SOIL – PLANT – ATMOSPHERE AERATION AND ENVIRONMENTAL PROBLEMS

EDITED BY JAN GLIŃSKI, GRZEGORZ JÓZEFACIUK, KARL STAHR

Centre of Excellence for
Applied Physics in Sustainable
Agriculture AGROPHYSICS

Hohenheim University

Institute of Agrophysics Polish
Academy of Sciences

Jan Gliński, Grzegorz Józefaciuk, Karl Stahr (Editors)

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PREFACE

Soil environment is influenced by the state of three soil phases: solid liquid and air, and by complex equilibria among them.

Soil aeration, for which this issue is devoted to the largest extent, relates to soil air composition, its role for plants and soil biota, and to all processes of absorption, production and transfer of gases. This term denotes also the gas exchange between the soil and the atmosphere, the oxygen content in the soil, and many other processes and phenomena as oxygen distribution in soil, its availability for microorganisms and plant roots or even artificial forcing air into the soil.

Soil air composition is a result of biological and chemical processes of uptake and evolution of gases on the one hand and of physical processes of their dissolution and transport, on the other.

All aspects of soil aeration and its role for plants were described in the book by Gliński and Stępniewski "Soil Aeration and Its Role for Plants" edited by CRC Press in 1985, however since today a new knowledge has been accumulated. The continuous studies of aeration problems are performed in the Institute of Agrophysics PAS in the frame of activity of the Centre of Excellence for Applied Physics in Sustainable Agriculture AGROPHYSICS (Workpackage 3). The main objectives of this activity are:

- measurement of macro- and microdiffusion of oxygen in soil profile
- investigation of the influence of moisture and redox conditions on the emission of greenhouse gases
- estimation of consequences of soil anoxia on plants

We like to present here some our most recent results.

Many environmental processes of soil aeration depend on physical and chemical properties of soil solid and liquid phases, therefore some place in this issue is devoted to the above topics, as well.

The above described problems were presented at Summer School in Stuttgart (26-29 July 2004) organized by Centre of Excellence AGROPHYSICS (WP 3), Department of Soil Science of the Hohenheim University in Stuttgart and the Institute of Agrophysics PAS in Lublin.

The main idea of publishing this issue was to provide a written background for the participants of the Summer School, however the Editors will be glad if this may serve for other scientific purposes.

Jan Gliński

CONTENTS

PART A: GAS EXCHANGE

Review of research on greenhouse gases in Finland
Jaakkola A. 9

Effect of soil tillage and compaction on greenhouse gas fluxes
Lipiec J., Hatano R. 18

Gas emission from wetlands
Stępniewska Z., Stępniewski W., Bennicelli R., Ostrowska A., Kotowska U. 30

Aeration and climatic global change
Stępniewski W., Stępniewska Z. 37

Oxygenology - a new scientific discipline
Stępniewski W., Stępniewska Z. 43

Nitrous oxide emission from soils
Włodarczyk T., Gliński J., Kotowska U. 48

PART B: AERATION AND BIOLOGICAL ASPECTS

Aeration status of soil and enzyme activity
Brzezińska M. 55

Mapping of soil aeration properties
Gliński J., Stępniewska Z., Ostrowski J., Stępniewski W. 60

Microbial ecology of soil porous medium
Gliński J., Brzezińska M., Włodarczyk T. 65

Redox relations in a loess soil on eroded hill slope
Gliński P., Stępniewska Z. 72

Structure formation and its consequences on gas and water transport
in unsaturated arable and forest soils
Horn R. 79

Fate of dna in soil
Nannipieri P. 86

The biochemistry of the rhizosphere soils
Nannipieri P. 89

Soil aeration and pesticide decomposition
Stępniewska Z., Fornal E., Kosiorowska I., Charytoniuk P. 94

Methanotrophic activity of coal mine rocks
Stępniewska Z., Stefaniak E., Szmagara A. 103

PART C: POROUS ENVIRONMENT

Determination of energetic status and evaporation from porous bodies on the base of infrared imaging
Baranowski P., Lamorski K., Mazurek W., Walczak R.T. 111

Surface properties of soils and their behavior in soil degradation processes
Jozefaciuk G. 118

Compaction effects on soil physical properties and root and shoot growth
Lipiec J. 124

Monitoring of porous media processes with the application of physical and chemical sensors
Skierucha W., Walczak R.T., Malicki M.A., Wilczek A. 134

Concepts and morphology of hydromorphism in soils
Stahr K. 140

Hydrophysical characteristics of porous body as input data for water transport models
Walczak R. T., Sławiński C., Witkowska-Walczak B. 141

AUTHORS 149

SOIL – PLANT – ATMOSPHERE AERATION AND ENVIRONMENTAL PROBLEMS

PART A: GAS EXCHANGE

REVIEW OF RESEARCH ON GREENHOUSE GASES IN FINLAND

Jaakkola A.

Greenhouse gases have been examined in Finland at least at Helsinki and Kuopio universities and at the Agricultural Research Centre in Jokioinen. Several researchers have participated in this research since 1980, more vigorously during decades of 1990 and 2000. The investigations have concentrated on nitrous oxide, carbon dioxide and methane emissions and methane absorption, but occasionally also other gases have been investigated. During those years, agricultural land and forest, different soil types as well as management practices on the field and in the forest have been compared as sources or sinks of greenhouse gases.

NITROUS OXIDE EMISSIONS AT JOKIOINEN IN 1983

An early attempt to measure N_2O emission was made at Jokioinen in 1983 (Jaakkola 1985). A closed chamber method was used with steel cylinders 168 mm in inner diameter and 250 mm in height, inserted 100 mm into the soil. An air sample was taken 12 times during the season from the headspace of the cylinder covered for one hour with a rubber sheet. N_2O was determined with a gas gromatograph equipped with a Porapak Q column and EC detector. Argon-methane was used as carrier gas.

The actual scope of that research was to determine losses of nitrogen from agricultural soil by denitrification. Therefore also acetylene treatment of part of the cylinders was used in order to prevent the reduction of N_2O to N_2. In those experiments acetylene probably also inhibited N_2O production by nitrification. There were six fields growing barley or grass for hay on clay, fine sand and peat soils. The determinations were made on four plots on each field. Two plots were not fertilised the other two were fertilised with 100 kg/ha of N. The emissions during the whole observation period are given in Table 1.

Table 1. Emission of N_2O from soil during May – October 1983 in Jokioinen, Finland, kg N ha^{-1}

Soil	Crop	Unfertilised		Fertilised with 100 kg N ha^{-1}		SD
		- C_2H_2	+ C_2H_2	- C_2H_2	+ C_2H_2	
Clay	Barley	2.3	4.4	2.2	4.5	0.7
	Grass	0.8	0.8	2.6	3.1	0.6
Fine sand	Barley	0.5	0.8	0.6	0.8	0.1
	Grass	0.6	0.8	2.0	2.3	0.3
Peat	Barley	4.9	6.7	6.2	6.6	0.9
	Grass	1.2	1.0	6.8	4.6	0.9

In single observations, rates of N_2O emission ranged from 0 to 280 g N ha^{-1} d^{-1}. I most cases the rates were highest in June. There was often also an increase in September. Acetylene treatment did not always produce more nitrous oxide, indicating an important role of nitrification as a source of N_2O.

Barley fields on mineral soils emitted 0.5 – 2.3 kg N_2O-N ha^{-1} during the observation period. Nitrogen application had no effect. On peat field the emission was higher and fertilisation raised it a little. Grass fields emitted less N_2O than the barley fields. Nitrogen application increased the emission. The effect of fertilisation became visible, in most cases, at two weeks after fertilisation. The different effect of N application to barley and grass might be caused by the application method: for barley fertiliser placement was used, for grass the fertiliser was broadcasted.

RESEARCH AT UNIVERSITY OF KUOPIO

Professor Pertti Martikainen at University of Kuopio has supervised a lot of research on greenhouse gases. Part of the work has been done in other institutes, e.g. National Public Health Institute in Kuopio, Regional Environment Centres, University of Joensuu and in Research Stations of various organisations.

Articles dealing with microbial production of nitrous oxide and nitric oxide in boreal peatlands have been collected and discussed in the PhD thesis by Regina (1998). There were twelve experimental sites located in central Finland and eastern Finland. The sites represented several types of peat soil according to nutrient status and management. N_2O fluxes were measured by determining the gas concentration increase in a 60-liter aluminium chamber placed on an aluminium collar (60 cm x 60 cm) inserted 30 cm deep into the soil. The gas concentrations were determined in air samples with a gas chromatograph equipped with an EC detector.

As a summary of several investigations on peatlands in the beginning of 1990's (Silvola et al. 1992, Regina et al. 1996, Lång et al. 1995, Regina et al. 1998a) following data was given by Regina (1998):

Site	N_2O-N, μg m^{-2} h^{-1}	NO-N, μg m^{-2} h^{-1}
Low-sedge *S. Papillosum* pine fen, natural	-13 to 13	<1.6
Herb-rich sedge birch-pine fen, drained	79	12.5
Grass field, cultivated	210	64

The emission of both gases varied widely. Some absorption of N_2O was also observed. In general, emission of NO was markedly lower than N_2O emission. The observation period did not last the whole year and there were rather few measurements during this period, hence annual emissions can not be estimated.

Regina et al. (1998b) showed that forests on drained N-rich peat soils may be significant sources of N_2O and NO and their production of nitrogenous trace gases is enhanced by additional N.

Regina et al. (1999) found that drying of wet peatlands increased the emission rate of N_2O. In the laboratory experiment with peat monoliths the increase was observed 10 weeks after lowering the water table from –2 cm to –25 cm or from –15 cm to –25 cm. Raising the water table close to soil surface almost ceased the emissions.

