucose concentrations of mineral nutrients. Higher initial rates of CO₂-release were noted after the addition of P and glucose to N amended soil at C:P ratios greater than 30:1. Concerning heavy metal treatments (Pb, Cd and Co), the highest CO₂-production was measured after the 1st week incubation followed by the 3rd and 6th week respectively. The same effect was found at counting the bacterial population in different ecosystems. It is also shown from such data presented in Figures 7 and 9 that heavy metals, Pb, Cd and Co have significant effect on CO₂-production of tested uncultivated and wheat cultivated soil at different incubation periods (1st week, 3rd week, and 6th week). It can be observed that the methods used for evolution of CO₂-production (Figures 7 and 9) and total aerobic bacterial counts (Figures 11 and 13) are both suitable to be indicators for detection of the soil contamination as well as an idea about the soil fertility. It is known that the microbial biomass plays an important role in mineral nutrition of soil. BÄATH (1989) studied the effect of heavy metals in soil microbial processes and populations. Author established that the relative decreasing order toxicity of investigated metals incubation was Cd > Cu > Zn > Pb. These results were similar to our presented results in which our investigations showed that the relative toxicity of tested metals decreased in the order Cd > Co > Pb. On the other hand, our results on the microbial activities in an ecosystem treated with heavy metals is in accordance with the result of LEITA et al. (1995) who reported that the addition of Pb did not have any significant inhibitory effect on the level of microbial biomass C.

VAN DER HEIJDEN et al. (2008) mentioned that soil microbes are important regulators of plant productivity, especially in nutrient poor ecosystems where plant symbionts are responsible for the acquisition of limiting nutrients. Mycorrhizal fungi and N₂-fixing bacteria are responsible for 5–20% (grassland and savannah) to 80% (temperate and boreal forests) of all N, and up to 75% of P, that is acquired by plants annually. Free-living microbes also strongly regulate plant productivity, through the mineralization of, and competition for, nutrients that sustain plant productivity. Soil microbes play key roles in ecosystems and influence a large number of important ecosystem processes, including nutrient acquisition (SMITH & READ, 1997; SPRENT, 2001), N cycling (TIEDJE, 1988; KOWALCHUK & STEPHEN, 2001), C cycling (HOGBERG et al., 2001) and soil formation (RILLIG & MUMMEY, 2006). MORGAN et al. (2007) mentioned that risk assessment of metal-contaminated habitats based on responses in the field is complicated by the evolution of local, metal-resistant ecotypes. NADA et al. (1997) mentioned that in industrialized countries contamination of soil with a variety of heavy metals has become very common. Microorganisms connect the soil and the plant, and present an important indicator of change in soil biological activity and depending on the concentration and the parameters under investigation, as well as on the element applied. All tested elements

reduced the total number of bacteria and fungi. OLIVEIRA & PAMPULHA (2006) established that the quantitative analysis of soil microbial populations shows a marked decrease in total culturable numbers of the different microbial groups of the contaminated soil samples. Certain groups of soil microbes were particularly sensitive to long-term contamination (e.g., asymbiotic N₂-fixers and heterotrophic bacteria).

This study is concerned with the effect of CNP and heavy metals (Pb, Cd and Co) on CO₂-production as well as bacteria populations of cultivated and uncultivated soils during one, three and six weeks incubation. After one week of incubation, the recovery of Pb, Cd and Co concentrations added to CNP treated cultivated soils was determined in the HNO₃ soluble fraction. Data presented in Figures 1–3 show that the addition of inorganic forms of Pb, Cd, and Co significantly increases the mobile (HNO₃ soluble) fraction of these metals but after one week incubation their concentration does not reach the 100% recovery. It can be observed that the methods used for biomass, CO₂-evolution and total bacteria number, are both suitable to be indicators for biomass measurements through which we can have an idea about the soil fertility. It is known that microbial biomass plays an important role in mineral nutrition of soil. KÁTAI et al. (2005) realized that the maximum amount of CO₂ production was found in the meadow chernozem, marshy meadow and brown forest soil, while the maximum amount of microbial biomass C was recorded in the meadow solonetz soil. VÁGÓ et al. (2005) found that the total number of microbes and the CO₂ production slightly increased in both investigated soils compared to the control. The treatments significantly increased the microbial biomass values. The total number of bacteria in the typical meadow soil was 1.5-2 times higher than that in the calcareous chernozem soil.

These results were published in:

ALGAIDI et al. (2005): Effect of heavy metals in soil microbial processes and population. *Magazine of Sebha University*. Sebha, Libya. **12**: 1-6.

ALGAIDI et al. (2006): Impact of lead, cadmium, and cobalt on soil respiration and microbial content under in vitro conditions. Proc. **VII**. Intern. Ph.D. Students Conference. RNDr. M. Slábová, Ing. Z. Sýkorová (Eds.). 4th April 2006. University of South Bohemia, Faculty of Agriculture, České Budějovice, Czech Republic. pp.: 7-16. ISBN 80-7040-847-2.

ALGAIDI et al. (2007): A szennyező nehézfémek hatása a talajbaktériumok mennyiségére, és a talajlégzésre *in vitro* körülmények között. *Agrokémia és Talajtan*, **56**: 353-366.

5.2. FACTORS INFLUENCING TRACE GASES EMISSIONS

The rate and composition of nitrogenous gas production depend on many factors, e.g. on soil temperature and moisture (MAHMOOD et al., 1998), on the chemical form of N in the fertilizer (BERECZ et al., 2000; DEBRECZENI & BERECZ, 1998) and on the amount of available C (SIMARMATA et al., 1991). The emission of N₂O and NO from soils by nitrification and denitrification processes depends not only on environmental and agricultural management factors, such as rain, temperature, fertilization, irrigation, and heavy metal accumulation, but also on soil properties such as pH, organic matter (OM) content, and particle size (SKIBA et al., 1998; INUBUSHI et al., 2000; VENTEREA & ROLSTON, 2000; KHALIL et al., 2002).

Laboratory experiments described here were used to demonstrate that soil moisture, soil temperature and heavy metals can influence the production and net fluxes of trace gases. These studies show that Cd and Pb inhibit N₂O and NO produced by nitrification and denitrification, and that nitrification is the major source of N₂O and NO at soil moistures relevant to the site from where the soils were collected. In terms of N₂O and NO production, nitrification was more sensitive to heavy metals application than denitrification. Furthermore, because a majority of NO production appears to occur from nitrification, heavy metals may be particularly effective at inhibiting NO emissions.

Soil aeration (SIMOJOKI & JAAKKOLA, 2000), N availability (BOUWMAN, 1996; DEL GROSSO et al., 2000) and acidity (GRANLI & BÖCKMANN, 1994) have been identified to be key factors influencing exchange dynamics of N₂O and NO between soils and the atmosphere. HOLLAND & LAMARQUE (1997) mentioned that the tropospheric and terrestrial N cycles are connected to one another through the emissions of NO_x and NH_x from soils and vegetation and the subsequent redeposition of these compounds and their products elsewhere. These connections play an important role in the Earth system influencing tropospheric concentrations of NO_x, ozone (O₃), and CO₂. Estimates of the biogenic sources of NO_x, soil emissions and biomass burning, are amongst the most variable terms in the global budget of NO_x and are eclipsed only by lightning.

Economic and energy budget analysis has to be done to verify the utility of agronomic impacts (JOLÁNKAI et al., 2007). JOLÁNKAI & BIRKAS (2005) mentioned that the climate change phenomena may be related to the rise in atmospheric CO₂. Long-term rise in atmospheric CO₂ highlights crop production regarding both adaptation and mitigation (JOLÁNKAI et al., 2005).

More recent findings suggested that denitrification can occur under aerobic soils. Though conditions in our incubation study might be favorable for nitrification, soil amendment with heavy metals might inhibit microbial growth and activity, and hence promoted O₂ consumption that created temporary anaerobic micro-sites (SAHRAWAT & KEENEY, 1986; GOEK & OTTOW, 1988). As a result, autotrophic nitrification might be reduced and N₂O production via denitrification enhanced. MCKENNEY et al. (1993) also observed higher denitrification rates in aerobic than in anaerobic conditions due to organic residues.

Management practices influencing GHG emissions from fertilizer include application rate, application technique, application timing, tillage practices, the use of other chemicals, irrigation, residual N and C from crops and fertilizer. Environmental factors influencing GHGs emissions from fertilizer include temperature, precipitation, soil moisture content, soil texture, soil N content, organic carbon content, O₂ availability, porosity, pH, freeze and thaw cycle annual variation and microorganisms (KULSHRESHTHA et al., 1999). The impact of increasing GHGs content in the atmosphere and climate change on the forest and the role of forestry in mitigating the impact of climate change were discussed by MUDRI et al. (2005).

5.2.1. NITRIC-OXIDE EMISSIONS (NO)

We introduced a ‘microcosm’ concept in the soil model to better account for the irregular nature of NO emissions, due to their dependence on soil conditions at the soil surface and particularly, in its topmost centimeters (JAMBERT et al., 1997; DUNFIELD & KNOWLES, 1999). The thickness of this layer was somewhat arbitrarily set to 5 cm, but followed the recommendations of MAHRT & PAN (1984), MARTINEZ et al. (2001) and NOILHAN & MAHFOUF (1996). DUNFIELD & KNOWLES, (1999) have also shown the importance of a better simulation of surface water dynamics to simulate NO production. SUN et al. (2008) mentioned that nitrate concentrations in the drainage water and nitrate leaching increased with increasing N application rate. ROLLAND et al. (2008) presented the implementation of a soil NO emissions submodel within the environmentally-orientated soil crop model. The submodel simulates NO production *via* the nitrification pathway, as modulated by soil environmental drivers. The model provided accurate predictions of NO emissions. The introduction of a 2 cm thick micro-layer in the topsoil, appeared improved the timing and magnitude of the predicted NO emissions in response to rapid weather changes, such as a heavy rainfall occurring after a dry spell. That was the reason of used 5 cm soil layer in our microcosms in the present investigations.

Previous studies have also shown that NO production in soils results predominantly from nitrification (ANDERSON & LEVINE, 1986; GÖDDE & CONRAD, 1999). The response of NO production to soil moisture was different than for N₂O. With only one exception, maximum production of NO typically occurred at soil moistures 30% WPFS. Our results recognized that at 30% WPFS and when the soil microcosms incubated at 15°C, NO emission from Ramann-type brown forest soil of Keszthely soil microcosms was more inhibited by Cd than by Pb. But

Pb more inhibited the NO emission than Cd in clay loam brown forest soil of Gödöllő soil microcosms. As regards diffusion control, linked with moisture content (due to low solubility of O₂) and soil structure, studies showed that the emission of NO may be limited by gaseous diffusion in soils, because of the high solubility of NO. Near the soil surface, any NO produced would be readily emitted due to a short diffusion path while in lower depths, NO tended to be converted to N₂O (McKENNEY & DRURY 1997). Experiments also showed that NO may be reduced with lateral diffusion while increasing emissions from adjacent areas (VENTERA & ROLSTON 2000). VENTERA & ROLSTON (2000) proposed a mechanistic modeling of chemical transport and transformation of the nitrification components (NH₄⁺, NO₂⁻, NO₃⁻, NO), with introducing a diffusion-reaction for each component for the different phases (solid, aqueous and gaseous). Our presented results are in agreement with one or with both suggestions. This model may improve simulations of NO emissions in accordance with soil gas diffusivity levels. With high soil moisture regime, simulated rates of NO emission peaks may be reduced to N₂O. Similar results were obtained in the presented study.

In the presented study, it was found that when the soil samples had 60% WFPS and incubated at 15°C, the amounts of NO detected were the lowest when compared with the soil samples incubated at 37°C or had 30% WFPS and incubated at 15°C. These results are in agreement with the following authors. WILLIAMS (1995) established that nitrification is regulated by a soil temperature factor, a soil moisture factor, and a soil pH factor. FANGUEIRO et al. (2008) stated that total N emissions (N₂O + N₂) as well as the sources of the N emissions (nitrification or denitrification) were also studied during this period. PÉREZ et al. (2007) found that soil water content and pH related negatively to NO emissions. NO emissions also showed an inverse relationship with WFPS in our linear regression models. This is in agreement with the “hole-in-the-pipe” model (FIRESTONE & DAVIDSON 1989) where the high emission of NO are explained by combined physical (lower water content) and biological processes. This could be explained if we consider that the sun heats on the soil directly. This would favor lower moisture in the surface soil layer enhancing NO emissions. This assumption is supported by our linear regression analysis where the only variable that was statistically significant and negatively related to NO emissions was WFPS.

A recent statistical model of global soil NO_x emissions (YAN et al. 2005), uses field measurement results of NO_x emissions with associated soil properties such as SOC content, pH, N fertilization rates, vegetation type, surface soil moisture, temperature and climate type, collected from the literature, to produce estimates of global soil NO_x emissions. These authors found that those parameters significantly influence NO_x emissions and that pH was the variable that mostly account for the variability in NO_x fluxes, which agree with our findings.

The hypothesis of a fixed ratio between NO emissions and nitrification rates from LAVILLE et al. (2005) may be challenged. Soil temperature was relatively high and may have enhanced this ratio (LI 2000). We thus tested the relationship of soil temperature and the NO to nitrification ratio proposed by the latter authors. The simulated NO emissions were closer to measurements in some cases. The net production of N₂O increased as soil moisture increased. The rate of NO production was greatest at the intermediate moistures investigated, between 14 and 19% gravimetric soil moisture, suggestive that nitrification is the dominant source of NO (KINNEY et al., 2005).

This is consistent with the results of experiments by PARTON et al. (1988b, 2001) and PATHAK & NEDWELL (2001). These results confirm that at moistures relevant to this field site, nitrification is the dominant source of N₂O (MOSIER & PARTON, 1985; PARTON et al., 1988a,b, 1996a). From soil incubations, BOLLMANN et al. (1999) observed a steady decrease in NO production as soil moisture was increased. A similar phenomenon was observed with the NO production rates in this study above 30% WFPS soil moisture. This demonstrates that nitrification is the dominant source of NO, which is supported by the results of the soil incubations and is consistent with ANDERSON & LEVINE (1986) and GÖDDE & CONRAD (1999). Other research has demonstrated that increased temperature and C sources can result in enhanced N₂O and NO production in soil (TORTOSO & HUTCHINSON, 1990; GÖDDE & CONRAD,

1999). Such variables were not addressed in this study. However, the soils used in the incubations of this study are not C rich, and would likely have a similar response to an added C source (MOSIER et al., 1996a,b).

Since the pioneering work of GALBALLY & ROY (1978), main controllers/influencing factors were identified. These are the soil water content, the soil temperature, the ambient NO concentration, and the substrate N availability. Coarse-scale models have already incorporated corresponding parameterizations to study the influence, interactions, and dynamics of influencing factors on regional to global and seasonal to inter-annual scales (HUTCHINSON et al., 1997). However, these algorithms/models usually fail when small scale, especially temporal effects of biogenic NO emissions are addressed.

There is a demand for more appropriate descriptions of the large pulses of biogenic NO emission commonly observed on a time scale of a few hours to a day following (a) wetting of dry soils by precipitation, thawing, and irrigation and (b) agricultural management practices like tilling, fertilization, harvesting, and burning (HUTCHINSON et al., 1997; MATSON, 1997). On comparative spatial scales (i.e., a few meters to kilometers), we need better descriptions of (a) the so-called 'canopy reduction' of soil NO emission (owing to its rapid conversion to NO₂, which is taken up by vegetation elements by an order of magnitude faster than NO) and (b) the consequences of atmospheric deposition of anthropogenic N on biogenic NO emission from soils (MATSON, 1997).

In this context, results of some recent models (POTTER et al., 1996a,b) and algorithms (YANG & MEIXNER, 1997; OTTER et al., 1999) are encouraging. Since they are based on mechanistic understanding of NO exchange, they enable description of biogenic NO emission (a) on the temporal and spatial dynamics of more general ecosystem variables (like gross mineralization) and (b) on rather short time scales. It should be mentioned in particular that present mesoscale meteorological – air chemistry models (VOGEL et al., 1995; GANZEVELD & LELIEVELD, 1995) are already able to tackle the problems of 'canopy reduction' of soil emitted NO, as well as dry and wet deposition of anthropogenic N by chemistry and small-scale surface exchange modules.

HORVÁTH et al. (2005) mentioned that during one year (2002–2003), emissions of NO and N₂O were measured from Sessile oak and Norway spruce forest soils in northeast Hungary. Accumulation in small static chambers followed by gas chromatography-mass spectrometry detection was used for the estimation of N₂O emission flux. Because there are rapid chemical reactions of NO and O₃, small dynamic chambers were used for *in situ* NO flux measurements. Average soil emissions of NO were 1.2 and 2.1 $\mu\text{g N m}^{-2} \text{ h}^{-1}$, and for N₂O were 15 and 20 $\mu\text{g N m}^{-2} \text{ h}^{-1}$, for spruce and oak soils, respectively. Thus, about 10–13% of N compounds deposited to the soil, mostly as NH₃/NH₄⁺ and HNO₃/NO₃⁻, are transformed in the soil and emitted back to the atmosphere, mostly as N₂O.

5.2.2. NITROUS-OXIDE EMISSIONS (N₂O)

Agricultural soils contribute approximately 80% of the total N₂O in the atmosphere, and as such are the most important anthropogenic source of N₂O (ISERMANN, 1994). N₂O is produced in soils mainly by nitrification and denitrification processes. Microbial activities, including nitrification and denitrification, are generally greatest during seasons with high soil temperatures (SOMMERFIELD et al., 1993). However, N₂O emissions have shown a great temperature anomaly.

Several parameters have been identified that affect the rate of N₂O emission from agricultural system, including N supply (BOUWMAN, 1996; BROWN et al., 2000; MAGGIOTTO et al., 2000), temperature (GOODROAD and KEENEY, 1984; CASTALDI, 2000), pH (DAUM and SCHENK, 1998; MOGGE et al., 1999) and soil moisture (DOBBIE et al., 1999; ZHENG et al., 2000, 2002).

As a practical manner to improve soil fertility, amendment of local organic residues has been gaining worldwide support. Incorporation of crop residues provides a source of readily available C and N in the soil, and subsequently influences the CO₂ and N₂O emissions (FLESSA & BEESE, 1995; COCHRAN et al., 1997; LEMKE et al., 1999). The residue type was thought to be

an important factor affecting N₂O emission (AULAKH et al., 1991; MCKENNEY et al., 1993; SHELP et al., 2000). Although the amount of N that recycles into agricultural fields through residues may add 25–100 Tg N yr⁻¹ into agricultural soils. NO and N₂O are known as intermediate products of nitrification and denitrification processes in soils, and forest soil may be an important source for these compounds. Recent research has shown that the emission of NO and N₂O depends, among other things, on forest type, soil characteristics, and on atmospheric deposition of N to the forest ecosystem (GROFFMAN & TIEDJE, 1989; HENRICH & HASELWANDTER, 1997; VERMES & MYROLD, 1992). In a cross-site study of 15 European forests sites (PILEGAARD & NOFRETETE Team, 2004), the ratio of NO_x emission to N-deposition ranged from very little up to 50%. Although denitrification has shown to be insignificant in many forest ecosystems (e.g. GUNDERSEN, 1991; MYROLD et al., 1989), it is clear that in some forests, and soils may contribute to the atmospheric N-budget at both a local and a global scale. As a large part of these N emissions may occur in the form of N₂O, such emissions have significant implications for global warming.

In accordance with our results, it was found that the emissions of NO and N₂O were depended on the incubation temperature of the soil microcosms and the moisture regime in the soil. The rate of N₂O production and emission primarily depends on the availability of a mineral N source (substrate for nitrification or denitrification), O₂ supply or WFPS, soil temperature, pH and salinity and (for denitrification) the availability of labile organic compounds (SMITH et al., 2003). These variables operate in different combination and order of importance in both space and time (SKIBA & SMITH, 2000; DALAL et al., 2003).

In our study, all gas flux rates were positively correlated with soil temperature and emission rates were negatively correlated with soil moisture. The positive correlation with soil temperature is not surprising, as many indices of soil microbial activity, such as respiration, are positively related to temperature (CHEN et al., 2000; CURIEL YUSTE et al., 2004; FRANZLUEBBERS et al., 2002). The negative correlation with soil moisture was surprising, as soil microbial processes are usually positively correlated with soil water, or other factors that control the supply of readily mineralisable substrates (QI & XU, 2001; FRANZLUEBBERS et al., 2002). Only when soil moisture becomes too high does microbial respiration tend to decrease (CHEN et al., 2000). This negative correlation suggests that our soils were wet enough that N₂O production was decreasing, and perhaps N₂ emissions from denitrification were increasing.

The properties of brown forest soil samples used in the present study of Ramann-type of Keszthely with pH 7.55 and clay loam of Gödöllő with pH 5.56 may gave up the differences in the emissions of trace gases. The pH was significantly positively correlated with the production of N₂O when soil was incubated at 50% WHC, but not at 100% WHC. Total gaseous emissions to the atmosphere (N₂O, NO and N₂) have repeatedly been shown to be less from acidic than in neutral or in slightly alkaline soils (ŠIMEK & COOPER, 2002). This may be due to an effect on nitrification and/or denitrification (SUZUKI et al., 1974; WEIER et al., 1993; ELLIS et al., 1996; VAN CLEEMPUT & SAMATER, 1996; BRADY & WEIL, 1999). The organic carbon and total soil N were significantly positively correlated with N₂O production at both 50% WHC and 100% WHC. It has often been reported that the C and N content of soils has a positive effect on N₂O production (WILLIAMS et al., 1998; RUDAZ et al., 1999; WULF et al., 1999; HADI et al., 2000), but not always (ANGOA PÉREZ et al., 2004). Larger amounts of soil OM content will lead to larger amounts of N being mineralized and formation of more NH₄⁺, which will increase nitrification and thus production of N₂O (DALAL et al., 2003). Comparatively, it was observed that at 60% WFPS and the microcosms incubated at 15°C, the amounts of N₂O emitted from Keszthely soil samples were more sensitive to Cd than the amounts of N₂O emitted from soil of Gödöllő. The N₂O release was larger at 100% WHC than at 50%. It is well known that increases in soil moisture content increase production of N₂O as denitrification is induced (BOLLMANN & CONRAD, 1997). Nitrification is the main source of N₂O emissions at lower moisture contents (YOSHIDA & ALEXANDER, 1970; BLACKMER et al., 1980). The balance between the two processes contributing to the N₂O emission will vary with climate, soil conditions and soil management. Generally, high rainfall, poor drainage, fine soil

texture and high organic carbon content promote denitrification and associated N₂O production, whereas low rainfall, good drainage and aeration and coarse texture promote nitrification and associated N₂O production (GROFFMAN & TIEDJE, 1991). However, in most soils the dominance of nitrification or denitrification as the main source of N₂O is not static and can switch very rapidly as the soil aeration state within the biologically active sites changes due to, e.g. rainfall or increased O₂ demand caused by the presence of easily mineralisable OM (SKIBA & SMITH, 2000).

There are several studies on the high N₂O fluxes at low soil temperatures in northern European and North American soils, showing that from 38 to 70% of the annual emissions can take place during winter (VAN BOVHOVE et al., 1996; WAGNER-RIDDLE et al., 1997; RÖVER et al., 1998; ALM et al., 1999; TEEPE et al., 2000). The highest N₂O fluxes at low temperatures have been associated with freezing and thawing cycles (FLESSA et al., 1995; KAISER et al., 1998; PREMIÉ & CHRISTENSEN, 2001; TEEPE et al., 2001).

Several alternative mechanisms have been proposed to explain the high N₂O release during thawing including physical release of the trapped N₂O (BURTON & BEAUCHAMP, 1994), an increase in the availability of substrates and associated denitrification activity (CHRISTENSEN & TIEDJE, 1990; CHRISTENSEN & CHRISTENSEN, 1991), a combination of physical N₂O release and increased microbial activity (GOODROAD & KEENEY, 1984; KAISER et al., 1998) and chemical production of N₂O (Christianson & CHO, 1983). Many observations have recorded of on high N₂O emissions from Finnish agricultural soils *in situ* during winter without freezing–thawing cycles (MALJANEN et al., 2003). The mechanism for these emissions is unknown. When soil temperature was lowered in a stepwise manner each of the two soils showed an increase in N₂O release at 15°C. However, the release rates were dependent on the soil type and soil water content. The liberation of N₂O stored in soil does not explain these increases, because the solubility of N₂O in water increases with decreasing temperature. Therefore, we consider that microbial processes were responsible for the increased N₂O production. Since the responsible microorganisms operate under various optimum conditions it is generally assumed that nitrification is the predominant N₂O producing process under moderately moist and that denitrification is the predominant process under wet conditions when NH₄⁺ and NO₃⁻ are available in soil (CONRAD, 1996a,b; BOUWMAN, 1998).

More recent findings suggested that denitrification can occur under aerobic soils. MÜLLER et al. (2003) found that the process of NO₃⁻ reduction is the predominant N₂O producing mechanism even under aerobic conditions in a temperate grassland soil. Their field observations indicated that soil volumetric water in the main rooting zone (top 10 cm) stayed at approximately 0.3 cm³ cm⁻³ during the main growth period and O₂ concentrations in the entire soil profile stayed between 15 and 21% throughout most of the observation period.

Though conditions in our incubation study might be favorable for nitrification, residue amendment might stimulate microbial growth and activity, and hence promoted O₂ consumption that created temporary anaerobic micro-sites (SAHRAWAT & KEENEY, 1986; GOEK & OTTOW, 1988; CANNAVO et al., 2003). As a result, autotrophic nitrification might be reduced and N₂O production *via* denitrification enhanced. MCKENNEY, et al. (1982, 1993) also observed higher denitrification rates in aerobic than in anaerobic conditions due to organic residues.

We simply don't know the contribution of nitrification and denitrification to the overall N₂O emission, because we didn't make any measurements under acetylene inhibition which is believed to block the build-up of NO₃⁻ and the subsequent N₂O production *via* denitrification. A further investigation is required to identify N₂O production *via* denitrification under aerobic conditions when organic C is incorporated.

Generally, a small amount of the N in the fertilizer ends up being released to the atmosphere as N₂O and NO_x (the rest ends up in the crop, in the soil, in water, in microorganisms, or in the air as N₂). The net amount of N₂O and NO_x released depends on many factors, including: the type of biomass being grown; the amount, type, depth, and frequency of application of fertilizer; the temperature, water content, and acidity of the soil; agricultural and harvesting practices; and others (BOWDEN et al., 1990; BRUMME & BEESE, 1992;

EICHNER, 1990; CONRAD et al., 1983; ANDERSON & LEVINE, 1987; LI et al., 1994, 1996; GROFFMAN et al., 2000)

N₂O is produced from complex microbial nitrification, denitrification, and decomposition processes in soils. Increases in the amount of N added to the soil typically result in increased N₂O emissions (WILLIAM et al., 1992a). One study suggests a roughly linear relationship between N lost as N₂O and N input, over a range of 0 to 600 kg of fertilizer N ha⁻¹ added to several different soil types (VELTHOF & OENEMA, 1995). Several studies have shown that typical values for the percentage of applied N that is emitted as N₂O-N range from about 0.2% to 3%, for corn, barley, and wheat fields in the U.S. and Europe, and that these emissions may represent increases of from a few to a few hundred percent above background levels (LI et al., 1994; VELTHOF & OENEMA, 1995). N₂O emissions are higher from saturated than from dryer soils, and peat soils and soils high in NO₂ and CaCO₃ content seem to have particularly high N₂O emissions (VELTHOF & OENEMA, 1995; BANDIBAS et al., 1994).

In general, researchers have a good understanding of many of the individual factors that regulate N₂O production from soils, but they cannot yet predict how these factors will interact to produce reliable N₂O emissions estimates for specific crop, soil, fertilizer, and management combinations. Thus, the direct and even total emissions of N₂O from soil fertilization can in principle be quantified, but pending further study there will be significant uncertainty in estimates of both direct and indirect emissions. GROFFMAN et al. (2000) come to a similar conclusion, suggesting that there are indeed coherent patterns in annual N₂O flux at the ecosystem scale in forest, cropland, and rangeland ecosystems but that these patterns vary by region and emerge only with continuous flux measurements over multiple years.

VERHAGEN & BOUMA (1998) postulated that farm management should aim at N profile in the fall that has a low risk of exceeding the present NO₃⁻ leaching limit during the wet season. Thus, the N application should match the crop demand on a spatial and on a temporal scale.

However, O₂ availability was not the key factor for the observed high N₂O production at low temperatures. When soil temperature is 15°C with constant soil water content, the O₂ content normally increases with decreasing temperature as a result of the decrease in microbial O₂ consumption (SMITH et al., 1998). This means that the developing O₂ conditions do not favour an increase in the total denitrification rate (sum of N₂O and N₂) when the temperature is 15°C. O₂ deficiency, and an associated increase in N₂O production, could occur at lower temperature in soils with high microbial activity. With good soil aeration (30 and 60% WFPS), Ramann-type soil samples of Keszthely and clay loam soil samples of Gödöllő revealed increase in N₂O production at a lower temperature, which could be associated with the higher respiration rate (O₂ consumption). High soil water content favours denitrification associated with the limitation of O₂ diffusion. Here, N₂O production was favoured by high soil water content in three out of the two soils. The increased N₂O release took place at a lower temperature with higher soil water content (lower O₂ diffusion rate) Gödöllő soil samples.

It is known that the ratio of N₂O-to-N₂ in denitrification increases with a decrease in temperature, and thus enhances N₂O production (KEENEY et al., 1979; MAAG & VINTHER, 1996). Presently, we do not have results to show the possible changes in the ratio of N₂O-to-N₂ in our soils. One possible explanation for the increase in the N₂O emissions lies in the temperature history of the soil during the experiment. In microcosm's studies, KOPONEN et al. (2004) found that stepwise decrease in soil temperature from 15°C induced an increase in the N₂O emissions close to the 0°C. These emissions peaked between -0.4 and 2.5°C depending on the soil type and water content. The results show that in addition to the well-documented thawing peak, soils also can have a maximum in their N₂O emission near 0°C when soil temperature decrease. The correlations between the N₂O and CO₂ emissions were weak. The results suggest that N₂O is produced in soils down to a temperature of -6°C.

The incubation of soil for 35 days at rather low and high temperatures (15 and 37°C), allows good conditions for growth of the microbial community. When the temperature in reaches at certain critical point, the populations probably started to decline and the decomposing cells released nutrients for the surviving microbes. This sudden increase in the

substrate availability could then account for increase in N₂O production. An interesting observation was that denitrifiers might benefit more from the extra substrates than the other heterotrophic microbes (CO₂ production) in general.

The high N₂O emissions during the incubation at low temperature of soils are well documented (SOMMERFIELD et al., 1993; RÖVER et al., 1998; TEEPE et al., 2000; PREMIÉ & CHRISTENSEN, 2001). However, the experiments on low temperature have not differentiated between the actual production and diffusion of N₂O at a particular temperature. When the incubation temperature of the soils microcosms was 37°C, the N₂O release increased. These emissions were much higher than the peaks in the N₂O release when the soil temperature was low. The key questions are, whether there was an extremely high production of N₂O just below 15°C, or was there liberation of the N₂O entrapped in the soils microcosms when the soil incubated at 37°C? Furthermore, the results from the gas sampling system in the soils show that there was an accumulation of N₂O in the soils at 37°C.

CONEN & SMITH (2000) predicted that N₂O concentration increases in the soil air immediately after closure of the chamber due to high gas concentrations in the upper part of the soil profile. CHRISTENSEN et al. (1996) compared 10 different closed, dynamic chambers and micro-meteorological methods and found a good agreement between results. However, they also reported that the magnitude of underestimation is 20% using small chambers.

DEBRECZENI et al. (2002) were conducted an experiment on the nitrogenous gas production in the rooting zone at two soil moisture levels, with or without the incorporation of maize crop residues into the soil, and with or without test plants. Gas traps were placed in the post at a soil depth of 20 cm. During the growing season, the trapped soil air was analysed for NO_x, N₂O and N₂. Practically the same N amounts evolved in the soil air with both chemical forms of N fertilizer at both soil moisture levels. Expressed as a percentage of fertilizer N, the total amount of gaseous N evolved averaged 12.8% and 12.9% in the planted, and 23.8% and 24.3% in the unplanted pots with KNO₃ and NH₄Cl fertilizer, respectively. Higher soil moisture and the incorporation of crop residues resulted in higher NO_x-N₂ and N₂O-N ratios within the total gaseous N evolved in the rooting zone. CHENG et al. (2004) determined the nitrification activities of soils by adding 200 mg N ((NH₄)₂SO₄) kg⁻¹ soil and incubating for 3 weeks at 25°C and 60% WFPS. The net nitrification rates obtained fitted one of two types of models, depending on the soil pH: a zero-order reaction model for acidic soils and one neutral soil; or a first-order reaction model for one neutral soil and alkaline soils. YANG et al. (2008) examined total denitrification losses using the acetylene inhibition technique and have not separated N₂O emissions from N₂ emissions. Additional studies would be required to separate out the influence of these treatments and soils on the speciation of denitrification gasses. During nitrification, N₂O can be formed by the oxidation of HNO or reduction of NO₂⁻ under low O₂ concentrations (GOREAU et al., 1980; POTH & FOCHT, 1985; FIRESTONE & DAVIDSON, 1989). NO is believed to also be formed from oxidation of HNO and reduction of NO₂⁻ during nitrification, although it may also be an intermediate between HNO and NO₂⁻ (FIRESTONE & DAVIDSON, 1989; CONRAD, 1996b).

5.2.3. CARBON-DIOXIDE EMISSIONS (CO₂)

In our experiments, the CO₂ production also showed a sudden increase just at 15°C, which might indicate the release of the accumulated CO₂. It has been suggested that low temperature inhibited the soil microbes and soil aggregates, increasing the availability of substrates for heterotrophic microbes including denitrifying bacteria (CHRISTENSEN & TIEDJE, 1990; CHRISTENSEN & CHRISTENSEN, 1991; SCHIMMEL & CLEIN, 1996; DENEFF et al., 2001). In fact, CO₂ production at 15°C was higher with Cd contaminated soil than that contaminated with Pb. However, there was no close association between N₂O and CO₂ production, indicating that the denitrifying bacteria had the capability to utilize any extra substrates released during soil temperature stress. The denitrifying bacteria might have increased their activity although the overall microbial communities did not increase their activity as assessed here by CO₂ production. Our results suggested that there was N₂O production in soils at 15°C. CAUSARANO et

al. (2008) mentioned that these results agree with a threshold value of 2 to distinguish historically degraded soils with improved soil conditions from degraded soils. This on-farm survey of SOC complements experimental data and shows that pastures and conservation tillage will lead to significant SOC sequestration throughout the region, resulting in improved soil quality and potential to mitigate CO₂ emissions.

5.3. HEAVY METAL INFLUENCE TRACE GASES EMISSIONS

The effect of heavy metals or soil moistures on NO production has not previously been measured in soil incubation experiments. However, because NO is produced by the same general pathways as N₂O, previous studies that investigated the effects of heavy metals on N₂O production, nitrification, and denitrification likely apply to NO production (Tu, 1994). As mentioned above, because Cd and Pb inhibited nitrification (Tu, 1994), the observed decrease in NO production *via* nitrification that resulted from heavy metal amendment was expected. Consequently, such heavy metals may be particularly effective at reducing NO emissions from soils, as most of the NO production appears to result from nitrification.

With increased concentration of heavy metal, the total production of NO decreased, and NO production from both nitrification and denitrification decreased. The fact that NO production by denitrification is inhibited by addition of Cd and Pb is contrary to previous research (Tu, 1994). However, as the concentration of Cd or Pb was increased, their inhibitory effect on NO production by nitrification was greater than that by denitrification. Compared to the fertilized control soils, the relative importance of nitrification to NO production decreased from approximately 84 to 52% and from approximately 83 to 43%, as Cd and Pb were added at the normal field application concentration. This is similar to the general trends also observed for N₂O production. Nitrification was the most significant source of NO production for the entire range of soil moistures tested. Cd inhibits NO production to a lesser degree than Pb. NO production is inhibited by Cd to a lesser amount than N₂O production. Nonetheless, nitrification still appears to be more sensitive to Cd than denitrification. With increasing amounts of Cd, inhibition of NO production *via* nitrification was proportionally greater than NO produced by denitrification.

The effect of the soil temperatures on N₂O and NO production by nitrification and denitrification at varying soil moistures and heavy metals concentrations was determined in microcosm's experiments. For the range of soil moistures (30 and 60% WFPS), nitrification was the most significant source of N₂O in the control and treated soil samples for Keszthely and Gödöllő soil sites. This is in agreement with previous studies at this field site (MOSIER & PARTON, 1985; PARTON et al., 1988a,b, 1996a,b). However, the rate of N₂O production from fertilized control incubations markedly increased as soil moisture increased from 30% to 60% WFPS. This suggests that denitrification, which will be favored under wetter conditions, is more proficient at producing N₂O in fertilized soils.

HOLTAN-HARTWIG et al. (2002) reported that the immediate effect (after 1 day of application) of heavy metals on denitrification. They found a general reduction of the denitrification rate, but also a decrease in N₂O reduction that was more pronounced than the decrease in N₂O production. Therefore, production of N₂O increased.

The production of N₂O was significantly negatively correlated to heavy metal content in soil incubated at 30% WFPS and 60% WFPS, i.e. production of N₂O decreased when concentrations of heavy metals in soil increased. Heavy metals affected both nitrification and denitrification. It has often been reported that nitrification is inhibited by heavy metals (INUBUSHI et al., 2000; HINOJOSA et al., 2004). As such, production of N₂O through nitrification will also be reduced (INUBUSHI et al., 2000). The different steps in the reduction of NO₃⁻ to N₂ in denitrification appear to differ in their heavy metal tolerance. The reduction of NO₂⁻ appears to be more sensitive than the reduction of NO₃⁻ (BOLLAG & BARABASZ, 1979; MCKENNEY & VRIESACKER, 1985); the same seems to be true for N₂O reductase (BOLLAG & BARABASZ, 1979).

The total inhibitory effects of the heavy metals on nitrification were greater than that on denitrification. There is also a change in N₂O production rates with changes in soil moisture. In particular, the N₂O production rate tends to increase as the soil moisture and denitrification potential increases. This suggests that denitrification can potentially result in greater N₂O production than nitrification, particularly at higher soil moisture. At moisture levels 30% WFPS denitrification will become more important for N₂O production than nitrification. Because the heavy metals tested here appeared to have a stronger effect on nitrification, they may have relatively less influence on N₂O production and emissions when applied to soils of higher moisture content or denitrification potential.

A similar trend was observed for denitrification, as NO and N₂O production by denitrification is not inhibited to the same degree. This suggests that various reduction steps in denitrification might be inhibited by heavy metal differently, thereby inhibiting NO and N₂O production by varying degrees (FIRESTONE & DAVIDSON, 1989; CONRAD, 1996b).

Independent of the amount of heavy metal added in this study a decrease in the rate of N₂O and NO and an increase in the rate of CO₂ production was measured as the soil moisture of the incubation was increased to more favorable conditions for denitrification. In general, larger fluxes of N₂O were observed at the field site with increasing temperature (KINNEY, 2004a,b), but this can be complicated when excessive desiccation occurs, which can subsequently inhibit N₂O production (STARK & FIRESTONE, 1995).

The influence of heavy metals on trace gas fluxes has not historically received little attention. The above description of agricultural practices that influence N₂O and NO fluxes helps assess the importance of the net effects that Cd and Pb can have on NO and N₂O production. Regardless of the soil moisture conditions of the incubations, total N₂O and NO production was substantially inhibited by addition of the heavy metals. It is common practice to add both of the heavy metals throughout the growing season and therefore this might lead to greater effects than observed here and in KINNEY et al. (2004a,b). Like soil type and weather, heavy metals use may also mask the effects of various other agricultural practices on soil trace gas fluxes (HÉNAULT et al., 1998). Due to a general lack of investigation of the effects that heavy metals have on soil trace gas fluxes, it may be difficult to ascertain how various individual agricultural practices affect the production and consumption of traces gas in soils.