Liikanen (2002) studied in her dissertation the greenhouse gas dynamics in lake sediments and water columns. She concluded that significant amounts of methane might be released from eutrophic lake sediments especially in summer and autumn from the deep profundal and littoral sediments with anoxic overlying water. Ebullition was an important mechanism in transporting CH_4 directly from the sediment to the atmosphere. When O_2 existed on the sediment surface or in the water column, CH_4 was effectively oxidised resulting in negligible emissions. Lake sediments were insignificant sources of N_2O due to limited availability of NO_3^-.

Saari (2003) studied methane oxidation in forest soils. She found that, in general, CH_4 oxidation rates in upland forests are highest in the uppermost mineral soil. Therefore, diffusion of CH_4 from the atmosphere, and thereby soil moisture, strongly affects CH_4 uptake. Finnish upland forests that have a low N deposition and a favourable soil texture exhibit higher CH_4 oxidation than Dutch upland forests. Methane oxidation in boreal forest soils is not sensitive to soil dryness.

Heikkinen (1983) measured in his dissertation carbon gas exchange in various wetland ecosystems in northernmost Finland (Kaamanen in sub-arctic area, Kevo in arctic area) and in Russia (Lek Vorkuta in tundra area). CO_2 and CH_4 fluxes over a range of terrestrial and aquatic ecosystems were measured using static chamber techniques. In general, wet *Sphagnum* sp. and *Carex* sp. dominated flarks and lawns were net sinks for CO_2 and net sources of CH_4. East European tundra lost approximately 8.1 Tg carbon during summer 2001 with mean temperature 1.6° higher than long-term mean. So, even in present climatic conditions the East European tundra is vulnerable to carbon loss to the atmosphere.

Maljanen (2003) studied in her dissertation the CO_2, CH_4 and N_2O dynamics of farmed and forested organic soils in Finland. In one study CO_2 dynamics were measured in an organic soil in eastern Finland (Maljanen et al. 2001). The annual balance was calculated for plots where barley or grass was grown. During the growing season, the grassland was a net source while barley was a net sink for CO_2. However, both soils were net sources when autumn, winter and spring were also included. The annual CO_2 emissions were 750 g CO_2-C m^{-2} and 400 g CO_2-C m^{-2} from grassland and barley soils, respectively. In another article (Maljanen et al. 2003a) nitrous oxide emissions on the same field were studied. The annual N_2O emission from cultivated soil, where barley was grown, was 8.3-11.0 kg N_2O-N ha^{-1} a^{-1} while an adjacent forest site emitted 4.2 kg N_2O-N ha^{-1} a^{-1}. Similar soils kept bare by regular cutting of the vegetation and tilling emitted 6.5-7.1 kg N_2O-N ha^{-1} a^{-1}. Maljanen et al. (2003b) measured CH_4 fluxes on the same site. They found that agricultural soils under grass or barley or without vegetation, generally acted as sinks for methane. However, during warm dry summer they emitted CH_4. A forested soil took up methane a rate of 3.9 kg C ha^{-1} a^{-1} while the rate in agricultural soils was on average one third of that ranging 0.1 – 3.7 kg C ha^{-1} a^{-1}. Diurnal variation in CO_2, N_2O and CH_4 fluxes was also recorded (Maljanen et al. 2002). CO_2 and N_2O emissions from agricultural and forest soils were higher during daytime than in the night while CH_4 uptake did not vary markedly. In an additional study Maljanen et al. (2003c) found rather good agreement between N_2O emissions determined with closed chamber method and those calculated according to Fick's law on the basis of gas concentration gradient in soil or snow.

In the summary of a PhD thesis by Nykänen (2003) is concluded that Finnish natural peatlands, especially the fertile ones, can be significant sources of CH_4 but they usually have no N_2O emissions. A permanently lowered water table decreased the emissions from minerotrophic boreal peatlands and occasionally led to CH_4 uptake while at nutrient poor peatlands the decrease in emission rate was small. In the former peatlands drainage led to increased N_2O emissions while there was no change in the latter ones.

RESEARCH AT MTT AGRIFOOD RESEARCH FINLAND, JOKIOINEN

N_2O emissions were monitored during 2000-2002 on loamy sand and on clay soil under grass, barley and fallow (Syväsalo et al. 2004a). The fluxes were measured with static chamber throughout the year. The annual fluxes from the clay soil ranged from 3.7 to 7.9 kg N ha^{-1} and those from sandy loam 1.5 – 7.5 kg N ha^{-1}. On average 60% of the fluxes occurred outside the growing season, from October to April. Amount of applied N fertiliser did not correlate closely with variation in N_2O fluxes. Soil pore size distribution explained the variation somewhat. On the clay field the highest fluxes came from the fallow plots and on the sandy field from the barley plots, but the differences were not statistically significant.

Emissions of N_2O were measured from field plots of grass, barley, potatoes and fallow on a peat field in northern Finland during 2000-2002 and in southern Finland in 1999-2002 (Regina et al. 2004). The mean annual fluxes were as follows, kg N ha^{-1} a^{-1}:

	grass		barley		fallow	
	mean	SD	mean	SD	mean	SD
North	4.0	1.2	13	3.0	4.4	0.8
South	7.3	1.2	15	2.6	25	6.9

The direct effect of adding N fertiliser on N_2O emissions was not important. Half of the annual flux entered the atmosphere outside the growing season (October – April). The authors conclude that the larger N_2O fluxes in the south might be due to the more humified status of the peat, more rapid mineralisation and weather with more cycles of freezing and thawing in the winter.

In an incubation experiment with peat, clay and loamy sand at soil moistures 40, 60, 80 and 100% Water Filled Pore Space the highest N_2O emission was recorded in the wettest soils (Pihlatie et al. 2004), being up to 10 000 times higher than in the dry soils. The emission from dry soils followed the sequence loamy sand < clay < peat while in the wet soils the order was clay < peat < loamy sand.

Nitrification the share of which was determined by acetylene inhibition was the dominant N_2O producing process in all the soils at 60% WFPS.

The emissions of N_2O, CH_4 and CO_2 were measured with closed chamber method in an experiment on fine sand soil where organic farming with livestock, conventional farming with livestock and cereal production without livestock were compared (Syväsalo et al. 2004b). Grass was growing in the two former treatments. The fluxes were as follows, kg ha^{-1}:

	N_2O annual	CH_4 annual	CO_2 winter
Organic grass	1.4	-0.51	1.4
Conventional grass	1.2	-0.72	1.1
Conventional cereal	3.5	-0.44	0.6

About half of the N_2O emission occurred during 1. Nov. – 31. May period. The respective share of CH_4 uptake varied between 9 and 31% in different treatments. Leaching of N was also measured. It varied between 8.7 and 10.8 kg ha^{-1} in the treatments.

RESEARCH AT DEPARTMENT OF FOREST ECOLOGY, UNIVERSITY OF HELSINKI

Studies dealing with carbon balance in forest soils have been carried out at the Department of Forest Ecology, University of Helsinki. Part of those studies consisted of measurements of CO_2 efflux from soil surface. The experiments were performed at Hyytiälä Forestry Field Station in southern Finland (61º51´N, 24º17´E) where a versatile measurement station (Station for Measuring Forest Ecosystem Atmosphere Relations) exists.

The studies on CO_2 efflux have started in 1997 by developing the method of measurement. Pumpanen et al. (2001) found out that closed chamber clearly underestimates the efflux. More reliable results are given by their non-vented non-steady state flow-through chamber where the assessing episode with closed cover lasted for 70 s. Also in these dynamic flow-through chambers there are error sources important to be aware. Differences between inflow to the chamber and outflow out of it are substantial sources of error, so they have to be adjusted equal.

In another study assessing seasonal patterns of CO_2 efflux from the soil in a Scots pine forest Pumpanen et al. (2003a) stated even 30% underestimation with the closed chamber technique while the flow-through chamber overestimated high CO_2 effluxes by 20% in comparison with known efflux. During two and a half years, efflux of CO_2 ranged from 0.0-0.1 g m^{-2} h^{-1} in winter to peak values of 2.3 g m^{-2} h^{-1} in late June and in July. The annual accumulated CO_2 efflux was 3100-3300 g CO_2 m^{-2} in 1998 and 1999. Soil air CO_2 concentration was highest in July-August ranging 580-780 μmol mol^{-1} in the humus layer and 13600 – 14500 μmol mol^{-1} in the C-horizon. In winter the concentrations were lower, especially in deeper soil layers. Drought decreased CO_2 efflux and soil air CO_2 concentration.

Pumpanen et al. (2003b) measured with the closed-chamber method an annual efflux of 1900 g CO_2 m^{-2} in a 130-year old coniferous forest. After clear-cutting the effluxes rose to 3200, 2800 and 2900 g CO_2 m^{-2} in three successive years after harvesting in places with logging residue left. When logging residue was removed, the annual efflux was smaller and gradually decreased to pre clear-cutting levels.

RESEARCH AT LABORATORY OF AGRICULTURAL CHEMISTRY AND PHYSICS, UNIVERSITY OF HELSINKI

The studies on air in agricultural soils and effects of soil properties on it began in 1986. They included determinations of CO_2 and N_2O concentration in soil air at different depths in various experiments as well as measuring N_2O emissions with closed chamber method. A summary of majority of the results is published as PhD thesis by Simojoki (2001).

The composition of soil air at different depths on two observation sites were monitored throughout the year (Jaakkola 1994). Emission of N_2O was measured with closed-chamber method during growing season. One soil profile (A) consisted of finesand-mixed humified peat underlain by a layer of Carex peat (25-50 cm) and finesand below it, the other profile (B) was a clay-rich silt. Both soils were in agricultural use. The nitrous oxide concentration in the soil air ranged from 0.3 to 70 µl l^{-1}, usually being higher in the deeper soil layers. The highest emission peaks were 0.3 kg N_2O-N ha^{-1} d^{-1}, not always coinciding with concentration peaks in soil air. The results are given in Fig.1

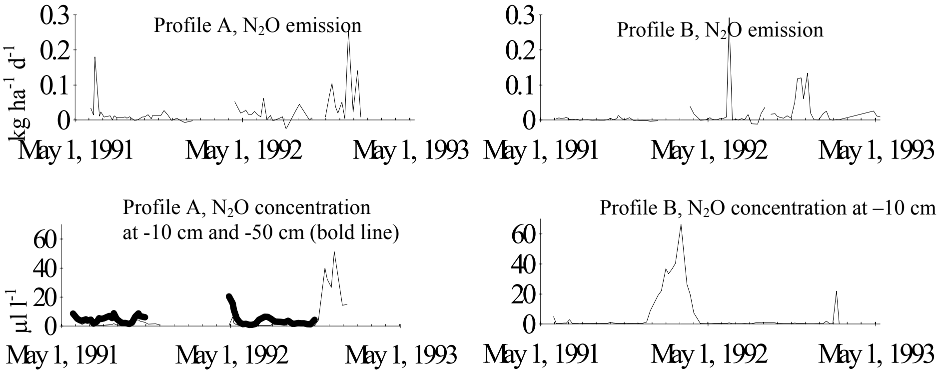

Fig. 1. Nitrous oxide emission and concentration in the soil air.

In a two-year field experiment on a loam soil classified as Aquic Cryochrept (Jaakkola and Simojoki 1998) concentration of N_2O in bare, unirrigated soil varied at various depths between 0.4 and 100 µl l^{-1} at 15 and 30 cm depths. A heavy irrigation in June (120 mm), saturating the topsoil with water, raised the concentrations for a couple of weeks in both bare soil and soil cropped with a cereal-grass mixture. Irrigation in the beginning of August (110 mm) raised the concentrations in bare soil only. Average emission during some periods is given in Table 2.

Table 2. Geometric means of N_2O concentrations, µl l^{-1}, on loam soil during various periods (values in each column not followed by a common letter differ significantly, $P = 0.05$)

	27.6. - 11.7. 93		1.8. - 15.8. 93		22.8. - 5.9. 93		22.8. - 19.9. 94	
	-15 cm	-30 cm	-15 cm	-30 cm	-15 cm	-30 cm	-15 cm	-30 cm
Bare soil	0.75	0.98	1.09^{ab}	1.38^{b}	6.86	10.02	0.91	0.83
Cropped soil	0.79	1.08	0.77^{a}	0.98^{ab}	0.73	0.54	0.48	0.63
Irrigated bare soil	2.67	3.36	4.44^{b}	6.54^{c}	2.09	3.91	0.83	1.27
Irrigated cropped soil	2.56	3.14	0.44^{a}	0.26^{a}	0.33	0.47	0.41	0.49

N_2O emissions were measured with closed-chamber method in some plots. They varied between 0 and 40 g N ha^{-1} d^{-1}. The mean daily emission over the whole observation period (growing seasons 1993 and 1994) was 7 g N ha^{-1} d^{-1}. In the total material of 234 observations including all treatments, the emissions were correlated with concentrations in soil air at 15 cm depth ($r = 0.80$) and 30 cm depth ($r = 0.65$).

Another field experiment was performed on a loamy clay soil classified as Eutric Cambisol according to FAO classification (Simojoki and Jaakkola 2000). The emission of N_2O from the bare soil was three to seven times larger than that from soil cropped with barley (Table 3). Irrigation and fertiliser nitrogen application increased it.

Table 3. Nitrous oxide emission from clay soil

		N_2O-N, g ha^{-1} during 1 June – 22 October, 1993	
		Unfertilised	N fertilised
Bare soil	Unirrigated	1680	2030
	Irrigated	2030	3540
Cropped with barley	Unirrigated	120	570
	Irrigated	850	1150

It was concluded that the N_2O emission from cropped soil originated mainly from shallower depth than 15 cm where the concentrations were measured. The largest emissions were observed at 0.6 – 0.9 WFPS.

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EFFECT OF SOIL TILLAGE AND COMPACTION ON GREENHOUSE GAS FLUXES

Lipiec J., Hatano R.

INTRODUCTION

Long term data indicate considerable uncertainty in the evaluation of anthropogenic greenhouse gas emissions. Recent evaluations imply greater input of greenhouse gases to the atmosphere from agricultural production than that previously estimated (Mosier et al., 1998). In this paper we summarize the effects of tillage practices and compaction with highliting recent literature.

CARBON DIOXIDE

Management practices significantly influence acting of soil as a sink or source for atmospheric CO_2 and therefore play an important role in sequestering C in soil (Fortin et al., 1996; Paustian et al., 2000).

Tillage practices

Usually, reduced tillage or no-till vs. conventional tillage results in lower CO_2 emission (e.g. Reicosky et al., 1997; La Scala et al., 2001; Sánchez et al., 2002) and greater gains of soil organic carbon in soil (Ball et al., 1999; McConkey et al., 2003). This effect is enhanced by clay content and to a higher extent under subhumid than semi-arid conditions (McConkey et al., 2003).

Emission of CO_2 is considerably different during and the time since tillage. It was shown that maximum emission in CO_2 taking place during tillage quickly decline with time passed after tillage. Comparison of results from different studies revealed that highest emission at tillage was up to approximately 1.6 g CO_2-C m^{-2} h^{-1} (Wuest et al. (2003) and 0.5 g CO_2-C m^{-2} h^{-1} after 1 day (Rochette and Angers, 1999) and 0.25g CO_2-C m^{-2} h^{-1} after 15 days (La Scala Jr. et al., 2001). Short-lasting effect of tillage on CO_2-C emission was enhanced during the summer seasons (Rochette and Angers, 1999; Alvarez et al., 2001) when plowing produces in the short-term an important soil temperature increase and thus more favorable conditions to microbial activity . The opposite was, however, observed following spring plowing under cool and wet conditions of Canada (Rochette and Angers, 1999). Figure 1 illustrates this.

Short-term responses to tillage may be less pronounced in soils with a long history of cultivation because of a relatively resilient microbial community and/or because lower initial microbial biomass and nutrient pools preclude a strong response to disturbance (Calderón et al., 2000). Greater fluxes of CO_2 in tilled soil went along with enhanced water vapor fluxes and associated soil water losses (Reicosky et al., 1999; Prior et al., 2000). The relative differences in carbon dixide emission decreased with time passed after tillage and were related to soil temperature (Ball et al., 1999) and soil wetness and crop type (Franzluebbers et al., 1995). CO_2 emissions after plowing were substantially higher from an established bermudagrass pasture compared with a no-till sorghum field or a continuously cultivated sorghum field (Reicosky et al., 1997). In addition minimum and no-till contributed to lower CO_2 compared to CT fluxes due to reduced fossil-fuel consumption C emissions associated with reduced number of farming operations (Sánchez et al., 2002; West and Marland, 2002).

The effect of tillage on CO_2 emissions is associated with depth of soil disturbance and equipment used. The data in Table 1 indicate that CO_2 fluxes immediately after tillage (30-60 s) to 5-8, 10 and 45 cm depths were respectively 1.3, 4 and 7 times greater than that from non disturbed control plot (0.079 CO_2-C m^{-2} h^{-1}). However, in study comparing various tillage implements (rotary tiller, chisel plough, disk plow and disk harrow) with the same working depth (20 cm) the fluxes were highest after applying disk harrow and in general increased with degree of soil disturbance. Response of CO_2 emissions to tillage is more pronounced in organic than mineral soils (Maljanen et al., 2001). The results stress the importance of no disturbing practices in order to reduce soil carbon loss induced by tillage treatments

Mechanisms

Greater flux from the soil during and shortly after tillage is often ascribed to lower resistance to gas transfer and related physical CO_2 release from soil pores and solution (Reicosky et al., 1997; Wuest et al., 2003). Other studies (Calderón et al. (2001) and Jackson et al. (2003) reporting greater CO_2 emissions from disturbed than non-disturbed in spite of lower respiration sustain this explanation. The CO_2 degassing from soil profile immediately after tillage can be pursued by increased soil respiration when temperatures are warm and eagerly decomposable organic matter or crop residue are available (Rochtte and Angers, 1999). When intense rainfall occurred immediately after tillage and reduced greatly soil roughness, significantly greater CO_2-C emission in plowed compared to unplowed soil appeared only few days later (Alvarez et al., 2001).

In some other studies, however, a diminishing effect of soil disturbance on CO_2 emission was also observed (Franzluebbers et al., 1995; Calderón et al., 2000) and was attributed to the effects of different soil temperature and soil water content on soil CO_2 evolution (Franzluebbers et al., 1995). In study of Kiese and Butterbach-Bahl (2002) CO_2 emission was positively related to water filled pore space at dry to moderate soil wetness during the dry season and negatively to the wetness changes in the wet season. In sandy soils lower CO_2 emission from tilled vs. untilled plots was attributed to low concentration of C and N and microbial activity (Calderón et al., 2000).