No significant difference in production rates of CO₂ was observed between soil incubated at 50% WHC and 100% WHC. The addition of C₂H₂ had a small, but significant effect on the production of CO₂. Increasing the O₂ concentration in the headspace to 100% also increased the production rate of CO₂ because it aerated the anaerobic micro-sites (DENDOOVEN et al., 1996).

Our results showed that the CO₂ production rate was affected by heavy metals. These results were consistent with those of BROOKES et al. (1986a,b). They reported a decrease in CO₂-C evolution (ca. 30%) in presence of Cu, Ni, Zn and Cd. DAI et al. (2004) also found that the respiration rate was negatively correlated with Zn, Pb, Cu and Cd content. There are different explanations for this (GILLER et al., 1998). *First*, the decrease in CO₂ production rate might be due to a decrease in substrate availability as CO₂ production rate was significant positive correlated with SOC content. *Second*, microbial activity might have been inhibited by increases in heavy metal concentrations. The effects of other soil characteristics, such as pH (e.g. SAGGAR et al., 1999), CEC, soil structure (AMATO & LADD, 1992), sodicity (NELSON et al., 1996), clay content (e.g. VAN VEEN et al., 1985), and specific surface area of the clay and the nature of the clay mineral (SAGGAR et al., 1996) on the production of CO₂ could not be excluded, either.

The temporal changes of N₂O and CO₂ concentration demonstrated the impact of the coupled microbial processes resulting in these GHGs. The gas production depended on the soil moisture level, temperature and C/N ratio significantly. The inhibitory effect of toxic heavy metals (e.g. Cd) could also be affected by the C/N ratio. The appearance of NO as an intermediate of microbial processes was observed as well (KAMPFL et al., 2007). To some extent, our results showed an agreement with the above mentioned recent works when the

presented results illustrated that At moisture regime was 30% WFPS and incubated at 15°C, the rates of CO₂ emissions were increased by Pb contamination in the soil microcosms of both brown forest soil samples from Keszthely (Ramann-type) and Gödöllő (clay loam). But the rates were decreased by increasing the concentrations of Cd in Gödöllő soil samples and in Keszthely soil samples; the emissions were decreased at 24 mg Cd. While, when the soil moisture regime was at 60% WFPS and soil microcosms contaminated by Cd or Pb and incubated at 15°C, the amounts of CO₂ emitted from microcosms of Gödöllő soil samples were more than those amounts emitted from Keszthely soil samples. The rate of emission from microcosms of clay loam soil of Gödöllő was approximately the double amount emitted from microcosms of Ramann-type brown forest soil samples of Keszthely. The increases in the emission may be due to the increases in concentrations. Based on these results, it appeared that soil characteristics were the primary factor affecting spatial emission variability in the soil sites. However, some of the spatial emission variability remained explained by simple linear regression and other statistical analyses. The correlation between the effects and measured gas emission provided information about the strength of the soil parameter affecting the N transformation within these soil sites. Additionally an optimum uniform management and an optimum variable-rate management were developed and measured. For these strategies also the different soil conditions patterns were taken into account (soil pH, soil temperature, soil moisture, soil contamination with cadmium or lead). All results were evaluated based on the influences of soil conditions.

It can be concluded that incubation time is an important factor for metal recovery in soil, soil respiration is a detectable method for measurement the toxicity of the metal and it can be considered that this method might be an indicator of soil metal contamination, and the heavy metals have the important concern in microbial populations in the investigated soil samples.

It can be stated that the applied microcosm experimental model proved to be a suitable tool for detecting the effect of factors influencing the CO₂, N₂O and NO release from agricultural soil. This study underlines the key role of contamination of soil sample with different concentrations of two heavy metals (Cd and Pb) in emissions of NO, N₂O, and CO₂ from 60% WFPS soils under different incubation temperatures conditions. The management of soil contamination and the temperature are key considerations for mitigating trace gases emissions from these micro-agroecosystems. It is necessary to take into account the incubation temperature at 37°C increased the production rates of the NO, N₂O, and CO₂ more than at 15°C., Pb concentration over 40 mg kg⁻¹ soil caused a reduction in trace gas production. Cd had lower toxicity toward the nitrification or denitrification at all concentrations compared with Pb effects. Cd and Pb significantly reduced the rate of NO production especially at 15°C. At 37°C, the higher rates of NO, N₂O production found in Cd contaminated soil at all tested concentrations.

These results were published in:

ALGAIDI et al. (2005): Effect of temperature and different C/N ratios on gas emissions (N₂O, NO and CO₂) from brown forest soil. "Agriculture in Central Europe Potentials and Risks" 47th Georgikon Scientific Conference and 15th ÖGA Annual Meeting, 2005. szeptember 29–30., Keszthely. CD-R adathordozón sokszorosítva, made by ///VTCD Gn20050929.

ISBN 963 9639 03

6.

ALGAIDI et al. (2005): Gas emission in brown forest soil in relation to C:N applied rate and soil temperature. In: Az MTA Szabolcs-Szatmár-Bereg Megyei Tudományos Testületének XIV. évi Közgyűléssel egybekötött Tudományos Ülésének Előadásai I. rész. 2005. szeptember 30.–október 01. Nyíregyháza. P. Nagy (Ed.). CD-R kiadvány a KÁLL-TRADE Kft, Nyíregyháza. pp: 9-15. ISBN-13:978-963-8048-32-5.

ALGAIDI et al. (2006): Predicting N₂O and CO₂ emission from agricultural soil amended with different C:N ratios. Proc. VI. Nat. Sci. Conf. Internat. Participation "Ecology & Health 2006" 18th May 2006. Plovdiv, Bulgaria. pp: 268-272.

KAMPFL GY.; KRISTÓF K.; ALGAIDI A.A.; BAYOUMI HAMUDA H.E.A.F.; HELTAI GY. (2007): Study of NO_x and CO₂ production of cultivated soil in closed microcosm experimental system. *Microchemical Journal*, 85: 31-38. IF: 1.806

ALGAIDI et al. (2008): A hőmérséklet hatása nehézfémekkel szennyezett talajok gázkibocsátására. *Agrokémia és Talajtan*, **57**: 147-160.

Further research is required to investigate how the large heavy metal concentrations might affect plant characteristics. The inhibitor/suppression technique used was confirmed to be flawed as negative values for nitrifier denitrification were obtained. Our study showed that the main factors that regulate the NO emissions in our studied soils are pH and WFPS. Our results can be used to improve current estimates of NO and N₂O emissions from the investigated ecosystems where information is limited.

Incorporation of heavy metals reduced NO, N₂O and CO₂ emissions (in some cases). This reduction was quantitatively dependent on heavy metal concentration, lower concentrations of heavy metals inducing higher emission rates than higher heavy metal concentrations. A further conclusion is that the trace gases emissions in soils amended with heavy metal is not a constant but dependent on other environmental factors such as soil conditions, moisture, temperature, etc.

6. SUMMARY

The present study titled “Predicting NO, N₂O and CO₂ emission from agricultural soil through related environmental parameters”. The background for the investigation could be seen in the increasing number of environmental pollution by agricultural land use. The dissertation was embedded in the context of the Framework of the Research Programme “Strategies to Reduce the Emission of Greenhouse Gases and Environmental Toxic Agents from Agriculture and Land Use” in the Department of Chemistry and Biochemistry, Institute of Environmental Science, Faculty of Agricultural and Environmental Science at the Szent István University, Gödöllő, Hungary. The present study is summarized in the followings:

A. Effect of heavy metals on the quantity of soil aerobic bacteria and soil respiration under *in vitro* conditions:

The effect of Pb, Co and Cd ions on the activity of aerobic soil heterotrophic bacteria was studied in cultivated and uncultivated soil samples of clay loam brown forest originating from Gödöllő. Soil samples each of were 500 g with 40% WFPS were activated by substrate-induced respiration (SIR) and contaminated by different concentrations of the investigated heavy metals. The soil samples of heavy metals free contaminations were investigated as main control for the run experiment. The soil samples were filled into glass vessels of 1500 cm³ containing small beaker filled with NaOH to trap the CO₂ release from soil. The glass vessels containing treated soil samples were incubated in the greenhouse at 28°C for one, three or six weeks. The metabolism of soil-borne aerobic heterotrophic bacteria was activated by adding C, N and P in the form of glucose, sodium nitrate and potassium phosphate, respectively, prior to the determination of SIR. Measurements were made on changes in the total mobilizable heavy metal fraction, the total aerobic heterotrophic bacterial count and the quantity of CO₂ produced during the incubation periods. The heavy metal compounds examined became immobilized largely within a week, but after further incubation, they gradually became re-mobilized. The results indicated that the addition of heavy metal ions reduced the total aerobic bacterial count and the physiological activity of the bacteria in the soil. In general, the aerobic bacterial populations declined to a similar extent as the CO₂ production in response to the toxic effect of the tested metal ions. The inhibition in the biological activity of the soil samples could already be observed at 3rd week, but this effect only became substantial at the end of the 6th week incubation period. Pb²⁺ reduced the CO₂ emission from both cultivated and uncultivated soils in various phases of incubation to the lowest extent. Gas emission was inhibited to the greatest extent by the Cd²⁺ ions, but a considerable decline could also be observed in the presence of Co²⁺ ions. The results of this experiment can summarize as:

1. The recoveries of the amounts of Pb, Cd and Co were significantly higher at the 6th week of the incubation intervals than at 1st and 3rd incubation week. Linear regression and

correlation indicated no significant differences between the metal recoveries in the uncultivated and wheat cultivated brown forest soil samples originated from Gödöllő.

2. The CO₂-released from uncultivated soil samples was more than CO₂-released from cultivated soils. Soil samples treated with SIR activated the biological processes in both soil samples. It was recognized that Cd was more inhibiting metal than Co and Pb in investigated soil samples. The amounts of CO₂-released were reduced by increasing the concentrations of heavy metals.

3. Cd was more toxic metal and causes a decrease in the population density of aerobic bacterial structure in both soil samples followed by Pb and Co. The inhibition of population density of aerobic bacterial structure was increased by increasing the incubation periods. The toxicity decreasing order of the tested metals was Cd > Co > Pb.

These results were published in:

ALGAIDI et al. (2005): Effect of heavy metals in soil microbial processes and population. *Magazine of Sebha University*. Sebha, Libya. **12**: 1-6.

ALGAIDI et al. (2006): Impact of lead, cadmium, and cobalt on soil respiration and microbial content under in vitro conditions. Proc. **VII**. Intern. Ph.D. Students Conference. RNDr. M. Slábová, Ing. Z. Sýkorová (Eds.). 4th April 2006. University of South Bohemia, Faculty of Agriculture, České Budějovice, Czech Republic. pp.: 7-16. ISBN 80-7040-847-2.

ALGAIDI et al. (2007): A szennyező nehézfémek hatása a talajbaktériumok mennyiségére, és a talajlégzésre *in vitro* körülmények között. *Agrokémia és Talajtan*, **56**: 353-366.

B. Impact of incubation temperature, moisture regime on the trace gases emission from heavy metals contaminated soils

Trace gases are produced in soil primarily by microbial processes. Soil temperature and moisture regime are the key factors controlling both decomposition and denitrification. Their production and emission from the soil are controlled by a number of environmental variables, including inorganic N availability, WFPS, soil temperature and soil contamination. Agricultural management practices, such as fertilization and irrigation, affect these environmental variables and thus have the potential to dramatically alter NO, N₂O and CO₂ emissions from the soil. Current models incorporate some of these variables, such as WFPS, heavy metal contamination and soil temperature as well as the soil types. The trace gases emission losses from two different soil types: 1) Ramann-type brown forest soil originated from Keszthely and 2) clay loam brown forest soil originated from Gödöllő contaminated with various concentrations of Cd and Pb at 30 and 60% WFPS were studied in a static closed microcosm model experiment at two incubation temperatures (15 and 37°C) for 35 days. The trapped soil air was analysed for N₂O and CO₂ by gas chromatography and for NO was measured using chemiluminescent method.

Independent soil microcosm experiments were used to investigate the effects of the different concentrations heavy metals Cd and Pb, under different soil conditions (soil pH, soil moisture, soil temperature), on N₂O, NO and CO₂ production by nitrifying and denitrifying bacteria in different soil sites. Soil sub-samples were amended with different concentrations of Cd or Pb, and the N₂O, NO and CO₂ concentrations were monitored periodically during approximately 35 days following amendment. Nitrification is the major source of N₂O and NO in these soils at soil moistures relevant to those observed at the field site where the soil samples were collected. At Cd concentrations from 6 mg kg⁻¹ soil to 24 mg kg⁻¹ soil and Pb concentrations from 40 mg kg⁻¹ soil to 160 mg kg⁻¹ soil, N₂O and NO production was inhibited by all concentrations of heavy metals. Generally N₂O production was inhibited by the heavy metal from 10 to 62% and 20 to 98% at the lowest and highest dosages, respectively. NO production was generally inhibited from about 5 to 47% and by 20 to 97% at the lowest and highest dosages, respectively. N₂O and NO production by nitrification were more susceptible to inhibition by these heavy metals than denitrification. Production of both N₂O and NO by

nitrification was inhibited by as much as 99%, at the highest concentration of heavy metal applied.

The results of this experiment can summarize as:

A. Emission of nitric oxide:

1. **At 30% WFPS, and when the soil microcosms incubated at 15°C:** The NO emission in Gödöllő soil samples was approximately 2 times more than the amounts emitted from Ramann-type brown forest soil samples of Keszthely when contaminated by Cd at different concentrations. NO emission rates were decreased by increasing the concentration and the time of incubation. But when Pb contaminated soil samples incubated in microcosms at 15°C, the detected NO emissions were higher in Ramann-type of Keszthely microcosms than those emitted from clay loam brown forest soil of Gödöllő soil samples. The amounts of NO were influenced by the metal contaminated doses and time of incubation. The results showed that when the soil microcosms incubated at 15°C, NO emission from Ramann-type soil microcosms was more inhibited by Cd than by Pb. But Pb more inhibited the NO emission than Cd in clay loam soil microcosms.

2. **At 60% WFPS, and when the soil microcosms incubated at 15°C:** When soil samples contaminated by Cd and incubated at 15°C, the NO emissions from Ramann-type were less than the NO emitted from clay loam soil samples. Clay loam brown forest soil samples were more sensitive to the highest concentration (24 mg Cd).

Pb concentrations were more inhibiting the NO emission in clay loam brown forest soil originated from Gödöllő than from Ramann-type brown forest soil type collected from Keszthely. Also, the NO emission rates from Keszthely and Gödöllő were more inhibited by Pb than Cd.

3. **When Ramann-type soil microcosms of 60% WFPS incubated at 37°C:** The amounts of NO detected from microcosms of soil contaminated by Pb is smaller than those detected when the soil contaminated by Cd.

4. It was found that when the soil samples had 60% WFPS and incubated at 15°C, the amounts of NO detected were the lowest when compared with the soil samples incubated at 37°C or had 30% WFPS and incubated at 15°C.

B. Emission of nitrous oxide:

1. At 60% WFPS, it was found that N₂O emission rates were more inhibited by highest concentrations of Cd than of Pb, when the soil samples incubated at 15°C. The amounts of N₂O emitted from Ramann-type from Keszthely soil samples were more sensitive to Cd than the amounts of N₂O emitted from clay loam soil samples from Gödöllő. The amounts of N₂O emitted from Keszthely soil samples were less than the amounts of N₂O emitted from Gödöllő when the soil samples contaminated by Pb.

2. In Ramann-type brown forest soil of Keszthely, N₂O emission rates were more inhibited by Pb than Cd when the soil microcosms contain 60% WFPS moisture regime and incubated at 37°C.

C. Emission of carbon dioxide:

1. When the two brown forest soil samples of Ramann-type and clay loam contained 30% WFPS, contaminated by different concentrations of Cd and Pb and incubated at 15°C, the detected amounts of CO₂ were lower in Keszthely Ramann-type soil samples than those amounts of CO₂ emitted from microcosms of clay loam of Gödöllő.

2. The amount of CO₂ emitted was less in Cd contaminated soil samples than those contaminated by Pb from Ramann-type and clay loam soil originated from Keszthely and Gödöllő, respectively, at moisture regime 30% WFPS and incubation temperature 15°C.

3. At moisture regime was 30% WFPS and incubated at 15°C, the rates of CO₂ emissions were increased by Pb contamination in the soil microcosms of both soils from Keszthely and Gödöllő. But the rates were decreased by increasing the concentrations of Cd in Gödöllő soil samples and in Keszthely soil samples; the emissions were decreased at 24 mg Cd.

4. When the soil moisture regime was at 60% WFPS and soil microcosms contaminated by Cd or Pb and incubated at 15°C, the amounts of CO₂ emitted from microcosms of clay loam soil of Gödöllő were more than those amounts emitted from Ramann-type soil of Keszthely. The rate of emission from clay loam soil microcosms was approximately the double amount emitted from Ramann-type soil. The increases in the emission may be due to the increases in concentrations.

5. Emission rates of CO₂ from Ramann-type soil with 60% WFPS contaminated by Cd and incubated at the 37°C were higher than those emitted from microcosms of Pb contaminated soil.

Based on these results, it appeared that soil characteristics were the primary factor affecting spatial emission variability in the soil sites. However, some of the spatial emission variability remained explained by simple linear regression and other statistical analyses. The correlation between the effects and measured gas emission provided information about the strength of the soil parameter affecting the N transformation within these soil sites.

Additionally an optimum uniform management and an optimum variable rate management were developed and measured. For these strategies also the different soil conditions patterns were taken into account (Soil type, soil pH, soil temperature, soil moisture regime, soil contamination with cadmium or lead). All results were evaluated based on the influences of soil conditions.

It was obvious, that variable rates of trace gases emissions were most advantageous compared to the control, especially, when the emission rates were differentiated for low and high moisture conditions. Adapted gas emission strategies, as variable rate management indicated a potential to reduce the amount of N, which is left in the soil after harvest. In a case study the denitrification under these soil conditions over the incubation time was reduced. The results indicated a reduction of cumulative denitrification under adapted ecological factors.

These results were published in:

ALGAIDI et al. (2005): Effect of temperature and different C/N ratios on gas emissions (N₂O, NO and CO₂) from brown forest soil. "Agriculture in Central Europe Potentials and Risks" 47th Georgikon Scientific Conference and 15th ÖGA Annual Meeting, 2005. szeptember 29–30., Keszthely. CD-R adathordozón sokszorosítva, made by //VTCD Gn20050929.

ISBN 963 9639 03

6.

ALGAIDI et al. (2005): Gas emission in brown forest soil in relation to C:N applied rate and soil temperature. In: Az MTA Szabolcs-Szatmár-Bereg Megyei Tudományos Testületének XIV. évi Közgyűléssel egybekötött Tudományos Ülésének Előadásai I. rész. 2005. szeptember 30.–október 01. Nyíregyháza. P. Nagy (Ed.). CD-R kiadvány a KÁLL-TRADE Kft, Nyíregyháza. pp: 9-15. ISBN-13:978-963-8048-32-5.

ALGAIDI et al. (2006): Predicting N₂O and CO₂ emission from agricultural soil amended with different C:N ratios. Proc. VI. Nat. Sci. Conf. Internat. Participation "Ecology & Health 2006" 18th May 2006. Plovdiv, Bulgaria. pp: 268-272.

KAMPFL GY.; KRISTÓF K.; ALGAIDI A.A.; BAYOUMI HAMUDA H.E.A.F.; HELTAI GY. (2007): Study of NO_x and CO₂ production of cultivated soil in closed microcosm experimental system. *Microchemical Journal*, **85**: 31-38. IF: 1.806

ALGAIDI et al. (2008): A hőmérséklet hatása nehézfémekkel szennyezett talajok gázkibocsátására. *Agrokémia és Talajtan*, **57**: 147-160.

Keywords: NO, N₂O and CO₂ emission; denitrification, nitrification; heavy metals, soil type; incubation temperature, moisture regime, soil respiration, aerobic heterotrophic bacterial population, bioavailability of heavy metals

7. ÖSSZEFOGLALÁS

Disszertációm címe: „Az NO, N₂O és CO₂ emisszió előrejelzése mezőgazdasági talajokból a környezeti paraméterek függvényében”. A munkám kapcsolódott a Szent István Egyetem Kémia és Biokémia Tanszékén folyó OTKA kutatási programokhoz, amelyeknek keretében az üvegházhatású gázok (CO₂, N₂O, NO) kibocsátását befolyásoló agroökológiai tényezők hatásait mérik fel. Ennek keretében kísérleteim célkitűzését két fő pontban fogalmaztam meg:

1. A nehézfémek (Cd, Co, Pb) hatásának felmérése a vizsgált talajok légzésére és baktérium populációjára.
2. Mikrokozmosz kísérletekben tanulmányozni a nehézfémek, a talajtulajdonságok, a nedvesség, a hőmérséklet hatását az üvegházhatású gázok (NO, N₂O és CO₂) kibocsátásának mértékére.

Disszertációm második fejezetében részletesen irodalmi áttekintést adtam az üvegházhatású gázok (NO, N₂O és CO₂) kibocsátását befolyásoló hatásokról a nitrogén biogekémiai ciklusaiban.

Az első célkitűzésnek megfelelő kísérleteimben nehézfémekkel kezelt talajokban vizsgáltam az alkalmazott nehézfémek (Cd, Co, Pb) mobilizálható frakciójának változását, továbbá az aerob heterotróf baktériumok mennyiségére, aktivitására gyakorolt nehézfém-hatást, ill. mértem a talajlégzést (CO₂ kibocsátást), mint a talaj szennyezettségének bioindikátorát. Ehhez ólom- (Pb²⁺), a kobalt- (Co²⁺) és a kadmium- (Cd²⁺) ionok különböző koncentrációjú vizes oldatait használtam. A nehézfémeket háromféle dózisban alkalmaztam: Cd (1,5, 3 és 6 mg/kg) CdCl₂ formában, Co (4, 8 és 16 mg/kg) CoCl₂ formában és Pb (40, 80 és 160 mg/kg) PbCl₂ formában. A talajminták Gödöllőről származó, mezőgazdasági művelés alatt álló (továbbiakban: művelt) és nem művelt barna erdőtalajok voltak. Az üvegedényekbe töltött talajmintákat üvegházban, 28°C-on inkubáltuk egy, három és hat hétig. A talajban élő baktériumok anyagcseréjét C, N és P hozzáadásával aktiváltuk, a tápanyagokat nátrium-nitrát, kálium-foszfát és glükóz formájában adtuk a talajhoz a szubsztrát-indukált légzés vizsgálatára (SIR: substrate induced respiration). Meghatároztam az összes mobilizálható nehézfém frakció, az összes aerob baktérium csíraszám és a fejlődött CO₂ mennyiségének változását az inkubációs idő alatt. Megállapítottam, hogy a vizsgált nehézfémek vegyületei egy héten belül nagymértékben immobilizálódtak, majd további inkubáció után fokozatosan újramobilizálódtak. A nehézfémionok adagolása csökkentette a talaj teljes aerob baktérium számát, valamint fiziológiai aktivitását. Az aerob baktérium-populációk általában a CO₂—termeléshez hasonlóan csökkentek a vizsgált fémionok toxikus hatására. A talajminták biológiai aktivitásában bekövetkezett gátlások már három hét után is érvényesültek, de igazán jelentős hatásokat a 6 hetes inkubációs periódus végén tapasztaltam. A különböző inkubációs szakaszokban az Pb²⁺ csökkentette a legkisebb mértékben a művelt és a nem művelt talajok CO₂-kibocsátását. A gázkibocsátást a Cd²⁺—ionok gátolták a leginkább, de Co²⁺—ionok jelenlétében is érzékelhető volt határozott csökkenés.

Második célkitűzésemnek megfelelő kísérleteimben kadmiummal (Cd) és ólommal (Pb) szennyezett Keszthely környékéről származó barna erdőtalaj és gödöllői barna erdőtalaj gázkibocsátását (NO, N₂O, CO₂) vizsgáltam gázkromatográfias és kemilumineszcenciás módszerrel zárt rendszerű, különböző hőmérsékleten (15 és 37°C), 35 napig inkubált kísérleti modellben. A mikrokozmosz rendszerű kísérletet hermetikusan, szilikon szeptummal lezárt, 1200 cm³ térfogatú üveg edényekben végeztük, amelyekbe 200 g jól homogenizált (2 mm-nél kisebb szemcseméretű), kis humusztartalmú talajmintát helyeztünk. A talajmintákat különböző mértékben szennyeztük a következő vegyületekkel: Pb(CH³COO)₂ · 3H₂O 40, 80 és 160 mg Pb kg⁻¹ talaj, illetve CdCl₂ · 2,5H₂O 0, 12 és 24 mg Cd kg⁻¹ talaj koncentrációban. Azt tapasztaltam, hogy a harmadik napon a kemilumineszcenciás detektorral mért NO-kibocsátás fokozatosan csökkent az alacsonyabb hőmérsékleten, és a 8. napon már nem volt mérhető a NO mennyisége. A 37°C-on inkubált, kadmiummal szennyezett talaj N₂O—kibocsátása napról napra emelkedett a kísérlet első hetében, majd

fokozatosan csökkenni kezdett. A CO₂–kibocsátás mértéke nem változott a kísérlet 15. napjáig, utána viszont csökkenő tendenciát mutatott. Megállapítottuk, hogy a Cd–szennyezett talajminták gázkibocsátása nagyobb volt, mint a mikrobákra toxikusabb Pb-szennyezett mintáké. A magasabb hőmérsékleten a talajminták gázkibocsátása meghaladta az alacsonyabb hőmérsékleten kapott gázkibocsátási értékeket.

Általánosságban elmondható, hogy a talajminták helyspecifikus jellemzői és a hőmérséklet volt a legfontosabb meghatározó tényező a gázkibocsátás mértékére. Az összes kísérletben az találtam, hogy a denitrifikálás volt a legfőbb oka a gázkibocsátásnak, mivel a vízzel kitöltött talajhézag tartalom (WFPS) 60%-os volt a legtöbb esetben, ami anaerob körülményeket teremtett, és ez elősegítette a mikrobák számára a NO-gáz újrafelhasználását. A kísérlet kezdeti szakaszában mind a CO₂ és az N₂O kibocsátás emelkedett, mivel a talaj mikrobiológiai tevékenysége és a talaj szervesanyag mineralizációja is fokozódott a talajminták szárítása és az újra nedvesítés következtében.

Kulcsszavak: nehézfémek hatása, talajbaktériumok mennyisége, talajlégzés, NO–, N₂O–, és CO₂ –emisszió, mikrokozmosz, hőmérséklet, talajnedvesség, talajszennyezettség.

8. NEW SCIENTIFIC RESULTS

The highlight of the most important results recognized from the present study can summarize as:

1. Heavy metal contamination strongly influences the respiration and aerobic bacterial community in agricultural soil. The recoveries and bioavailability of contaminant amounts of Pb, Cd and Co were significantly higher at the 6th week of the incubation intervals than at 1st and 3rd incubation week. Linear regression and correlation indicated no significant differences between the metal recoveries in the uncultivated and wheat cultivated clay loam brown forest soil samples originated from Gödöllő. Also, the CO₂-released was more from uncultivated than cultivated soil samples. Cd was more toxic metal and causes a decrease in the bacterial population density in both soil samples followed by Pb and Co. The toxicity decreasing order of the tested metals was Cd > Co > Pb.
2. The microcosm's experimental model proved to be a suitable tool for detecting the effect of factors (moisture, temperature and heavy metal) influencing the CO₂, N₂O and NO release from two agricultural soil types (1. Ramann-type brown forest soil originated from Keszthely, and 2. clay loam brown forest soil originated from Gödöllő). Based on these results, it appeared that soil characteristics are the primary factors affecting spatial emission variability in the soil sites. In my experiments in this sense the following result were achieved:
 - 2.1. When the microcosms of Keszthely (pH = 7.55) and Gödöllő (pH = 5.56) soil samples of moisture regime 30% WFPS, contaminated with various contamination doses of Cd and Pb and incubated at 15°C, NO emission from Keszthely soil was more inhibited by Cd than by Pb. While Pb more inhibited the NO emission than Cd in Gödöllő soil microcosms. Moreover, at soil moisture 60% WFPS, and incubated at 15°C the NO emissions from Keszthely microcosms were less than the emission from Gödöllő soil. When Keszthely soil microcosms of 60% WFPS incubated at 37°C, the amounts of NO detected from microcosms of soil contaminated by Pb is smaller than those detected when the soil contaminated by Cd.
 - 2.2. The amounts of N₂O emitted from Keszthely soil microcosms were less than the amounts of N₂O emitted from Gödöllő microcosms when the soil samples had moisture regime of 60% WFPS, contaminated by Pb and incubated at 15°C. In Keszthely soil microcosms. N₂O emission rates were more inhibited by Pb than Cd when the microcosms incubated at 37°C.
 - 2.3. At moisture regime was 30% WFPS and incubated at 15°C, the rates of CO₂ emissions were increased by Pb contamination in the soil microcosms of both soils, and the emission rates were decreased by increasing the concentrations of Cd in Gödöllő and Keszthely microcosms. When the soil moisture regime was at 60% WFPS and soil

microcosms contaminated by Cd or Pb and incubated at 15°C, the amounts of CO₂ emitted from microcosms of Gödöllő were more than the detected amounts emitted from the microcosms of Keszthely.

- 2.4. The emission rates from clay loam of Gödöllő microcosms were approximately the double amount emitted from Ramann-type of Keszthely soil. The increases in the emission may be due to the increases in concentrations. In Keszthely soil of 60% WFPS contaminated by Cd and Pb and incubated at the emission rates of 37°C, the amounts of CO₂ emitted from Cd contaminated soil in the microcosms were higher than those amounts of CO₂ emitted from microcosms of Pb contaminated soil of Keszthely, too.

9. PROPOSALS

1. The common management practices

Several options for the mitigation of trace gases emissions have been suggested in a recent review. These options are aimed at increasing the efficiency of N fertilizer use and on reducing the amount of N cycling through an agricultural system. For example, the primary consideration for mitigating N₂O emissions from soils is to match the supply of mineral N (from fertilizer and manure applications, legume-fixed N) to the spatial and temporal needs of the pasture plants. Although it is possible to achieve uniform application of N fertilizers, it is difficult to control the uneven excretal distribution in the pastures that are grazed throughout the year. The common management practices include optimum N supply to pasture crops, proper animal residue management, and use of controlled release fertilizers, NIs, and proper water management. Strategies and best management practices for mitigation of gaseous N emission include:

- Improvement of overall N-use efficiency
- Manipulation of N economy of the animal to reduce N excretion
- Lower N content of pastures – supplementary feed
- Winter management – stand-off pads
- Strategic application of farm effluents
- Use of controlled-release N-transformation inhibitors
- Reduction of livestock numbers

2. Options for Reducing the Environmental Effects of N in Agriculture

After addition of N to farms as animal excreta, fertilizer, crop residues or biological fixation, it can be lost by gaseous emissions to the atmosphere as NH₃, N₂O and other NO_x, by runoff or leaching of NO₃, and by soil erosion. The predominant loss process and the amounts lost are influenced by the ecosystem, soil characteristics, farming practice, fertilizer techniques, and prevailing weather conditions. The lost N can acidify soils and water bodies, deplete stratospheric O₃, change climate, produce blooms of toxic algae, eutrophic coastal ecosystems, and produce respiratory and cardiac disease in humans. Many approaches have been suggested for increasing the efficiency of N fertilizer and reducing losses, including optimal use of fertilizer form, rate and method of application, matching supply with crop demand, optimizing split application schemes, supplying fertilizer in the irrigation water, applying fertilizer to the plant rather than the soil, changing the fertilizer type to suit the conditions, and use of slow-release fertilizers and nitrification inhibitors. In addition, agronomic practices such as higher plant densities, weed and pest control and balanced fertilization with other nutrients can increase efficiency of N use and result in reduced loss of N. If the options proposed for reducing emissions from fertilizer use were implemented, they would not only reduce impacts on the environment, but they would increase farm's income.

3. N₂O Emission Reducing Management Techniques

In order to reduce N₂O emissions from crop production activities, it is important to focus on managerial techniques. Managerial techniques that affect N₂O emissions include tillage technology, tillage techniques and tillage timing, crop rotations, method and timing of fertilizer application, and type of N applied. Fertilizer applied in the fall is subject to spring thaw environmental conditions. Fertilizer applied after the spring thaw will not be subject to the spring thaw environmental conditions there by generally reducing N₂O emissions from fertilizer N

(NYBORG et al. 1997). MOSIER et al. (1996) suggested the management practices that optimize the crop's ability to uptake N as it becomes available will reduce N₂O emissions from mineral and organic N. N use efficiency (NUE) examines a crop's N uptake, relative to the amount of N applied. Strategies that increase NUE can also reduce N losses. GAUER et al. (1992) found that NUE is generally the greatest with low levels of applied N and decreases as the amount of N applied increases. Improved moisture conditions increase NUE through increased yield potential and improvement of N mobility in the soil. MOSIER et al. (1996) and BEAUCHAMP (1997) gave the following practical strategies to mitigate N₂O emission from agricultural soils:

- 11) Match N supply with crop demand
- 0a) Use soil/plant testing to determine fertilizer N needs
- 1b) Minimize fallow periods to limit mineral nitrate accumulation
- 2c) Optimized split application schemes
- 3d) Match N application to reduced production goals in regions of crop over production
- 22) Close N flow cycles
- 0a) Integrate animal and crop production systems in terms of manure reuse and plant production
- 1b) Maintain plant residue N on the production site
- 33) Use advanced fertilization techniques
- 0a) Controlled release fertilizers
- 1b) Place fertilizers below the soil surface
- 2c) Foliar application of fertilizers
- 3d) Use nitrification inhibitors
- 4e) Match fertilizer amount and type to seasonal precipitation
- 44) Optimize tillage, irrigation and drainage

4. Strategies and best management practices for mitigation of gaseous N emission include:

1. Improvement of overall N-use efficiency.
2. Manipulation of N economy of the animal to reduce N excretion.
3. Lower N content of pastures – supplementary feed.
4. Winter management – stand-off pads.
5. Strategic application of farm effluents.
6. Use of controlled-release N-transformation inhibitors.
7. Reduction of livestock numbers.

5. The ideal inhibitor for use in agriculture should:

The general theory behind the use of these inhibitors is that they slow down N turnover by slowing the oxidation of N to NO₃⁻, causing N to stay in the form of NH₄⁺. However, the NI does not inhibit nitrification indefinitely. Therefore, a quantitative understanding of interrelations between N₂O and NH₃ emissions, and NO₃⁻ and NH₄⁺ leaching, is central both to understanding how pasture systems behave and respond to inhibitors, and to determining the effectiveness of land management strategies to reduce overall N losses. Mitigation strategies neglecting these interrelations may be sub-optimal. The value of inhibitors in mitigating N₂O emissions also depends on their rate of degradation and persistence in soils, but key soil and environmental factors influencing NIs are poorly understood.

The ideal inhibitor for use in agriculture should:

1. Specifically block an enzymatic reaction (e.g., NI should block NH₄⁺ oxidation to NO₂⁻, but not NO₂⁻ oxidation to NO₃⁻, during the nitrification process).
2. Remain in close contact with N compounds (UIs must move with urea molecules which are not readily adsorbed by soil, whereas NI must be close to NH₄⁺ ions which are readily retained by soil).
3. Not adversely affect other beneficial soil organisms and higher plants.
4. Remain effective in soil for several weeks after N input through fertilizer addition and excretal deposition.
5. Not be toxic to animals and humans in the amounts used to effectively inhibit nitrification.
6. Be cost effective to use.

6. The key questions regarding the NIs that need future attention are:

Furthermore, there is little information on the long-term impact these inhibitors could have in altering the N cycle of agricultural systems, and on the issues of toxicity. **The key questions regarding the NIs that need future attention are:**

- What processes regulate the efficacy of NIs at site/point application scales, and what conclusions can be drawn about their likely short-, medium- and long-term effectiveness and required application rates/frequencies?
- What impacts do NIs have on medium- to long-term N storage and indirect N₂O emissions, and are there any deleterious implications for soil CO₂ gas exchange?
- Can present measurement techniques quantitatively demonstrate emissions reductions due to application of NIs at paddock/herd scales, and to what level of precision? Is there evidence of bias in the assessment of effectiveness between measurement approaches?
- What level of emissions reduction is achieved with inhibitors through time, as a function of changes in animal excretal inputs and climate?
- What are the requirements for long-term monitoring/demonstration of mitigation effectiveness, and what is the cost/precision trade-offs for monitoring instrumentation?

10. The Scientific Publications related to the Dissertation Work (2004-2008)

1. LEKTORÁLT FOLYÓIRATOKBAN MEGJELENT KÖZLEMÉNYEK:

1.1. Idegyen nyelv:

1. Kampfl Gy. - Kristóf K. - **Algaidi A.A.** - Bayoumi Hamuda H.E.A.F. - Heltai Gy. (2007): Study of NO_x and CO₂ production of cultivated soil in closed microcosm experimental system. *Microchemical Journal*, **85**: 31-38. IF: 1.806
2. Kristóf Krisztina - Kampfl Györgyi - Heltai György - Nótás Erika - **Algaidi Ahmed Abdousalam** (2007): Examination of NO_x and CO₂ production in agricultural soils. *Cereal Research Communications*, **35**: 689-692. IF: 1.027

1.2. Magyar nyelv:

3. **Algaidi A.A.** - Bayoumi Hamuda H.E.A.F. - Nótás E. - Kristóf K. - Kampfl Gy. - Hamid Y.S. - Heltai Gy. (2007): A szennyező nehézfémek hatása a talajbaktériumok mennyiségére, és a talajlégzésre *in vitro* körülmények között. *Agrokémia és Talajtan*, **56**: 353-366.
4. **Algaidi A.** Abdousalam - Bayoumi Hamuda H.E.A.F. - Horváth Márk - Nótás Erika - Heltai György (2008): A hőmérséklet hatása nehézfémekkel szennyezett talajok gáz kibocsátására. *Agrokémia és Talajtan*, **57**: 147-160.

2. IDEGYEN NYELV: HAZAI EGYETEMI BULLETINBEN MEGJELENT KÖZLEMÉNYEK:

5. **Algaidi A.A.** - Bayoumi Hamuda H.E.A.F. - Nótás Erika - Kristóf K. - Kampfl Gy. - Heltai Gy. (2005): Effect of some heavy metals on soil microbial biomass. *Scientific Bulletin of Szent István University*, Gödöllő, Hungary. pp: 97-105.
6. Kristóf K. - Kampfl Gy. - **Algaidi A.A.** - Bálint Á. - Bakony G. - Heltai Gy. (2005): Study of several factors of influencing the N₂O and CO₂ release of cultivated soil in microcosm experiments. *Scientific Bulletin of Szent István University*, Gödöllő, Hungary. pp: 133-146.
7. Hamid Y.S. - Füleky Gy. - **Algaidi A.A.** - Bayoumi Hamuda H.E.A.F. - Issa Ibrahim A. (2008): Rapid determination of CaCO₃ dissolution in soil horizons. *Scientific Bulletin of Szent István University*, Gödöllő, Hungary. pp: 81-92.

3. KÜLFÖLDI EGYETEMI BULLETINBEN MEGJELENT KÖZLEMÉNYEK:

8. **Algaidi A.A.** - Bayoumi Hamuda H.E.A.F. - Nótás Erika - Kristóf K. - Kampfl Gy. - Issa Ibrahim A. - Hamid Y.S. - Heltai Gy. (2005): Effect of heavy metals in soil microbial processes and population. *Magazine of Sebha University*. Sebha, Libya. **12**: 1-6.