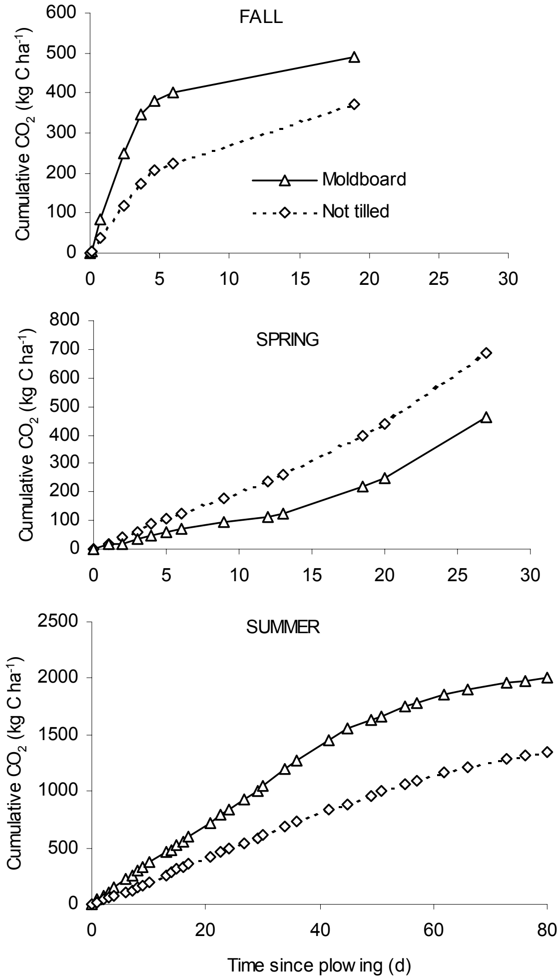

Fig. 1. *CO_2-C losses from a plowed and a non-tilled soil following plowing (after Rochette and Angers, 1999).*

Lower rates of organic matter decomposition and CO_2 evolution with decreasing tillage intensity resulted in sequestration of crop-derived C and thereby increase the soil's ability to remove CO_2 from the atmosphere (Dick et al., 1998; Halvorson et al., 2002; West and Marland, 2002). Using a global database of 67 long-term experiments in US West and Post (2002) indicated that a change from conventional tillage to no-till sequestered on average 57 g C m^{-2} y^{-1} (0.0065 g C m^{-2} h^{-1}). This figure was more than doubled (125 g C m^{-2} y^{-1} or 0.0143 g C m^{-2} h^{-1}) under Spanish conditions (Sánchez et al., 2002). This impact can be enhanced when the C-building practices are maintained because soil C sequestered due to reduced tillage is not stable and rapidly mineralized to CO_2 (Dick et al., 1998; McConkey et al., 2003).

Table 1. CO_2 emissions as related to tillage operations

Implement: **Norfolk sandy loam, Alabama, USA**	**Emissions CO_2 [g -C m^{-2} h^{-1}]**	**Reference**
None	0.079*	Prior et al. (2000)
Kinze planter (5-8 cm)	0.101	
Coulter (10cm)	0.317	
Ro-til, coulters and rolling basket (45 cm)	0.554	
Implement: Acid dark red latosol, Sao Paulo State, Brazil		
None	0.055**	La Scala et al. (2001)
Rotary tiller (20 cm)	0.087	
Chisel plough (20 cm)	0.131	
Disk plow (20 cm)	0.106	
Disk harrow (20 cm)	0.35	

*Means over 30-60 s after tillage; ** means over 2-week period.

NITROUS OXIDE

Agricultural soils are a major source of atmospheric nitrous oxide (N_2O). Production of nitrous oxide in soils is mainly from mineral N by the microbial process of nitrification and denitrification (Bandibas et al., 1994; MacKenzie et al., 1997) that are affected by soil tillage and compaction (Soane snd Ouwerkerk, 1995).

Effects of tillage and compaction

In general N_2O emision is greater in no-tilled compared with conventionall-tilled soils (Lal et al., 1995; Jacinthe and Dick, 1997; Mummey et al., 1998) although the opposite effect was also reported (Arah et al., 1991). Greater N_2O emission from no-tilled soil can be partly associated with lower air-filled porosity (Ball et al., 1999) increased availability of C (Palma et al., 1997) and contribution of large aggregates (Linn and Doran, 1984) with anoxic centers (Horn et al., 1994; Hatano and Sakuma 1991) under no-till. Faster emission of N_2O from no-tilled than ploughed soil took place despite low diffusivity near the soil surface in the former (Fig…). This can be to the production sites close to the soil surface, as shown by the high concentrations at shallow depth (Ball et 1999).

Modelling studies of Mummey et al. (1998) revealed that differences between the two tillage scenarios were strongly regional and suggest conversion of conventionally tilled soil to no-till may have a greater effect on N_2O emissions in drier regions.

Several studies showed increased denitrification (Bakken et al., 1987; Hatano and Sawamoto (1997) and N_2O emissions (Hansen et al., 1993; Ruser et al., 1998) with increasing soil and subsoil compaction. The enhanced N_2O-N emission from compacted soil was often accompanied by greater N_2O concentration in the soil air.

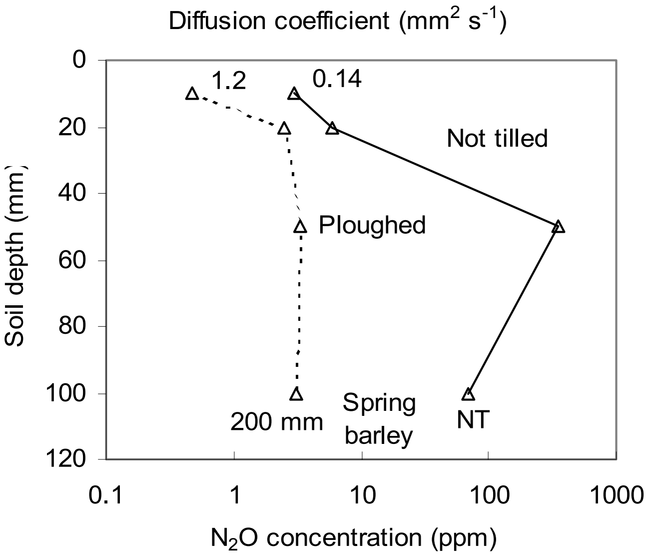

Fig. 2. *N_2O concentrations in the ploughed and not tilled (NT) soil (9 occasions, April-May) (after Ball et al., 1999).*

Greater N_2O emissions from compacted soil were associated with increased water filled pore space (WFPS) or reduced air-filled porosity (Douglas and Crawford, 1993; Lipiec and Stępniewski, 1995). Because of this enhanced N_2O emissions follow rain events (Hansen et al., 1993; Hatano and Sawamoto, 1997; Ball et al., 1999; Kusa et al, 2002) and should be included in measurement schedule to improve the accuracy of the estimates.

In general N_2O emissions are positively correlated with WFPS (e.g. Simojoki and Jaakkola, 2000; Kiese and Butterbach-Bahl, 2002, temperature (e.g. Smith et al., 1998; Kusa et al., 2002) and availability of NH_4^+ and NO_3^- (Kusa et al., 2002). They are also affected by soil organic carbon content (Skiba et al., 1998; Włodarczyk et al., 2002), acidity (Bandibas et al., 1994; Tokuda and Hayatsu, 2001) texture (Gliński et al., 2000) and redox potential (Stępniewska et al., 2000; Inubushi et al., 2003).

Spatial and temporal variability

In arable soils spatial variability of N_2O emission was associated with extremely high N_2O emission rates from areas of a few square centimeters to a few square meters (Ball et al., 1997; Röver et al., 1999; Choudhary et al., 2002). The hot spots were often attributed to high soil nitrogen concentration and management direction and tillage induced microreliefs (Jacinthe and Dick, 1997; Clemens et al., 1999; Röver et al., 1999), natural soil heterogeneity and the measurement technique used (Choudhary et al., 2002). In no-tilled soil, substantially higher N_2O emission was recorded from soil enclosing a drill slit (458 μg N m^{-2} h^{-1} or 110 g N ha^{-1}day^{-1}) than between slits (207 μg N m^{-2} h^{-1} or 49 g N ha^{-1}day^{-1}) (Ball et al., 1999). Knowledge of the small-scale spatial variability helps better estimates of the emissions over large scale (Mummey et al., 1997). Under potato field N_2O emission is spatially variable due to specific configuration and soil compaction (Fig. 3). The most pronounced dynamics in ridges is ascribed to soil temperature and increased soil respiration, which casues an increased anaerobic volume in which denitrification takes place (Flessa et al., 2002b) The mean share of the ridges, uncompacted interrows and tractor-compacted interrows in the total field N_2O emission in this study was 66%, 10% and 24%, respectively.

N_2O emissions from grasslands depend on soil compaction by livestock hooves and associated high inputs of of excretal N. The effects of both factors resulted in large temporal and spatial variability of the N_2O flux.

Given spatial patterns of N_2O fluxes often persist for short time and diurnal changes are largely influenced by cycles in soil temperature (Smith et al., 1998; Williams et al., 1999; Choudhary et al., 2002; Flessa et al., 2002a) and rainfall and irrigation events through effects on air-filled porosity (Stępniewska et al., 2000).

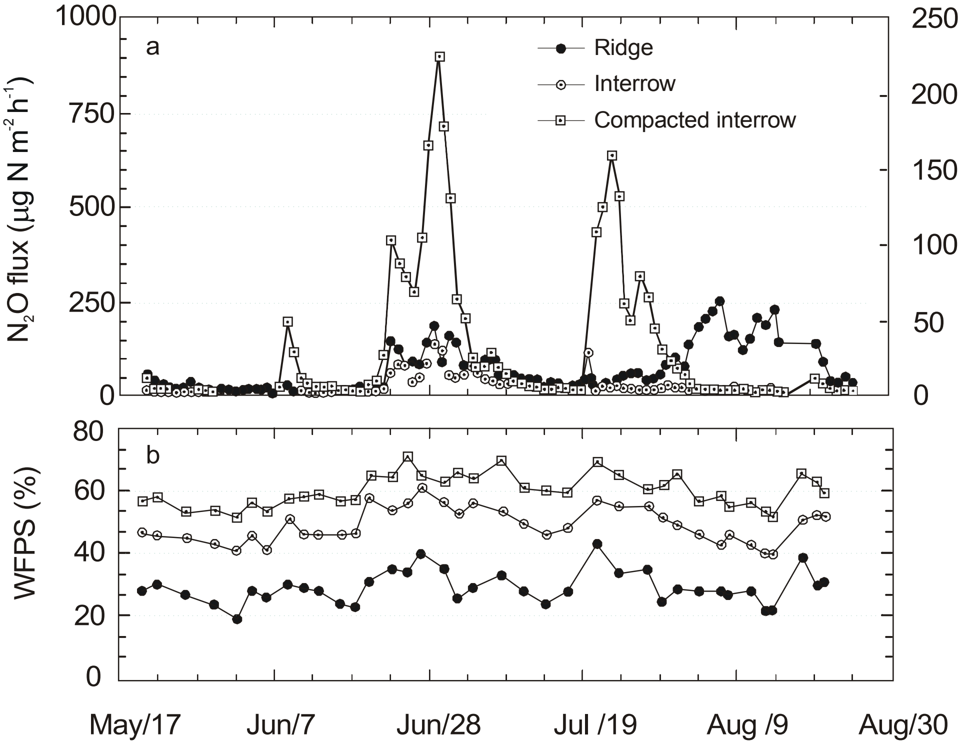

Fig. 3. *N_2O fluxes and water-filled pore space (WFPS) during the potato growing period (after Flessa et al., 2002b).*

METHANE

Main suppliers to the atmospheric methane concentration are cultivated wetlands (rice fields) and natural wetlands (Le Mer and Roger, 2001). Soil management may account for 20% of overall CH_4 emissions (Neue et al., 1996).

Effects of tillage and compaction on methane exchange

Information about the effect of different tillage systems on CH4 oxidation is limited. Some studies showed that methane oxidation potential (uptake) of upland soils may best be preserved by no-tillage (Ball et al., 1997,1999; Kessavalou et al., 1998; Hütsch, 2001; Le Mer and Roger, 2001) because soil tillage disturbs methano-oxidising microorganisms (consumers of CH_4) by disruption soil structure and increases gaseous diffusivity resulting in release soil-entrapped methane. The degree to which soil cultivation reduces CH_4 oxidation depends on the soil texture. In well aggregated fine textured soil microorganisms in the crumbs seem to have some protection against disturbance, whereas those around sand grains can easily loose their niches of high activity. (Ball et al., 1997).

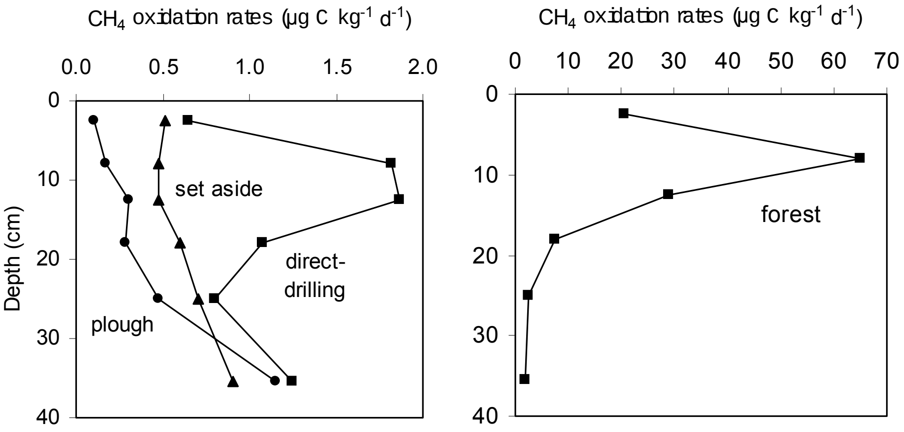

__Fig. 4.__ Methane oxidation rates in different soil layers as related to method of tillage and land use (after Hütsch, 2001).

Tillage method and land use has a clear effect on vertical zonation of methane oxidation (Fig. 4). This oxidation increased substantially below the plough layer (0-25 cm) and showed a subsurface maximum under direct-drilling (5-15 cm) and under forest (5-10 cm). Under set aside the zonation was similar to that under ploughing. In general the highest oxidation rates occurred in the uppermost mineral soil horizon. The most dominant factor for the spatial variation in CH_4 production on the micro-scale is the distribution of fresh organic material, which activates and possibly attracts methanogenic Archaea (methanogens) (Wachinger et al. (2000).

An important factor influencing methane oxidation and emission is soil compaction (Ruser et al., 1998; Le Mer and Roger, 2001). In potato-cropped field the ridge soil and the uncompacted inter-row soil had mean CH_4-C oxidation rates of 3.8 and 0.8 μg m^{-2} h^{-1} (0.0038 and 0.0008 g CH_4-C m^{-2} h^{-1}), respectively, whereas the tractor-compacted soil in this study emitted CH_4-C at 2.1 μg m^{-2} h^{-1} (0.0021 g CH_4-C m^{-2} h^{-1})(Ruser et al., 1998). Similar reaction was reported by Flessa et al. (2002a).

NITRIC OXIDE

Production and release of NO are largely controlled by environmental variables such as inorganic nitrogen availability, soil water content and soil temperature. Land use and cultural practices largely influence these variables.

In general, tillage increases NO emissions by rising the amount of exposed soil allowing for easier physical transfer of NO out of the soil. It was reported that conventional tillage can increase NO emissions by a factor of 2 to 7 (Skiba et al., 1997; Civerolo and Dickersen, 1998). This effect can be enhanced by incorporation of green manure (Skiba et al., 1997). Peirce and Aneja (2000) reported that more than forty percent of the total NO flux comes from the top 1 cm of soil and it decreases exponentially with soil depth and very little from soil at a depth of 20 cm or greater. In general, production and of NO increase with increasing soil WFPS, temperature and NO_3 concentration (Skiba et al., 1997; Tabachow et al., 2001) .

MULTIPLE GREENHOUSE GASES

The measurements of multiple greenhouse gases fluxes allow minimizing the effect of site conditions while comparing the fluxes in response to management practices. Effect of the practices depends on type of the trace gas and experimental conditions.

Ball et al. (1999) reported that ploughing and control of compaction can minimize losses of CO_2 and N_2O whereas CH_4 oxidation may be preserved by no-tillage. The accumulated N_2O emissions corresponded to 5.3% and 3.9 % of added fertilizer in compacted and in uncompacted soil, respectively and the accumulated CH_4 uptake was reduced by 52% by soil compaction (Hansen et al. (1993). Flessa et al (2002b) observed similar effect of compaction on potato-cropped fields. An integrated emission of the CO_2, CH_4 and N_2O was lower with organic farming vs. conventional farming (Flessa et al., 2002a).

CONCLUSIONS

1. Tillage practices and compaction largely affect greenhouse gas emission and uptake through changes in soil physical, chemical and biological properties of soil and crops. These effects depend on type of greenhouse gas and site conditions.
2. Tillage increases CO_2 emission by reducing resistance to gas transport and elevated temperature. This is most pronounced during tillage and immediately after. Tillage depth and degree of soil disturbance enhance and rainfall events diminish this effect.

3. Emission of N_2O is higher from not tilled than tilled and from compacted than not compacted soil is ascribed to greater contribution of larger aggregates with anoxic centres and reduced gas diffusivity and air-filled porosity. With not tilled soil this effect is enhanced by increased availability of C. Oxidation potential and uptake of methane is greater in not tilled than tilled upland soils because soil tillage disturbs methano-oxidising microorganisms that consume CH_4. Soil compaction enhances the methane emission.

4. Tillage increases NO emissions by rising the amount of exposed soil allowing easier physical transfer of NO from the soil. Incorporation of green manure enhances this emission.

5. Experiments with measurements of multiple greenhouse gases showed that soil compaction led to increased N_2O emission and reduced CH_4 uptake. Further research is needed to weigh beneficial against negative effects of management practices with consideration site-relative importance of particular gases.

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GAS EMISSION FROM WETLANDS

Stępniewska Z., Stępniewski W., Bennicelli R., Ostrowska A., Kotowska U.

SUMMARY

The aim of this paper was to investigate the formation of gases in Łęczyńsko-Włodawskie Lake District in the middle-east part of Poland.

Gas samples were collected from several natural (Moszne, Rotcze, Uściwierz, Piaseczno) and two anthropogenic lakes (Nadrybie and Szczecin). The investigated lakes were differentiated by trophy (oligo-,mezo-, eu- or dystrophy), depths (1.5-18m) and sizes (17.6-100ha). The gases emitted from the water surface at different distance from the shore were collected by a floating chamber technique. Samples of gasses were taken with a syringe and analyzed by gas chromatography technique, using different detectors: Flame Ionization Detector (FID) for CH4 detection and Thermal Conductivity Detector (TCD) for O_2 and CO_2 were used. The highest methane concentrations in the collected gases ranged from 2.92% (mezo-trophic Piaseczno lake) to 62.6 % (dystrophic Moszne lake).

Methane fluxes from the surface of the tested lakes ranged from 0.002 to 0.25 t/ha/day and were the highest during summer time from anthropogenic Nadrybie lake, while from mezzo-trophic Piaseczno lake did non exceed 1% of this amount.

In the tested peat profiles the ranges of methane fluxes were higher and maximally reached up to 300% of the values obtained for the collection chambers. This results indicated that oxidation of methane during its penetration from deeper layer to the peat surface reaches almost 75% of the generated methane.

BACKGROUND

Wetlands are recognized as sites with significant sources of atmospheric methane. Natural and cultivated wetlands represent approximately 40% of the sources of atmospheric CH_4 (increasing roughly by 1% annually) contributing to about 15% of the greenhouse effect. The global methane emission from wetlands is about 145 Tg yr –1 of which 92 Tg yr –1 come from natural wetlands and 53 Tg yr –1come from rice paddies (Raport IEA, 1999).

The ability of methane to absorb infrared radiation is 20-30 times higher then that of CO_2. The estimation of emission of greenhouse gases from restored wetlands in relation to water table position and prediction of its dependence on the expected climate changes is an essential problem of restored peatlands. It is assessed that predicted increase of temperature by 2^oC and of precipitation by 10% will elevate CH_4 emission from northern wetlands by 21% (Kammen and Marino, 1993).