4. HAZAI TUDOMÁNYOS RENDEZVÉNYEKEN MEGJELENT KÖZLEMÉNYEK:

4.1. Idegyen nyelv:

9. **Algaidi A.A.** - Bayoumi Hamuda H.E.A.F. - Nótás Erika - Kristóf K. - Kompfl Gy. - Issa Ibrahim A. - Hamid Y.S. - Heltai Gy. (2004): Bioavailability of Zn²⁺ and Pb²⁺ on soil microbial respiration and population. *In: Az MTA Szabolcs-Szatmár-Bereg Megyei Tudományos Testülete évkönyvei Vol.: 13.* Tudományos Ülés, Nyíregyháza. S. Kókai (Ed.). Káпитális Nyomdaipari és Kereskedelmi Kft, Debrecen. pp: 411-416.
10. **Algaidi A.A.** - Bayoumi Hamuda H.E.A.F. - Kristóf K. - Kampfl Gy. - Heltai Gy. (2005): Effect of temperature and different C/N ratios on gas emissions (N₂O, NO and CO₂) from brown forest soil. "Agriculture in Central Europe Potentials and Risks" **47th** Georgikon Scientific Conference and **15th** ÖGA Annual Meeting, 2005. szeptember 29-30., Keszthely. CD-R adathordozón sokszorosítva, made by //VTCD Gn20050929, ISBN 963 9639 03 6.
11. **Algaidi A.A.** - Bayoumi Hamuda H.E.A.F. - Kristóf K. - Kampfl Gy. - Hamid Y.S. - Issa Ibrahim A. - Heltai Gy. (2005): Gas emission in brown forest soil in relation to C:N applied rate and soil temperature. *In: Az MTA Szabolcs-Szatmár-Bereg Megyei Tudományos Testületének XIV. évi Közgyűléssel egybekötött Tudományos Ülésének Előadásai I. rész.* 2005. szeptember 30. – október 01. Nyíregyháza. P. Nagy (Ed.). CD-R kiadvány a KÁLL-TRADE Kft, Nyíregyháza. pp: 9-15. ISBN-13:978-963-8048-32-5.

5. KÜLFÖLDI TUDOMÁNYOS RENDEZVÉNYEKEN MEGJELENT KÖZLEMÉNYEK:

12. **Algaidi A.A.** - Bayoumi Hamuda H.E.A.F. - Nótás Erika - Kristóf K. - Kampfl Gy. - Hamid Y.S. - Heltai Gy. (2006): Impact of lead, cadmium, and cobalt on soil respiration and microbial content under *in vitro* conditions. *Proceeding of the VII. International Ph.D. Students Conference.* RNDr. M. Slábová, Ing. Z. Sýkorová (Eds.). **4th** April 2006. University of South Bohemia, Faculty of Agriculture, České Budějovice, Czech Republic. pp.: 7-16. ISBN 80-7040-847-2.
13. **Algaidi A.A.** - Kristóf K. - Kampfl GY. - Hamid Y.S. - Bayoumi Hamuda H.E.A.F. - Nótás Erika - Issa I.A. - Heltai GY. (2006): Predicting N₂O and CO₂ emission from agricultural soil amended with different C:N ratios. *Proceedings of VI. National Scientific Conference with International Participation "Ecology & Health 2006"* 18th May 2006. Plovdiv, Bulgaria. pp: 268-272.
14. Kristóf K. - **Algaidi A.A.** - Bayoumi Hamuda H.E.A.F. - Kampfl Gy. - Hamid Y.S. - Heltai Gy. (2006): Study of NO_x and CO₂ production of cultivated soil in closed microcosm experimental system. *Proceeding of the VII. International Ph.D. Students Conference.* RNDr. M. Slábová, Ing. Z. Sýkorová (Eds.). **4th** April 2006. University of South Bohemia, Faculty of Agriculture, České Budějovice, Czech Republic. pp.: 39-47. ISBN 80-7040-847-2.
15. Kristóf K. - **Algaidi A.A.** - GY Kampfl GY. - Hamid Y.S. - Bayoumi Hamuda H.E.A.F. - Bálint Á. - Heltai GY. (2006): Effect of soil moisture and temperature on NO_x and CO₂ production from brown forest soil. *Proceedings of VI. National Scientific Conference with International Participation "Ecology & Health 2006"* 18th May 2006. Plovdiv, Bulgaria. pp: 273-278.

6. HAZAI NEMZETKÖZI TUDOMÁNYOS RENDEZVÉNYEKEN MEGTARTOTT ELŐADÁSOK ÖSSZEFOGLALÓI:

16. Kristóf Krisztina - **Algaidi Abdousalam A.** - Kampfl Györgyi - Bayoumi Hosam - Heltai György (2005): Influence of C/N Ratio on NO_x and CO₂ Production of Cultivated Soil in Closed Microcosm System. **XII** Hungarian–Italian Symposium on Spectrochemistry: Environmental Pollution and Human Health. Abstract Book edited by G. Viktor, Z. Gyula. 23-27 October 2005, Pécs. pp: 82. ISBN 963 463 800 7.

7. KÜLFÖLDI TUDOMÁNYOS RENDEZVÉNYEKEN MEGTARTOTT POSZTEREK ÖSSZEFOGLALÓI:

17. **Algaidi A.A.** - Hamid Y.S. - Bayoumi Hamuda H.E.A.F. - Kristóf K. - Kampfl Gy. - Heltai Gy. (2007): Impacts of some environmental factors on the emission of trace gases. International Workshop on Practical Solutions **IV.** For managing optimum C and N content in Agricultural soils. 20th to 22nd June 2007, Prague, Czech. pp: 01. ISBN 978-80-87011-02-7.

18. Krisztof K. - Kampfl Gy. - **Algaidi A.A.** - Hamid Y.S. - Bayoumi Hamuda H.E.A.F. - Heltai Gy. (2007): Organic and inorganic fertilisers influencing the CO₂ and NO_x production. International Workshop on Practical Solutions IV. For managing optimum C and N content in Agricultural soils. 20th to 22nd June 2007, Prague, Czech. pp: 33. ISBN 978-80-87011-02-7.

8. HAZAI NEMZETKÖZI TUDOMÁNYOS RENDEZVÉNYEKEN BEMUTATOTT POSZTEREK ÖSSZEFOGLALÓI:

19. **Algaidi A.A.** - Bayoumi Hamuda H.E.A.F. - Kristóf K. - Kampfl Gy. - Heltai Gy. (2005): Effect of temperature and different C/N ratios on gas emissions (N₂O, NO and CO₂) from brown forest soil. "Agriculture in Central Europe Potentials and Risks" 47th Georgikon Scientific Conference and 15th ÖGA Annual Meeting 2005. szeptember 29-30., Keszthely. pp: 217.

9. HAZAI NEMZETKÖZI TUDOMÁNYOS RENDEZVÉNYEKEN BEMUTATOTT POSZTEREK:

20. **Algaidi A.A.** - Bayoumi Hamuda H.E.A.F. - Kristóf K. - Kampfl Gy. - Heltai Gy. (2005): Effect of temperature and different C/N ratios on gas emissions (N₂O, NO and CO₂) from brown forest soil. "Agriculture in Central Europe Potentials and Risks" 47th Georgikon Scientific Conference and 15th ÖGA Annual Meeting, Keszthely. 2005. szeptember 29-30.

10. HAZAI NEMZETKÖZI TUDOMÁNYOS RENDEZVÉNYEKEN MEGTARTOTT ELŐÁSOK:

21. Kristóf K. - **Algaidi Abdousalam A.** - Kampfl Gy. - Bayoumi Hosam - Heltai György (2005): Influence of C/N Ratio on NO_x and CO₂ Production of Cultivated Soil in Closed Microcosm System. XII. Hungarian – Italian Symposium on Spectrochemistry "Environmental Pollution and Human Health". Pécs. 23-27 October 2005.

11. HAZAI TUDOMÁNYOS RENDEZVÉNYEKEN MEGTARTOTT ELŐÁSOK:

22. **Algaidi A.A.** - Bayoumi Hamuda H.E.A.F. - Kristóf K. - Kampfl Gy. - Hamid Y.S. - Issa Ibrahim A. - Heltai Gy. (2005): Gas emission in brown forest soil in relation to C:N applied rate and soil temperature. Az MTA Szabolcs-Szatmár-Bereg Megyei Tudományos Testülete 14. éves Tudományos Ülés. Nyíregyháza. September 30.-October 01. 2005.

23. **Algaidi A.A.** - Kristóf K. - Kampfl Gy. - Bayoumi Hamuda H.E.A.F. - Heltai Gy. (2006): Role of thermal factor on the mobilization of soil N-biotransformation. *In: Az MTA Szabolcs-Szatmár-Bereg Megyei Tudományos Testületének XV. évi Közgyűléssel egybekötött Tudományos Ülést.* 2006. szeptember 22. - 23. Nyíregyháza.

24. Kristóf K. - Kampfl Gy. - **Algaidi A.A.** - Bayoumi Hamuda H.E.A.F. - Heltai Gy. (2006): Effect of different nitrogen sources on the soil N-biotransformation. *In: Az MTA Szabolcs-Szatmár-Bereg Megyei Tudományos Testületének XV. évi Közgyűléssel egybekötött Tudományos Ülést.* 2006. szeptember 22. - 23. Nyíregyháza.

12. KÜLFÖLDI TUDOMÁNYOS RENDEZVÉNYEKEN MEGTARTOTT ELŐADÁSOK:

25. **Algaidi A.A.** - Bayoumi Hamuda H.E.A.F. - Nótás Erika - Kristóf K. - Kampfl Gy. - Hamid Y.S. - Heltai Gy. (2006): Impact of lead, cadmium, and cobalt on soil respiration and microbial content under *in vitro* conditions. VII. International Ph.D. Students Conference. University of South Bohemia, Faculty of Agriculture, České Budějovice, Czech Republic. 4th April 2006.

26. Kristóf K. - **Algaidi A.A.** - Bayoumi Hamuda H.E.A.F. - Kampfl Gy. - Hamid Y.S. - Heltai Gy. (2006): Study of NO_x and CO₂ production of cultivated soil in closed microcosm experimental system. VII. International Ph.D. Students Conference. University of South Bohemia, Faculty of Agriculture, České Budějovice, Czech Republic. 4th April 2006.

13. KÜLFÖLDI TUDOMÁNYOS RENDEZVÉNYEKEN BEMUTATOTT POSZTEREK:

27. **Algaidi A.A.** - Kristóf K. - Kampfl Gy. - Hamid Y.S. - Bayoumi Hamuda H.E.A.F. - Nótás Erika - Issa I.A. - Heltai GY. (2006): Predicting N₂O and CO₂ emission from agricultural soil amended with different C:N ratios. VI. *National Scientific Conference of International Participation "Ecology & Health 2006"* Plovdiv, Bulgaria. 18th May 2006.

28. Kristóf K. - **Algaidi A.A.** - Kampfl Gy. - Hamid Y.S. - Bayoumi Hamuda H.E.A.F. - Bálint Á. - Heltai Gy. (2006): Effect of soil moisture and temperature on NO_x and CO₂ production from brown forest soil. **VI. National Scientific Conference of International Participation "Ecology & Health 2006"** Plovdiv, Bulgaria. 18th May 2006.
29. **Algaidi A.A.** - Hamid Y.S. - Bayoumi Hamuda H.E.A.F. - Krisztof K. - Kampfl Gy. - Heltai Gy. (2007): Impacts of some environmental factors on the emission of trace gases. International Workshop on Practical Solutions **IV**. For managing optimum C and N content in Agricultural soils. 20th to 22nd June 2007, Prague, Czech.
30. Krisztof K. - Kampfl Gy. - **Algaidi A.A.** - Hamid Y.S. - Bayoumi Hamuda H.E.A.F. - Heltai Gy. (2007): Organic and inorganic fertilisers influencing the CO₂ and NO_x production. International Workshop on Practical Solutions **IV**. For managing optimum C and N content in Agricultural soils. 20th to 22nd June 2007, Prague, Czech.
31. Kristóf Krisztina - Kampfl Györgyi - Heltai György - Nótás Erika - **Algaidi Ahmed Abdousalam** (2007): Examination of NO_x and CO₂ production in agricultural soils. **6th Alps-Adria Scientific Workshop** on Environmental consequences of sustainability, Obervellach, Austria, 30 April - 5 May, 2007.

11. FURTHER TASK

The results of the presented study pointed out the possibility to use microcosm model in order to measure the emissions rates of trace gases under control environment and developing reduction strategies. The implementation of the microcosm model formed the basis of developing adapted reduction strategies of trace gases emissions in consideration of underlying environmental-limiting factors. However, modeling complex systems requires good and valuable information about the basis securities.

Thus, in future research the developed N fertilization strategies (by the means of measuring the emissions rates of trace gases) using the crop growth (maize, wheat, beans, and etc.) model should be realized and tested with regard to the reduction of N losses. Additionally, there is a need to validate the model in consideration of the indicated yield-limiting factors, the positive effects of variable rate N fertilization strategies on reducing N oxides emissions seem to be limited.

A further investigation is required to identify N₂O production *via* denitrification under aerobic conditions when organic C is incorporated.

Further research is required to investigate how the large heavy metal concentrations might affect plant characteristics. The inhibitor/suppression technique used was confirmed to be flawed as negative values for nitrifier denitrification were obtained. Our study showed that the main factors that regulate the NO emissions in our studied soils are pH and WFPS. Our results can be used to improve current estimates of NO and N₂O emissions from the investigated ecosystems where information is limited.

Incorporation of heavy metals reduced NO, N₂O and CO₂ emissions (in some cases). This reduction was quantitatively dependent on heavy metal concentration, lower concentrations of heavy metals inducing higher emission rates than higher heavy metal concentrations. A further conclusion is that the trace gases emissions in soils amended with heavy metal is not a constant but dependent on other environmental factors such as soil conditions, moisture, temperature, etc.

12. ACKNOWLEDGEMENTS

At first, I would like to thank the General Peoples Committee of High Education and the Great Libyan Arab Jamahiriya for providing generous financial support for this research work.

I extend my heartfelt gratitude to my advisors:

Prof. Dr. *György Heltai*, for his guidance constant encouragement, advice, constructive criticism and scientific challenges.

I would like to extend my earnest gratitude to my advisor:

Prof. Dr. habil *Hosam E.A.F. Bayoumi Hamuda*, for his support and guidance provided throughout my Doctorate program and allowing me to benefit from his experience, kindness and patience.

Without their help, it wouldn't be possible to complete my dissertation in a timely manner.

My appreciation is extended to my colleague Györgyi Kampfl for her technical support. Special thanks are extended to the Department staff members, secretarial staff and the technician staff of the Department of Chemistry and Biochemistry, and the members of the Institute of Environmental Science, Faculty of Agricultural and Environmental Science at Szent István University for their support and help during my time at the University.

I extend my deep appreciation to my fellow graduate students in the Department for their strong support and timely help during my stay in Hungary. I am grateful to my friends, for their critical thoughts, input, moral support, and encouragement in professional and personal aspects of my life.

My special thanks to The University of Szent István and the staff members of the Doctorate and Habilitation Committee of the University and the administration office of Doctorate and Habilitation Committee of the University. Also, I would like to thank the Ph.D. School of Environmental Science for their kindness and support to finish my Dissertation.

In a special way we would like to thank the staff of Central Laboratory at the University

I thank my parents, for ingraining me with love, laughter, continuous encouragement and moral ethic. I especially appreciate my children for sharing their love with me. Finally, special thanks are extended to my wife for her patience, moral support, sharing my burden, and her help in preparing this Dissertation.

13. REFERENCES

- Abbasi, M.K., Adams, W.A. (1998): Loss of nitrogen in compacted grassland soil by simultaneous nitrification and denitrification. *Plant and Soil*, **200**: 265–277.
- Agriculture and Agri-Food Canada (1998): The Health of Our Air. Toward sustainable Agriculture in Canada. Government Services Canada. 98 pp.
- Agriculture and Agri-Food Canada (2000): Prairie Agricultural Landscapes. A Land Resource Review. Prairie Farm Rehabilitation Administration, Regina, Saskatchewan. 179 pp.
- Agriculture and Agri-Food Canada (2002): "Environment Bureau" http://www.agr.gc.ca/policy/environment/eb/public_html/ebe/climate.html accessed Dec. 2002.
- Akiyama, H., Tsuruta, H., Watanabe, T. (2000): N₂O and NO emissions from soils after the application of different chemical fertilizers. *Chemosphere*, **2**: 313–320.
- Al-Kaisi, M.M., Kruse, M.L., Sawyer, J.E. (2008): Effect of Nitrogen Fertilizer Application on Growing Season Soil Carbon Dioxide Emission in a Corn–Soybean Rotation. *J Environ. Qual.*, **37**: 325–332.
- Algaidi, A.A., Bayoumi Hamuda, H.E.A.F., Nótás, E., Kristóf, K., Kampfl, Gy., Hamid, Y.S., Heltai, Gy. (2007): A szennyező nehézfémek hatása a talajbaktériumok mennyiségére, és a talajlégzésre in vitro körülmények között. *Agrokémia és Talajtan*, **56**: 353–366.
- Algaidi, A., Abdousalam, Bayoumi Hamuda, H.E.A.F., Horváth, Márk, Nótás, Erika, Heltai, Gy. (2008): A hőmérséklet hatása nehézfémekkel szennyezett talajok gázkibocsátására. *Agrokémia és Talajtan*, **57**: 147–160.
- Alley, R., Berntsen, T., Bindoff, N.L., Chen, Z., Chidthaisong, A., Friedlingstein, P., Gregory, J., Hegerl, G., Heimann, M., Hewitson, B., Hoskins, B., Joos, F., Jouzel, J., Kattsov, V., Lohmann, U., Manning, M., Matsuno, T., Molina, M., Nicholls, N., Overpeck, J., Qin, D., Raga, G., Ramaswamy, V., Ren, J., Rusticucci, M., Solomon, S., Somerville, R., Stocker, T. F., Stott, P., Stouffer, R.J., Whetton, P., Wood, R.A., Wratt, D. (2007): Climate change. The Physical Science Basis, Contribution of working group I to the fourth assessment report of the IPCC, Paris.
- Alm, J., Saarnio, S., Nykänen, H., Silvola, J., Martikainen, P.J. (1999): Winter CO₂, CH₄ and N₂O on some natural and drained boreal peatlands. *Biogeochem.*, **44**: 163–189.
- Amato, M., Ladd, J.N. (1992): Decomposition of ¹⁴C-labelled glucose and legume material in soils: properties influencing the accumulation of organic residue C and microbial biomass C. *Soil Biol. Biochem.*, **24**: 455–464.
- Ambus, P., Zechmeister-Boltenstern, S., Butterbach-Bahl, K. (2006): Sources of nitrous oxide emitted from European forest soils. *Biogeosci.*, **3**: 135–145.
- Anderson, I.C., Levine, J.S. (1986): Relative rates of nitric oxide and nitrous oxide production by nitrifiers, denitrifiers, and nitrate respirers. *Appl. Environ. Microbiol.*, **51**: 938–945.
- Anderson, I.C., Levine, J.S. (1987): Simultaneous field measurements of biogenic emissions of nitric oxide and nitrous oxide. *J. Geophys. Res.*, **92**: 965–976.
- Anderson, I.C., Levine, J.S., Poth, M.A., Riggan, P.J. (1988): Enhanced biogenic emissions of nitric oxide and nitrous oxide following surface biomass burning. *J. Geophys. Res.* **93**: 3893–3898.
- Anderson, J.P.E., Domsch, K.H. (1978): A physiological method for the quantitative measurement of microbial biomass in soils. *Soil Biol. Biochem.*, **10**: 215–221.
- Andreae, M.O., Crutzen, P.J., Culf, A.D., Grace, J., Kabat, K., Lelieveld, J., Valentini, R., Meixner, F.X. (2000): European studies on trace gases and atmospheric chemistry as a contribution to the large-scale biosphere atmosphere experiment in Amazonia (EUSTACH - LBA), European studies on trace gases and atmospheric chemistry as a contribution to the large scale biosphere atmosphere experiment in Amazonia (EUSTACH - LBA), Proceedings of the European Climate Science Conference, October 19-23, 1998, Vienna, Austria. Commission of the European Communities (DG XII), Brussels, Belgium.
- Aneja, V.P., Roelle, P.A., Li, Y. (2001): Effect of environmental variables on NO emissions from agricultural soils. *Phyton*, **41**: 27–38.
- Angoa Pérez, M.V., González Castañeda, J., Frías-Hernández, J.T., Franco-Hernández, O., van Cleemput, O., Dendooven, L., Olalde, V. (2004): Trace gas emissions from soil of the central highlands of Mexico as affected by natural vegetation: a laboratory study. *Biol. Fertil. Soils*, **40**: 252–259.

- Arah, J.R.M., Smith, K.A. (1990): Factors influencing the fraction of the gaseous products of soil denitrification evolved to the atmosphere as nitrous oxide. *In: Soils and the Greenhouse Effect* (Ed.: Bouwman, A.F.) 475–480. John Wiley and Sons, New York.
- Assennato, G., Paci, C., Baser, M.E., Molinini, R., Candela, R.B., Altamura, B.M., Giorgino, R. (1986): Sperm count suppression without endocrine dysfunction in lead-exposed men. *Arch. Environ. Health*, **4**: 387–390.
- Aulakh, M.S., Rennie D.A., Paul, E.A. (1983): Field studies on gaseous nitrogen losses from soils under continuous wheat versus a wheat-fallow rotation. *Plant and Soil*, **75**: 15–27.
- Aulakh, M.S., Doran, J.W., Walter, D.T., Mosier, A.R., Francis, D.D. (1991): Crop residue type and placement effects on denitrification and mineralization. *Soil Sci. Soc. Am. J.*, **55**: 1020–1025.
- Ausmus, B.S., Dodson, G.J., Jackson, D.R. (2004): Behavior of heavy metals in forest microcosms. *Water, Air and Soil Pollut.*, **10**: 19–26.
- Bach, M. (1987): Die potentielle Nitratbelastung des Sickerwassers durch die Landwirtschaft in der Bundesrepublik Deutschland. *Gött. Bodenkd. Ber.*, **93**: 1–186.
- Bååth, E. (1989): Effects of heavy metals in soil metals on microbial processes and population. *Water Air Soil Pollut.*, **47**: 335–346.
- Bailey, L.D. (1976): Effects of the temperature and root on denitrification in a soil. *Can. J. Soil Sci.* **56**: 79–87.
- Ball, B.C., Scott, A., Parker, J.P. (1999): Field N₂O, CO₂ and CH₄ fluxes in relation to tillage, compaction and soil quality in Scotland. *Soil Till. Res.*, **53**: 29–39.
- Bardgett, R.D., Speir, T.W., Ross, D.J., Yeates, G.W., Kettles, H.A. (1994): Impact of pasture contamination by copper chromium and arsenic timber preservative on soil microbial properties and nematodes. *Biol. Fertil. Soils*, **18**: 71–79.
- Baker, A.J.M., Walker, P.L. (1990): *In: Heavy Metal Tolerance in Plants: Evolutionary Aspects.* (ed.: Shaw, A.J.) 155–177. Boca Raton: CRC Press.
- Bakken, L.R. (1988): Denitrification under different cultivated plants: effects of soil moisture tension, nitrate concentration, and photosynthetic activity. *Biol. Fertil. Soils*, **6**: 271–278.
- Bandibas, J., Vermoesen, A., Groot, J.D., Cleemput, O.V. (1994): The effect of different moisture regimes and soil characteristics on nitrous oxide emission and consumption by different soils. *Soil Sci.*, **158**: 106–114.
- Basta, N.T., Pantone, D.J., Tabatabai, M.A. (1993): Path analysis of heavy metal adsorption by soil. *Agron. J.*, **85**: 1054–1057.
- Baumgärtner, D., Conrad, R. (1992): Effects of soil variables and season on the production and consumption of nitric oxide in oxic soils. *In: Fertility of Soils.* 166–174. Springer-Verlag.
- Bayoumi Hamuda, H.E.A.F., Kecskés, M. (2003): Correlation between the efficiencies of CO₂ release, FDA, and dehydrogenase activity in the determination of the biological activity in soil amended with sewage sludge. *Az MTA Sz-Sz-B. Megyei Tudományos Testülete 12 éves Tudományos Ülés (Konferencia kiadvány).* Nyíregyháza, Hungary. pp: 11–16.
- Bayoumi Hamuda H.E.A.F., Kucsma N., Várady Gy., Kiss Z., Kecskés M. (1996): Nehézfémek és kombinációik hatása különböző *Rhizobium leguminosarum* törzsek szaporodására. *Agrokémia és Talajtan*, **45**: 153–168.
- Bayoumi Hamuda H.E.A.F., Kiss Z., Várady Gy., Balázsy S., Kucsma N., Kecskés M. (1995): The influence of nitrapyrin and sodium azide on the growth and respiration of some *Rhizobium* strains. *Microbiol. Res.*, **150**: 247–251.
- Beauchamp, E.G. (1997): Nitrous oxide emission from agricultural soils. *Can. J. Soil Sci.*, **77**: 113–123.
- Beck, H., Christensen, S. (1987): The effect of grass maturing and root decay on N₂O production in soil. *Plant and Soil*, **103**: 269–273.
- Behrendt, H., Bach, M., Kunkel, R., Opitz, D., Pagenkopf, W.-G., Scholz, G., Wendland, F. (2002): Quantifizierung der Nährstoffeinträge der Flussgebiete Deutschlands auf der Grundlage eines harmonisierten Vorgehens. UFO-Plan des BMU Forschungsberichts 29922285, Abschlussbericht.
- Bellinger, D., Leviton, A., Watermaux, C., Needleman, H.L., Rabinowitz, M. (1987): Longitudinal analyses of prenatal and postnatal lead exposure and early cognitive development. *N. Engl. J. Med.*, **316**: 1037–1043.

- Beloso, M.C., Villar, M.C., Cabaneiro, A., Carballas, N.M., Gonzalez-Prieto, S.J., Carballas, T. (1993): Carbon and nitrogen mineralization in an acid soil fertilized with composted urban refuses. *Bioresource Technol.*, **45**: 123–129.
- Benavides, M.P., Gallego, M.S., Tomaro, M.L. (2005): Cadmium toxicity in plants. *Braz. J. plant physiol.*, **17**: 21–34.
- Benckiser, G., Haider, K., Sauerbeck, D. (1986): Field measurements of gaseous nitrogen losses from an Alfisol planted with sugarbeets. *Z. Pflanzenernahr. Bodenk.*, **149**: 249–261.
- Benjamin, M.M., Leckie, J.D. (1980): Analysis, Chemistry, Biology, Vol. 2. (eds.: Baker, R.A., Arbor, A.) – MI: Ann Arbor Science Publishers, Inc.
- Benstead, J., Lloyd, D. (1996): Spatial and temporal variations of dissolved gases (CH₄, CO₂ and O₂) in peat cores. *Microb. Ecol.*, **31**: 57–66.
- Berecz, K., Debreczeni, K., Heltai, Gy. (2000): Studying nitrogenous gas production in soil air affected by different nitrogen fertilizer forms applied to wheat in pot experiments. In: Biogenic Emission of Greenhouse Gases Caused by Arable and Animal Agriculture. (eds.: Freibauer, A., Kaltschmitt, M.) 23–30. Institute für Energiewirtschaft und Rationelle Energieanwendung, Stuttgart.
- Berti, W.R., Jacobs, L.W.P. (1996): Chemistry and Phytotoxicity of Soil Trace Elements from Repeated Sewage Sludge Applications. *J. Environ. Qual.*, **25**: 1025–1032.
- Bhandral, R., Bolan, N.S., Saggar, S., Hedley, M.J. (2007a): Nitrogen transformations and nitrous oxide emissions from various types of farm effluents. *Nutr. Cycl. Agroecosyst.*, doi: 10.1007/s10705-007-9107-5.
- Bhandral, R., Saggar, S., Bolan, N.S., Hedley, M.J. (2007b): Transformation of nitrogen and nitrous oxide emission from grassland soils as affected by compaction. *Soil Till. Res.*, **94**: 482–492.
- Billore, S.K., Numata, M., Minami, K. (1996): Nitrous oxide emission from grassland and forest soils through nitrification. *Curr. Sci.*, **70**: 1010–1012.
- Blackmer, A.M., Bremner, J.M., Schmidt, E.L. (1980): Production of nitrous oxide by ammonia-oxidizing chemoautotrophic microorganisms in soil. *Appl. Environ. Microbiol.*, **40**: 1060–1066.
- Blackmer, A.M., Robbins, S.G., Bremner, J.M. (1982): Diurnalvariability in rate of emission of nitrous oxide from soils. *Soil Sci. Soc. Am. J.*, **46**: 937–942.
- Blake, G.R. (1965): Particle density. In: Methods of Soil Analysis. Part 1. Physical and Mineralogical Methods (ed.: Klute, A.) 371–373. Soil Sci. Soc. Am., Madison.
- Bleakly, B.H., Tiedje, J.M. (1982): Nitrous oxide production by organisms other than nitrifiers or denitrifiers. *Appl. Environ. Microbiol.*, **44**: 1342–1348.
- van Bochove, E., Jones, H.G., Pelletier, F., Prevost, D. (1996): Emission of N₂O from agricultural soil under snow cover: a significant part of N budget. *Hydrol. Proc.*, **10**: 1545–1549.
- Bøckmann, O.C., Olf, H.W. (1998): Fertilizer, agronomy and N₂O. *Nutr. Cycl. Agroecosyst.*, **52**: 165–170.
- Bollag, J.M., Tung, G. (1972): Nitrous oxide release by soil fungi. *Soil Biol. Biochem.*, **4**: 271–276.
- Bollag, J.M., Barabasz, W., 1979. Effect of heavy metals on the denitrification process in soil. *J. Environ. Qual.*, **8**: 71–79.
- Bollmann, A., Conrad, R. (1997): Recovery of nitrification and production of NO and N₂O after exposure of soil to acetylene. *Biol. Fertil Soils*, **25**: 41–46.
- Bollmann, A., Koshorreck, M., Meuser, K., Conrad, R. (1999): Comparison of two different methods to measure nitric oxide turnover in soils. *Biol. Fertil. Soils*, **29**: 104–110.
- Bouwman, A.F. (1990): Exchange of greenhouse gases between terrestrial ecosystems and the atmosphere. In: Soils and the Greenhouse Effect. (ed.: Bouwman, A.F.) 100–120. Wiley, Chichester.
- Bouwman, A.F. (1996): Direct emissions of nitrous oxide from agricultural soils. *Nutr. Cycl. Agroecosyst.*, **46**: 53–70.
- Bouwman, A.F. (1998): Nitrogen oxides and tropical agriculture. *Nature*, **392**: 866–867.
- Bouwman, A.F., Taylor, J.A., Kroeze, C. (2000): Testing hypothesis on global emissions of nitrous oxide using atmospheric models. *Glob. Change Sci.*, **2**: 475–492.

- Bowden, R.D., Steudler, P.A., Melillo, J.M. (1990): Annual nitrous oxide fluxes from temperate forest in the Northeastern United States. *J. Geophys. Res.*, **95**: 13997–14005.
- Boyer, J.N., Groffman, P.M. (1996): Bioavailability of water extractable organic carbon fractions in forest and agricultural soil profiles. *Soil Biol. Biochem.*, **28**: 783–790.
- Boyle, J.F., Rose, N.L., Bennion, H., Yang, H., Appleby, P.G. (1999): Environmental impacts in the Jiangnan Plain: Evidence from lake sediments. *Water, Air, Soil Pollut.*, **112**: 21–40.
- Brady, N.C., Weil, R.R. (1999): *The Nature and Properties of Soils*. Prentice-Hall, New Jersey, p. 881.
- Bremner, J.M. (1997): Sources of nitrous oxide in soils. *Nutr. Cycl. Agroecosyst.* **49**: 7–16.
- Bremner, J.M. (1996): Total nitrogen. In: *Methods of Soil Analysis: Chemical Methods* (ed.: Sparks, D.L.) 1085–1121. Soil Science Society of America, Madison.
- Bremner, J.M., Blackmer, A.M. (1978): Nitrous oxide: emissions from soils during nitrification. *Science*, **199**: 295–296.
- Bremner, J.M., Blackmer, A.M. (1979): Effects of acetylene and soil water content on emissions of nitrous oxide from soils. *Nature*, **208**: 380–381.
- Bremner, J.M., Blackmer, A.M. (1981): Terrestrial nitrification as a source of atmospheric nitrous oxide. In: *Denitrification, Nitrification and Atmospheric Nitrous Oxide* (ed.: Delwiche, C.C.) 151–170. John Wiley and Sons, New York, Chichester, Brisbane, Toronto.
- Bremner, J.M., Robbins, S.G., Blackmer, A.M. (1980): Seasonal variability in emission of nitrous oxide from soil. *Geophys. Res. Lett.*, **7**: 641–644.
- Bremner, J.M., Breitenbeck, G.A., Blackmer, A.M. (1981a): Effect of anhydrous ammonia fertilization on emission of nitrous oxide from soils. *J. Environ. Qual.*, **10**: 77–80.
- Bremner, J.M., Breitenbeck, G.A., Blackmer, A.M. (1981b): Effect of nitrapyrin on emission of nitrous oxide from soil fertilized with anhydrous ammonia. *Geophys. Res. Lett.*, **8**: 353–356.
- Brumme, R., Beese, F. (1992): Effects of liming and nitrogen fertilization on emissions of CO₂ and N₂O from a temperate forest. *J. Geophys. Res.*, **96**: 9321–9328.
- Brumme, R., Borken, W., Finke, S. (1999): Hierarchical control on N₂O emissions in forest ecosystems. *Glob. Biogeochem. Cycl.*, **13**: 1137–1148.
- Breuer, L., Papen, H., Butterbach-Bahl, K. (2000): N₂O emission from tropical forest soils of Australia. *J. Geophys. Res. Atmos.*, **105**: 26353–26367.
- Brookes, P.C., McGrath, S.P., Heijnen, C.E. (1986a): Metal residues in soils previously treated with sewage sludge and their effects on growth and nitrogen fixation by blue-green algae. *Soil Biol. Biochem.*, **18**: 345–355.
- Brookes, P.C., Heijnen, C.E., McGrath, S.P., Vance, E.D. (1986b): Soil microbial biomass estimates in soils contaminated with metals. *Soil Biol. Biochem.*, **18**: 383–388.
- Brookes, P.C., McGrath, S.P., de Klein, D.A., Elliott, E.T. (1984): Effects of heavy metals on microbial activity and biomass in field soils treated with sewage sludge. *Environ. Contam.* (Internat. Conf., London, July 1984) CEP Ltd, Edinburgh, UK, pp. 574–583.
- Brown, H.A., Waggner-Riddle, C., Thurtell, G.W. (2000): Nitrous oxide flux from solid dairy manure in storage as affected by water content and redox potential. *J. Environ. Qual.*, **29**: 630–638.
- Brown, J.C., Jones, W.E. (1975): Heavy metal toxicity in plants. 1. A crisis in embryo. *Commun. Soil Sci. Plant Anal.*, **6**: 421–438.
- Bundesregierung (2004a): Mitteilung der Regierung der Bundes Republik Deutschland, August 2004. 3. Bericht gemäß Artikel 10 der Richtlinie 91/676/EWG des Rates vom 12. Dezember 1991 zum Schutz der Gewässer vor Verunreinigungen durch Nitrat aus landwirtschaftlichen Quellen. <http://www.lawa.de/pub/kostenlos/gw/Nitratbericht-2004.pdf>
- Bundesregierung (2004b): Am 16. Februar tritt das Kyoto-Protokoll in Kraft. <http://www.bundesregierung.de/Politikthemen/Kyoto-Protokoll,12005.722593/artikel/Am-16.-Februar-2005-tritt-das-.htm>
- Bundesregierung (2004c): Climate change – a major challenge of our time. <http://www.bundesregierung.de/en/-/10001.756263/artikel/Climate-change-major-challenge.htm>
- Burton, D.L., Beauchamp, E.G. (1994): Profile of nitrous oxide and carbon dioxide concentrations in a soil subject to freezing. *Soil Sci. Soc. Am. J.*, **58**: 115–122.

- Butterbach-Bahl, K., Gasche, R., Breuer, L., Papen, H. (1997): Fluxes of NO and N₂O from temperate forest soils: Impact of forest type, N deposition and of liming on the NO and N₂O emissions. *Nutr. Cycl. Agroecosyst.*, **48**: 79–90.
- Butterbach-Bahl, K., Stange, F., Papen, H., Li, C. (2001): Regional inventory of nitric oxide and nitrous oxide emissions for forest soils of Southeast Germany using the biogeochemical model PnET-N-DNDC. *J. Geophys. Res. Atmos.*, **106**: 34155–34166.
- Butterbach-Bahl, K., Willibald, G., Papen, H. (2002): Soil core method for direct simultaneous determination of N₂ and N₂O emissions from forest soils. *Plant and Soil*, **240**: 105–116.
- Butterbach-Bahl, K., Kesik, M., Miehle, P., Papen, H., Li, C. (2004a): Quantifying the regional source strength of N-trace gases across agricultural and forest ecosystems with process based models. *Plant and Soil*, **260**: 311–329.
- Butterbach-Bahl, K., Kock, M., Willibald, G., Hewett, B., Buhagiar, S., Papen, H., Kiese, R. (2004b): Temporal variations of fluxes of NO, NO₂, N₂O, CO₂, and CH₄ in a tropical rain forest ecosystem. *Glob. Biogeochem. Cycl.*, **18**(3): GB3012.
- Cannavo, P., Richaume, A., Lafolie, F. (2003): Fate of nitrogen and carbon in the vadose zone: *in situ* and laboratory measurements of seasonal variations in aerobic respiratory and denitrifying activities. *Soil Biol. Biochem.*, **36**: 463–478.
- Cardenas, L., Rondon, A., Johansson, C., Sanhueza, E. (1993): Effects of soil moisture, temperature, and inorganic nitrogen on nitric oxide emissions from acidic tropical savannah soils. *J. Geophys. Res.*, **98**: 14783–14790.
- Carran, R.A., Theobald, P.W., Evans, J.P. (1995): Emission of nitrous oxide from some grazed pasture soils in New Zealand. *Aust. J. Soil Res.*, **33**: 341–35.
- Castaldi, S. (2000): Responses of nitrous oxide, dinitrogen and carbon dioxide production and oxygen consumption to temperature in forest and agricultural light-textured soils determined by model experiment. *Biol. Fertil. Soils*, **32**: 67–72.
- Castaldi, S., Smith, K.A. (1998): Effect of cycloheximide on N₂O and NO₃⁻ production in a forest and an agricultural soil. *Biol. Fertil. Soils*, **27**: 27–34.
- Causarano, H.J., Franzluebbers, A.J., Shaw, J.N., Reeves, W.D., Randy, L.R., Wood, W.C. (2008): Soil organic carbon fractions and aggregation in the southern piedmont and coastal plain. *Soil Sci. Soc. Am. J.*, **72**: 221–230.
- Cela, S., Sumner, M.E. (2002a): Soil zinc fractions determine inhibition of nitrification. *Water, Air, Soil Pollut.*, **141**: 91–104.
- Cela, S., Sumner, M.E. (2002b): Critical concentrations of copper, nickel, lead, and cadmium in soils based on nitrification. *Commun. Soil Sci. Plant Anal.*, **33**: 19–30.
- Cela, S., Sumner, M.E. (2003): Relationship between released nickel and zinc and nitrification in two soils amended with biosolids. *Commun. Soil Sci. Plant Anal.*, **34**: 2727–2743.
- Chalk, P.M., Smith, C.J. (1983): Chemodenitrification. *In: Gaseous Loss of Nitrogen from Plant–Soil Systems Developments in Plant and Soils Sciences* (eds.: Freney, J.R., Simpson, J.R.) vol. **9**: 65–89.
- Chameides, W.L., Fehsenfeld, F., Rodgers, M.O., Cardelina, C., Martinez, J., Parrish, D., Lonneman, W., Lawson, D.R., Rasmussen, R.A., Zimmerman, P., Greenberg, J., Middleton, P., Wang, T. (1992): Ozone precursor relationships in the ambient atmosphere. *J. Geophys. Res.*, **97**: 6037–6055.
- Chander, K., Brookes, P.C. (1991): Effects of heavy metals from past applications of sewage sludge on microbial biomass and organic matter accumulation in sandy loam and silty loam U.K. soil. *Soil Biol. Biochem.*, **23**: 927–932.
- Chander, K., Brookes, P.C. (1993): Residual effects of zinc, copper and nickel in sewage sludge on microbial biomass in a sandy loam. *Soil Biol. Biochem.*, **25**: 1231–1239.
- Checkai, R.T., Corey, R.B., Helmke, P.A. (1987): Effects of ionic and complexed metal concentrations on plant uptake of cadmium and micronutrient metals from solution. *Plant and Soil*, **99**: 335–345.
- Chen, H.M., Zheng, C.R., Tu, C., Zhu, Y.G. (1999): Heavy metal pollution in soils in China: status and countermeasures. *Ambio.*, **28**: 130–134.
- Chen, H.M., Harmon, M.E., Griffiths, R.P., Hicks, W. (2000): Effects of temperature and moisture on carbon respired from decomposing woody roots. *Forest Ecol. Manag.*, **138**: 51–64.
- Cheng, W. (1999): Rhizosphere feedbacks in elevated CO₂. *Physiol.*, **19**: 313–320.

- Cheng, W., Tsuruta, H., Chen, G., Yagi, K. (2004): N₂O and NO production in various Chinese agricultural soils by nitrification. *Soil Biol. Biochem.*, **36**: 953–963.
- Cheng, W., Nakajima, Y., Sudo, S., Akiyama, H., Tsuruta, H. (2002): N₂O and NO emissions from Chinese cabbage field as influenced by band application of urea or controlled-release urea fertilizers. *Nutr. Cycl. Agroecosyst.*, **63**: 231–238.
- Cho, U., Seo, N. (2004): Oxidative stress in *Arabidopsis thaliana* exposed to cadmium is due to hydrogen peroxide accumulation. *Plant Sci.*, **168**: 113–120.
- Choi, M.J., Cho, D.H. (2008): Research Activities on the Utilization of Carbon Dioxide in Korea. *Clean J.*, **36**: 5–6.
- Christensen, S., Christensen, B.T. (1991): Organic matter available for denitrification in different soil fractions: effect of freeze/thaw cycles and straw disposal. *J. Soil Sci.*, **42**: 637–647.
- Christensen, S., Tiedje, J.M. (1990): Brief and vigorous N₂O production by soil at spring thaw. *J. Soil Sci.* **41**: 1–4.
- Christensen, S., Simkins, S., Tiedje, J.M. (1990): Spatial variation in denitrification: dependency of activity centers on the soil environment. *Soil Sci. Soc. Am. J.*, **54**: 1608–1613.
- Christensen, S., Ambus, P., Arah, J.R.M., Clayton, H., Galle, B., Griffith, D.W.T., Hargreaves, K.J., Klemetsson, L., Lind, A.M., Maag, M., Scot, A., Skiba, U., Smith, K.A., Welling, M., Wienhold, F.G. (1996): Nitrous oxide emission from an agricultural field: comparison between 15 measurements by flux chamber and micro-meteorological techniques. *Atmos. Environ.*, **30**: 4183–4190.
- Christianson, C.B., Cho, C.M. (1983): Chemical denitrification of nitrite in frozen soils. *Soil Sci. Soc. Am. J.*, **47**: 38–42.
- Cicerone, R.J. (1987): Changes in stratospheric ozone. *Science*, **237**: 35–42.
- Clemens, S., Palmgreen, M.G., Kramer, U. (2002): A long way ahead: understanding and engineering plant metal accumulation. *Trends Plant Sci.*, **7**: 309–315.
- Cochran, V.L., Sparrow, E.B., Schlentner, S.F., Knight, C.W. (1997): Longterm tillage and crop residue management in the subarctic: fluxes of methane and nitrous oxide. *Can. J. Soil Sci.*, **77**: 565–570.
- Colbourn, P., Dowdell, R.J. (1984): Denitrification in field soils. *Plant and Soil*, **76**: 213–226.
- Colbourn, P., Ryden, J.C., Dollard, G.J. (1987): Emission of NO_x from urine-treated pasture. *Environ. Pollut.*, **46**: 253–261.
- Conen, F., Smith, A. (2000): An explanation of linear increases in gas concentration under closed chambers used to measure gas exchange between soil and the atmosphere. *Eur. J. Soil Sci.*, **51**: 111–117.
- Connell, D.W., Miller, G.J. (1984): Chemistry and Ecotoxicology of Pollution. pp. 444. John Wiley & Sons, NY.
- Conrad, R. (1990): Flux of NO_x between soil and atmosphere: Importance of soil microbial metabolism. *In: Denitrification in soil and sediment.* (eds.: Revsbech, N.P., Sorensen, J.) 105–128. Plenum Press, New York.
- Conrad, R. (1994): Compensation concentration as critical variable for regulating the flux of trace gases between soil and atmosphere. *Biogeochem.*, **27**: 155–170.
- Conrad, R. (1995): Soil microbial processes involved in production and consumption of atmospheric trace gases. *Adv. Microbial Ecol.*, **14**: 207–250.
- Conrad, R. (1996a): Soil microorganisms as controllers of atmospheric trace gases (H₂, CO, CH₄, OCS, N₂O, and NO). *Microbiol. Rev.*, **60**: 609–640.
- Conrad, R. (1996b): Metabolism of nitric oxide in soil and soil microorganisms and regulation of flux into the atmosphere. *In: Microbiology of Atmospheric Trace Gases: Sources, Sinks, and Global Change Processes.* (ed.: Kelly, D.P.) 167–203. Springer, Berlin Heidelberg, New York.
- Conrad, R. (2002): Microbiological and biochemical background of production and consumption of NO and N₂O in soil. *In: Trace Gas Exchange in Forest Ecosystems* (eds.: Gasche, R., Papen, H., Rennenberg, H.) 3–33. Kluwer Academic Publishers, Dordrecht, Netherlands.
- Conrad, R., Seiler, W., Bunse, G. (1983): Factors influencing the loss of fertilizer nitrogen into the atmosphere as N₂O. *J. Geophys. Res.*, **88**: 6709–6718.

- Cote, L., Brown, S., Pare, D., Fyles, J., Bauhus, J. (2000): Dynamics of carbon acid nitrogen mineralization in relation to stand type, stand age and soil texture in the boreal mixed wood. *Soil Biol. Biochem.*, **32**: 1079–1090.
- Cotrufo, M.F., Gorissen, A. (1997): Elevated CO₂ enhances belowground C allocation in three perennial grass species at different levels of N availability. *New Phytol.*, **137**: 421–431.
- Cotrufo, M.F., Ineson, P., Rowland, A.P. (1994): Decomposition of tree leaf litters grown under elevated CO₂: effect of litter quality. *Plant and Soil*, **163**: 121–130.
- Cox, R.M., Betts, R.A., Jones, C.D., Spall, S.A., Totterdell, I.J. (2000): Acceleration of global warming due to carbon-cycle feedbacks in a coupled climate model. *Nature*, **408**: 184–187.
- Crill, P., Keller, M., Weitz, A., Grauel, B., Veldkamp, E. (2000): Intensive field measurements of N₂O emissions from a tropical agricultural soil. *Glob. Biogeochem. Cycl.*, **14**: 85–96.
- Crutzen, P.J. (1979): The role of NO and NO₂ in the chemistry of the troposphere and stratosphere. *Ann. Rev. Earth Planet. Sci.*, **7**: 443–472.
- Crutzen, P.J., Mosier, A.R., Smith, K.A., Winiwarer, W. (2008): N₂O release from agro-biofuel production negates global warming reduction by replacing fossil fuels. *Atmos. Chem. Phys.*, **8**: 389–395.
- Curiel Yuste, J., Janssens, I.A., Carrara, A., Ceulemans, R. (2004): Annual Q10 of soil respiration reflects plant phenological patterns as well as temperature sensitivity. *Glob. Change Biol.*, **10**: 161–169.
- Curtis, P.S., Wang, X. (1998): A meta-analysis of elevated CO₂ effects on woody plant mass, form and physiology. *Oecologia*, **113**: 299–313.
- Dai, J., Becquer, T., Rouiller, J.H., Reversat, G., Bernhard-Reversat, F., Lavelle, P. (2004): Influence of heavy metals on C and N mineralisation and microbial biomass in Zn-, Pb-, Cu-, and Cd-contaminated soils. *Appl. Soil Ecol.*, **25**: 99–109.
- Dalal, R.C., Wang, W., Robertson, G.P., Parton, W.J. (2003): Nitrous oxide emission from Australian agricultural lands and mitigation options: a review. *Aust. J. Soil*, **61**: 292–292.
- Dalsgaard, T., Canfield, D.E., Petersen, J., Thamdrup, B., Acuña-González, J. (2003): N₂ production by the anammox reaction in the anoxic water column of Golfo Dulce, Costa Rica. *Nature*, **422**: 606–608.
- Das, P., Samantaray, S., Rout, G.R. (1997): Studies on cadmium toxicity in plants. *Environ. Pollut.*, **98**: 29–36.
- Daum, D., Schenk, M.K. (1998): Influence of nutrient solution pH on N₂O and N₂ emissions from a soilless culture system. *Plant and Soil*, **203**: 279–287.
- Davidson, E.A. (1991): Fluxes of nitrous oxide and nitric oxide from terrestrial ecosystems. *In*: Microbial production and consumption of greenhouse gases: Methane, nitrogen oxides, and halomethanes (eds.: Rogers, J.E., Whitman, W.B.) 219–235. Am. Soc. Microbiol., Washington, DC.
- Davidson, E.A. (1992): Sources of nitric oxide and nitrous oxide following wetting of dry soil. *Soil Sci. Soc. Am. J.*, **56**: 95–102
- Davidson, E.A. (1993): Soil water content and the ratio of nitrous oxide to nitric oxide emitted from soil. *In*: The biogeochemistry of global change: radiative trace gases. (ed.: Oremland, R.S.) 369–386. Chapman and Hall, London, New York.
- Davidson, E.A., Kinglerlee, W. (1997): A global inventory of nitric oxide emissions from soils. *Nutr. Cycl. Agroecosyst.*, **48**: 37–50.
- Davidson, E.A., Stark, J.M., Firestone, M.K. (1990): Microbial consumption and consumption of nitrate in an annual grassland. *Ecology*, **71**: 1968–1975.
- Davidson, E.A., Potter, C.S., Schlesinger, P., Klooster, S.A. (1998): Model estimates of regional nitric oxide emissions from soils of the southeastern United States. *Ecol. Appl.*, **8**: 748–759.
- Davidson, E.A., Keller, M., Erickson, H.E., Verchot, L.V., Veldkamp, E. (2000): Testing a conceptual model of soil emissions of nitrous and nitric oxides. *BioScience*, **50**: 667–680.
- Davidson, E.A., Vitousek, P.M., Matson, P.A., Riley, R., Garcia-Méndez, G., Maass, J.M. (1991): Soil emissions of nitric oxide in a seasonally dry tropical forest of Mexico. *J. Geophys. Res.*, **96**: 15439–15445.
- Davidson, E.A., Matson, P.A., Vitousek, P.M., Riley, R., Dunkin, K., Garcia-Mendez, G., Maass, J.M. (1993): Processes regulating soil emissions of NO and N₂O in a seasonally dry tropical forest. *Ecology*, **74**: 130–139.

- Davies, B.E. (1990): Lead. *In: Heavy Metals in Soils* (ed.: Alloway, B.J.) 177–196. Blackie and Son, Glasgow, UK.
- Davies, K.J.P., Lloyd, D., Boddy, L. (1989): The effect of oxygen on denitrification in *Paracoccus denitrificans* and *Pseudomonas aeruginosa*. *J. Gen. Microbiol.*, **136**: 2945–2951.
- Dean, J.V., Harper, J.E. (1986): Nitric oxide and nitrous oxide production by soybean and winged bean during the in vivo nitrate reductase assay. *Plant Physiol.*, **82**: 718–723.
- Debreczeni, K., Berecz, K. (1998): Monitoring of gaseous nitrogen losses from nitrogen fertilizers in model experiments. *Commun. Soil Sci. Plant Anal.*, **29**: 2207–2216.
- Debreczeni, K., Fischl, K., Wittmann, Z. (2002): Nitrogenous gas production in the air as affected by different n fertilizer forms and water supplies in model experiments. *Acta Agron. Hung.*, **50**: 433–440.
- Debreczeni, K., Fischl, K., Heltai, G., Bálint, Á. (1997): Effect of N fertilization the N-containing gases of the soil. *Acta Agron. Hung.*, **45**: 163–172.
- De Haan, F.A.M., Bourg, A.C.M., Brookes, P.C., Verstraete, W., van Riemsdijk, W.H., van der Zee, S.E.A.T.M., Giraldez, J.V., McGrath S.P. (1989): Soil quality assessment. State of the art report on soil quality. Final report to the C.E.E. Directorate-General XII, Science, Research and Development Directorate E., Environment and Non-Nuclear Energy Contract EV4A/0008/NL.
- de Klein, C.A.M., Barton, L., Sherlock, R.R., Li, Z., Littlejohn, R.P. (2003): Estimating a nitrous oxide emission factor for animal urine from some New Zealand pastoral soils. *Aust. J. Soil Res.*, **41**: 381–399.
- Delany, A.C., Fitzjarrald, D.R., Lenschow, D.H., Pearson, Jr. R., Wendel, G.J., Woodruff, B. (1986): Direct measurements of nitrogen oxides and ozone fluxes over grassland. *J. Atmos. Chem.*, **4**: 429–444.
- Del Grosso, S.J., Parton, W.J., Mosier, A.R., Ojima, D.S., Kulmala, A.E., Phongpan, S. (2000): General model for N₂O and N₂ gas emissions from soils due to denitrification. *Glob. Biogeochem. Cycl.*, **14**: 1045–1060.
- DeLucia, E.H., Hamilton, J.G., Naidu, S.L., Thomas, R.B., Andrews, J.A., Finzi, A., Lavine, M., Matamala, R., Mohan, J.E., Hendrey, G.R., Schlesinger, W.H. (1999): Net primary production of a forest ecosystem with experimental CO₂ enrichment. *Science*, **289**: 1177–1179.
- Dendooven, L., Pemberton, E., Anderson, J.M. (1996): Denitrification potential and reduction enzymes dynamics in a Norway spruce plantation. *Soil Biol. Biochem.*, **28**: 151–157.
- Denef, K., Six, J., Pausian, K., Merckx, R. (2001): Importance of macroaggregate dynamics in controlling soil carbon stabilization: short term effects of physical disturbance by dry–wet cycles. *Soil Biol. Biochem.*, **8**: 751–755.
- Dobbie, K.E., McTaggart, I.P., Smith, K.A. (1999): Nitrous oxide emissions from intensive agricultural systems: Variations between crops and seasons, key driving variables, and mean emission factors. *J. Geophys. Res.*, **104**: 26891–26899.
- Dorland, S., Beauchamp, E.G. (1991): Denitrification and ammonification at low soil temperatures. *Can. J. Soil Sci.*, **71**: 293–303.
- Dowdell, R.J., Burford, J.R., Cress, R. (1979): Losses of nitrous oxide dissolved in drainage water from agricultural land. *Nature*, **278**: 342–343.
- Dunfield, P.F., Knowles, R. (1999): Nitrogen monoxide production and consumption in an organic soil. *Biol. Fertil. Soils*, **30**: 153–159.
- Duxbury, J.M. (1994): The significance of agricultural sources of greenhouse gases. *Fertil. Res.*, **38**: 151–163.
- EC-Council Directive (1991): Council Directive 91/676/EEC concerning the protection of waters against pollution caused by nitrates from agricultural sources.
- Eichner, M.J. (1990): Nitrous oxide emissions from fertilized soils: Summary of available data. *J. Environ. Qual.*, **19**: 272–280.
- Eick, M.J., Peak, J.D., Brady, P.V., Pesek, J.D. (1999): Kinetics of lead absorption/desorption on goethite: residence time effect. *Soil Sci.*, **164**: 28–39.
- Elliot, H.A., Liberali, M.R., Huang, C.P. (1986): Competitive adsorption of heavy metals by soils. *J. Environ. Qual.*, **15**: 214–219.

- Ellis, S., Dendooven, L., Goulding, K.W.T. (1996): Quantitative assessment of soil nitrate disappearance and N₂O evolution during denitrification: nitrate disappearance during denitrification. *Soil Biol. Biochem.*, **28**: 589–595.
- Emmerling, C., Edelhoven, T., Schröder, D. (2001): Response of soil microbial biomass and activity to agricultural de-intensification over a 10 year period. *Soil Biol. Biochem.*, **33**: 2105–2114.
- Enquête-Kommission “Schutz der Erdatmosphäre” des deutschen Bundestages (1994): Schutz der Grünen Erde. Klimaschutz durch umweltgerechte Landwirtschaft und Erhalt der Wälder. Economica Verlag, Bonn. 702 pp.
- Epron, D., Farque, L., Lucot, E., Badot, P.M. (1999): Soil CO₂ efflux in a beech forest: the contribution of root respiration. *Ann. For. Sci.*, **56**: 289–295.
- Ernst, W.H.O., Verkleij, J.A.C., Schat, H. (1992): Metal tolerance in plants. *Acta Bot. Neerl.*, **41**: 229–248.
- Fangueiro, D., Pereira, J., Chadwick, D., Coutinho, J., Moreira, N., Trindade, H. (2008): Laboratory assessment of the effect of cattle slurry pre-treatment on organic N degradation after soil application and N₂O and N₂ emissions. *Nutr. Cycl. Agroecosyst.*, **80**: 107–120.
- Firestone, M.K., Davidson, E.A. (1989): Microbiological basis of NO and N₂O production and consumption in soil. In: Exchange of trace gases between terrestrial ecosystems and the atmosphere (eds.: Andreae, M.O., Schimel, D.S.) 7–21. John Wiley & Sons, New York.
- Firestone, M.K., Firestone, R.B., Tiedje, J.M. (1980): Nitrous oxide from soil denitrification: factors controlling its biological production. *Science*, **208**: 749–751.
- Flessa, H., Beese, F. (1995): Effect of sugarbeet residues on soil redox potential and nitrous oxide emission. *Soil Sci. Soc. Am. J.*, **59**: 1044–1051.
- Flessa, H., Dörsch, P., Beese, F. (1995): Seasonal variation of N₂O and CH₄ fluxes in differently managed arable soils in southern Germany. *J. Geophys. Res.*, **100**: 23115–23124.
- Flessa, H., Dörsch, P., Beese, F., König, H., and Bouwman, A. F.: (1996): Influence of cattle wastes on nitrous oxide and methane fluxes in pasture land. *J. Environ. Qual.*, **25**: 1366–1370.
- Focht, D.D. (1974): The effect of temperature, pH and aeration on the production of nitrous oxide and gaseous nitrogen – a zero order kinetic model. *Soil Sci.*, **118**: 173–179.
- Focht, D.D. (1978): Methods for analysis of denitrification in soils. In: Nitrogen in the Environment. (eds.: Nielsen, D., MacDonald, J.) 2, 433–490. Academic Press.
- Food and Agriculture Organization, FAO (1996): Control of Water Pollution from Agriculture. FAO Irrigation and Drainage Paper 55, FAO, UN, Rome.
- Fowler, D., Duyzer, J.H. (1989): Micrometeorological techniques for the measurement of trace gas exchange. In: Exchange of trace gases between terrestrial ecosystems and the atmosphere (eds.: Andreae, M.O., Schimel, D.S.) 189–207. John Wiley & Sons, New York.
- Foy, C.D., Chaney, R.L., White, M.C. (1978): The physiology of metal toxicity in plants. *Ann. Rev. Plant Physiol.*, **29**: 511–566.
- Franzluebbers, K., Franzluebbers, A.J., Jawson, M.D. (2002): Environmental controls on soil and whole-ecosystem respiration from a tallgrass prairie. *Soil Sci. Soc. Am. J.*, **66**: 254–262.
- Freney, J.R. (1997): Strategies to reduce gaseous emission of nitrogen from irrigated agriculture. *Nutr. Cycl. Agroecosyst.*, **48**: 155–160.
- Frolking, S.E., Mosier, A.R., Ojima, D.S., Li, C., Parton, W.J., Potter, C.S., Priesack, E., Stenger, R., Haberbosch, C., Dörsch, P., Flessa, H., Smith, K.A. (1998): Comparison of N₂O emissions from soils at three temperate agricultural sites: simulations of year-round measurements by four models. *Nutr. Cyc. Agroecosyst.*, **52**: 77–105.
- Gabrielle, B., Laville, P., Hénault, C., Nicoullaud, B., Germon, J.C. (2006a): Simulation of nitrous oxide emissions from wheat cropped soils using CERES. *Nutr. Cycl. Agroecosyst.*, **74**: 133–146.
- Gabrielle, B., Laville, P., Duval, O., Nicoullaud, B., Germon, J.C., Hénault, C. (2006b): Process-based modelling of nitrous oxide emissions from wheat-cropped soils at the subregional scale. *Glob. Biogeochem. Cycl.*, **20**: GB4018.
- Gabrielle, B., Roche, R., Angas, P., Cantero-Martinez, C., Cosentino, L., Mantineo, M., Langensiepen, M., Hénault, C., Laville, P., Nicoullaud, B., Gosse, G. (2002): A priori parameterization of the CERES soil-crop models and tests against several European data sets. *Agron.*, **22**: 25–38.

- Galbally, I.E. (1989): Factors controlling NO_x emissions from soils. *In: Exchange of trace gases between terrestrial ecosystems and the atmosphere.* (eds.: Andreae, M.O., Schimel, D.S.) 23–37. John Wiley & Sons, New York.
- Galbally, I.E., Roy, C.R. (1978): Loss of fixed nitrogen from soils by nitric oxide exhalation. *Nature*, **275**: 734–735.
- Galbally, I.E., Johansson, C. (1989): A model relating laboratory measurements of rates of nitric oxide production and field measurements of nitric oxide emission from soils. *J. Geophys. Res.* **94**: 6473–6480.
- Galloway, J.N., Dentener, F.J., Capone, D.G., Boyer, E.W., Howarth, R.W., Seitzinger, S.P., Asner, G.P., Cleveland, C.C., Green, P.A., Holland, E.A., Karl, D.M., Michaels, A.F., Porter, J.H., Townsend, A.R., Vorosmarty, C.J. (2004): Nitrogen cycles: past, present and future. *Biogeochem.*, **70**: 153–226.
- Ganz, C., Saggart, S., Arnold, G.C., Lambie, S.J. (2006): Estimating nitrous oxide emissions from grazed pastures using small and large chambers. In: New Zealand Society of Soil Science Conference 27–30 November. Rotorua, New Zealand, p 63.
- Ganzeveld, L.N., Lelieveld, J. (1995): Dry deposition parameterization in a chemistry-general circulation model and its influence on the distribution of chemically reactive trace gases. *J. Geophys. Res.*, **100**: 20999–21012.
- Garcia-Montiel, D., Steudler, P., Piccolo, M., Neill, C., Melillo, J., Cerri, C. (2003): Nitrogen oxide emissions following wetting of dry soils in forest and pastures in Rondônia, Brazil. *Biogeochem.*, **64**: 319–336.
- Gareia, M. (1984): *J. Soil Science*, **138**: 147–152.
- Garrido, F., Hénault, C., Gaillard, H., Perez, S., Germon, J.C. (2002): N₂O and NO emissions by agricultural soils with low hydraulic potentials. *Soil Biol. Biochem.*, **34**: 559–575.
- Gauer, L.E., Grant, C.A., Gehl, D.T., Bailey, L.D. (1992): Effects of nitrogen fertilization on grain protein content, nitrogen use efficiency of six spring wheat (*Triticum aestivum* L.) cultivars, in relation to estimated moisture supply. *Can. J. Plant Sci.*, **72**: 235–241.
- Gestel, M., Van Ladd, J.N., Amato, M. (1991): Carbon and nitrogen mineralization from two soils of contrasting texture and microaggregate stability: influence of sequential fumigation, drying and storage. *Soil Biol. Biochem.*, **23**: 313–322.
- Ghannoum, O., Von Caemmerer, S., Ziska, L.H., Conroy, J.P. (2000): The growth response of C₄ plants to rising atmospheric CO₂ partial pressure: a reassessment. *Plant Cell Environ.*, **23**: 931–942.
- Giller, K.E., Witter, E., McGrath, S.P. (1998): Toxicity of heavy metals to microorganisms and microbial processes in agricultural soil. *Soil Biol. Biochem.*, **30**, 1389–1414.
- Godbold, D.L., Kettner, C. (1991): Lead influences root growth and mineral nutrition of *Picea abies* seedlings. *J. Plant Physiol.*, **139**: 95–99.
- Gödde, M., Conrad, R. (1999): Immediate and adaptational temperature effects on nitric oxide production and nitrous oxide release from nitrification and denitrification. *Biol Fertil Soils*, **30**: 33–40.
- Gödde, M., Conrad, R. (2000): Influence of soil properties on the turnover of nitric oxide and nitrous oxide by nitrification and denitrification at constant temperature and moisture. *Biol. Fertil. Soils*, **32**: 120–128.
- Goek, M., Ottow, J.C.G. (1988): Effect of cellulose and straw incorporation in soil on total denitrification and nitrogen immobilization at initially aerobic and permanent anaerobic conditions. *Biol. Fertil. Soils*, **5**: 317–322.
- Goodroad, L.L., Keeney, D.R. (1984): Nitrous oxide production in aerobic soils under varying pH, temperature and water content. *Soil Biol. Biochem.*, **16**: 39–43.
- Goreau, T.J., Kaplan, W.A., Wofsy, S.C., McElroy, M.B., Valois, F.W., Watson, S.W. (1980): Production of NO₂ and N₂O by nitrifying bacteria at reduced concentrations of oxygen. *Appl. Environ. Microbiol.*, **40**: 526–532.
- Granli, T., Bøckmann, O.C. (1994): Nitrous oxide from agriculture. *Norw. J. Agric. Sci. Suppl.* **12**: 48–53.
- Groffman, P.M., Tiedje, J.M. (1989): Denitrification in north temperate forest soils: relationships between denitrification and environmental factors at the landscape scale. *Soil Biol. Biochem.*, **21**: 621–626.

- Groffman, P.M., Tiedje, J.M. (1991): Relationships between denitrification, CO₂ production and air-filled porosity in soils of different texture and drainage. *Soil Biol. Biochem.*, **23**: 299–302.
- Groffman**, P.M., Crawford, M.K. (2003): Denitrification potential in urban riparian zones. *J. Environ. Qua.*, **32**: 1144–1149.
- Groffman, P.M., Brumme, R., Butterbach-Bahl, K., Eobbie, K.E., Moser, A.R., Ojima, D., Papen, H. A., Parton, W.J., Smith, K.A., Wagner-Riddle, C. (2000): Evaluating annual nitrous oxide fluxes at the ecosystem scale. *Glob. Biogeochem. Cycl.*, **14**: 1061–1070.
- Grønlund, A., Hauge, A., Hovde, A., Rasse, D.P. (2008): Carbon loss estimates from cultivated peat soils in Norway: a comparison of three methods. *Nutr. Cycl. Agroecosyst.*, **81**: 157–167.
- Gumealius, L., Smith, E.H., Dalhammar, G. (1996): Potencial biomarker for denitrification of wastewater: effects of process variables and cadmium toxicity. *Water Res.*, **30**: 3025–3031.
- Gundersen, P. (1991): Nitrogen deposition and the forest nitrogen cycle: role of denitrification. *Forest Ecol. Manag.*, **44**: 15–28.
- Haag, D., Kaupenjohann, M. (2001): Landscape fate of nitrate fluxes and emissions in Central Europe – A critical review of concepts, data, and models for transport and retention. *Agric. Ecosyst. Environ.* **86**: 1–21.
- Hadi, A., Inubushi, K., Purnomo, E., Razie, F., Yamakawa, K., Tsuruta, H. (2000): Effect of land-use changes on nitrous oxide (N₂O) emission from tropical peatlands. *Chemosphere*, **2**: 347–358.
- Hall, J.L. (2002): Cellular mechanisms for heavy metal detoxification and tolerance. *J. Exp. Bot.*, **53**: 1–11.
- Hall, S.J., Matson, P.A. (1999): Nitrogen oxide emissions after nitrogen additions in tropical forests. *Nature*, **400**: 152–155.
- Hall, S.J., Matson, P.A., Roth, R. (1996): NO_x emission from soil: Implications for air quality modelling in agricultural regions. *Ann. Rev. Energy Environ.*, **21**: 311–346.
- Hall, S.J., Asner, G., Kitayama, K. (2004): Substrate, climate, and land use controls over soil N dynamics and N-oxide emissions in Borneo. *Biogeochem.*, **70**: 27–58.
- Hanson, P.J., Lindberg, S.E. (1991): Dry deposition of reactive nitrogen compounds: A review of leaf, canopy and non-foliar measurements. *Atmos. Environ.*, **25**: 1615–1634.
- Harris, G.W., Wienhold, F.G., Zenker, T. (1996): Airborne observation of strong biogenic NO_x emissions from the Namibian savanna at the end of the dry season. *J. Geophys. Res.* **101**: 23707–23711.
- Hatch, D., Goulding, K., Murphy, D. (2002): Nitrogen. *In: Agriculture, Hydrology, and Water Quality* (eds.: Haygarth, P.M., Jarvis, S.C.) 7–28. CABI Publishing, New York, NY.
- Haynes, R.J. (1986): Nitrification. *In: Mineral nitrogen in the plant–soil system.* (ed.: Haynes, R.J.) 127–165. Orlando, FL. Academic Press.
- Hedley, C.B., Saggar, S., Dando, J. (2002): Use of intact soil cores to assess the effect of soil water content on nitrous oxide emissions from a poorly drained pasture soil. *In: Back to the Future, New Zealand Soil Science Society Golden Jubilee Conference, Programme and Abstracts.* p 85, Victoria University, Wellington, New Zealand.
- Hedley, C.B., Saggar, S., Tate, K.R. (2006): Procedure for fast simultaneous analysis of the greenhouse gases: methane, carbon dioxide, and nitrous oxide in air samples. *Commun. Soil Sci. Plant Anal.*, **37**: 1501–1510.
- Herman, F., Smidt, S., Englisch, M., Feichtinger, F., Gerzabek, M., Haberhauer, G., Jandl, R., Kalina, M., Zechmeister-Boltenstern, S. (2002): Investigations of nitrogen fluxes and pools on a limestone site in the Alps. *ESPR – Environ. Sci. Pollut. Res.*, **2**: 46–52.
- Henrich, M., Haselwandter, K. (1997): Denitrification and gaseous nitrogen losses from an acid spruce forest soil. *Soil Biol. Biochem.*, **29**: 1529–1537.
- Henry, J.R. (2000): An Overview of Phytoremediation of Lead and Mercury. NNEMS Report. Washington, D.C.; pp, 3–9.
- Hénault, C., Devis, X., Lucas, J.L., Germon, J.C. (1998): Influence of different agricultural practices (type of crop, form of N-fertilizer) on soil nitrous oxide emission. *Biol. Fertil. Soils*, **27**: 299–306.

- Hénault, C., Bizouard, F., Laville, P., Gabrielle, B., Nicoulaud, B., Germon, J.C., Cellier, P. (2005): Predicting “*in situ*” soil N₂O emission using a NOE algorithm and soil database. *Glob. Change Biol.*, **11**: 115–127.
- Hernandez, L.E., Cárpena-Ruiz, R., Garate, A. (1996): Alternation in the mineral nutrition of pea seedlings exposed to cadmium. *J. Plant Nutr.*, **15**: 1981–1598.
- Hill, A.C. (1971): Vegetation: A sink for atmospheric pollutants. *J. Air Pollut. Control Ass.* **21**: 341–346.
- Hinojosa, M.B., García-Ruiz, R., Vinēgla, B., Carreira, J.A. (2004): Microbiological rates and enzyme activities as indicators of functionality in soils affected by the Aznalcóllar toxic spill. *Soil Biol. Biochem.*, **36**: 1637–1644.
- Hirsch, R.E., Lewis, B.D., Spalding, E.P., Sussman, M.R. (1998): A role for the AKT1 potassium channel in plant nutrition. *Science*, **280**: 918–921.
- Hogberg, P., Nordgren, A., Buchmann, N., Taylor, A.F.S., Ekblad, A., Hogberg, M.N. (2001): Large-scale forest girdling shows that current photosynthesis drives soil respiration. *Nature*, **411**: 789–792.
- Holland, E.A.; Lamarque, J.F. (1997): **Modeling bio-atmospheric coupling of the nitrogen cycle through NO_x emissions and NO_y deposition.** *Nutr. Cycl. Agroecosyst.*, **48**: 7–24.
- Holtan-Hartwig, L., Bechmann, M., Risnes Høyas, T., Linjordet, R., Reier Bakken, L. (2002): Heavy metals tolerance of soil denitrifying communities: N₂O dynamics. *Soil Biol. Biochem.*, **34**: 1181–1190.
- Hooper, A.B., Terry, K.R. (1979): Hydroxylamine oxidoreductase of *Nitrosomonas*: Production of nitric oxide from hydroxylamine. *Biochim. Biophys. Acta*, **571**: 12–20.
- Hooper, A.B., Arciero, D.M., DiSpirito, A.A., Fuchs, J., Johnson, M., LaQuier, F., Mundfrom, G., McTavish, H. (1990): Production of nitrite and N₂O by ammonia-oxidizing nitrifiers. *In: Nitrogen Fixation: Achievements and Objectives.* (eds.: Gresshoff, P.M., Roth, L.E., Stacey, G., Newton, W.E.) 387–392. Chapman & Hall, New York, London.
- Horváth, L., Führer, E., Lajtha K. (2005): Nitric oxide and nitrous oxide emission from Hungarian forest soils; link with atmospheric N-deposition. *Biogeosci. Discuss.*, **2**: 703–723.
- Hossain, A.K.M.A., Raison, R.J., Khanna, P.K. (1995): Effects of fertilizer application and fire regime on soil microbial biomass carbon and nitrogen, and nitrogen mineralization in an Australian subalpine eucalypt forest. *Biol. Fertil. Soils*, **19**: 246–252.
- Hou, A., Akiyama, H., Nakajima, Y., Sudo, S., Tsuruta, H. (2000): Effects of urea form and soil moisture on N₂O and NO emissions from Japanese Andosols. *Chemosphere*, **2**: 321–327.
- Houghton, J. (1997): *Global Warming: the Complete Briefing*, 2nd Edn. Cambridge University Press, Cambridge, UK.
- Houot, S., Chaussod, R. (1995): Impact of agricultural practices on the size and activity of the microbial biomass in a long-term field experiment. *Biol. Fertil. soils*, **19**: 309–316.
- Howard, D.M., Howard, P.J. (1993): Relationships between CO₂ evolution, moisture content and temperature for a range of soil types. *Soil Biol. Biochem.*, **25**: 1537–1546.
- Hutchinson, G.L. (1995): Biosphere-atmosphere exchange of gaseous N oxides. *In: Soils and Global Change.* (eds.: Lal, R., Kimble, J., Levine, E., Stewart, B.A.) 219–236. CRC Press, Inc., Boca Raton, FL.
- Hutchinson, G.L., Brams, E.A. (1992): NO versus N₂O emissions from an NH₄⁺ amended bermuda grass pasture. *J. Geophys. Res.*, **97**: 9889–9896.
- Hutchinson, G.L., Davidson, E.A. (1993): Processes for production and consumption of gaseous nitrogen oxides in soil. *In: Agricultural Ecosystem Effects on Trace Gases and Global Climate Change* (eds.: Harper, L.A., Mosier, A.R., Duxbury, J.M., Rolston, D.E.) 79–93. ASA, CSSA, SSSA, Spec. Publ. 55, Madison, WI.
- Hutchinson, G.L., Livingston, G.P., Brams, E.A. (1993): Nitric and nitrous oxide evolution from managed subtropical grassland. *In: The biogeochemistry of global change: Radiatively active trace gases* (ed.: Oremland, R.S.) 290–316. Chapman and Hall, New York.
- Hutchinson, G.L., Vigil, M.F., Doran, J.W., Kessavalou, A. (1997): Coarse-scale soil atmosphere NO_x exchange modeling: status and limitations. *Nutr. Cycl. Agroecosyst.*, **48**: 25–35.
- Hwang, S., Hanaki, K. (2000): Effects of oxygen concentration and moisture content refuse on nitrification, denitrification and nitrous oxide production. *Bioresource Technol.*, **71**: 159–165.

- Intergovernment Panel on Climate Change, IPCC (1997): Revised 1996 IPCC Guidelines for national greenhouse gas inventories. The Organisation for Economics Co-operation and Development, Paris.
- IPCC (1997): Intergovernmental panel on climate change guidelines for national greenhouse gas inventories chapter 4: agriculture: nitrous oxide from agricultural soils and manure management. OECD, Paris.
- IPCC (2000a): Land use, land use change and forestry IPCC. pp 377. Cambridge University Press, UK.
- IPCC (2000b): Special report on emissions scenarios. Cambridge University Press, Cambridge, UK.
- IPCC (2001a): Climate change 2001. The Scientific Basis. IPCC Third Assessment Report, IPCC Summary for Policy Makers. <http://www.ipcc.ch/pub/guide/htm>.
- IPCC (2001b): Climate Change 2001: Synthesis Report. A Contribution of Working Groups I, II, and III to the third Assessment Report of the IPCC (ed.: Watson, R.T.), the core Writing Team. Cambridge University Press, Cambridge United Kingdom, and New York, NY, USA, 398 pp.
- IPCC (2004): Intergovernmental Panel of Climate Change. <http://www.ipcc.ch/>.
- IPCC, WGIII (2007): Summary for policy makers. Working Group III contribution to the IPCC 4th Assessment Report. Climate Change 2007: Mitigation of Climate Change. Cambridge University Press, Cambridge.
- International Fertilizer Industry Association and Food and Agriculture Organization of the United Nations, IFA and FAO (2001): Global estimates of gaseous emissions of NH₃, NO and N₂O from agricultural land (based on work by Bouwman, A.F., Boumans, L.J.M., Batjes, N.H.). Rome. 106 pp.
- International Fertilizer Industry Association, IFA (1992): IFA World Fertilizer Use Manual. International Fertilizer Industry Association, Paris.
- Inubushi, K., Goyal, S., Sakamoto, K., Wada, Y., Yamakawa, K., Arai, T. (2000): Influences of application of sewage sludge compost on N₂O production in soils. *Chemosphere – Glob. Change Sci.*, **2**: 329–334.
- Isermann, K. (1994): Agriculture's share in the emission of trace gases affecting the climate and some cause-oriented proposals for sufficiently reducing this share. *Environ. Pollut.*, **83**: 95–111.
- Ishizuka, S., Tsuruta, H., Murdiyarso, D. (2002): An intensive field study on CO₂, CH₄, and N₂O emissions from soils at four land-use types in Sumatra, Indonesia. *Glob. Biogeochem. Cycl.*, **16**: 1049.
- Ishizuka, S., Iswandi, A., Nakajima, Y., Yonemura, L., Sudo, S., Tsuruta, H., Murdiyarso, D. (2005a) Spatial patterns of greenhouse gas emission in a tropical rainforest in Indonesia. *Nutr. Cycl. Agroecosyst.*, **71**: 55–62.
- Ishizuka, S., Iswandi, A., Nakajima, Y., Yonemura, S., Sudo, S., Tsuruta, H., Murdiyarso, D. (2005b): The variation of greenhouse gas emissions from soils of various landuse/cover types in Jambi province, Indonesia. *Nutr. Cycl. Agroecosyst.*, **71**: 17–32.
- Jacob, D.J., Bakwin, P.S. (1991): Cycling of NO_x in tropical forest canopies. *In: Microbial production and consumption of greenhouse gases: Methane, nitrogen oxide, and halomethanes* (eds.: Rogers, J.E., Whitman, W.B.) 237–253. American Society for Microbiology, Washington, DC.
- Jambert, C., Serça, D., Delmas, R. (1997): Quantification of N losses as NH₃, NO, and N₂O and N₂ from fertilized maize fields in southwestern France. *Nutr. Cycl. Agroecosyst.*, **48**: 91–104.
- Ji, G.L., Wang, J.H., Zhang, X.N. (2000): Environmental problems in soil and groundwater induced by acid rain and management strategies in China. *In: Soils and Groundwater Pollution and Remediation: Asia, Africa and Oceania* (eds.: Huang, P.M., Iskandar, I.K.) 201–224. CRC Press, London.
- Johansson, C. (1984): Field measurements of emission of nitric oxide from fertilized and unfertilized forest soils in Sweden. *J. Atmos. Chem.*, **1**: 429–442.