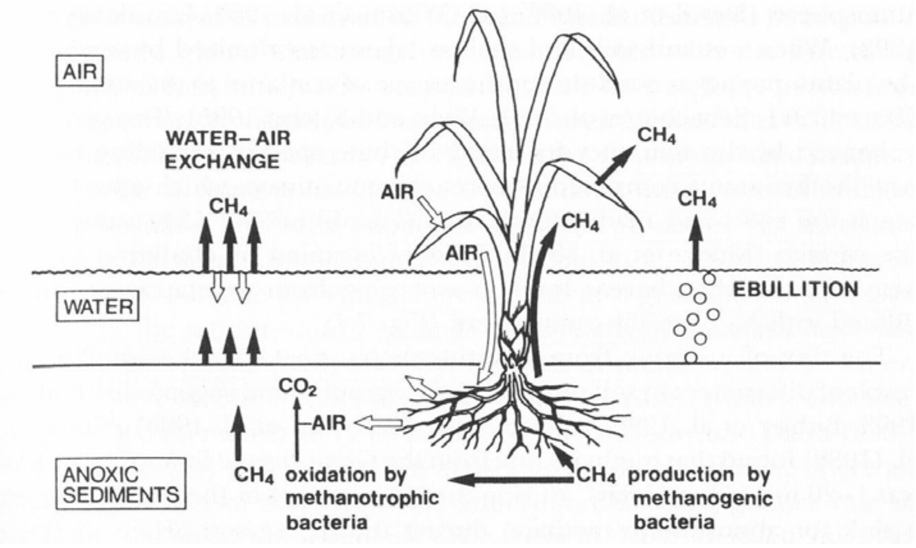

Fig.1. *Methane production and oxidation in wetland soils. Schutz et al. 1991.*

Distribution and availability of oxygen in sediments and soils is an important regulator of CH_4 and N_2O emissions (which is highest between 1% and 0.5 % of O_2 concentration) and of aerobic methane oxidation (Valentine and Reeburgh, 2000). Is should be emphasised that oxygen can be produced by phototrophs even in lake sediments. Methane oxidation during its migration through soil and/or water constitutes 15% to 76% of the potential diffusive methane flux (resulting from methanogenesis). Thus increasing of methane oxidation in wetlands can be done by regulation of water table position (Schipper and Reddy, 1994) .

Methanogenesis can occur via several different metabolic pathways: by acetate splitting (from 50 to 60% of CH_4 production) or by CO_2 reduction in which hydrogen is available as a product of fermentation (Augustin et all.1998). Sulphate-redusing bacteria can use H_2 as a source of electrons and they are more efficient then methanogens. Thus, in most environments there is a little or no overlap between the zone of metanogenesis and sulphate reduction zone. In the sediments methanogenesis took place when sulfate is depleted Shlesinger, 1997.

SITE DESCRIPTION

The investigations were carried out in the Polesie district in the east part of Poland. Water retention capacity in this province called Western Polesie which covers the area over 140 thousand ha, showed a tendency to increase. This area is rich in natural lakes (68), swamps and peat soils subjected to dewatering during last 60 years by construction of numerous ditches and drainage channels.

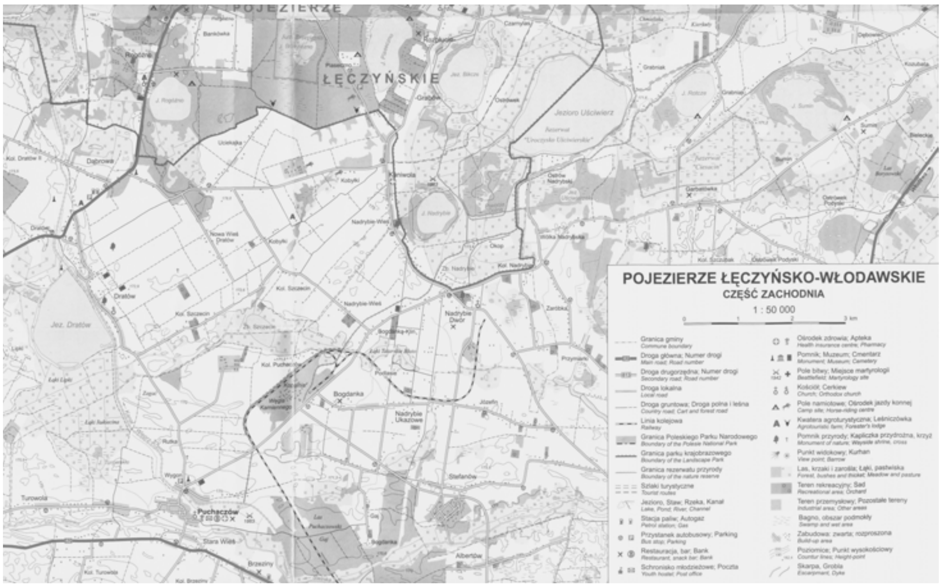

Fig.2. Map of Łęczyńsko-Włodawskie Lake District (Western Part).

Another deformation of earth surface in this territory, called "depression reservoirs" is connected with land subsidence and formation of the new artificial lakes (Nadrybie and Szczecin) as an effect of an activity of coal mine, which has operated there since 1975 and disturbs the previously developed water system.

Fig.3. *View on Nadrybie anthropogenic lake and coal mine factory in the deep.*

During 2000-2002, periodic gas studies at both on natural and anthropogenic lakes as well as on peat soils were performed. Gases emitted from the surface of the tested lakes at transect (litoral, sublitoral and pelagial zone) were studied using static closed chamber technique. In the peat soils the surface flux and vertical concentrations of the emitted gases were measured. The gas samples were taken periodically after 30, 60 and 90 min and anlyzed by Varian gas chromatograph configured together in 3-columns and 3-detectors (TCD/FID/ECD). This enabled routine analysis for gases of interest (CH_4, CO_2, O_2, N_2 and N_2O) over multiple ranges with a single injection.

Fig.4. *Floating chamber (for collecting gas samples) on the surface of Moszne lake.*

RESULTS

Methane emissions from natural and anthropogenic lakes at different seasons of the year and transect are presented in Tabs.1- 2 and Fig.5.

Natural lakes and newly formed anthropogenic lakes were differentiated with respect to the composition of the emitted gas (N_2 in the range 40-80% and O_2 in the range 6-28%). The concentration of CO_2 was at a level 0-4%, but methane was the most dynamic component of emitted gases. Its concentration reached up to 60% v/v.

Table 1. Seasonal methane emission [t/ha/day] from the tested natural lakes

	Moszne	Uściwierz	Rotcze	Piaseczno
Spring	0,002	0,0015	0,0008	0,0005
Summer	0,035	0,0016	0,0077	0,0028
Autumn	0,008	0,0035	0,0021	0,0005

Higher methane emissions were noted in Szczecin anthropogenic lake and in natural Moszne lake in lithoral zone. The central part of lakes were characterized by much smaller methane and carbon dioxide concentrations and higher those of oxygen and nitrogen. Comparison of the both anthropogenic lakes shows that one of them (Szczecin) has shown a wide range of differentiation in the gas composition. This indicates an advanced methanogenesis process in lithoral and sublithoral zone, while in Nadrybie lake the level of methane emission was four time higher than in the pelagial of Szczecin lake.

Table 2. Seasonal methane emission [t/ha/day] from the anthropogenic lakes under study.

	Spring	Summer	Autumn
Nadrybie lithoral	0,012	0,252	0,002
Nadrybie sublithoral	0,043	0,002	0,001
Nadrybie pelagial	-	0,012	-
Szczecin lithoral	0,086	0,008	-
Szczecin sublhitoral	0.178	0,028	0,0002
Szczecin pelagial	0,007	0,002	0,0002

The collected results of emitted gases from natural and anthropogenic lakes are presented in Fig.5.

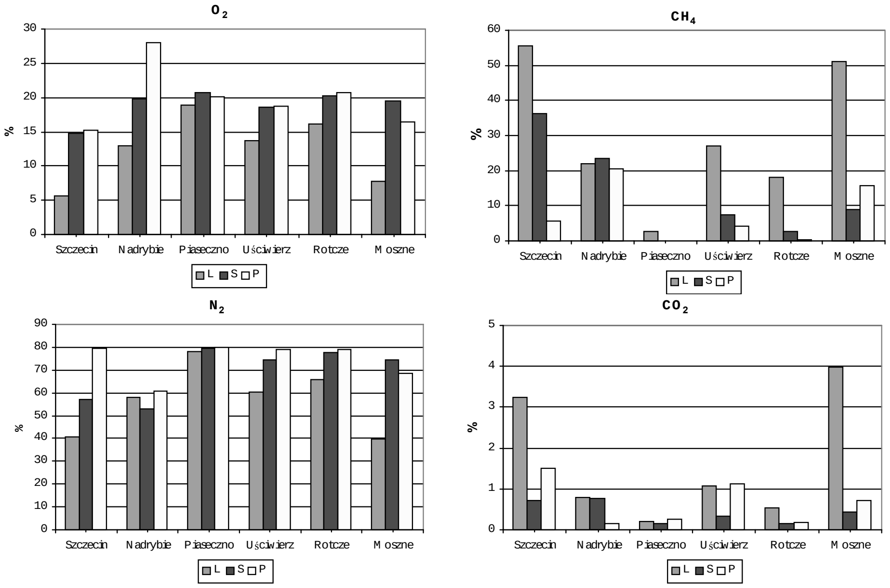

Fig.5. Gas composition from Szczecin and Nadrybie anthropogenic lakes as well as from Piaseczno, Uściwierz, Rotcze and Moszne natural lakes at transect :L-lithoral, S-sublithoral, P-pelagial .

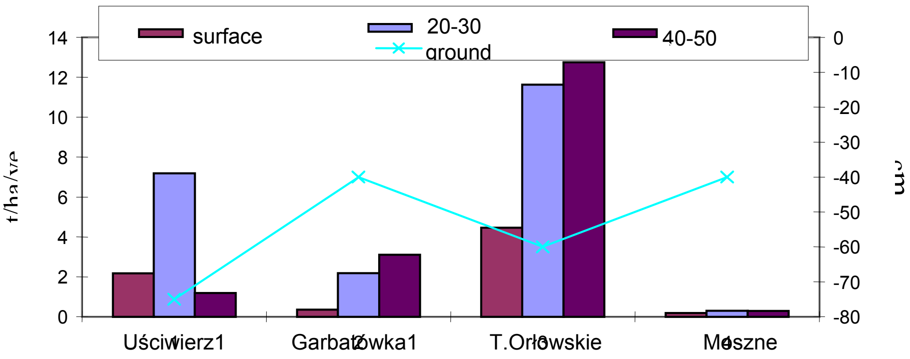

Fig.6. *Ground water level and methane emission from surface and at different depths (t/ha/year) of tested peat soil.*

Methane released from the anthropogenic lake (Szczecin) was the highest during spring time after 30 min and recived 35,5% v/v and even 67,24% during summer time in lithoral zone and 32,2 and 64,26% from Nadrybie lake, respectively.