- Johansson, C. (1989): Fluxes of NO_x above soil and vegetation. In: Exchange of trace gases between terrestrial ecosystems and the atmosphere (eds.: Andreae, M.O., Schimel, D.S.) 229–246. John Wiley & Sons, New York.
- Johansson, C., Galbally, I.E. (1984): Production of nitric oxide in loam under aerobic and anaerobic conditions. *Appl. Environ. Microbiol.*, **47**: 1284–1289.
- Johansson, C., Granat, L. (1984): Emission of nitric oxide from arable land. *Tellus*, **36**: 25–37.
- Johansson, C., Sanhueza, E. (1988): Emission of NO from savanna soils during rainy season. *J. Geophys. Res.*, **93**: 14193–14198.
- Johansson, C., Rohde, H., Sanhueza, E. (1988): Emission of NO in a tropical savanna and a cloud forest during the dry season. *J. Geophys. Res.*, **93**: 7180–7192.
- Jolánkai, M., Birkás, M. (2005): Carbon Sequestration of Crops Influenced by Nitrogen Fertilization. Proceedings. 43rd Croatian and 3rd International Symposium on Agriculture. Opatija, Croatia. pp.: 540–543.
- Jolánkai, M., Máté, A., Nyárai, H.F. (2005): The carbon cycle: a sink-source role of crop plants. *Cereal Res. Commun.*, **33**: 13–17.
- Jolánkai, M., Nyárai, F.H., Farkas, I., Szentpétery, Zs. (2007): Agronomic impacts on energy crop performance. *Cereal Res. Commun.*, **35**: 537–540.
- Jones, C., Kiniry, J. (1986): CERES-N Maize: a simulation model of maize growth and development. Texas A&M University Press, College station.
- Jongen, M., Jones, M.B., Hebeisen, T., Blum, H., Hendrey, G. (1995): The effects of elevated CO₂ concentrations on the root growth of *Lolium perenne* and *Trifolium repens* grown in a FACE system. *Glob. Change Biol.*, **1**: 361–371.
- Jørgensen, B.J., Jørgensen, R.N. (1997): Field-scale and laboratory study of factors affecting N₂O emissions from a rye stubble field on sandy loam soil. *Biol. Fertil. Soils*, **25**: 366–371.
- Julistuti, S.R., Baeyens, J., Creemers, C., Bixio, C., Lodewyckx, E. (2003): The inhibitory effects of heavy metals and organic compounds on the net maximum specific growth rate of the autotrophic biomass in activated sludge. *J. Hazardous Materials*, **100**: 271–283.
- Kabata-Pendias, A., Pendias, H. (1984): Trace Elements in Soils and Plants, CRC Press Inc, Florida, pp. 154–163.
- Kaiser, E.A., Kohrs, K., Kücke, M., Schnug, E., Heinemeyer, O., Munch, J.C. (1998): Nitrous oxide release from arable soil: importance of N fertilisation, crops and temporal variation. *Soil Biol. Biochem.*, **30**: 1553–1563.
- Kakareka, S., Gromov, S., Pacyna, J., Kukharchyk, T. (2004): Estimation of heavy metal emission fluxes on the territory of the NIS. *Atmos. Environ.*, **38**: 7101–7109.
- Kampf, Gy., Kristóf, K., Algaidi, .A.A., Bayoumi Hamuda, H.E.A.F., Heltai, .Gy. (2007). Study of NO_x and CO₂ production of cultivated soil in closed microcosm experimental system. *Microchem. J.*, **85**: 31–38.
- Kanwar, J.S. (1972): *Fertil. News.*, **17**: 17.
- Kasimir-Klemedtsson, A., Klemedtsson, L., Berglund, K., Martikainen, P.J., Silvola, J., Oenema, O. (1997): Greenhouse gas emissions from farmed organic soils: a review. *Soil Use Manag.*, **13**: 245–250.
- Kastori, R., Petrovic, M., Petrovic, N. (1992): Effect of excess lead, cadmium, copper and zinc on water relations in sunflower. *J. Plant Nutr.*, **15**: 2427–2439.
- Kátai, J., Vágó, I., Lukács, V.E. (2005): Relationships between the carbon content and some microbial characteristics in the different soil types. *Cereal Res. Commun.*, **33**: 389–392.
- Keeney, D.R., Fillery, I.R., Marx, G.P. (1979): Effect of temperature on the gaseous nitrogen products of denitrification in a silt loam soil. *Soil Sci. Soc. Am. J.*, **43**: 1124–1128.
- Keller, M., Reiners, W.A. (1994): Soil atmosphere exchange of nitrous oxide, nitric oxide, and methane under secondary succession of pasture to forest in the Atlantic lowlands of Costa Rica. *Glob. Biogeochem Cycl.*, **8**: 399–409.
- Kennish, M.J. (1992): Ecology of Estuaries: Anthropogenic Effects. CRC Press, Inc., Boca Raton, FL.; pp. 494
- Kerr, R.A. (2005): How hot will the greenhouse world be. *Science*, **309**: 100.
- Kesik, M., Ambus, P., Baritz, R., Brüggemann, N., Butterbach-Bahl, K., Damm, M., Duyzer, J., Horváth, L., Kiese, R., Kitzler, B., Leip, A., Li, C., Pihlatie, M., Pilegaard, K., Seufert, G., Simpson, D., Skiba, U., Smiatek, G., Vesala, T., Zechmeister-Boltenstern, S. (2005):

- Inventories of N₂O and NO emissions from European forest soils. *Biogeosciences*, **2**: 353–375.
- Kester, R.A., de Boer, W., Laanbroek, H.J. (1996): Short exposure to acetylene to distinguish between nitrifier and denitrifier nitrous oxide production in soil and sediment samples. *FEMS Microbiol. Ecol.*, **20**: 111–120.
- Khalil, M.I., Rosenani, A.B., Cleemput, O.V., Boeckx, P., Shamshuddin, J., Fauziah, C.I. (2002): Nitrous oxide production from an ultisol of the humid tropics treated with different nitrogen sources and moisture regimes. *Biol. Fert. Soils*, **36**: 59–65.
- Kiese, R., Butterbach-Bahl, K. (2002): N₂O and CO₂ emissions from three different tropical forest sites in the wet tropics of Queensland, Australia. *Soil Biol. Biochem.*, **34**: 975–987.
- Kiese, R., Hewett, B., Graham, A., Butterbach-Bahl, K. (2003): Seasonal variability of N₂O emissions and CH₄ uptake by tropical rainforest soils of Queensland, Australia. *Glob. Biogeochem. Cycl.*, **17**: 1043. doi:10.1029/2002GB002014
- Kiese, R., Li, C., Hilbert, D., Papen, H., Butterbach-Bahl, K. (2005): Regional application of PnET-N-DNDC for estimating the N₂O source strength of tropical rainforests in the Wet Tropics of Australia. *Glob. Change Biol.*, **11**: 128–144.
- Kim, D.S., Aneja, V.P., Robarge, W.P. (1994): Characterization of nitrogen oxide fluxes from soil of a fallow field in the central Piedmont of North Carolina. *Atmos. Environ.*, **28**: 1129–1137.
- Kinney, C.A. (2002): Agricultural and biogeochemical influences on fluxes and stable isotope composition of trace gases from Colorado grassland soils. *In: Chemistry and Geochemistry*. Colorado School of Mines, Golden.
- Kinney, C.A., Mandernack, K.W., Mosier, A.R. (2005): Laboratory investigations into the effects of the pesticides mancozeb, chlorothalonil, and prosulfuron on nitrous oxide and nitric oxide production in fertilized soil. *Soil Biol. Biochem.*, **37**: 837–850.
- Kinney, C.A., Mosier, A., Ferrer-Felis, I., Furlong, E., Mandernack, K.W. (2004a): The effects of the fungicides mancozeb and chlorothalonil on fluxes of N₂O, CH₄, and CO₂ in a grassland soil. *J. Geophys. Res.*, **109**: No. D5, D05303 10.1029/2003JD003655.
- Kinney, C.A., Mosier, A., Ferrer-Felis, I., Furlong, E., Mandernack, K.W. (2004b): The effects of the herbicides prosulfuron and metolachlor on trace gas fluxes (CO₂, N₂O, and CH₄) in a Colorado grassland soil. *J. Geophys. Res.*, **109**: No. D5, D05304 10.1029/2003JD003656.
- Kitzler, B., Zechmeister-Boltenstern, S., Holtermann, C., Skiba, U., Butterbach-Bahl, K. (2006): Controls over N₂O, NO_x and CO₂ fluxes in a calcareous mountain forest soil. *Biogeosciences*, **3**: 383–395.
- Klemetsson, L., Svensson, B.H., Rosswall, T. (1987): Dinitrogen and nitrous oxide produced by denitrification and nitrification in soil with and without barley plants. *Plant and Soil*, **99**: 303–319.
- Klepper, L. (1979): Nitric oxide (NO) and nitrogen dioxide (NO₂) emissions from herbicide treated soybean plants. *Atmos. Environ.*, **13**: 537–542.
- Knowles, R. (2000): Nitrogen cycle. *In: Encyclopedia of Microbiology*. vol. **3**. 2nd ed (ed.: Lederberg, J.) 379–391. Academic, San Diego, CA.
- Koponen, H.T., Pertti, L.F., Martikainen, J. (2004): Nitrous oxide emissions from agricultural soils at low temperatures: a laboratory microcosm study. *Soil Biol. Biochem.*, **36**: 757–766.
- Kowalchuk, G.A., Stephen, J.R. (2001): Ammonia-oxidizing bacteria: a model for molecular microbial ecology. *Ann. Rev. Microbiol.*, **55**: 485–529.
- Krauss, A. (1999): Regional nutrient balances in view of sustainability of soil fertility and safeguarding natural sources. *In: 11th international World Fertilizer Congress of Fertilization for Sustainable Plant Production and Soil Fertility* (eds.: Van Cleemput, O., Haneklaus, S., Hofman, G., Schnug, E., Vermoesen, A.) 312–324. Get, Belgium. International Science Centre of Fertilizers (CIEC). Braunschweig, Vol. 1.
- Kroeze, C., Mosier, A., Bouwman, L. (1999): Closing the global N₂O budget: a retrospective analysis 1500–1994. *Glob. Biogeochem. Cycl.*, **13**: 1–8.
- Kuenen, G.J., Robertson, L.A. (1994): Combined nitrification-denitrification processes. *Microbiol. Rev.*, **15**: 109–117.
- Kulshreshtha, S.N., Bonneau, M., Boehm, M., Giraldez, J. (1999): Canadian Economic and Emissions Model for Agriculture. Economic and Policy Analysis Directorate Policy Branch, Agriculture and Agri-Food Canada. Ottawa, Canada. 102 pp.

- Kumar, U., Jain, M.C., Kumar, S., Majumdar, D. (2000): Role of nitrification inhibitors on nitrous oxide emissions in a fertilized alluvial clay loam under different moisture regimes. *Curr. Sci.*, **79**: 224–228.
- Læg Reid, M., Bøckman, O.C., Kaarstad, O. (1999a): Global challenge – to feed the people. *In: Agriculture, Fertilizer and the Environment*. 25–75. Norsk hydro ASA, Porsgrunn, Norway. No 12.
- Læg Reid, M., Bøckman, O.C., Kaarstad, O. (1999b): Concerns related to fertilizer use. *In: Agriculture, Fertilizer and the Environment*. 77–182. Norsk hydro ASA, Porsgrunn, Norway. No 12.
- Lal, R. (2004): Soil carbon sequestration impacts on global climate change and food security. *Science* **304**: 1623–1627.
- Lal, R. (2008): Soil carbon stocks under present and future climate with specific reference to European ecoregions. *Nutr. Cycl. Agroecosyst.*, **81**: 113–127.
- Lal, R., Kimble, J., Levine, E., Stewart, B.A. (1995): Soils and Global Change. *In: Advances in Soil Science*, Lewis publishers, Chelsea, MI, 440 pp.
- Lamb, D., Erskine, P.D., Parrota, J.A. (2005): Restoration of degraded tropical forest landscapes. *Science*, **310**: 1628–1632.
- La Scala, N., Marques, J., Pereira, G.T., Corá, J.E. (2000): Carbon dioxide emission related to chemical properties of a tropical bare soil. *Soil Biol. Biochem.*, **32**: 1469–1473.
- Laudelout, H., Germain, L., Chabalier, P.F., Chiang, C.N. (1977): Computer simulation of loss of fertilizer nitrogen through chemical decomposition of nitrite. *J. Soil Sci.*, **28**: 329–339.
- Laverman, A.M., Zoomer, H.R., Engelbrecht, D., Berg, M.P., van Straalen, N.M., van Verseveld, H.W., Verhoef, H.A. (2000): Soil layer-specific variability in net nitrification and denitrification in an acid coniferous forest. *Biol. Fertil. Soils*, **32**: 427–434.
- Laville, P., Jambert, C., Cellier, P., Delmas, R. (1999): Nitrous oxide fluxes from a fertilised maize crop using micrometeorological and chamber methods. *Agric. For. Meteorol.*, **96**: 19–38.
- Laville, P., Hénault, C., Gabrielle, B., Serça, D. (2005): Measurement and modelling of NO fluxes on maize and wheat crops during their growing seasons: effect of crop management. *Nutr. Cycl. Agroecosyst.*, **72**: 159–171.
- Leita, L., De-Nobil, M., Muhlbachova, G., Mondini, C., Zerbi, G. (1995): Bioavailability and effects of heavy metals on soil microbial biomass survival during laboratory incubation. *Biol. Fertil. Soils*, **19**: 103–108.
- Le Mer, J., Roger, P. (2001): Production, oxidation, emission and consumption of methane by soils: a review. *Eur. J. Soil Biol.*, **37**: 25–50.
- Lemke, R.L., Izaurralde, R.C., Nyborg, M., Solberg, E.D. (1999): Tillage and N source influence soil-emitted nitrous oxide in the Alberta Parkland region. *Can. J. Soil Sci.*, **79**: 15–24.
- Lemke, R.L., Zhong, Z., Campbell, C.A., Zentner, R. (2007): Can Pulse Crops Play a Role in Mitigating GHG from North American Agriculture? *Agron. J.*, **99**: 1719–1725.
- Lensi, R., Chalamet, A. (1979): Relations nitrate-oxyde nitreux lors de la dénitrification dans un sol hydromorphe. *Rev. Ecol. Biol. Soil.*, **16**: 315–323.
- Levine, J.S., Cofer III, W.R., Sebacher, D.I., Winstead, E.L., Sebacher, S., Boston, P.J. (1988): The effects of fire on biogenic soil emissions of nitric oxide and nitrous oxide. *Glob. Biogeochem. Cycl.*, **2**: 445–449.
- Li, C.S. (2000): Modeling trace gas emissions from agricultural ecosystems. *Nutr. Cycl. Agroecosyst.*, **58**: 258–276.
- Li, C.S., Frohling, S.E., Frohling, D.A. (1992a): A model of nitrous oxide evolution from soil driven by rainfall events: I. model structure and sensitivity, *J. Geophys. Res.*, **97**: 9759–9776.
- Li, C.S., Frohling, S.E., Frohling, D.A. (1992b): A model of nitrous oxide evolution from soil driven by rainfall events: II. model applications. *J. Geophys. Res.*, **97**: 9777–9783.
- Li, C.S., Frohling, S.E., Harriss, A.C., Terry, A.E. (1994): Modeling Nitrous Oxide Emissions from Agriculture: A Florida Case Study. *Chemosphere*, **28**: 1401–1415.
- Li, C.S., Aber, J., Stange, F., Butterbach-Bahl, K., Papen, H. (2000): A process-oriented model of N₂O and NO emissions from forest soils: 1. model development. *J. Geophys. Res. Atmos.*, **105**: 4369–4384.

- Li, X.D., Wai, O.W.H., Li, Y.S., Coles, B.J., Ramsey, H., Thornton, I. (2000): Heavy metal distribution in sediment profiles of the Pearl River estuary. *South China Appl. Geochem.*, **15**: 567–581.
- Linn, D.M., Doran, J.W. (1984): Effect of water-filled pore space on carbon dioxide and nitrous oxide production in tilled and nontilled soils. *Soil Sci. Soc. Am. J.*, **48**: 1667–1672.
- Liu, J., Li, K., Xu, J., Zhang, Z., Ma, T., Lu, X., Yang, J., Zhu, Q. (2003): Lead toxicity, uptake, and translocation in different rice cultivars. *Plant Sci.*, **165**: 793–802.
- Liu, S.C., Trainer, M., Fehsenfeld, F.C., Parish, D.D., Williams, E.J., Fahey, D.W., Hübler, G., Murphy, P.C. (1987): Ozone production in the rural troposphere and the implications for regional and global ozone distributions. *J. Geophys. Res.* **92**: 4191–4207.
- Lloyd, D., Boddy, L., Davies, K.J.P. (1987): Persistence of bacterial denitrification capacity under aerobic conditions: the rule rather than the exception. *FEMS Microbiol. Ecol.*, **45**: 185–190.
- Logan, J.A. (1983): Nitrogen oxides in the troposphere: Global and regional budgets. *J. Geophys. Res.* **88**: 10785–10807.
- Logan, J.A., Prather, M.J., Wofsy, S.C., McElroy, M.B. (1981): Tropospheric chemistry: A global perspective. *J. Geophys. Res.* **86**: 7210–7254.
- Ludwig, J. (1994): Untersuchungen zum Austausch von Stickoxiden zwischen Biosphäre und Atmosphäre. PhD Thesis, Universität Bayreuth, Bayreuth.
- Ludwig, J., Meixner, F.X. (1994): Surface exchange of nitric oxide (NO) over three European ecosystems. In: Proceedings of the Sixth European Symposium on the Physico-Chemical Behaviour of Atmospheric Pollutants (eds.: Angeletti, G., Restelli, G.) 587–593. Commission of the European Communities, Luxembourg.
- Ludwig, J., Weber, P., Meixner, F.X., Rennenberg, H. (1992): Surface fluxes of NO and NO₂ by a dynamic chamber technique – Laboratory studies on wheat. In: Field measurements and interpretation of species related to photooxidants and acid deposition (eds.: Angeletti, G., Beilke, S., Slanina, J.) 257–265. Commission of the European Communities, Brussels, Belgium.
- Ludwig, J., Meixner, F.X., Vogel, B., Förstner, J. (2001): Soil-air exchange of nitric oxide: An overview of processes, environmental factors, and modeling studies. *Biogeochem.*, **52**: 225–257.
- Lump, L.R. (2002): Reducing uncertainty about CO₂ as a climate driver. *Nature*, **419**: 188–190.
- Luo, J., Ledgard, S.F., Lindsay, S. (2007a): Nitrous oxide emissions from application of urea on New Zealand pasture. *N. Z. J. Agric. Res.*, **50**: 1–11.
- Luo, J., Saggar, S., Bhandral, R., Lindsay, S., Bolan, N.S., Qiu, W., Kear, M., Sun, W. (2007b): Nitrous oxide emissions from a livestock stand-off pad and from dairy farm effluent applied to pastoral soils. In: Proceedings for the annual New Zealand Land Treatment Collective Conference, Technical session (eds.: Wang, H., Quinter, M.) 139–149. 28. Rotorua, New Zealand.
- Maag, M., Vinther, F.P. (1996): Nitrous oxide emissions by nitrification and denitrification in different soil types and at different soil moisture contents and temperatures. *Appl. Soil Ecol.*, **4**: 5–14.
- Macfarlane, G.R., Burchett, M.D. (2001): Photosynthetic pigments and peroxidase activity as indicators of heavy metal stress in the greymangrove, *Avicennia marina* (Forsk.) Vierh. *Mar. Pollut. Bull.*, **42**: 233–240.
- Maggiotto, S.R., Webb, J.A., Wagner-Riddle, C., Thurtell, G.W. (2000): Nitrous and nitrogen oxide emissions from turfgrass receiving different forms of nitrogen fertilizer. *J. Environ. Qual.*, **29**: 621–630.
- Mahmood, T., Ali, R., Malik, K.A., Shamsi, S.R.A. (1998): Nitrous oxide emissions from an irrigated sandy-clay loam cropped to maize and wheat. *Biol. Ferti. Soils*, **27**: 189–196.
- Mahrt, L., Pan, H. (1984): A two-layer model of soil hydrology. *Boundary-Layer Meteorol.*, **29**: 1–20.
- Malhi, S.S., McGill, W.B., Nyborg, M. (1990): Nitrate losses in soils: effect of temperature, moisture and substrate concentration. *Soil Biol. Biochem.*, **22**: 733–737.
- Marja, M., Pertti, J.M., Heikki, A., Jouko, S. (2002): Short-term variation in fluxes of carbon dioxide, nitrous oxide and methane in cultivated and forested organic boreal soils. *Soil Biol. Biochem.*, **34**: 577–584.

- Maljanen, M., Martikainen, P.J., Waden, J., Silvola, J. (2001): CO₂ exchange in an organic field growing barley or grass in eastern Finland. *Glob. Change Biol.*, **7**: 679–692.
- Maljanen, M., Liikanen, A., Silvola, J., Martikainen, P.J. (2003): Nitrous oxide emissions from boreal organic soil under different land-use. *Soil Biol. Biochem.*, **35**: 689–700.
- Marschner, H. (1986): Mineral Nutrition of Higher Plants. 2nd edition. Academic Press. 889 pp.
- Martinez, C.E., Motto, H.L. (2000): Solubility of lead, zinc, and copper added to mineral soils. *Environ. Pollut.*, **107**: 153–158.
- Martinez, J.E., Duchon, C.E., Crosson, W.L. (2001): Effect of the number of soil layers on a modeled surface water budget. *Water Resour. Res.*, **37**: 367–377.
- Matson, P. (1997): NO_x emission from soils and its consequences for the atmosphere and biosphere: critical gaps and research directions for the future. *Nutr. Cycl. Agroecosyst.*, **48**: 1–6.
- Matthews, E. (1994): Nitrogenous fertilizers: Global distribution of consumption and associated emissions of nitrous oxide and ammonia. *Glob. Biogeochem. Cycl.*, **8**: 411–439.
- McElroy, M.B., Woofsy, S.C. (1985): Nitrous oxide sources and sinks: atmospheric ozone. vol. 1. NASA, Washington, 81 pp.
- McKenney, D.J., Drury, C.F. (1997): Nitric oxide production in agricultural soils. *Glob. Change Biol.*, **3**: 317–326.
- McKenney, D.J., Vriesacker, J.R., (1985): Effect of cadmium contamination on denitrification processes in Brookston clay and Fox sandy loam. *Environ. Pollut.*, **38**: 221–233.
- McKeeney, D.R., Fillery, I.R., Marx, J.P. (1979): Effect of temperature on the gaseous nitrogen products of denitrification in a silt loam soil. *Soil Sci. Soc. Am. J.*, **43**: 1124–1128.
- McKenney, D.J., Shuttleworth, K.F., Vriesacker, J.R., Findlay W.I. (1982): Production and loss of nitric oxide from denitrification in anaerobic Brookston clay. *Appl. Environ. Microbiol.*, **43**: 534–541.
- McKenney, D.J., Wang, S.W., Drury, C.F., Findlay, W.I. (1993): Denitrification and mineralization in soil amended with legume, grass, and corn residues. *Soil Sci. Soc. Am. J.*, **57**: 1013–1020.
- McLaughlin, M.J., Parker, D.R., Clarke, J.M. (1999): Metals and micronutrients-food safety issues. *Field Crop. Res.*, **60**: 143–163.
- McNeil, K. R., Waring, S. (1992): In Contaminated Land Treatment Technologies (ed.: Rees, J.F.), Society of Chemical Industry. Elsevier Applied Sciences, London; pp. 143–159.
- McTaggart, I., Clayton, H., Smith, K. (1994): Nitrous oxide emission from fertilized grassland: Strategies for reducing emissions. In: Non-CO₂ Greenhouse Gases. (ed.: Ham, J.) 421–426. Kluwer, Dordrecht.
- Meixner, F.X. (1994): Surface exchange of odd nitrogen oxides. *Nova Acta Leopoldina*, **70**: 299–348.
- Meixner, F.X. (1997): The surface exchange of nitric oxide. In: Measurements and modeling in environmental pollution (eds.: San, J.R., Brebbia, C.A.) 325–334. Computational Mechanics Publications, Southampton, UK.
- Meixner, F.X., Fickinger, T., Marufu, L., Serça, D., Nathaus, F.J., Makina, E., Mukurumbira, L., Andreae, M.O. (1997): Preliminary results on nitric oxide emission from a southern African savanna ecosystem. *Nutr. Cycl. Agroecosyst.*, **48**: 123–138.
- Merino, A., Pérez-Batallón, P., Macías, F. (2004): Responses of soil organic matter and greenhouse gas fluxes to soil management and land use changes in a humid temperate region of southern Europe. *Soil Biol. Biochem.*, **36**: 917–925.
- Merino, P., Estavillo, J.M., Besga, G., Pinto, M., González-Murua, C. (2001): Nitrification and denitrification derived N₂O production from a grassland soil under application of DCD and Actilith F2. *Nutr. Cycl. Agroecosyst.*, **60**: 9–14.
- Merry, R.H., Tiller, K.G., Alston, A.M. (1983): Accumulation of copper, lead and arsenic in Australian orchard soils. *Aust. J. Soil Res.*, **21**: 549–561.
- MI-08-1735-1990 (1990): A szennyvízben megengethető káros és mérgező komponensek határértékei szántóföldi szennyvízhasznosítás esetén.
- Mogge, B., Kaiser, E.A., Munch, J.C. (1999): Nitrous oxide emissions and denitrification N-losses from agricultural soils in the Bornhöved lake region: Influence of organic fertilizers and land-use. *Soil Biol. Biochem.*, **31**: 1245–1252.

- Moreno, J.L., Hernandez, T., Garcia, C. (1999): Effects of a cadmium-containing sewage sludge compost on dynamics of organic matter and microbial activity in an arid soils. *Biol. Fert. Soils*, **28**: 230–237.
- Morgan, A.J., Kille, P., Stürzenbaum, S.R. (2007): Microevolution and ecotoxicology of metals in invertebrates. *Environ. Sci. Technol.*, **41**: 1085–1096.
- Mosier, A.R. (1989): Chamber and isotope techniques. *In*: Exchange of trace gases between terrestrial ecosystems and the atmosphere (eds.: Andreae, M.O., Schimel, D.S.) 175–187. John Wiley & Sons, New York.
- Mosier, A.R., Mack, L. (1980): Gas-chromatographic system for precise, rapid analysis of nitrous-oxide. *Soil Sci. Soc. Am. J.*, **44**: 1121–1123.
- Mosier, A.R., Parton, W.J., (1985): Denitrification in a shortgrass prairie: a modeling approach, *In*: Planetary Ecology. (eds.: Caldwell, D.E., Brierley, J.A., Brierley, C.L.) 441–451. Van Nostrand Reinhold Co., New York.
- Mosier, A.R., Kroeze, C. (1998): A new approach to estimate emissions of nitrous oxide from agriculture and its implications for the global N₂O budget. *IGBP Newsletter*, **34**: 8–13.
- Mosier, A.R., Kroeze, C. (2000): **Potential impact on the global atmospheric N₂O budget of the increased nitrogen input required to meet future global food demands.** *Chemosphere*, **2**: 465–473.
- Mosier, A., Wassmann, R., Verchot, L., King, J., Palm, C. (2004): Methane and nitrogen oxide fluxes in tropical agricultural soils: sources, sinks and mechanisms. *Environ. Dev. Sustainabil.*, **6**: 11–49
- Mosier, A.R., Duxbury, J.M., Freeny, J.R., Heinemeyer, O., Minami, K. (1996): Nitrous oxide emissions from agricultural fields: Assessment, Measurement and Mitigation. *J. Plant Soil Sci.*, **181**: 95–108.
- Mosier, A.R., Parton, W.J., Valentine, D.W., Ojima, D.S., Schimel, D.S., Delgado, J.A. (1996): CH₄ and N₂O fluxes in the Colorado shortgrass steppe: 1. Impact of landscape and nitrogen addition. *Glob. Biogeochem. Cycl.*, **10**: 387–399.
- Mosier, A.R., Kroeze, C., Navison, C., Oenema, O., Seitzinger, S., van Cleemput, O. (1998): Closing the global atmospheric N₂O budget: nitrous oxide emissions through the agricultural nitrogen cycle. *Nutr. Cycl. Agroecosyst.*, **52**: 225–248.
- Moustakas, M., Lanaras, T., Symeonidis, L., Karataglis, S. (1994): Growth and some photosynthetic characteristics of field grown *Avena sativa* under copper and lead stress. *Photosynthetica*, **30**: 389–396.
- Mudri, G., Singh, M.K., Ujj, A., Ligetvári, F. (2005): Prevention and mitigation measure for climate change: Impacts on forest vegetation. *Cereal Res. Commun.*, **33**: 65–67
- Mummey, D.L., Smith, J.L., Bolton, H. Jr. (1994): Nitrous oxide flux from a shrub–steppe ecosystem: sources and regulation. *Soil Biol. Biochem.*, **26**: 279–286.
- Murillo, J.M., Marañón, T., Cabrera, F., Lopez, R. (1999): Accumulation of heavy metals in sunflower and sorghum plants affected by the Guadiamar spill. *Sci. Total Environ.*, **242**: 281–292.
- Myrold, D.D., Matson, P.A., Peterson, D.L. (1989): Relationships between soil microbial properties and aboveground stand characteristics of conifer forests in Oregon. *Biogeochem.*, **8**: 265–281.
- Nada, M., Govedarica, M., Mirjana, J., Petrovic, N. (1997): The effect of heavy metals on total soil microbiological activity in lettuce. *Acta Hort.*, **462**: 133–138.
- Nádasy, E., Nádasy, M. (2006): Some harmful or useful environmental effect of nitrogen fertilizers. *Cereal Res. Commun.*, **34**: 49–52.
- Nannipieri, P., Grego, S., Ceccanti, B. (1990): Ecological significance of the biological activity in soil. *Soil Biochem.*, **6**: 293–355.
- Needleman, H.L., Schell, A., Bellinger, D., Leviton, A., Allred, E. (1990): The long-term effects of exposure to low doses of lead in childhood: an 11-year follow-up report. *N. Engl. J. Med.*, **322**: 83–88.
- Neill, C., Piccolo, M.C., Steudler, P.A., Melillo, J.M., Feigl, B.J., Cerri, C.C. (1995): Nitrogen dynamics in soils of forests and active pastures in the western Brazilian Amazon Basin. *Soil Biol. Biochem.*, **27**: 1167–1175

- Nelson, D.W. (1982): Gaseous losses of nitrogen other than through denitrification. *In: Nitrogen in agricultural soils* (ed.: Stevenson, F.J.) 327–344. ASA, Madison, WI.
- Nelson, P.N., Ladd, J.N., Oades, J.M. (1996): Decomposition of ¹⁴C labelled plant material in salt-affected soil. *Soil Biol. Biochem.*, **28**: 433–441.
- Németh, T., AbdEl-Galil, A., Radimszky, L., Baczó, G.Y. (1996): Effect of plant residues on ammonium and nitrate content of soils during incubation. *In: Progress in Nitrogen Cycling Studies* (eds.: Van Cleemput, O., Hofman, G., Vermoesen, A.) 109–114. Kluwer, London.
- Nieder, R., Schollmayer, G., Richter, J. (1989): Denitrification in the rooting zone of cropped soils with regard to methodology and climate. *Biol. Fertil. Soils*, **8**: 219–226.
- Niess, D.H. (1999): Microbial heavy metal resistance. *Appl. Microbiol. Biotechnol.*, **51**: 730–750.
- Nishio, T., Fujimoto, T. (1990): Kinetics of nitrification of various amounts of ammonium added to soils. *Soil Biol. Biochem.*, **22**: 51–55.
- Noilhan, J., Mahfouf, J.F. (1996): The ISBA land surface parameterization scheme. *Glob. Planet Change*, **1–3**: 145–159.
- Nyborg, M., Laidlaw, J.W., Solberg, E.D., Malhi, S.S. (1997): Denitrification and nitrous oxide emissions from a Black Chernozemic soil during spring thaw in Alberta. *Can. J. Soil Sci.*, **77**: 153–160.
- Nykänen, H., Alm, J., Lång, K., Silvola, J., Martikainen, P.J. (1995): Emissions of CH₄, N₂O and CO₂ from a virgin fen and a fen drained for grassland in Finland. *J. Biogeogr.*, 351–357.
- Oliveira, A., Pampulha, E.M. (2006): Effects of long-term heavy metal contamination on soil microbial characteristics. **102**: 157–161.
- Otter, L.B., Yang, W.X., Scholes, M.C., Meixner, F.X. (1999): Nitric oxide emissions from a Southern African savanna. *J. Geophys. Res.*, **104**: 18,471–18,485.
- Pacala, S., Socolow, R. (2004): Stabilization wedges: solving the climate problem for the next 50 years with current technologies. *Science*, **305**: 968–972.
- Pajari, B. (1995): Soil CO₂ effluxes in a poor upland site of Scots pine stand subjected to elevated temperatures and atmospheric carbon concentration. *Plant and Soil*, **169**: 563–570.
- Papen, H., Butterbach-Bahl, K. (1999): A 3-year continuous record of nitrogen trace gas fluxes from untreated and limed soil of a N-saturated spruce and beech forest ecosystem in Germany 1. N₂O emissions. *J. Geophys. Res. Atmos.*, **104**: 18487–18503.
- Pathak, H., Nedwell, D.B. (2001): Nitrous oxide emission from soil with different fertilizers, water levels and nitrification inhibitors. *Water, Air, and Soil Pollut.*, **129**: 217–228.
- Patten, D.K., Bremner, J.M., Blackmer, A.M. (1980): Effects of drying and air-dry storage of soils on their capacity for denitrification of nitrate. *Soil Sci. Soc. Am. J.*, **44**: 67–70.
- Parton, W.J., Stewart, J.W.B., Cole, C.V. (1988a): Dynamics of C N P and S in grassland soils. A model. *Biogeochem.*, **5**: 109–131.
- Parton, W.J., Mosier, A.R., Schimel, D.S., (1988b): Rates and pathways of nitrous oxide production in a shortgrass steppe. *Biogeochem.*, **6**: 45–58.
- Parton, W.J., Mosier, A.R., Ojima, D.S., Valentine, D.W., Schimel, D.S., Weier, K., Kulmala, A.E. (1996): Generalized model for N₂ and N₂O production from nitrification and denitrification. *Glob. Biogeochem. Cycl.*, **10**: 401–412.
- Parton, W.J., Holland, E.A., Del Grosso, S.J., Hartman, M.D., Martin, R.E., Mosier, A.R., Ojima, D.S., Schimel, D.S. (2001): Generalized model for NO_x and N₂O emissions from soils. *J. Geophys. Res.*, **106**: 17403–17419.
- Paul, K.I., Polglase, P.J., Nyakuengama, J.G., Khanna, P.K. (2002): Change in soil carbon following afforestation. *Forest Ecol. Manag.*, **168**: 241–257.
- Payne, W.J. (1981): The status of nitric oxide and nitrous oxide as intermediates in denitrification. *In: Denitrification, nitrification, and atmospheric nitrous oxide* (ed.: Delwiche, C.C.) 85–103. Wiley-Interscience, New York.
- Peterjohn, W.T. (1991): Denitrification: enzyme content and activity in desert soils. *Soil Biol. Biochem.*, **23**: 845–855.
- Pérez, T., Romero, J., Sanhueza, E. (2007): Effect of conversion of natural grassland to cropland on nitric oxide emissions from Venezuelan savanna soils. A four-year monitoring study. *Nutr. Cycl. Agroecosyst.*, **77**: 101–113.
- Pilegaard, K., the NOFRETETE Team (2004): Nitrogen load and forest type determine soil emission of nitrogen oxides (NO and N₂O). *Geophys. Res. Abstr.*, **6**: No. 05693.

- Pinto, A.P., Mota, A.M., de Varennes, A., Pinto, F.C. (2004): Influence of organic matter on the uptake of cadmium, zinc, copper and iron by sorghum plants. *Sci. Tot. Environ.*, **326**: 239–247.
- Poth, M., Focht, D.D. (1985): ¹⁵N kinetic analysis of N₂O production by *Nitrosomonas europaea*: An examination of nitrifier denitrification. *Appl. Environ. Microbiol.*, **49**: 1134–1141.
- Potter, C.S., Davidson, E.A., Verchot, L.V. (1996a): Estimation of global biogeochemical controls and seasonality in soil methane consumption. *Chemosphere*, **32**: 2219–2246.
- Potter, C.S., Matson, P.A., Vitousek, P.M., Davidson, E.A. (1996b): Processes modeling of controls on nitrogen trace gas emissions from soil worldwide. *J. Geophys. Res.*, **101**: 1361–1377.
- Potter, C.S., Randerson, J.T., Field, C.B., Matson, P.A., Vitousek, P.M., Mooney, H.A., Klooster, S.A. (1993): Terrestrial ecosystem production: A process model based on global satellite and surface data. *Glob. Biogeochem. Cycl.*, **7**: 811–841.
- Prather, M., Ehhalt, D. (2001): Atmospheric chemistry and greenhouse gases. In: Climate change 2001: the scientific basis (eds.: Houghton, J., Ding, J., Griggs, M., Noguer, P., van der Linden, P., Xiaosu, D.) Ch. 4. Cambridge University Press.
- Prather, M., Ehhalt, D., Dentener, F., Derwent, R., Dlugokencky, E., Holland, E., Isaksen, I., Katima, J., Kirchhoff, P., Matson, P., Midgley, P., Wang, M. (2001): Atmospheric chemistry and greenhouse gases. In: Climate change 2001 the scientific basis. Contribution of Working Group I to the Third Assessment Report of the IPCC. (eds.: Houghton, J. T., Ding, Y., Griggs, D. J., Noguer, M., van der Linden, P. J., Dai, X., Maskell, K., Johnson C.A.) 240–287. Cambridge University Press, Cambridge, UK.
- Premié, A., Christensen, S. (2001): Natural perturbations, drying–wetting and freezing–thawing cycles, and the emissions of nitrous oxide, carbon dioxide and methane from farmed organic soils. *Soil Biol. Biochem.*, **33**: 2083–2091.
- Probanza, A., Gutiérrez Mañero, F.J., Ramos, B., Acero, N., Lucas, J.A.** (1996): Effect of heavy metals on soil denitrification and CO₂ production after short term incubation. *Microbiol.*, **12**: 417–24.
- Qi, Y., Xu, M. (2001): Separating the effects of moisture and temperature on soil CO₂ efflux in a coniferous forest in the Sierra Nevada mountains. *Plant and Soil*, **237**: 15–23.
- Raich, J.W. (1998): Aboveground productivity and soil respiration in three Hawaiian rain forests. *Forest Ecol. Manag.*, **107**: 309–318.
- Raich, J.W., Schlesinger, W.H. (1992): The global carbon dioxide flux in soil respiration and its relationship to vegetation and climate, *Tellus*, **44**: 81–99.
- Raich, J.W., Potter, C.S., Bhagawati, D. (2002): Interannual variability in global soil respiration 1980–1994. *Glob. Change Biol.*, **8**: 800–812.
- Remde, A., Conrad, R. (1990): Production of nitric oxide in *Nitrosomonas europaea* by reduction of nitrite. *Arch. Microbiol.*, **154**: 187–191.
- Remde, A., Conrad, R. (1991a): Metabolism of nitric oxide in soil and denitrifying bacteria. *FEMS Microbiol. Ecol.*, **85**: 81–93.
- Remde, A., Conrad, R. (1991b): Role of nitrification and denitrification for NO metabolism in soil. *Biogeochem.*, **12**: 189–205.
- Remde, A., Slemr, F., Conrad, R. (1989): Microbial production and uptake of nitric oxide in soil. *FEMS Microbiol. Ecol.*, **62**: 221–230.
- Remde, A., Ludwig, J., Meixner, F.X., Conrad, R. (1993): A study to explain the emission of nitric oxide from a marsh soil. *J. Atmos. Chem.*, **17**: 249–275.
- Renault, P., Sierra, J., (1994): Modelling oxygen diffusion in aggregated soils. 2. Anaerobiosis in topsoil layers. *Soil Sci. Soc. Am. J.*, **58**: 1023–1030.
- Reth, S., Graf, W., Gefke, O., Schilling, R., Seidlitz, H.K., Munch, J.C. (2008): Whole-year-round Observation of N₂O Profiles in Soil: A Lysimeter Study. *Water, Air, Soil Pollut.*, **8**: 129–137.
- Ritchie, G.A.F., Nicholas, D.J.D. (1972): Identification of the sources of nitrous oxide produced by oxidative and reductive processes in *Nitrosomonas euopea*. *Biochem. J.*, **126**: 1181–1191.
- Rillig, M.C., Mummey, D.L. (2006): Mycorrhizas and soil structure. *New Phytol.*, **171**: 41–53.

- Robertson, G.P. (1989): Nitrification and denitrification in humid tropical ecosystems: Potential controls on nitrogen retention. *In: Mineral nutrients in tropical forest and savanna ecosystems* (ed.: Procter, J.) 55–69. Blackwell Scientific, Boston, Mass.
- Robertson, G.P., Tiedje, J.M. (1987): Nitrous oxide sources in aerobic soils: nitrification, denitrification, and other biological processes. *Soil Biol. Biochem.*, **19**: 187–193.
- Robertson, L.A., Kuenen, J.G. (1990): Physiological and ecological aspects of aerobic denitrification, a link with heterotrophic nitrification? *In: Denitrification in Soils and Sediments* (eds.: Revsbech, N.P., Sørensen, J.) 91–104. Plenum Press, New York.
- Robertson, G.P., Vitousek, P.M., Matson, P.A., Tiedje, J.M. (1997): Denitrification in a clear-cut Loblolly pine (*Pinus taeda* L.) plantation in the southeastern US. *Plant and Soil*, **99**: 119–129.
- Robertson, L.A., Cornelisse, R., de Vos, P., Hadjioetomo, R., Kuenen, J.G. (1989): Aerobic denitrification in various heterotrophic nitrifiers. *Antoine van Leeuwenhoek*, **57**: 139–152.
- Roberson, T.K., Reddy, C., Reddy, S.S., Nyakatawa, E.Z., Raper, R.L., Reeves, D.W., Lemunyon J. (2008): Carbon dioxide efflux from soil with poultry litter applications in conventional and conservation tillage systems in Northern Alabama. *J. Environ. Qual.*, **37**: 535–541.
- Rogers, H.H., Runion, G.B., Krupa, S.V. (1994): Plant responses to atmospheric CO₂ enrichment with emphasis on roots and the rhizosphere. *Environ. Pollut.*, **83**: 155–189.
- Rolland, M.N., Gabrielle, B., Laville, P., Serça, D., Cortinovis, J., Larmanou, E., Lehuger, S., Cellier, P., (2008): Modeling of nitric oxide emissions from temperate agricultural soils. *Nutr. Cycl. Agroecosyst.*, **80**: 75–93.
- Röver, M., Heinemeyer, O., Kaiser, E.A. (1998): Microbial induced nitrous oxide emissions from an arable soil during winter. *Soil Biol. Biochem.*, **30**: 1859–1865.
- Rudaz, A.O., Waëlti, E., Kyburz, G., Lehmann, P., Fuhrer, J. (1999): Temporal variation in N₂O and N₂ fluxes from a permanent pasture in Switzerland in relation to management, soil water content and soil temperature. *Agric. Ecosyst. Environ.*, **73**: 83–91.
- Ruddiman, W.F. (2003): The anthropogenic greenhouse erabegan thousands of years ago. *Climatic Change*, **61**: 292–292.
- Rudolph, J., Conrad, R. (1996): Flux between soil and atmosphere, vertical concentration profiles in soil, and turnover of nitric oxide: 2. Experiments with naturally layered soil cores. *J. Atmos. Chem.* **23**: 275–300.
- Rudolph, J., Rothfuss, F., Conrad, R. (1996): Flux between soil and atmosphere, vertical concentration profiles in soil, and turnover of nitric oxide: 1. Measurements on a model soil core. *J. Atmos. Chem.* **23**: 253–273.
- Rusk, J.A., Hamon, R.E., Stevens, D.P., McLaughlin, M.J. (2004): Adaptation of soil biological nitrification to heavy metals. *Environ. Sci. Technol.*, **38**: 3092–3097.
- Russow, R., Sich, I., Neue, H.U. (2000): The formation of the trace gases NO and N₂O in soils by the coupled processes of nitrification and denitrification: results of kinetic ¹⁵N tracer investigations. *Chemosphere*, **2**: 359–366.
- Ruzicka, S., Edgerton, D., Norman, M., Hill, T. (2000): The utility of ergosterol as a bioindicator of fungi in temperate soils. *Soil Biol. Biochem.*, **32**: 989–1005.
- Ruz-Jerez, B.E., White, R.E., Ball, P.R. (1994): Long-term measurement of denitrification in 3 contrasting pastures grazed by sheep. *Soil Biol. Biochem.*, **26**: 29–39.
- Sadowsky, M.J., Schortemeyer, M. (1997): Soil microbial response to increased concentrations of atmospheric CO₂. *Glob. Change Biol.*, **3**: 217–224.
- Saggar, S., Tate, K.R., Hedley, C.B., Carran, R.A. (2004a): Methane emissions from cattle dung and methane consumption in New Zealand grazed pastures. *In: Proceedings of the Trace Gas Workshop 18–19 March 2004. Wellington, New Zealand*, pp 102–106.
- Saggar, S., Bolan, N.S., Bhandral, R., Hedley, C.B., Luo, J. (2004b): A review of emissions of methane, ammonia, and nitrous oxide from animal excreta deposition and farm effluent application in grazed pastures. *N. Z. J. Agric. Res.*, **47**: 513–544.
- Saggar, S., Andrew, R.M., Tate, K.R., Hedley, C.B., Rodda, N.J., Townsend, J.A. (2004c): Modelling nitrous oxide emissions from dairygrazed pastures. *Nutr. Cycl. Agroecosyst.*, **68**: 243–255.
- Saggar, S., Clark, H., Hedley, C.B., Tate, K.R., Carran, R.A., Rys, G. (2004d): Methane emission estimates from animal dung and waste management systems in New Zealand. *In:*

- Proceedings of the Trace Gas Workshop 18–19 March 2004. Wellington, New Zealand, pp.: 98–101.
- Saggar, S., Bhandral, R., Bolan, N.S., Luo, J. (2005): Nitrous oxide emissions from land-applied effluents. *In: 3rd Internat. N Conf.*, Nanjing, China (eds.: Zhu, Z., Minami, K., Xing, G.) 796–804. Science Press USA Inc.
- Saggar, S., Giltrap, D.L., Li, C., Tate, K.R. (2007a): Modelling nitrous oxide emissions from grazed grasslands in New Zealand. *Agric. Ecosyst. Environ.*, **119**: 205–216.
- Saggar, S., Hedley, C.B., Giltrap, D.L., Lambie, S.J. (2007b): Measured and modelled estimates of nitrous oxide emission and methane consumption from sheep-grazed pasture. *Agric. Ecosyst. Environ.*, **122**: 357–365.
- Saggar, S., Parshotam, A., Hedley, C., Salt, G. (1999): ¹⁴C-labelled glucose turnover in New Zealand soils. *Soil Biol. Biochem.*, **31**: 2025–2037.
- Saggar, S., Parshotam, A., Sparling, G.P., Feltham, C.W., Hart, P.B.S. (1996): ¹⁴C-labelled ryegrass in soils varying in clay content and mineralogy. *Soil Biol. Biochem.*, **28**: 1677–1686.
- Sahrawat, K.L., Keeney, D.R. (1986): Nitrous oxide emission from soils. *Adv. Soil Sci.*, **4**: 103–148.
- Sakadevan, K., Zheng, H., Bavor, H.J. (1999): Impact of heavy metals on denitrification in surface wetland sediments receiving wastewater. *Water Sci. Technol.*, **40**: 349–355.
- Sanhueza, E., Hao, W.M., Scharffe, D., Donoso, L., Crutzen, P.J. (1990): N₂O and NO emissions from soils of the northern part of the Guayana shield, Venezuela. *J. Geophys. Res.*, **95**: 22481–22488.
- Sanità di Toppi, L., Gabrielli, R. (1999): Response to cadmium in higher plants. *Environ. Exp. Bot.*, **41**: 105–130.
- Satoh, T.H., Hom, S.S.M., Shanmugam, K.T. (1981): Production of nitrous oxide as a product of nitrite metabolism by enteric bacteria. *In: Genetic Engineering of Symbiotic Nitrogen Fixation and Conservation of Fixed Nitrogen* (eds.: Lyons, J.M., Valentine, R.C., Phillips, D.A., Rains, D.W., Huffaker, R.C.) 481–497. Plenum Press, New York.
- Schafer, F., Conrad R. (1993): Metabolism of nitric oxide by *Pseudomonas stutzeri* in culture and in soil. *FEMS Microbiol. Ecol.*, **102**: 119–127.
- Schimel, J. (1995): Ecosystem consequences of microbial diversity and community structure. *Ecol. Stud.* (Berlin), **113**: 239–254.
- Schimel, J.P., Clein, J.S. (1996): Microbial response to freeze–thaw cycles in tundra and taiga soils. *Soil Biol. Biochem.*, **28**: 1061–1066.
- Schimel, D.S., Weintraub, M.N. (2003): The implications of exoenzyme activity on microbial carbon and nitrogen limitation in soil: a theoretical model. *Soil Biol. Biochem.*, **35**: 549–563.
- Schindlbacher, A., Zechmeister-Bolternstern, S., Butterbach-Bahl, K. (2004): Effects of soil moisture and temperature on NO, NO₂, and N₂O emissions from European forest ecosystems. *J. Geophys. Res.*, **109**: 1–12.
- Schmidt, I., Bock, E. (1998): Anaerobic ammonia oxidation by cell-free extracts of *Nitrosomonas eutropha*. *Antonie Leeuwenhoek*, **73**: 271–278.
- Schoun, H., Kim, D., Uchiyama, H., Sugiyama, J. (1992): Denitrification by fungi. *FEMS Microbiol. Lett.*, **94**: 277–282.
- Schortemeyer, M., Hartwig, U.A., Hendrey, G.R., Sadowsky, M.J. (1996): Microbial community changes in the rhizosphere of white clover and perennial ryegrass exposed to free air carbon dioxide enrichment (FACE). *Soil Biol. Biochem.*, **28**: 1717–1724.
- Schuster, M., Conrad, R. (1992): Metabolism of nitric oxide and nitrous oxide during nitrification and denitrification in soil at different incubation conditions. *FEMS Microbiol. Ecol.*, **101**: 133–143.
- Serça, D., Delmas, R., Jambert, C., Labroue, L. (1994): Emissions of nitrogen-oxides from equatorial rainforests in Central-Africa—Origin and regulation of NO emissions from soils. *Tellus*, **46**: 243–254.
- Sharma, A., Johri, B.N. (2003): Combat of iron-deprivation through a plant growth promoting fluorescent *Pseudomonas* strain GRP3A in mung bean (*Vigna radiata* L. Wilzeck). *Microbiol. Res.*, **158**: 77–81.

- Sharma, S., Szele, Z., Schilling, R., Munch, J. C., Schloter, M. (2006): Influence of freeze-thaw on the structure and function of microbial communities and denitrifying population in soil. *Appl. Environ. Microbiol.*, **72**: 2148–2154.
- Shelp, M.L., Beauchamp, E.G., Thurell, G.W. (2000): Nitrous oxide emissions from soil amended with glucose, alfalfa, or corn residues. *Commun. Soil Sci. Plant Ann.*, **31**: 877–892.
- Shepherd, M.F., Barzetti, S., Hastie, D.R. (1991): The production of atmospheric NO_x and N₂O from a fertilized agricultural soil. *Atmos. Environ.*, **25**: 1961–1969.
- Silbergeld, E.K., Waalkes, M., Rice, J.M. (2000): Lead as a carcinogen: experimental evidence and mechanisms of action. *Am. J. Ind. Med.*, **38**: 316–323.
- Silvola, J., Välijoki, J., Aaltonen, H. (1985): Effect of draining and fertilization on soil respiration at three ameliorated peatland sites. *Acta Forestalia Fennica*, **191**: 1–32.
- Simarmata, T., Penckiser, G., Ottow, J.C.G. (1991): The effect inorganic N in combination with straw or compost on denitrification losses (Acetylene inhibition technique) from a silty loam soil. *Mitteilgn. Dtsch. Bodenk. Ges.*, **66**: 731–734.
- Šimek, M., Cooper, J.E. (2002): The influence of soil pH on denitrification: progress towards the understanding of this interaction over the last 50 years. *Eur. J. Soil Sci.*, **53**: 345–354.
- Simojoki, A., Jaakkola, A. (2000): Effect of nitrogen fertilization, cropping and irrigation on soil air composition and nitrous oxide emission in a loamy clay. *Eur. J. Soil Sci.*, **51**: 413–424.**
- Singer, M.J., Munns, D. N. (1996): *Soils An Introduction*. 3rd Edition. Prentice Hall Inc. 480 pp.
- Singh, J., Saggar, S., Bolan, N. (2004): Mitigating gaseous losses of N from pasture soil with urease and nitrification inhibitors. *In: Proceedings of the Australia New Zealand Super Soil 2004 Conference, December 2004, Sydney, Australia* <http://www.regional.org.au/au/asssi>.
- Skiba, U., Smith, K.A. (2000): The control of nitrous oxide emissions from agricultural and natural soils. *Chemosphere*, **2**: 379–386.
- Skiba, U., Smith, K.A., Fowler, D. (1993): Nitrification and denitrification as sources of nitric oxide and nitrous oxide in a sandy loam soil. *Soil Biol. Biochem.*, **25**: 1527–1536.
- Skiba, U., Fowler, D., Smith, K.A. (1994): Emissions of NO and N₂O from soils. *Environ. Monitor. Assess.*, **31**: 153–158.
- Skiba, U., Fowler, D., Smith, K.A. (1997): Nitric oxide emissions from agricultural soils in temperate and tropical climates: sources, controls and mitigation options. *Nutr. Cycl. Agroecosyst.*, **48**: 139–153.
- Skiba, U., McTaggart, I.P., Smith, K.A., Hargreaves, K.J., Fowler, D. (1996): Estimates of nitrous oxide emissions in the UK. *Energy Convert. Manag.*, **37**: 1303–1308.
- Skopp, J., Jawson, M.D., Doran, J.W. (1990): Steady-state aerobic microbial activity as a function of soil water content. *Soil Sci. Soc. Am. J.*, **54**: 1619–1625.
- Slemr, F., Seiler, W. (1984): Field measurement of NO and NO₂ emissions from fertilized and unfertilized soils. *J. Atmos. Chem.*, **2**: 1–24.
- Slemr, F., Seiler, W. (1991): Field study of environmental variables controlling the NO emission from soil and the NO compensation point. *J. Geophys. Res.*, **96**: 13017–13031.
- Smith, K.A. (1980): A model of the extent of anaerobic zones in aggregated soils and its potential application to estimates of denitrification. *J. Soil Sci.*, **31**: 263–277.
- Smith, P. (2004): Carbon sequestration in croplands: the potential in Europe and the global context. *Eur. J. Agron.*, **20**: 229–236.
- Smith, P. (2008): Land use change and soil organic carbon dynamics. *Nutr. Cycl. Agroecosyst.*, **81**: 169–178.
- Smith, S.E., Read, D.J. (1997): *Mycorrhizal Symbiosis*, 2nd edn. Academic Press. London, UK.
- Smith, M.S., Tiedje, J.M. (1979): The effect of roots on soil denitrification. *Soil Sci. Soc. Am. J.*, **43**: 951–955.
- Smith, M.S., Parsons, L.L. (1985): Persistence of denitrifying enzyme activity in dried soils. *Appl. Environ. Microbiol.*, **49**: 316–320.
- Smith, P., Martino, D., Cai, Z. (2007): Policy and technological constraints to implementation of greenhouse gas mitigation options in agriculture. *Agric. Ecosyst. Environ.*, **118**: 6–28.
- Smith, K.A., Thompson, P.E., Clayton, H., McTaggart, L.P., Conen, F. (1998): Effect of temperature, water content and nitrogen fertilisation on emissions of nitrous oxide by soil. *Atmos. Environ.*, **32**: 3301–3309.

- Smith, K.A., Ball, T., Conen, F., Dobbie, K.E., Massheder, J., Rey, A. (2003): Exchange of greenhouse gases between soil and atmosphere: interactions of soil physical factors and biological processes. *Eur. J. Soil Sci.*, **54**: 779–791.
- Smolders, E., McGrath, S.P., Lombi, E., Karman, C.C., Bernhard, R., Cools, D., Van Den Brande, K., Van Os, B., Walrave, N. (2003): Comparison of toxicity of zinc for soil microbial processes between laboratory-contaminated and polluted field soils. *Environ. Toxicol. Chem.*, **22**: 2592–2598.
- Sommerfeld, R.A., Mosier, A.R., Musselman, R.C. (1993): CO₂, CH₄ and N₂O flux through a Wyoming snowpack and implications for global budgets. *Nature*, **361**: 140–142.
- Sprent, J.I. (2001): Nodulation in Legumes. Royal Bot. Gardens, Kew, UK.
- Stange, F., Butterbach-Bahl, K., Papen, H., Zechmeister-Boltenstern, S., Li, C., Aber, J. (2000): A process-oriented model of N₂O and NO emissions from forest soils 2. Sensitivity analysis and validation. *J. Geophys. Res. Atmos.*, **105**: 4385–4398.
- Stark, J.M., Firestone, M.K. (1995): Mechanisms for soil moisture effects on activity of nitrifying bacteria. *Appl. Environ. Microbiol.*, **61**: 218–221.
- Steffens, J.C. (1990): The heavy metal-binding peptide of plants. *Ann. Rev. Plant Physiol. Plant Mol. Biol.*, **41**: 553–575.
- Stehfest, E., Bouwman, L. (2006): N₂O and NO emissions from agricultural fields and soils under natural vegetation: summarizing available measurement data and modeling of global annual emissions. *Nutr. Cycl. Agroecosyst.*, **74**: 207–228.
- Stern, N. (2006): Stern review: the economics of climate change. Available at: <http://www.sternreview.org.uk>.
- Stuedler, P.A., Melillo, J.M., Feigl, B.J., Neill, C., Piccolo, M.C., Cerri, C.C. (1996): Consequence of forest-to-pasture conversion on CH₄ fluxes in the Brazilian Amazon Basin. *J. Geophys. Res. Atmos.*, **101**: 18547–18554.
- Stohl, A., Williams, E., Kromp-Kolb, G.W.H. (1996): An European inventory of soil nitric oxide emissions and the effect of these emissions on the photochemical formation of ozone. *Atmos. Environ.*, **30**: 3741–3755.
- Stohs, S.J., Bagchi, D. (1995): Oxidative mechanisms in the toxicity of metal ions. *Free Rad. Biol. Med.*, **18**: 321–336.
- Stoorvogel, J.J., Smaling, E.M.A. (1998): Research on soil fertility decline in tropical environments: integration of spatial scales. *Nutr. Cycl. Agroecosyst.*, **50**: 151–158.
- Stuczynski, T.I., McCarty, G.W., Siebielec, G. (2003): Response of soil microbiological activities to cadmium, lead, and zinc salt amendments. *J. Environ. Qual.*, **32**: 1346–1355.
- Sun, B., Chen, D., Li, Y., Wang, X. (2008): Nitrogen leaching in an upland cropping system on an acid soil in subtropical China: lysimeter measurements and simulation. *Nutr. Cycl. Agroecosyst.*, **81**: 291–303.
- Suzuki, I., Dular, U., Kwok, S.C. (1974): Ammonia and ammonium ion as substrate for oxidation by *Nitrosomonas* cells and extracts. *J. Bacteriol.*, **176**: 6623–6630.
- Sváb, J. (1981): Biometriai módszerek a kutatásban. Mezőgazdasági Kiadó, Budapest, pp. 37–355.
- Tanimoto, T., Hatano, K., Kim, D., Uchiyama, H., Shoun, H. (1992): Co-denitrification by the denitrifying system of the fungus *Fusarium oxysporum*. *FEMS Microbiol. Lett.*, **93**: 177–180.
- Tate, K.R., Ross, D.J., Scott, N.A., Rodda, N.J., Townsend, J.A., Arnold, G.C. (2006): Post-harvest patterns of carbon dioxide production, methane uptake and nitrous oxide production in a *Pinus radiata* D. Don plantation. *Forest Ecol. Manag.*, **228**: 40–50.
- Tate, K.R., Ross, D.J., Saggar, S., Hedley, C.B., Dando, J., Singh, B.K., Lambie, S.M. (2007): Methane uptake in soils from *Pinus radiata* plantations, a reverting shrubland and adjacent pastures: effects of land-use change, and soil texture, water and mineral nitrogen. *Soil Biol. Biochem.*, **39**: 1437–1449.
- Teepe, R., Brumme, R., Beese, F. (2000): Nitrous oxide emissions from frozen soils under agricultural, fallow and forest land. *Soil Biol. Biochem.*, **32**: 1807–1810.
- Teepe, R., Brumme, R., Beese, F. (2001): Nitrous oxide emissions from soil during freezing and thawing period. *Soil Biol. Biochem.*, **33**: 1269–1275.
- Tiedje, J.M. (1988): Ecology of denitrification and dissimilatory nitrate reduction to ammonium. In: *Biology of Anaerobic Microorganisms* (ed. Seinder, A.J.B.) 179–244. Wiley, New York.

- Tietema, A., van Dam, D. (1996): Calculating microbial carbon and nitrogen transformations in acid forest litter with ¹⁵N enrichment and dynamic simulation modeling. *Soil Biol. Biochem.*, **28**: 953–965.
- Thompson, A.M. (1992): The oxidizing capacity of the earth's atmosphere: probable past and future changes. *Science*, **256**: 1157–1165.
- Thornton, F.C., Valente, R.J. (1996): Soil emissions of nitric oxide and nitrous oxide from no-till corn. *Soil Sci. Soc. Am. J.*, **60**: 1127–1133.
- Thornton, F.C., Shurpall, N.J., Bock, B.R., Reddy, K.C. (1998): N₂O and NO emission from poultry litter and urea applications to Bermuda grass. *Atmos. Environ.*, **32**: 1623–1630.
- Tilman, D., Fargione, J., Wolff, B., D'Antonio, C., Dobson, A., Howarth, A., Schindler, D., Schlesinger, W.H., Simberloff, D., Swackhamer, D. (2001): Forecasting agriculturally driven global environmental change. *Science*, **292**: 281–284.
- Todd, A.C., Wetmur, J.G., Moline, J.M., Godbold, J.H., Levin, S.M., Landrigan, P.J. (1996): Unraveling the chronic toxicity of lead: an essential priority for environmental health. *Environ. Health Perspec.*, **104**: 141–146.
- Topp, E., Pattey, E. (1997): Soils as sources and sink for atmospheric methane. *Can. J. Soil Sci.*, **77**: 167–178.
- Tortoso, A.C., Hutchinson, G.L. (1990): Contributions of autotrophic and heterotrophic nitrifiers to soil NO and N₂O emissions. *Appl. Environ. Microbiol.*, **56**: 1799–1805.
- Trevors, J.T., Stratton, G.W., Gadd, G.M. (1986): Cadmium transport, resistance, and toxicity in bacteria, algae, and fungi. *Can. J. Bacteriol.*, **32**: 447.
- Troeh, F.R., Thompson, L.M. (1993): *Soils and Soil Fertility*. 5th edn. Oxford University Press. New York, New York. 462 pp.
- Tsuruta, S., Takaya, N., Zhang, L., Shoun, H., Kimura, K., Hamamoto, M., Nakase, T. (1998): Denitrification by yeasts and occurrence of cytochrome P450nor in *Trichosporon cutaneum*. *FEMS Microbiol. Lett.*, **168**: 105–110.
- Tu, C.M. (1994): Effects of fungicides on microbial activities in sandy soil. *Internat. J. Environ. Health Res.*, **4**: 133–140.
- Tyler, G., Tyler, G. (1981): Heavy metals in soil biology and biochemistry. In: *Soil Biochemistry* (eds.: Paul, E.A., Ladd, J.N.) 371–414. Marcel Dekker, New York.
- United States Environmental Protection Agency, USEPA (1997): *Ecological Risk Assessment Guidance for Superfund: Process for Designing and Conducting Ecological Risk Assessments*. Interim Final. U.S. Environmental Protection Agency, Environmental Response Team (ed.: Edison, N.J.). June 5, 1997.
- United States Environmental Protection Agency, USEPA (1998): *Guidelines for Ecological Risk Assessment*. Risk Assessment Forum. U.S. Environmental Protection Agency, Washington DC. EPA/630/R-95/002F. April. May 14, 1998 Federal Register **63**: 26846–26924.
- United States Environmental Protection Agency, USEPA (1999): *Ecological Risk Assessment and Risk Management Principles for Superfund Sites*. Office of Emergency and Remedial Response, Washington, DC. OSWER Directive 92857–28.
- United States Environmental Protection Agency, USEPA (2003): *Guidance for Developing Ecological Soil Screening Levels*. November. Office of Solid Waste and Emergency and Remedial Response. OSWER Directive 92857–55.
- United Nations Framework Convention on Climate Change, UNFCCC (2004a): Kyoto Protocol. http://unfccc.int/essential_background/kyoto_protocol/items/2830.phf.
- UNFCCC. (2004b): http://unfccc.int/files/essential_background/application/pdf/beginner_02_en.pdf.
- UNFCCC. (1998): Review of the implementation of commitment and of other provisions of the convention. Review of information communicated under Article 12. National Communication from parties included in the annex 1 to the convention. Summary compilation of annual greenhouse gas emissions inventory data from Annex I Parties. Note by the secretariat. United Nations Framework Convention on Climate Change. Conference of the Parties. <http://unfccc.de>.
- UNFCCC. (1992): United Nations Framework Convention on Climate Change, <http://www.unfccc.de/resource/conv/index.htm>.

- Upendra, M.S., Jabro, J.D., William, B.S. (2008): Soil carbon dioxide emission and carbon content as affected by irrigation, tillage, cropping system, and nitrogen fertilization. *J. Environ. Qual.*, **37**: 98–106.
- Valente, R.J., Thornton, F.C. (1993): Emissions of NO from soil at a rural site in Central Tennessee. *J. Geophys. Res.*, **98**: 16745–16753.
- Van Cleemput, O., Baert, L. (1984): Nitrite: a key compound in N loss processes under acid conditions? *Plant and Soil*, **76**: 233–241.
- Van Cleemput, O., Samater, A.H. (1996): Nitrite in soils: Accumulation and role in the formation of gaseous N compounds. *Fertil. Res.*, **45**: 81–89.
- Van der Heijden, M.G.A., Bardgett, R.D., van Straalen, N.M. (2008): The unseen majority: soil microbes as drivers of plant diversity and productivity in terrestrial ecosystems. *Ecol. Lett.*, **11**: 296–310.
- Van der Ploeg, R.R., Machulla, G., Ringe, H. (1995): Ein Mischzellenmodell zur Abschätzung der Nitratauswaschung aus landwirtschaftlich genutzten Böden im Winterhalbjahr. *Z. Pflanzenernähr Bodenkd.* **158**: 365–373.
- Van Veen, J.A., Ladd, J.N., Amato, M. (1985): Turnover of carbon and nitrogen through the microbial biomass in a sandy loam and a clay soil incubated with [¹⁴C(U)] glucose and [¹⁵N] (NH₄)₂SO₄ under different moisture regimes. *Soil Biol & Biochem*, **17**: 747–756.
- Vágó, I., Kátai, J., Kovács, A.B. (2005): Changes in the carbon cycle parameters in a pot experiment under ryegrass. *Cereal Res. Commun.*, **33**: 381–384.
- Vásquez-Murrieta, M.S., Cruz-Mondragón, C., Trujillo-Tapia, N., Herrera-Arreola, G., Govaerts, B., Cleemput, O. Van, Dendooven, L. (2006): Nitrous oxide production of heavy metal contaminated soil. *Soil Biol. Biochem.*, **38**: 931–940.
- Veldkamp, E., Keller, M. (1997): Fertilizer-induced nitric oxide emissions from agricultural soils. *Nutr. Cycl. Agroecosyst.*, **48**: 69–77.
- Velthof, G.L., Oenema, O. (1995): Nitrous oxide fluxes from grassland in the Netherlands: II. Effects of soil type, nitrogen fertilizer application and grazing. *Eur. J. Soil Sci.*, **46**: 541–549.
- Venterea, R.T., Rolston, D.E. (2000): Mechanistic modeling of nitrite accumulation and nitrogen oxide gas emissions during nitrification. *J. Environ. Qual.*, **29**: 1741–1751.
- Verchot, L.V., Davidson, E.A., Cattânio, J.H., Ackerman, I.L., Erickson, H.E., Keller, M. (1999): Land use change and biogeochemical controls of nitrogen oxide emissions from soils in eastern Amazonia. *Glob. Biogeochem. Cycl.*, **13**: 31–46.
- Verhagen, A.J., Bouma, J. (1998): Defining threshold values for residual soil N levels. *Geoderma*, **85**: 199–211.
- Verma, S., Dubey, R.S. (2003): Lead toxicity induces lipid peroxidation and alters the activities of antioxidant enzymes in growing rice plants. *Plant Science*, **164**: 645–655.
- Vermes, J.F., Myrold, D.D. (1992): Denitrification in forest soils of Oregon. *Can. J. For. Res.*, **22**: 504–512.
- Vermoesen, A., de Groot, C.J., Nollet, L., Boeckx, P., Cleemput, O. (1996): Effect of ammonium and nitrate application on the NO and N₂O emission out of different soils. *Plant and Soil*, **181**: 153–162.
- Vig, K., Megharaj, M., Sethunathan, N., Naidu, R. (2003): Bioavailability and toxicity of cadmium to microorganisms and their activities in soil. *Adv. Environ. Res.*, **8**: 121–135.
- Vinther, F.P. (1984): Total denitrification and the ratio between N₂O and N₂ during the growth of spring barley. *Plant and Soil*, **76**: 227–232.
- Vitousek, P., Matson, C., Volkman, C., Maass, M., Garcia, G. (1989): Nitrous oxide flux from dry tropical forests. *Glob. Biogeochem. Cycl.*, **3**: 375–382.
- Vogel, B., Fiedler, F., Vogel, H. (1995): The influence of topography and biogenic VOC emissions in the state of Baden-Württemberg on the ozone concentrations during episodes of high air temperature. *J. Geophys. Res.*, **100**: 22907–2298.
- Vos, G.J.M., Bergevoet, I.M.J., Vedy, J.C., Neyroud, J.A. (1994): The fate of spring applied fertilizer N during the autumn-winter period: Comparison between winter-fallow and green manure cropped soil. *Plant and Soil*, **160**: 201–214.

- Wagner-Riddle, C., Thurtell, G.W., Kidd, G.K., Beauchamp, E.G., Sweetman, R. (1997): Estimates of nitrous oxide emissions from agricultural fields over 28 months. *Can. J. Soil Sci.*, **77**: 135–144.
- Wang, X., Wu, Y.Y. (1997): Behavior property of heavy metals in soil-rice system. *Chinese J. Ecol.*, **16**: 10–14.
- Wardle, D.A., Parkinson, D. (1991): Analysis of co-occurrence in a fungal community. *Mycol. Res.*, **95**: 504–507.
- Warneck, P. (1988): Chemistry of the natural atmosphere, Academic Press, San Diego, Calif., USA.
- Wasserman, G.A., Liu, X., Lolocono, N.J., Factor-Litvak, P., Kline, J.K., Popovac, D., Morina, N., Musabegovic, A., Vrenezi, N., Capuni-Paracka, S., Lekic, V., Preteni-Redjepi, E., Hadzialjevic, S., Slavkovich, V., Graziano, J.H. (1997): Lead exposure and intelligence in 7-year-old children: the Yugoslavia prospective study, *Environ. Health Perspect.*, **105**: 956–962.
- Weathers, P.J. (1984): N₂O evolution by green algae. *Appl. Environ. Microbiol.*, **48**: 1251–1253.
- Webster, E.A., Hopkins, D.W. (1996): Contributions from different microbial processes to N₂O emission from soil under different moisture regimes. *Biol. Fertil. Soils*, **22**: 331–335.
- Weier, K.L., MacRae, I.C., Myers, R.J.K. (1993): Denitrification in a clay soil under pasture and annual crop: Losses from ¹⁵N-labelled nitrate in the subsoil in the field using C₂H₂ inhibition. *Soil Biol. Biochem.*, **25**: 999–1004.
- Weiske, A., Benckiser, G., Herbert, T., Ottow, J.C.G. (2001): Influence of the nitrification inhibitor 3,4-dimethylpyrazole phosphate (DMPP) in comparison to dicyandiamide (DCD) on nitrous oxide emissions, carbon dioxide fluxes and methane oxidation during 3 years of repeated application in field experiments. *Biol. Fertil. Soils*, **34**: 109–117.
- Werner, C., Zheng, X., Tang, J., Xie, B., Liu, C., Kiese, R., Butterbach-Bahl, K. (2006): N₂O, CH₄ and CO₂ emissions from seasonal tropical rainforests and a rubber plantation in Southwest China. *Plant and Soil*, **289**: 335–353.
- West, R.C. (1984): CRC Handbook of Chemistry and Physics. 64th edn. RCR Press, Boca Raton.
- Wildt, J., Kley, D., Rockel, A., Rockel, P., Segschneider, H.J. (1996): Emission of NO from several higher plant species. *J. Geophys. Res.*, **102**: 5919–5927.
- Williams, J.R. (1995): The EPIC model. In: Computer models of watershed hydrology (ed.: Singh, V.P.). Water Resources Publications, Highlands Ranch.
- Williams, E., Fehsenfeld, F. (1991): Measurement of soil nitrogen oxide emissions at three North American ecosystems. *J. Geophys. Res.*, **96**: 1033–1042.
- Williams, E.J., Parrish, D.D., Fehsenfeld, F.C. (1987): Determination of nitrogen oxide emissions from soils: Results from a grassland site in Colorado, United States. *J. Geophys. Res.*, **92**: 2173–2179.
- Williams, E.J., Guenther, A., Fehsenfeld, F.C. (1992a): An inventory of nitric oxide emissions from soils in the United States. *J. Geophys. Res.*, **97**: 7511–7519.
- Williams, E.J., Hutchinson, G.L., Fehsenfeld, F.C. (1992b): NO_x and N₂O emissions from soil. *Glob. Biogeochem. Cycl.*, **6**: 351–388.
- Williams, P.H., Jarvis, S.C., Dixon, E. (1998): Emission of nitric oxide and nitrous oxide from soil under field and laboratory conditions. *Soil Biol. Biochem.*, **30**: 1885–1893.
- Williams, E.J., Parrish, D.D., Buhr, M.P., Fehsenfeld, F.C., Fall, R. (1988): Measurement of soil NO_x emissions in central Pennsylvania. *J. Geophys. Res.*, **93**: 9539–9546.
- World Meteorological Organization, WMO (2006): Greenhouse gas bulletin: the state of greenhouse gases in the atmosphere using global observations up to December 2004. Env. Div., Geneva.
- Wolf, I., Brumme, R. (2002): Contribution of nitrification and denitrification sources for seasonal N₂O emissions in an acid German forest soil. *Soil Biol. Biochem.*, **34**: 741–744.
- Wong, S.C., Li, X.D., Zhang, G., Qi, S.H., Min, Y.S. (2000): Heavy metal in agricultural soils of the Pearl River Delta. South China. *Environ. Pollut.*, **119**: 33–44.
- Wrage, N. (2003): Pitfalls in measuring nitrous oxide production in nitrifiers. PhD Thesis. Wageningen University, Wageningen, The Netherlands. ISBN 990-5808-781-6. 140p.

- Wrage, N., Velthof, G.L., Laanbroek H.J., Oenema, O. (2004): Nitrous oxide production in grassland soils: assessing the contribution of nitrifier denitrification. *Soil Biol. Biochem.*, **36**: 229–236.
- Wrage, N., Velthof, G.L., van Beusichem, M.L., Oenema, O. (2001): Role of nitrifier denitrification in the production of nitrous oxide. *Soil Biol. Biochem.*, **33**: 1723–1732.
- Wulf, S., Lehmann, J., Zech, W., (1999): Emissions of nitrous oxide from runoff irrigated and rainfed soils in semiarid north-west Kenya. *Agric. Ecosyst. Environ.*, **72**: 201–205.
- Yamulki, S., Goulding, K.W.T., Webster, C.P., Harrison, R.M. (1995): Studies of NO and N₂O fluxes from a wheat field. *Atmos. Environ.*, **29**: 1627–1635.
- Yan, X., Ohara, T., Akimoto, I. (2005): Statistical modeling of global soil NO_x emissions. *Glob. Biogeochem. Cycl.*, **19**:GB3019.
- Yan, X., Shimizu, K., Akimoto, H., Ohara, T. (2003): Determining fertilizer-induced NO emission ratio from soils by a statistical distribution model. *Biol. Fertil. Soils*, **39**: 45–50.
- Yang, W.X., Meixner, F.X. (1997): Laboratory studies on the release of nitric oxide from subtropical grassland soils: The effect of soil temperature and moisture. *In: Gaseous Nitrogen Emissions from Grasslands* (eds.: Jarvis, S.C., Pain, B.F.) 67–71. CAB International, Wallingford, UK.
- Yang, X.M., Drury, C.F., Zhang, T.Q., Ajakaiye, A., Forsberg, C.W., Fan, M.Z., Philip, J.P. (2008): Short-term carbon dioxide emissions and denitrification losses from soils amended with low-P manure from genetically modified pigs. *Nutr. Cycl. Agroecosyst.*, **80**: 153–160.
- Yano, Y., McoDowell, W.H., Kinner, N.E. (1998): Quantification of biodegradable dissolved organic carbon in soil solution with flowthrough bioreactors. *Soil Sci. Soc. Am. J.*, **62**: 1556–1564.
- Yienger, J.J., Levy, H. (1995): Empirical model of global soil biogenic NO_x emissions. *J. Geophys. Res.*, **100**: 11447–11464.
- Yoshida, T., Alexander, M. (1970): Nitrous oxide formation by *Nitrosomonas europaea* and heterotrophic microorganisms. *Soil Sci. Soc. Am. Proc.*, **34**: 880–882.
- Zak, D.R., Pregitzer, K.S., Curtis, P.S., Holmes, W.E. (1993): Elevated atmospheric CO₂ and feedback between carbon and nitrogen cycles. *Plant and Soil*, **151**: 105–117.
- Zechmeister-Boltenstern, S., Hahn, M., Meger, S., Jandl, R. (2002): Nitrous oxide emissions and nitrate leaching in relation to microbial biomass dynamics in a beech forest soil. *Soil Biol. Biochem.*, **34**: 823–832.
- Zheng, X., Wang, M., Wang, Y., Shen, R., Gou, J., Li, J., Jin, J., Li, L. (2000): Impacts of soil moisture on nitrous oxide emission from croplands: a case study on the rice-based agroecosystem in Southeast China. *Chemosphere*, **2**: 207–224.
- Zheng, X., Fu, C., Xu, X., Yan, X., Huang, Y., Chen, G., Han, S., Hu, F. (2002): The Asian nitrogen cycle case study. *Ambio*, **31**: 79–87.
- Zhou, Z., Takaya, N., Sakairi, M.A.C., Shoun, H. (2001): Oxygen requirement for denitrification by the fungus *Fusarium oxysporum*. *Arch. Microbiol.*, **175**: 19–25.
- Zumft, W.G. (1997): Cell biology and molecular basis of denitrification. *Microbiol. Mol. Biol. Rev.*, **61**: 533–616.