In the case of natural lakes the highest concentration of CH4 in the emitted gas equal to 52% i 4% was found in the lithoral zone of Moszne lake while that from Rotcze and Piaseczno lakes not exceed 15% .

Oxygen concentration was the smallest (8%) in lithoral what indicates on the highest a demand in this zone. In all tested lakes concentration of O_2 increase ones translocation to sublithoral and pelagial.

The highest oxygen demand was observed in the lithoral zone of Moszne lake where concentration of oxygen was at the level of 0,74%, (summer 2001), reaching at the same moment 17,78% in sublithoral and 8,36% in pelagial zone. From Uściwierz lake O_2 concentration in the emitted was on the level 10,3% and 14,3 % while from Rotcze and Piaseczno19,3 and 20,7%, respectively.

Concentration of carbon dioxide was negatively correlated with oxygen concentration and was the highest in gas samples from Moszne lake, while from Uściwierz lake was on the level 7,36%. In the case of the lakes indicate maximal concentration of CO_2 2,77%, while in Rotcze and Piaseczno lake did not exceed 1%.

Distribution of Eh in the particular lake zone of the lakes under study is presented in Fig.7. The highest differentiation was observed in Uściwierz lake and between shore (piezometr-Pz) and pelagial (P) zone exceeded 200mV, while in Piaseczno lakes was about 300mV.

The most advanced anaerobic conditions were found in anthropogenic lakes rich in organic matter Szczecin (surface ca. 100 ha) and Nadrybie (surface ca.18 ha) which emit to atmosphere 1020 t and 169 t of methane per year, respectively.

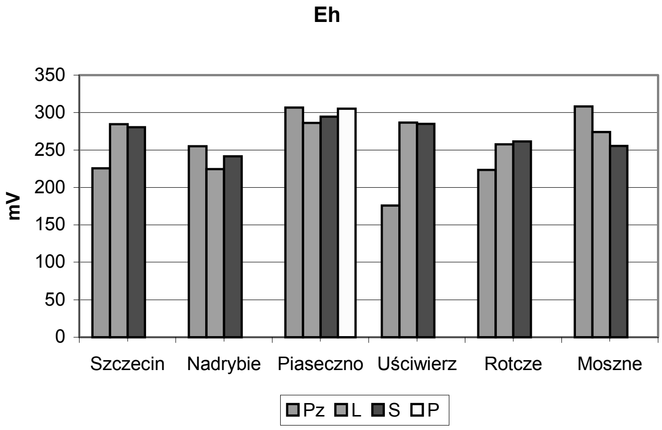

Fig.7. *Redox potential (Eh) in anthropogenic lakes (Szczecin i Nadrybie) and natural lakes (Piaseczno, Uściwierz, Rotcze i Moszne) in different zone (Pz – piezometr; L – lithoral; S – sublithoral; P - pelagial).*

From natural lakes the range of methane emission varies from 11.54 t/ha/year (Moszne) to 0.41 t/ha/year. These values are comparable with CH4 emission from rice field (Piaseczno) or even many times higher (Moszne) which according to Murase and Kimura(1994) remain on the level about 0,65 t/ha/year. Methane emission from the tested peat soil did not exceed 0.82 t/ha/year.

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AERATION AND CLIMATIC GLOBAL CHANGE

Stępniewski W., Stępniewska Z.

INTRODUCTION

The list of greenhouse gases comprises water vapor, carbon dioxide, methane, nitrous oxide and others. Total greenhouse effect is evaluated to be about 32°C. Of this about 20°C is caused by the presence of water vapor in the atmosphere, 7°C by carbon dioxide, 2.4°C by ozone, 1,4°C - by nitrous oxide, and 0.8°C by methane (Kożuchowski and Przybylak, 1995). The present day concern about global warming is caused by expected further increase of the global temperature by 2-4°C during 21 century. Talking about interrelation between soil aeration and global warming usually methane and nitrous oxide are taken into consideration. However, this relationship is also valid for water vapor and carbon dioxide.

WATER VAPOR

Water vapor pressure in the atmosphere is not related directly to soil aeration status. However, anoxic conditions in soil occur predominantly in wetlands, which generate higher humidity in the atmosphere. Thus the presence of wetlands should increase the temperature through elevated humidity of atmospheric air.

CARBON DIOXIDE

Carbon dioxide is the second important greenhouse gas. Under natural conditions its primary source was the respiration of soil (assessed at present to be about 60 Pg of C), of plants and animals (also about 60 Pg of C), while its essential sink was the photosynthesis (121 Pg C) (Lal, 2002). The equilibrium between them has been modified by anthropogenic emission presented in Table 1. The total organic C pool in soil is assessed as 1550 Pg, atmospheric C pool as 750 Pg and pool in biota – as 610 Pg (Lal, 2002). Change of soil carbon pool by 1 Pg is equivalent to 0.47 ppm change in the atmospheric CO_2 (Lal, 2002).

Availability of oxygen is of primary importance for the process of organic matter mineralization due to microbial respiration. The rate of annual increase of the atmospheric pool of carbon dioxide is 0.4% and the residence time is 50-200 years. Anoxic conditions in wetlands lead to reduction of respiration rate and to net carbon accumulation in soil. This, in turn, leads to reduction of its amount in the atmosphere. However it should be kept in mind that in anoxic wetlands part of the assimilated carbon is returned to the atmosphere in the form of methane, which is much more active radiatively (see further). Thus the net effect of wetlands is the increase of the global temperature because the methane evolved and the increased humidity of the atmosphere prevail over the accumulation of organic carbon under such conditions.

Table 1. Sources and sinks of atmospheric carbon dioxide according to Lal 2002.

Source/sink	Flux Pg/year
1. Sources	
a. Fossil fuel combustion	6.8
b. Deforestation, land use and world soils	1.6
Total	**8.4**
2. Sinks	
a. increase of atmospheric concentration	3.5
b. ocean uptake	2.0
Total	**5.5**
Unknown sink (probably soils)	**2.7**

METHANE

Methane is the next important greenhouse gas. Its contribution to the future increase of the greenhouse effect can be important, despite its low concentration in the atmosphere (1.73 ppmv). This importance is a result of capacity to absorb infrared radiation, which is about 30 times higher compared to that of carbon dioxide. Its residence time in the atmosphere is 10 years and its concentration increases by about 1% per year. Main sinks and sources of atmospheric methane are presented in Table 2. Most of methane is formed under anoxic conditions of which anoxic soil plays an extremely important role. This is valid for natural wetlands being the most important methane source as well as for rice fields, and landfills.

It should be emphasized that soil can be a source and sink of methane dependently on its aeration status. Oxic soil absorbs methane, while anoxic soil is the methane source. Conversion of a given soil from the sink to source of methane depends on its aeration status. As it has been shown in Fig. 1. methane is produced at redox potentials below –50 mV. At higher values it undergoes oxidation. The effect of redox potential on methanotrophic activity of a sand flushed with methane is shown in Fig. 2. So in the same site deeper soil horizons can produce methane which can be partly or entirely oxidized in the surface layer during migration to the atmosphere. An idealized distribution of methane sources and sinks in soil is presented in Fig. 3. The effect of oxygen concentration on methane oxidation rate as measured by the methane and oxygen consumption and by carbon dioxide production is demonstrated for the sand incubated in the presence of methane in Fig. 4.

Table 2. Sources and sinks of atmospheric methane (Tg rok^{-1}) according to different authors.

Authors*	A	B		C	D	E	F
Sources of CH_4	value	value	range	value	value	value	range
Total natural sources					345	145	
Natural wetlands	125±70	115	55-150	100		100	92-232
Other natural sources:		50	25-140				
- termites	30±30					20	2-22
- oceans	10±5					4	0,2-2
- marine sedim.						5	0,4-12,2
- geological	5±5					14	12-36
- fresh waters	5±5						
Agric. sources total						141	
Rice fields	70±50	60	20-100	50		60	25-90
Fuminants and animal wastes	105±30	105	85-130	100		81	65-100
Anthropogenic non-agric sources together.						217	
Energy production and use:		100	70-120	100		30	25-50
- natural gas	80±45					46	15-64
- coal	35±10					30	6-60
Lanfills	40±25	30	20-70	22		61	40-100
Biomas burning	30±15	40	20-80			50	27-80
Municipal waste waters	25±10	25					
Total sources	**560±90**	**525**		**540**		**503**	**410-660**
CH_4 sinks							
Decomposition in the atmosphere:		470	420-520				
- reactions with OH in throposph.	455±50				490	445	360-530
- Reactions with OH, Cl, $O^\bullet$ in strtosphere	45±10				40	40	32-48
Oxidation of atmospheric CH_4 in soil	30±25	30	15-45		38	30	15-45
CH_4 sinks together	**530±85**	**500**			**568**	**515**	**430-600**
Annual increase in atmosphere	+30	+25				-12	+20-60

* Abbreviations: A: Lelieveld and Crutzen, 1993; B: IPCC, 1995; C: Mosier, 1998; D: Etiope and Klusman, 2002; E: Khalil, 2000 after Wuebbles and Hayhoe, 2002; F: Different sources after Wuebbles and Hayhoe, 2002