14. APPENDIX

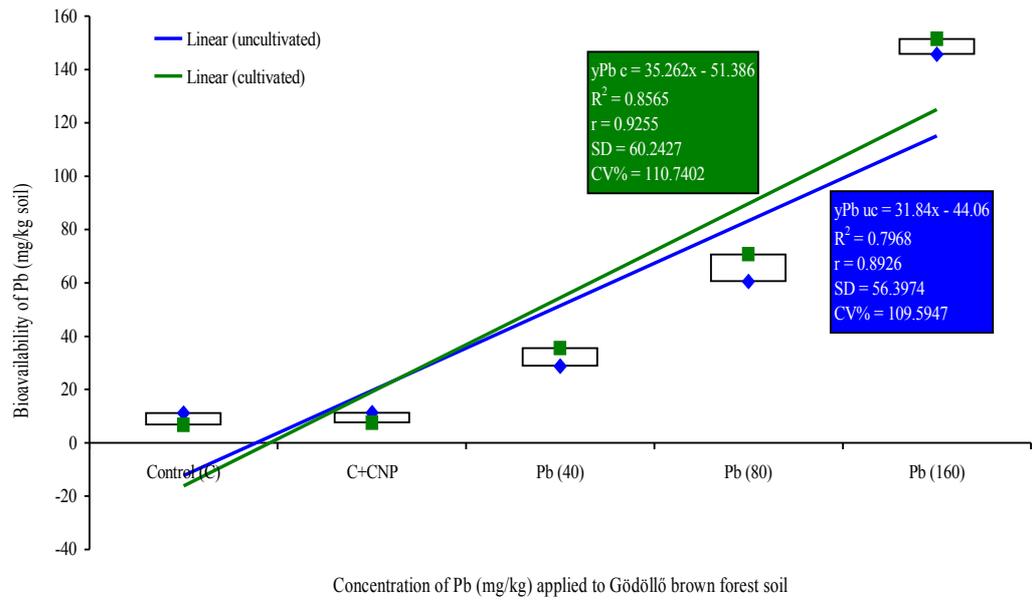


Fig. A-1. Linear regression and other statistical determinants indicate the relationships between the different Pb doses applied to cultivated (c) and uncultivated (uc) brown forest soils (Gödöllő) and its bioavailability

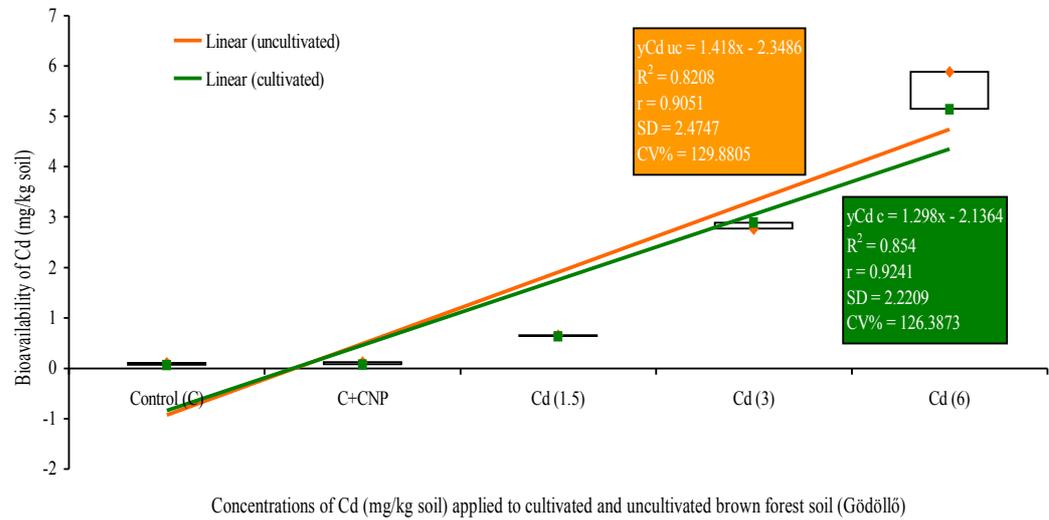


Fig. A-2. Linear regression and other statistical determinants indicate the relationships between the different Cd doses applied to cultivated (c) and uncultivated (uc) brown forest soils (Gödöllő) and its bioavailability

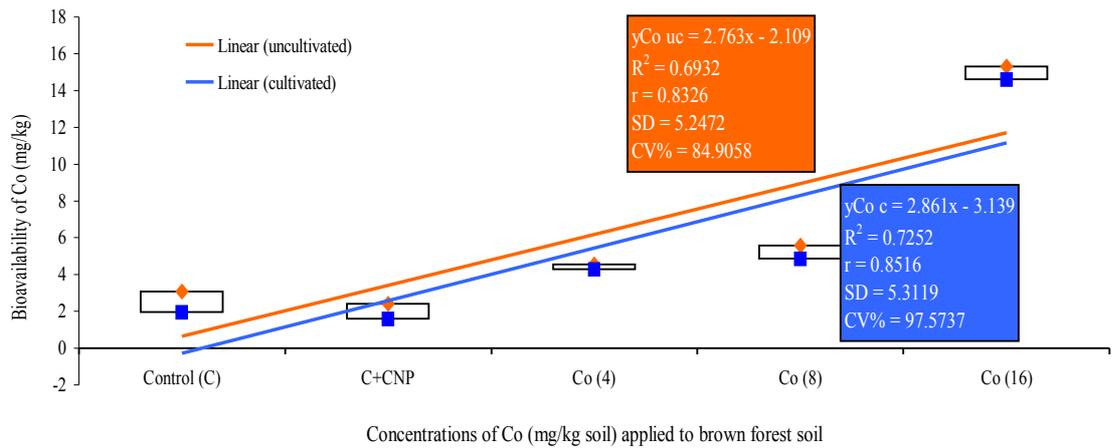


Fig. A-3. Linear regression and other statistical determinants indicate the relationships between the different Co doses applied to cultivated (c) and uncultivated (uc) brown forest soils (Gödöllő) and its bioavailability

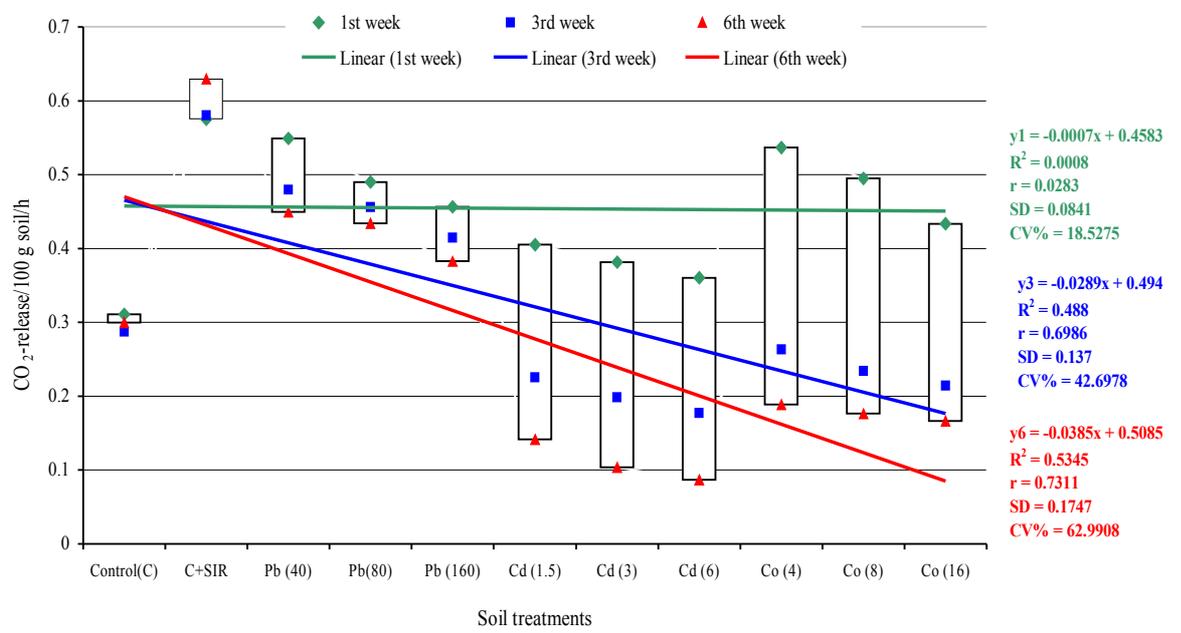


Fig. A-4. Linear regression and other statistical determinants indicate the relationships between the different Pb, Cd, and Co doses (mg/kg soil) applied to uncultivated brown forest soils (Gödöllő) and CO₂-release

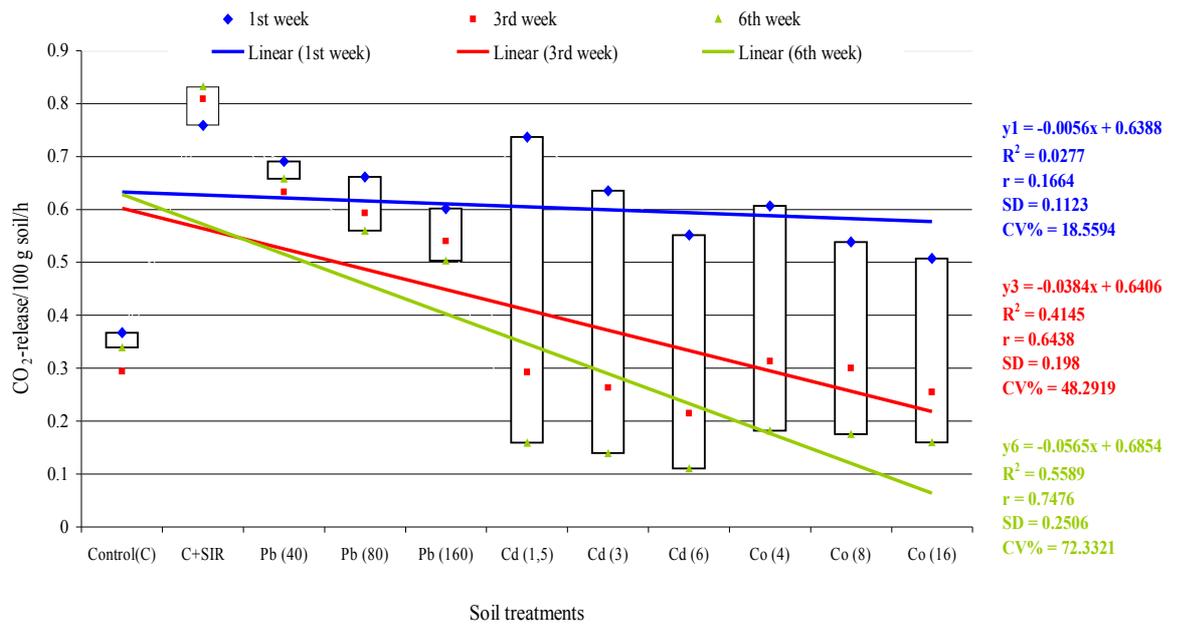


Fig. A-5. Linear regression and other statistical determinants indicate the relationships between the different Pb, Cd, and Co doses (mg/kg soil) applied to cultivated brown forest soils (Gödöllő) and CO₂-release

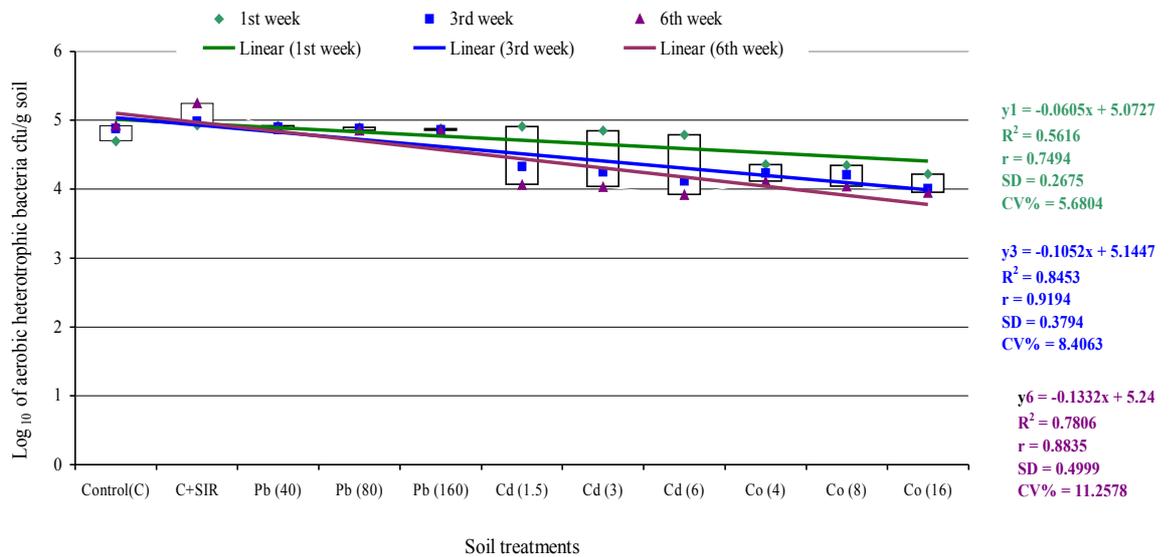


Fig. A-6. Log₁₀ of aerobic heterotrophic bacterial count (cfu/g soil) from uncultivated brown forest soil (Gödöllő) contaminated by different concentrations (mg/kg soil) of Pb, Cd, and Co

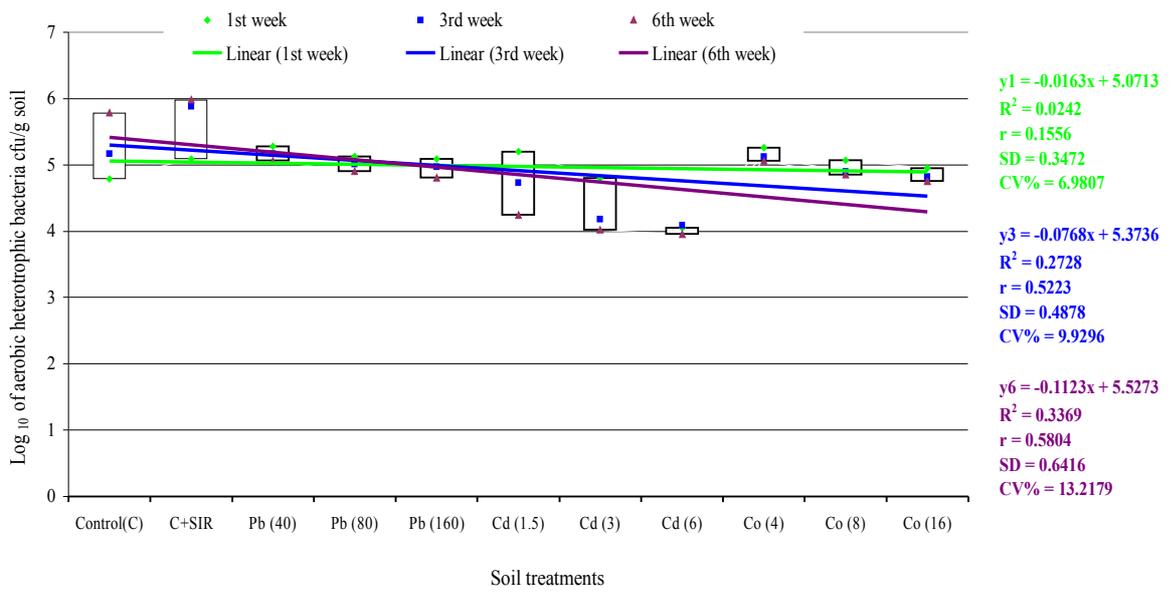


Fig. A-7. Log_{10} of aerobic heterotrophic bacterial count (cfu/g soil) from cultivated brown forest soil (Gödöllő) contaminated by different concentrations (mg/kg soil) of Pb, Cd, and Co

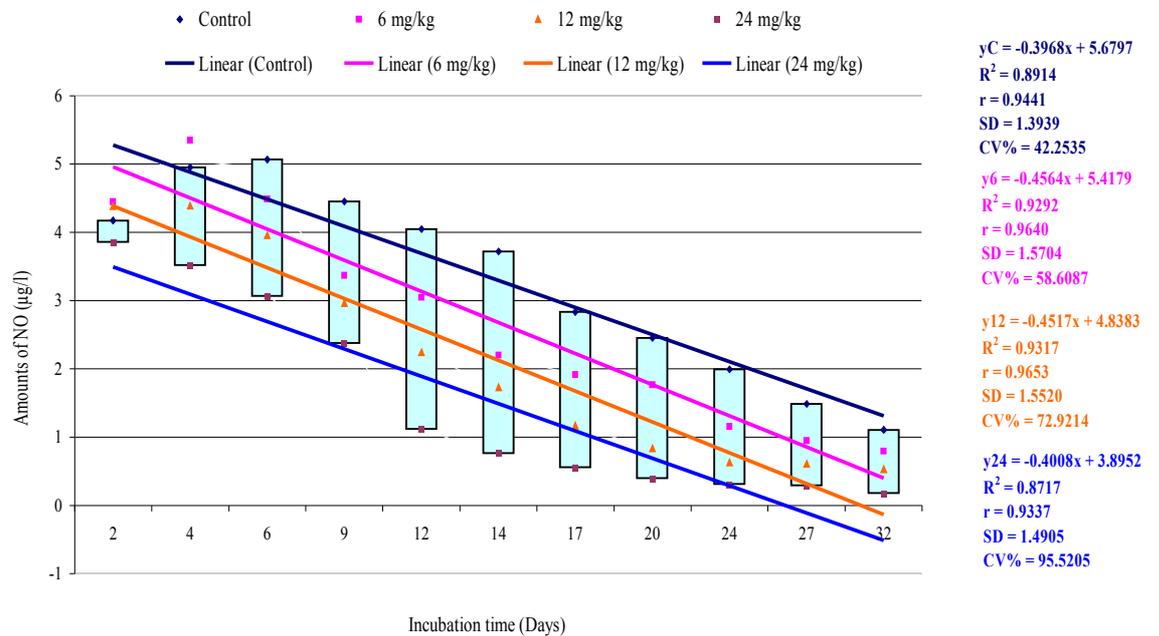


Fig. A-8. Linear regression and some statistical determinants indicate the relationship between NO amounts detected in microcosm containing brown forest soil (Keszthely) of 30% WFPS treated with different concentrations of Cd and incubated at 15°C

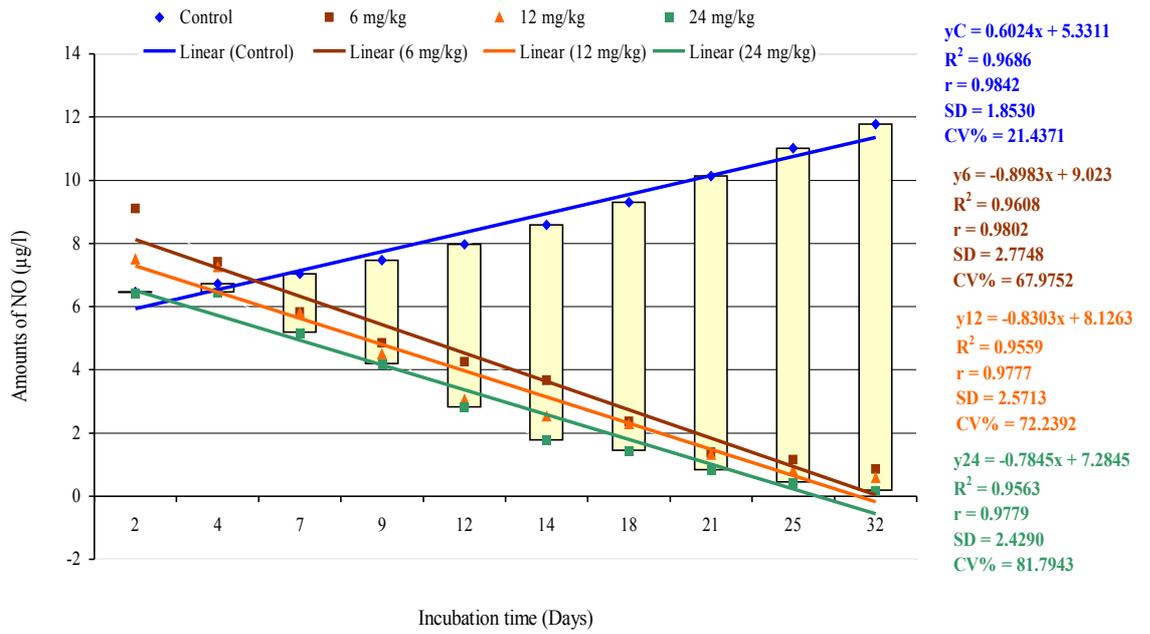


Fig. A-9. Linear regression and some statistical determinants indicate the relationship between NO amounts detected in microcosm containing brown forest soil (Gödöllő) of 30% WFPS treated with different concentrations of Cd and incubated at 15°C

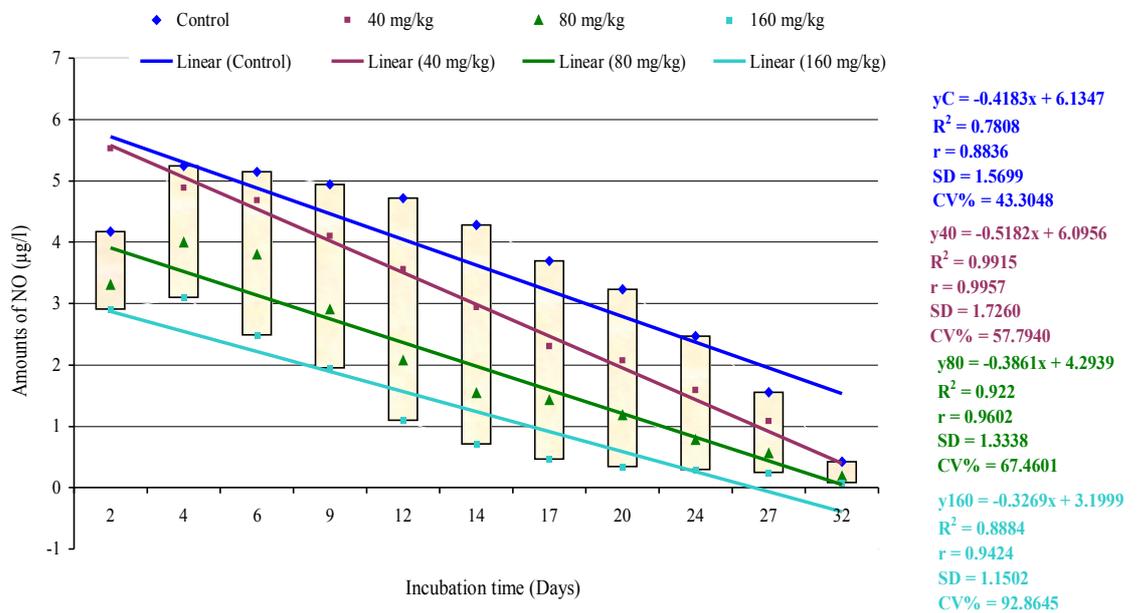


Fig. A-10. Linear regression and some statistical determinants indicate the relationship between NO amounts detected in microcosm containing brown forest soil (Keszthely) of 30% WFPS treated with different concentrations of Pb and incubated at 15°C

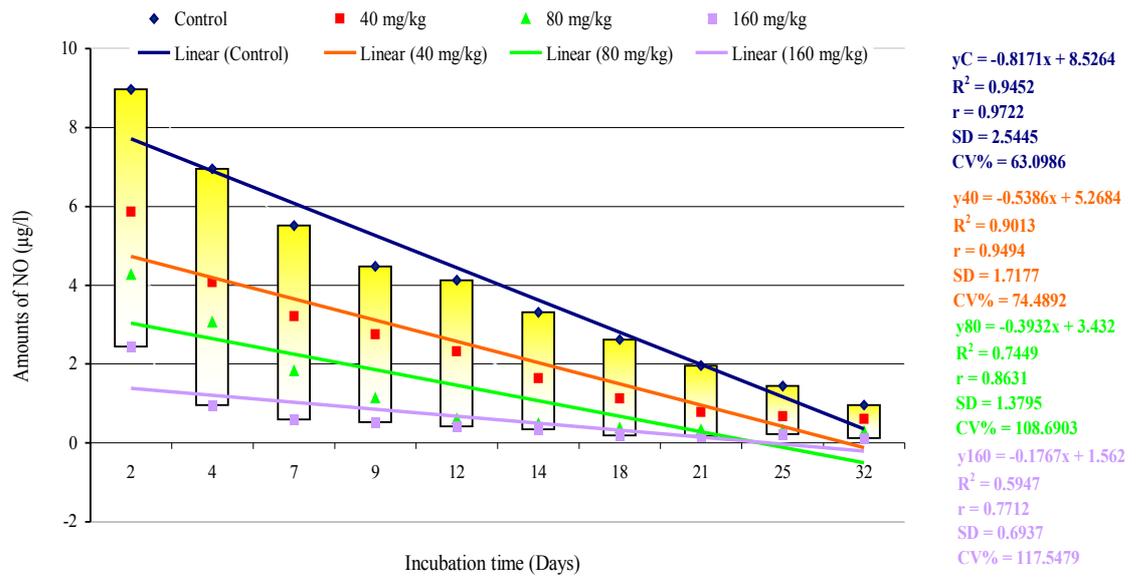


Fig. A-11. Linear regression and some statistical determinants indicate the relationship between NO amounts detected in microcosm containing brown forest soil (Gödöllő) of 30% WFPS treated with different concentrations of Pb and incubated at 15°C

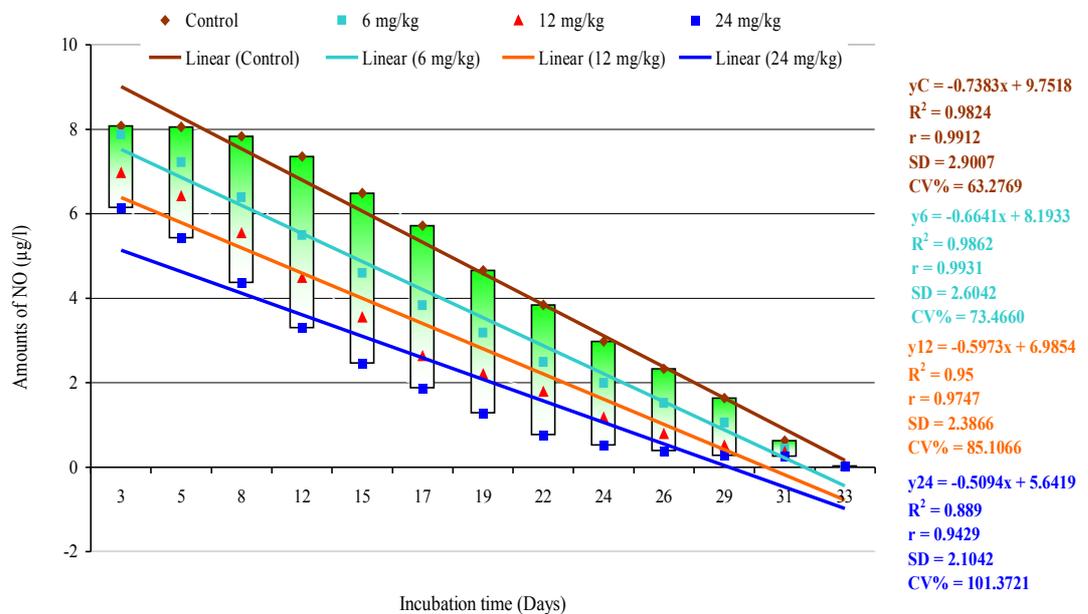


Fig. A-12. Linear regression and some statistical determinants indicate the relationship between NO amounts detected in microcosm containing brown forest soil (Keszthely) of 60% WFPS treated with different concentrations of Cd and incubated at 15°C

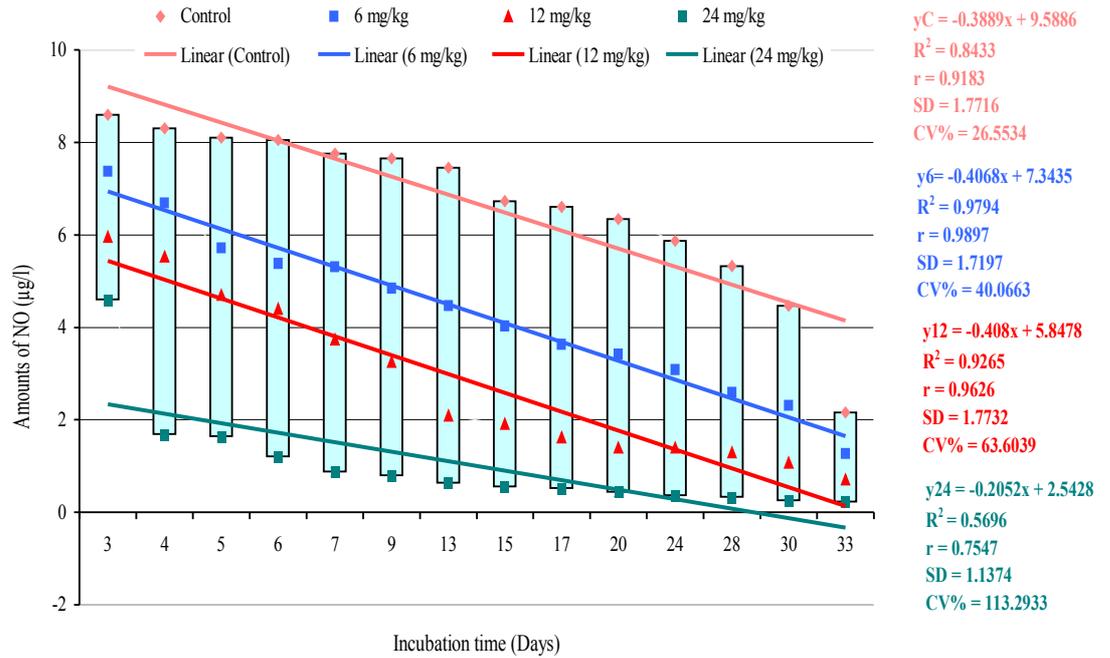


Fig. A-13. Linear regression and some statistical determinants indicate the relationship between NO amounts detected in microcosm containing brown forest soil (Gödöllő) of 60% WFPS treated with different concentrations of Cd and incubated at 15°C

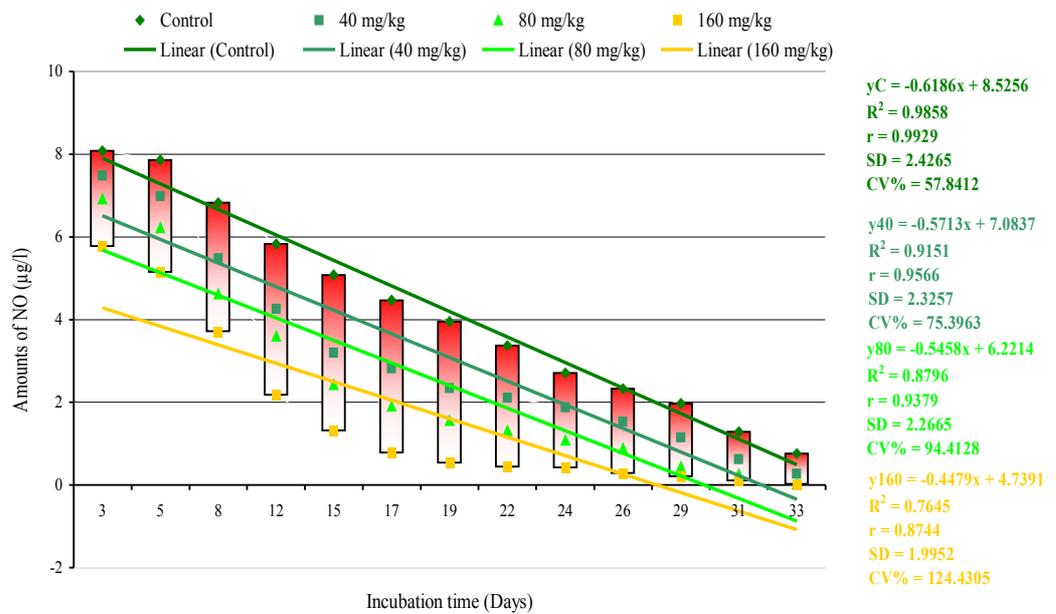


Fig. A-14. Linear regression and some statistical determinants indicate the relationship between NO amounts detected in microcosm containing brown forest soil (Keszthely) of 60% WFPS treated with different concentrations of Pb and incubated at 15°C

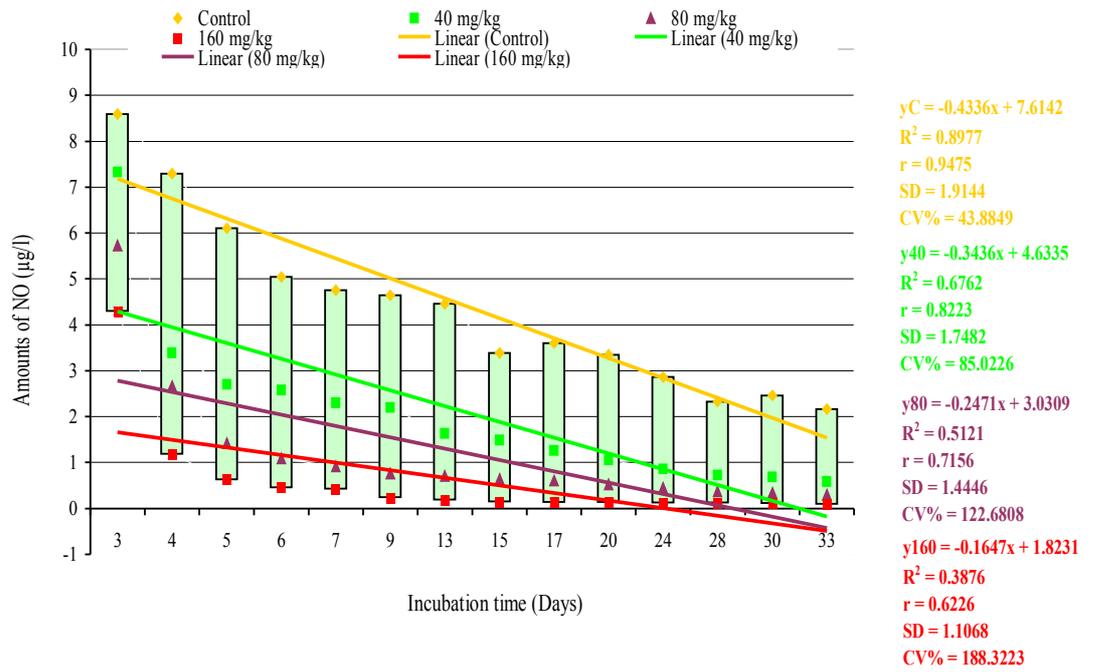


Fig. A-15. Linear regression and some statistical determinants indicate the relationship between NO amounts detected in microcosm containing brown forest soil (Gödöllő) of 60% WFPS treated with different concentrations of Pb and incubated at 15°C

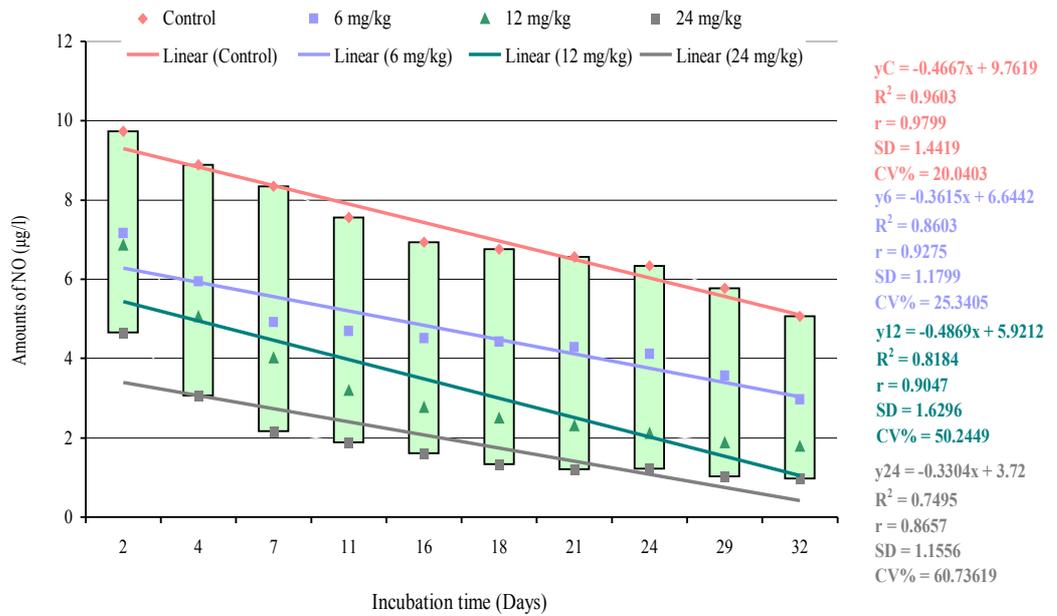


Fig. A-16. Linear regression and some statistical determinants indicate the relationship between NO amounts detected in microcosm containing brown forest soil (Keszthely) of 60% WFPS treated with different concentrations of Cd and incubated at 37°C

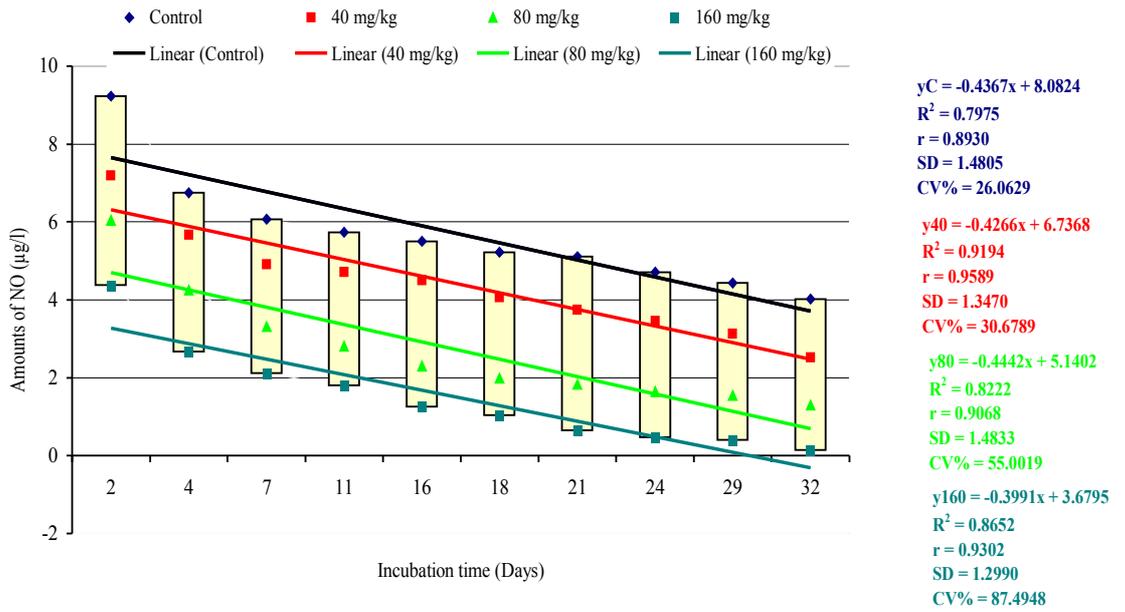


Fig. A-17. Linear regression and some statistical determinants indicate the relationship between NO amounts detected in microcosm containing brown forest soil (Keszthely) of 60% WFPS treated with different concentrations of Pb and incubated at 37°C

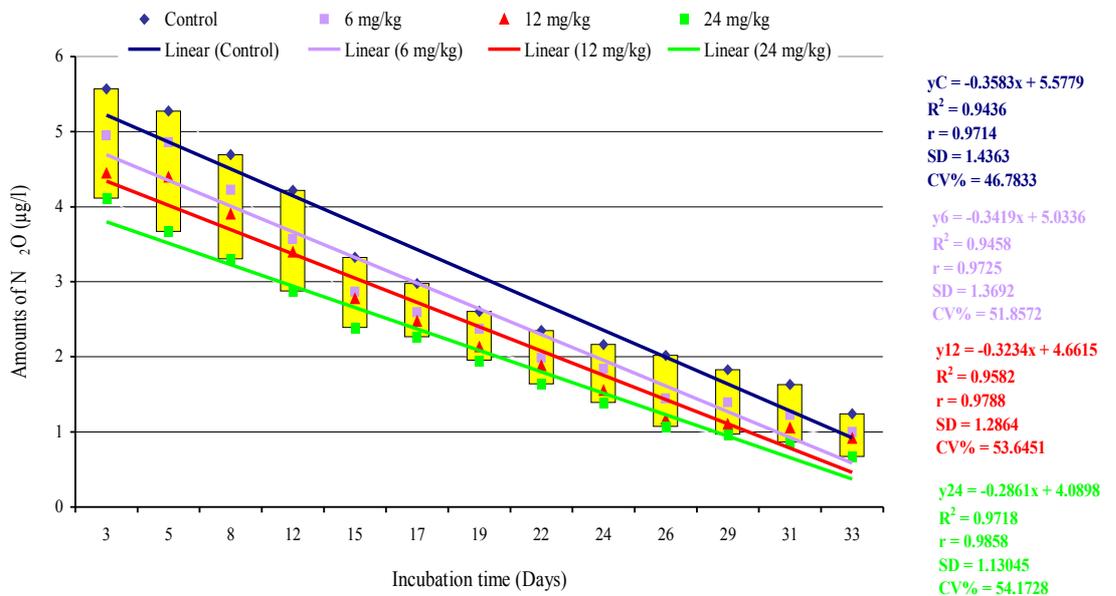


Fig. A-18. Linear regression and some statistical determinants indicate the relationship between N₂O amounts detected in microcosm containing brown forest soil (Keszthely) of 60% WFPS treated with different concentrations of Cd and incubated at 15°C

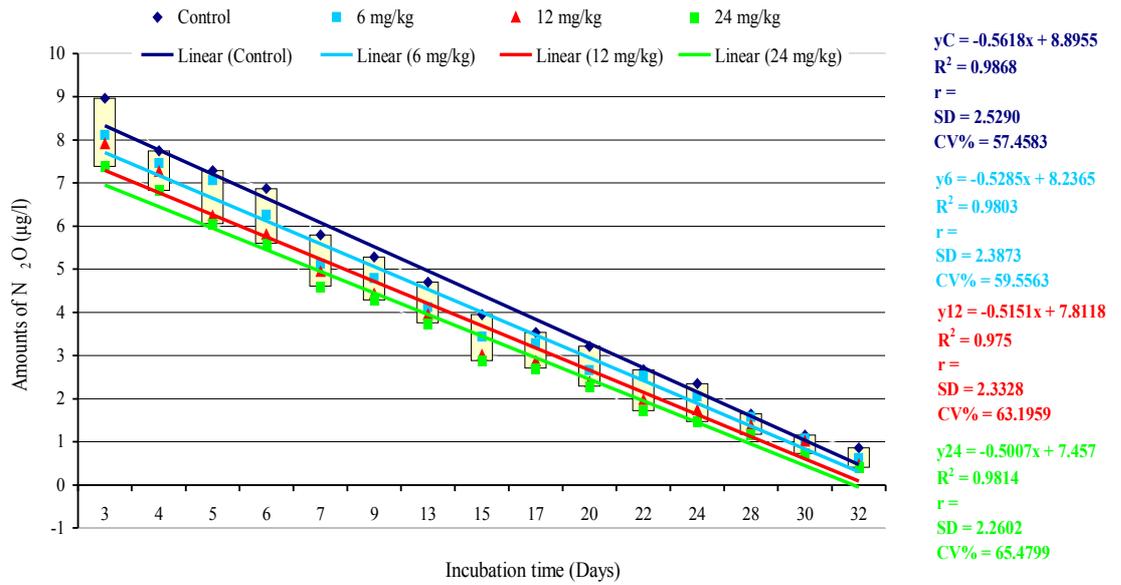


Fig. A-19. Linear regression and some statistical determinants indicate the relationship between N₂O amounts detected in microcosm containing brown forest soil (Gödöllő) of 60% WFPS treated with different concentrations of Cd and incubated at 15°C

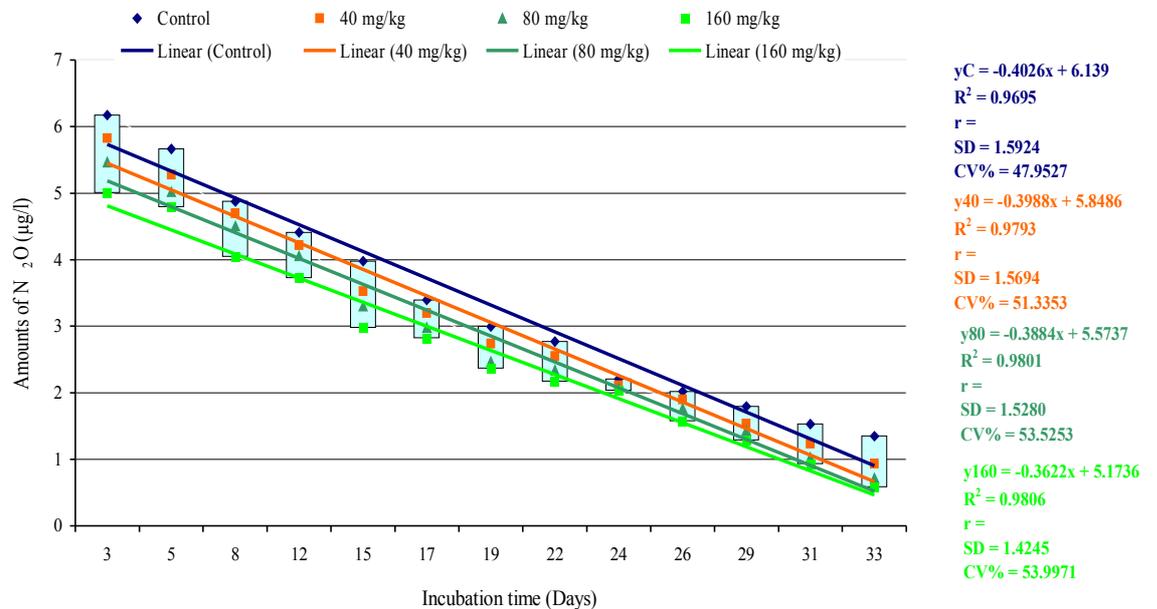


Fig. A-20. Linear regression and some statistical determinants indicate the relationship between N₂O amounts detected in microcosm containing brown forest soil (Keszthely) of 60% WFPS treated with different concentrations of Pb and incubated at 15°C

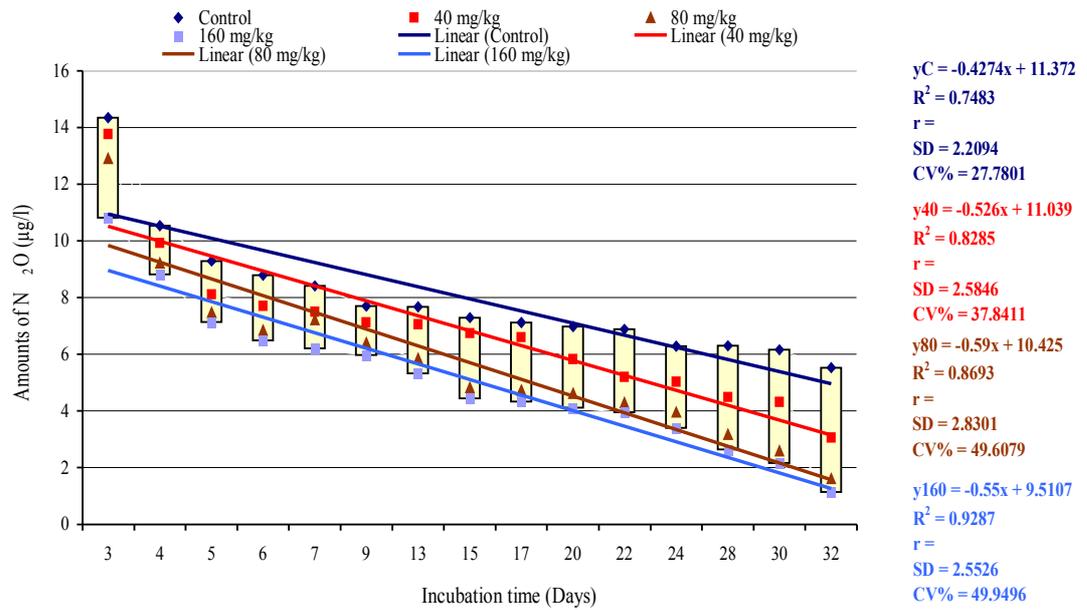


Fig. A-21. Linear regression and some statistical determinants indicate the relationship between N₂O amounts detected in microcosm containing brown forest soil (Gödöllő) of 60% WFPS treated with different concentrations of Pb and incubated at 15°C

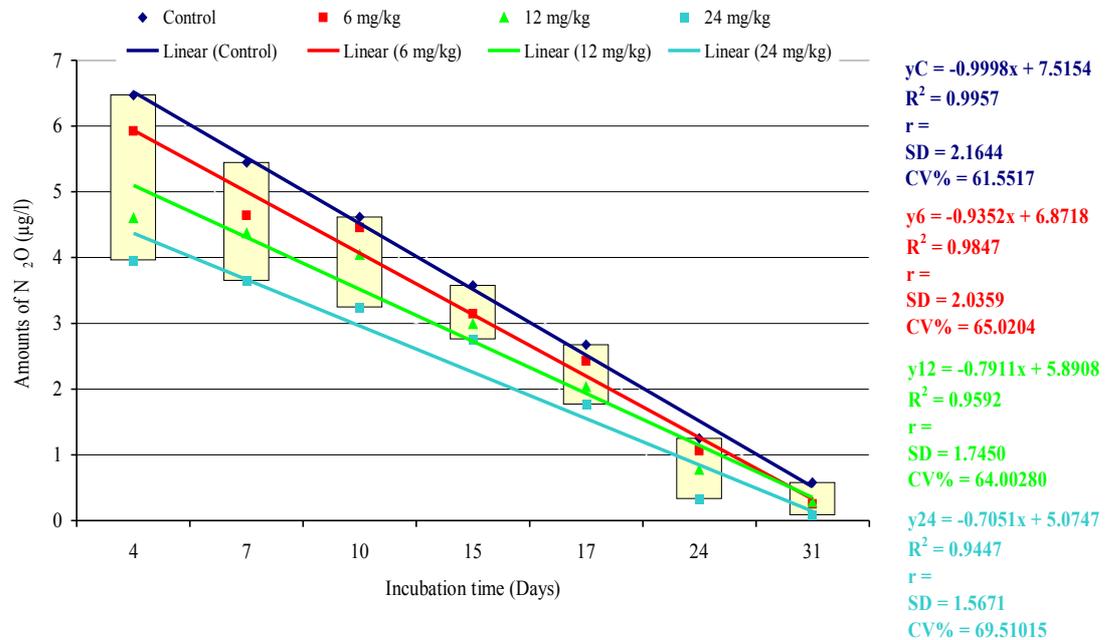


Fig. A-22. Linear regression and some statistical determinants indicate the relationship between N₂O amounts detected in microcosm containing brown forest soil (Keszthely) of 60% WFPS treated with different concentrations of Cd and incubated at 37°C

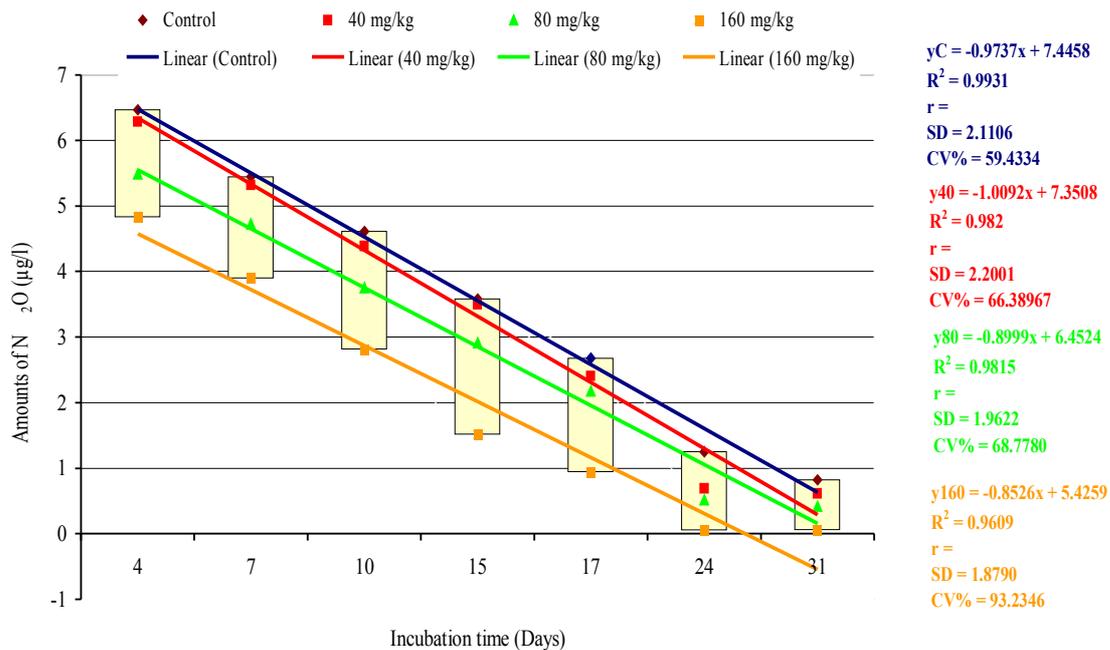


Fig. A-23. Linear regression and some statistical determinants indicate the relationship between N₂O amounts detected in microcosm containing brown forest soil (Keszthely) of 60% WFPS treated with different concentrations of Pb and incubated at 37°C

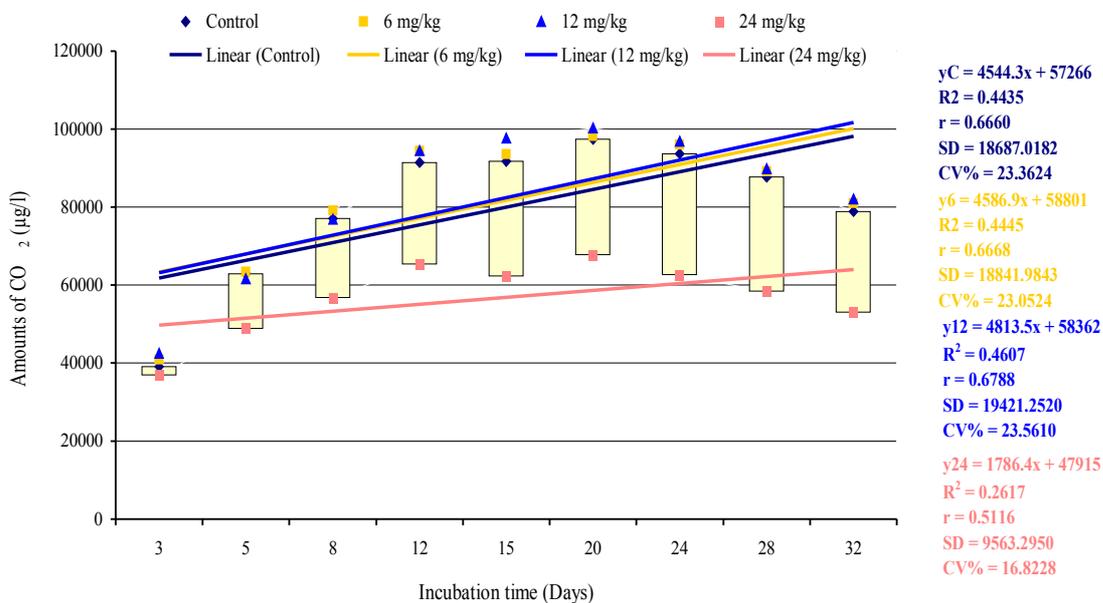


Fig. A-24. Linear regression and some statistical determinants indicate the relationship between CO₂ amounts detected in microcosm containing brown forest soil (Keszthely) of 30% WFPS treated with different concentrations of Cd and incubated at 15°C

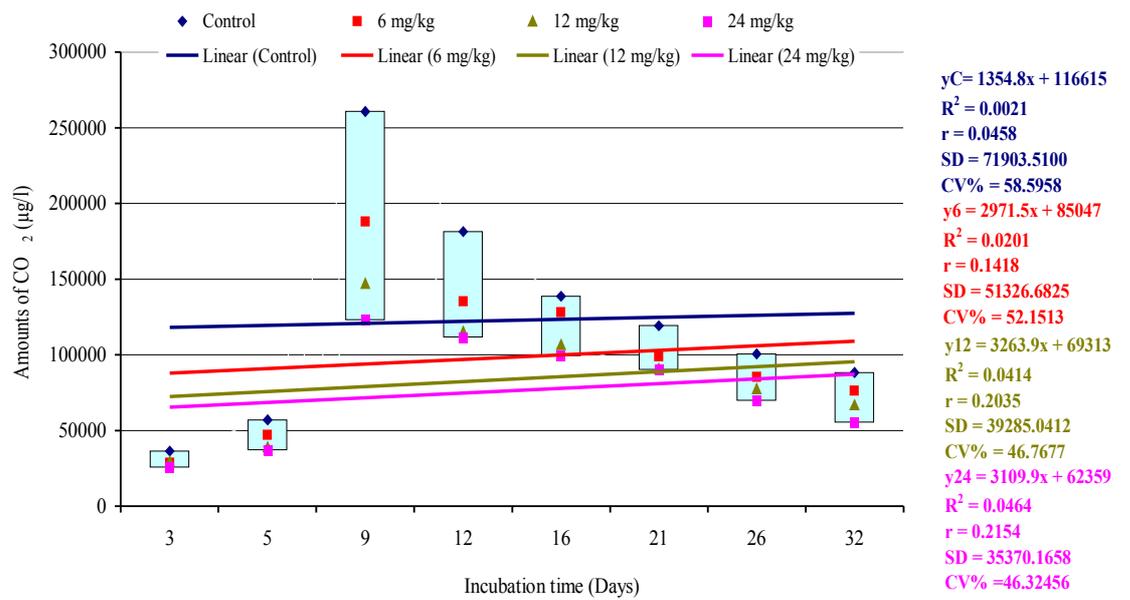


Fig. A-25 Linear regression and some statistical determinants indicate the relationship between CO₂ amounts detected in microcosm containing brown forest soil (Gödöllő) of 30% WFPS treated with different concentrations of Cd and incubated at 15°C

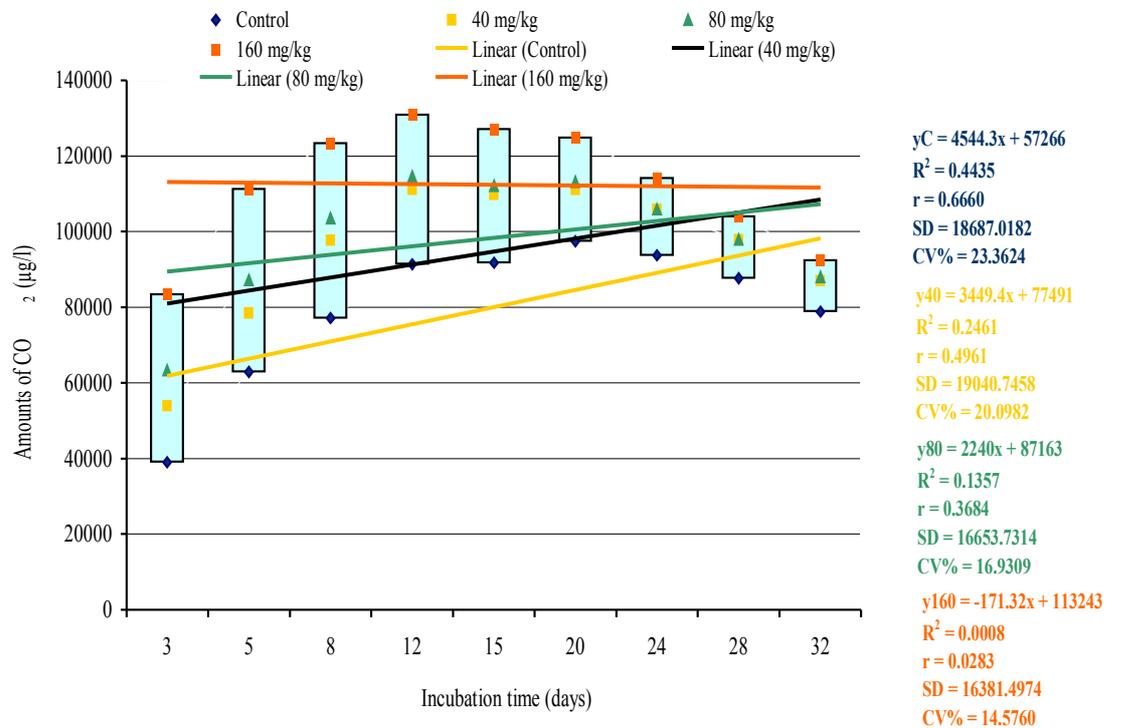


Fig. A-26. Linear regression and some statistical determinants indicate the relationship between CO₂ amounts detected in microcosm containing brown forest soil (Keszthely) of 30% WFPS treated with different concentrations of Pb and incubated at 15°C

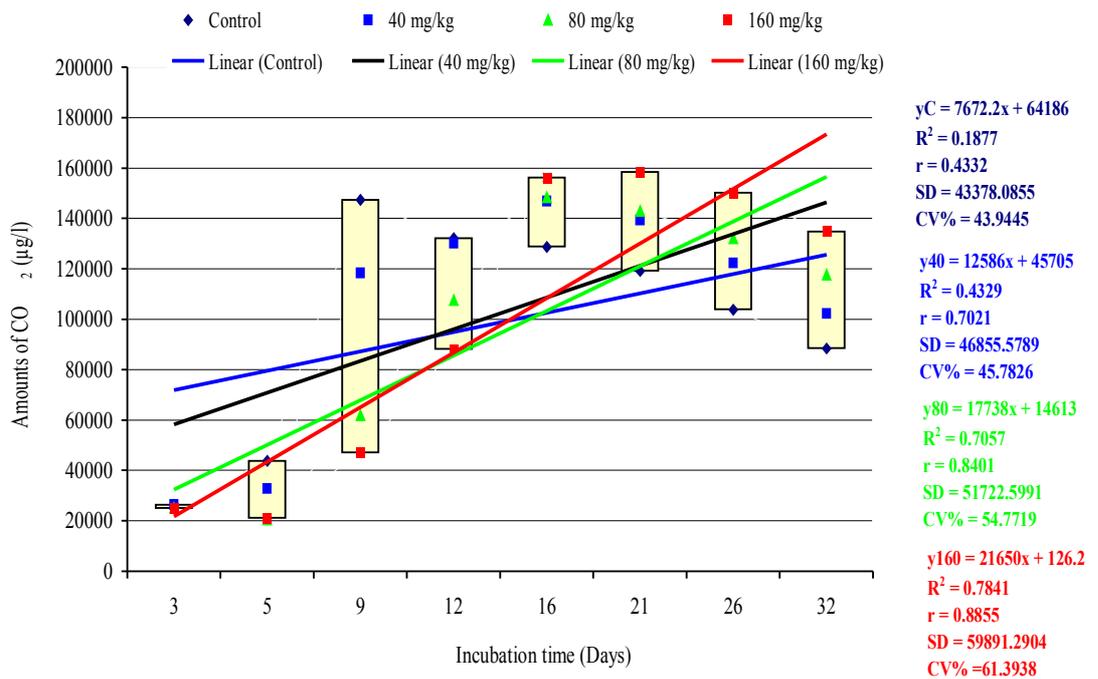


Fig. A-27. Linear regression and some statistical determinants indicate the relationship between CO₂ amounts detected in microcosm containing brown forest soil (Gödöllő) of 30% WFPS treated with different concentrations of Pb and incubated at 15°C

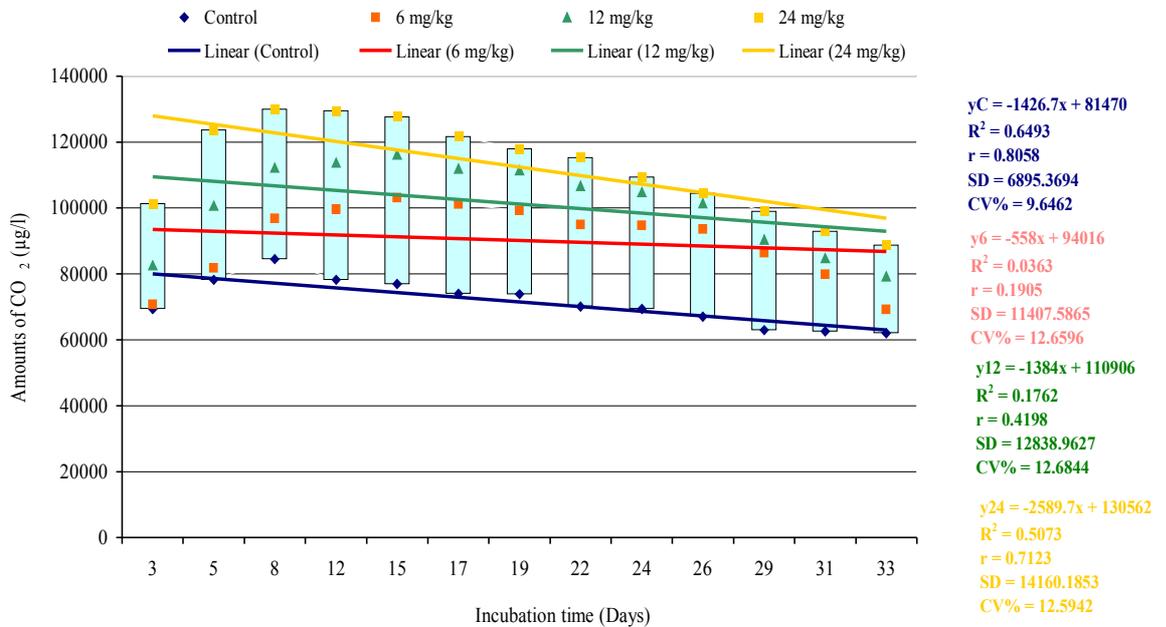


Fig. A-28. Linear regression and some statistical determinants indicate the relationship between CO₂ amounts detected in microcosm containing brown forest soil (Keszthely) of 60% WFPS treated with different concentrations of Cd and incubated at 15°C

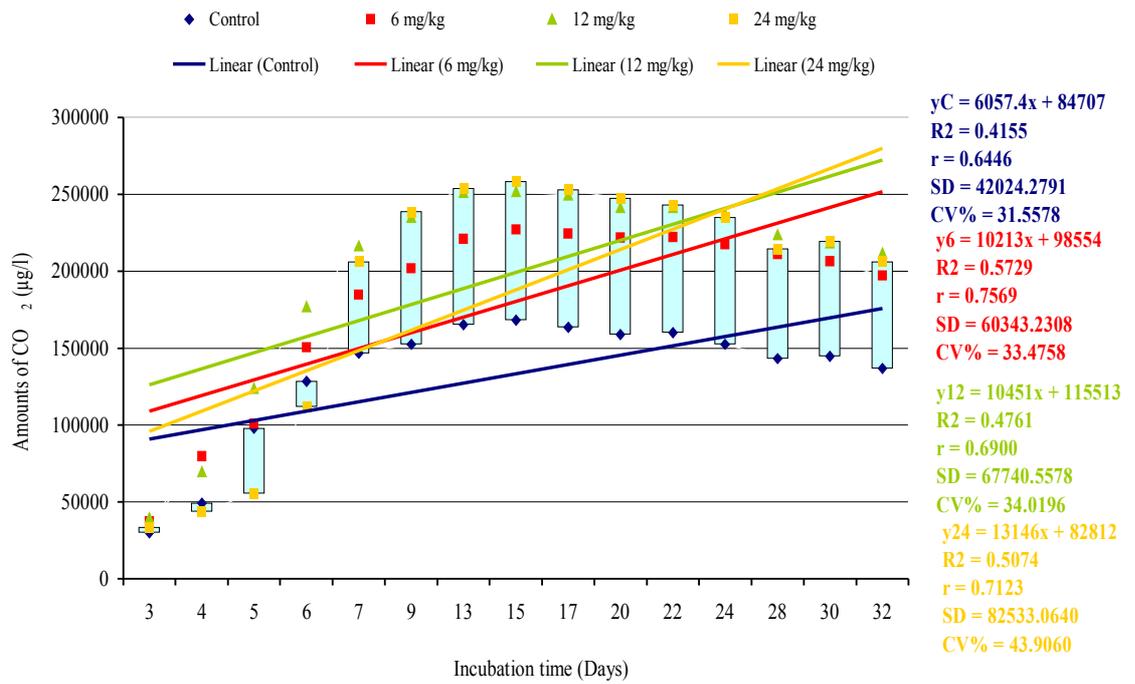


Fig. A-29. Linear regression and some statistical determinants indicate the relationship between CO₂ amounts detected in microcosm containing brown forest soil (Gödöllő) of 60% WFPS treated with different concentrations of Cd and incubated at 15°C

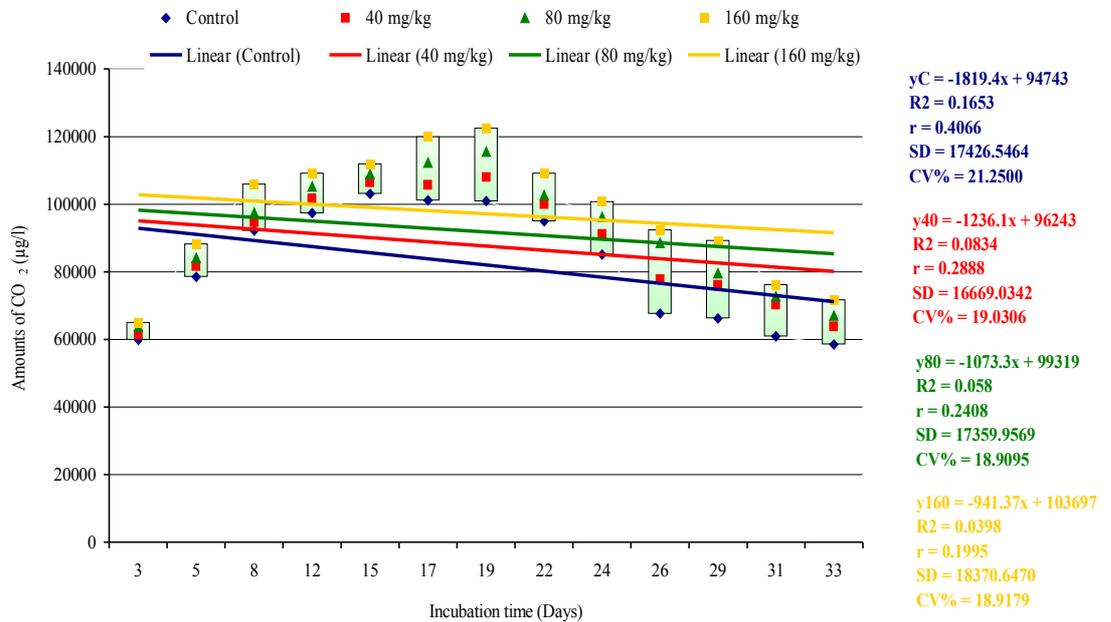


Fig. A-30. Linear regression and some statistical determinants indicate the relationship between CO₂ amounts detected in microcosm containing brown forest soil (Keszthely) of 60% WFPS treated with different concentrations of Pb and incubated at 15°C

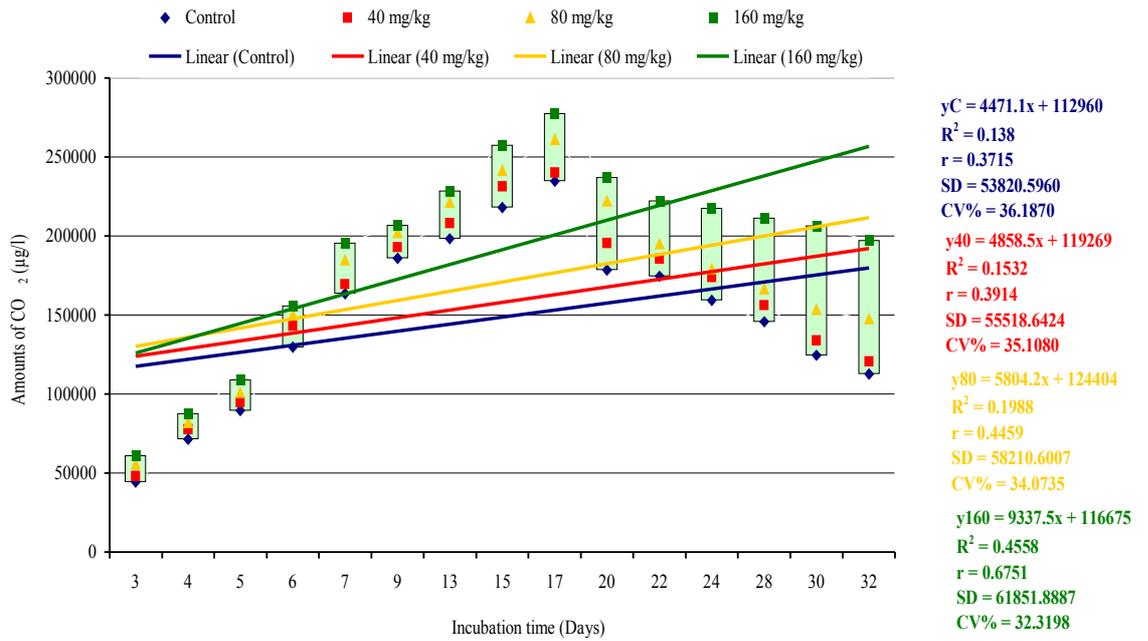


Fig. A-31. Linear regression and some statistical determinants indicate the relationship between CO₂ amounts detected in microcosm containing brown forest soil (Gödöllő) of 60% WFPS treated with different concentrations of Pb and incubated at 15°C

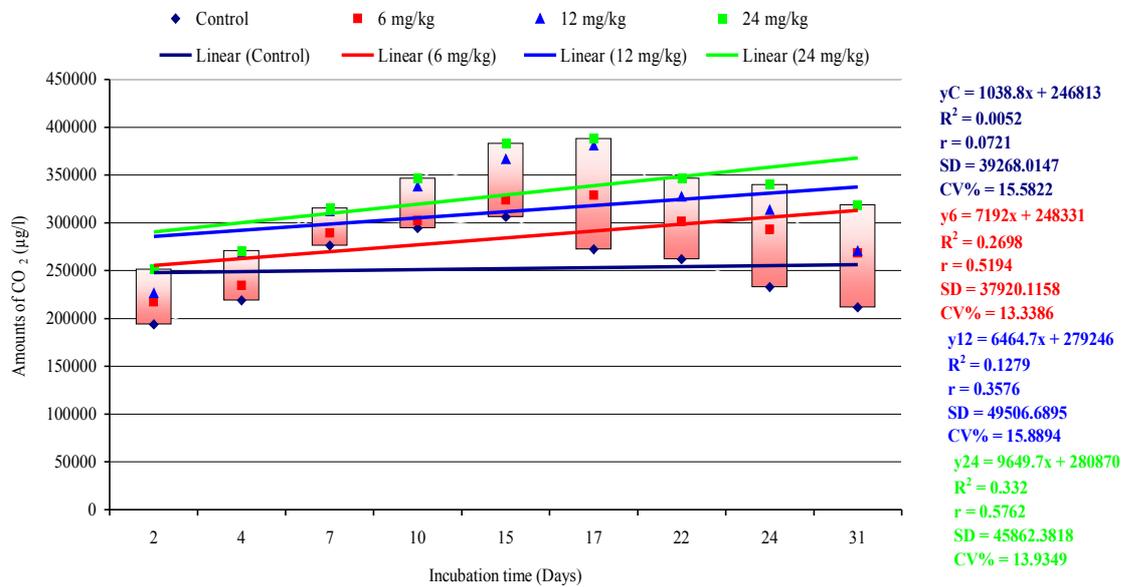


Fig. A-32. Linear regression and some statistical determinants indicate the relationship between CO₂ amounts detected in microcosm containing brown forest soil (Keszthely) of 60% WFPS treated with different concentrations of Cd and incubated at 37°C

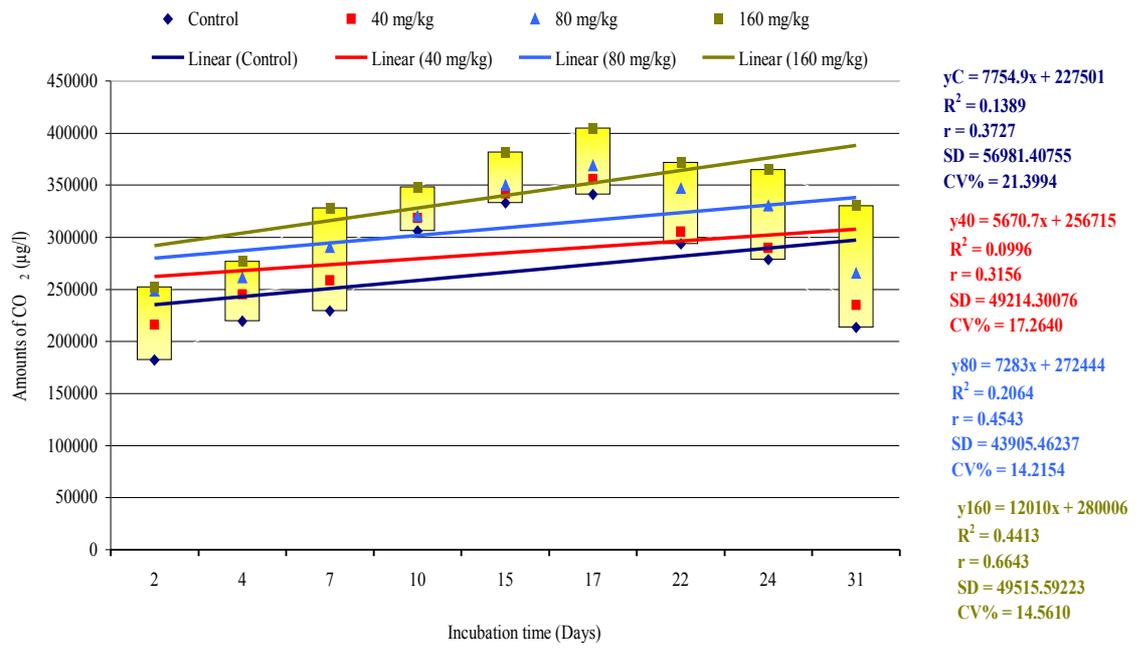


Fig. A-33. Linear regression and some statistical determinants indicate the relationship between CO₂ amounts detected in microcosm containing brown forest soil (Keszthely) of 60% WFPS treated with different concentrations of Pb and incubated at 37°C