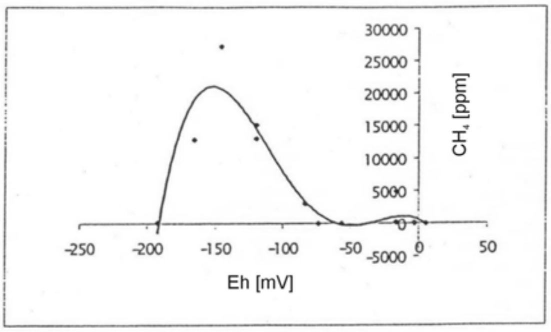


Fig. 1. *Quasi – equilibrium methane concentration versus soil redox potential in a peat soil irrigated with municipal waste-water after mechanical and biological treatment. (modified from Stepniewski and Stepniewska, 2000)*

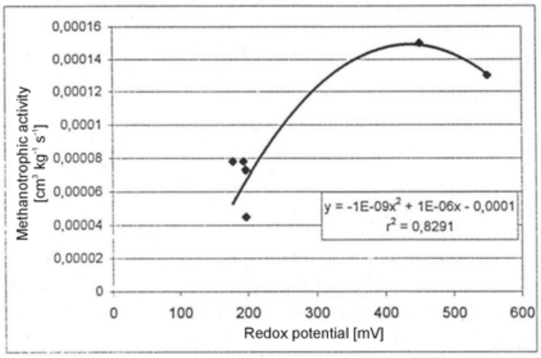


Fig. 2. *Methanotrophic activity of a sand flushed with methane versus redox potential (from Pawłowska, 1999).*

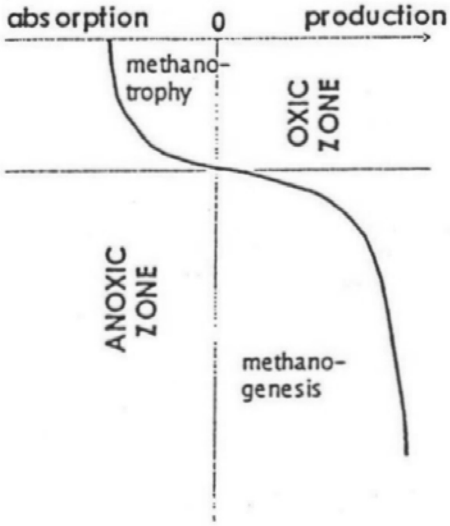


Fig. 3. *An idealized distribution of sources and sinks of methane in a soil profile with oxic and anoxic zone (modified from Stepniewski and Stepniewska, 2000).*

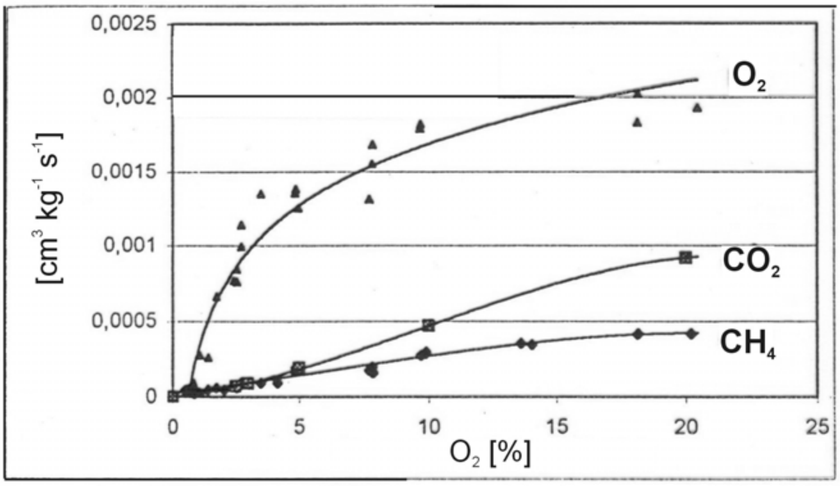


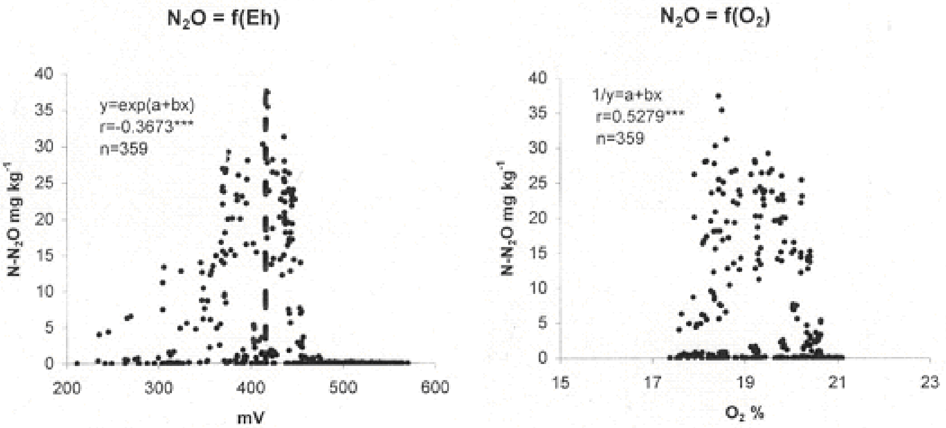
Fig. 4. *The effect of oxygen concentration on methane oxidation rate as measured by the methane and oxygen consumption and by carbon dioxide production for a sand incubated in the presence of methane in Fig. 4. (After Pawłowska, 1999).*

NITROUS OXIDE

Nitrous oxide concentration in the atmosphere is about 313 ppb v/v. i.e. abut five times less than that of methane, but its activity in the absorption of infrared radiation is more than 200 times that of carbon dioxide. Its lifetime in the atmosphere is about 166 years and the annual increase by 0.7 ppbv each year (Freney, 2002).

Out of about 23,1 Tg of nitrous oxide emitted to the atmosphere every year 14.1 Tg is a result of natural processes (4.7 Tg from the oceans, and 9.4 from soils) and about 9 Tg is the result of human activity. The pool emitted due to human activity consists of 5.5 Tg emitted from agricultural soils, 2.1 Tg from industry and automobiles, 0.8 Tg from biomass burning and 0.6 Tg from cattle and feedlots. Despite some uncertainty of these figures in should be emphasized that the most of nitrous oxides is produced in soils (Freney, 2002).

The nitrous oxide concentration in the soil air versus soil redox potential and versus oxygen concentration is shown in Fig. 5. It shows that nitrous oxide coexists within, soil in a rather narrow range of oxygen concentration and of redox potentials. Both at lower and at higher redox potentials nitrous oxide is absorbed by the soil. In the first case due to its reduction and in the second – due to oxidation. Thus during migration to the atmosphere nitrous oxide can face the layer capable to reduce it and then by the layer capable to oxidize it. Additional complication can be introduced by soil heterogeneity, as such processes can overlap even within single soil aggregates.



$N_2O = f(Eh)$

$N_2O = f(O_2)$

Fig. 5. *Concentration of nitrous oxide in equilibrium with different Cambisols versus oxygen concentration and soil redox potential – laboratory incubation in closed vessels. (After Włodarczyk, 2000).*

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OXYGENOLOGY - A NEW SCIENTIFIC DISCIPLINE

Stępniewski W., Stępniewska Z.

THE CONCEPT

Oxygenology has been defined by Stępniewski and Stępniewska (1998) as the scientific discipline related to the presence and the role of oxygen in nature on Earth. It constitutes a branch of environmental sciences and comprises issues of storage, transport, generation, absorption, turnover, functions and measurement of oxygen content in the environment. The name of this new discipline is analogous to that of hydrology.

The proposal of identification of oxygenology as a separate branch of science was justified not only by the unique role of oxygen as the most abundant component of the lithosphere and as an exceptional component, on the cosmic scale, of the atmosphere of our planet, but also by the need for a holistic approach to the oxygen related problems faced in aquatic, wetland and dry-land ecosystems because of their common nature and structure.

Oxygen plays an essential role in the life of all macro- and microorganisms, as well as in the biochemical and chemical processes occurring in environment.

Having limited our interest only to Earth's oxygenology (i.e without oxygenology related to other planets), and more precisely only to the contemporary oxygenology (omitting paleooxygenology related to previous geological periods) such subbranches as atmospheric oxygenology, aquatic oxygenology, lithospheric oxygenology and biooxygenology have been distinguished. The aim of this paper is to present only few selected examples of the issues involved in the oxygenology as presentation of the entire scope of this discipline would require several books. As an illustration of this fact is the book devoted solely to soil oxygenology (Gliński and Stêpniewski, 1985) made reference to more than 820 publications.

ATMOSPHERIC OXYGENOLOGY

Oxygenology of atmosphere is related to the problems of oxygen distribution, production, absorption and turnover in the atmosphere as well as to the formation, distribution and reactivity of ozone in the troposphere and stratosphere, etc. Within the atmospheric oxygenology such research areas as. tropospheric oxygenology and stratospheric oxygenology can be distinguished.

AQUATIC OXYGENOLOGY

Hydrooxygenology or aquatic oxygenology has been defined as the oxygenology of the hydrosphere. It comprises issues of oxygen generation, absorption, transformation, distribution, storage, and transport in aquatic media. Within hydrooxygenology, such subbranches as ocean oxygenology, limnooxygenology (oxygenology of lakes), and potamic oxygenology (i.e. oxygenology of rivers) have been distinguished.

In many situations the saturation of lake water with oxygen in summer at a depth of several meters can exceed 140% due to generation of oxygen by photosynthesis of phytoplankton. Thus the oxygenological situation can be better here compared even to the surface of water, characterized by 100% saturation with atmospheric oxygen. It has to be emphasised that even under transparent ice-cover the production of oxygen due to photosynthesis can take place.

Waters with seasonal or permanent (eg. Arctic Ocean or Antarctic lakes) ice-cover create special oxygenological situation. A curious example is the oxygenological situation in antarctic lakes covered during all the year with a thick ice-cover. However, under the ice - cover the water is almost saturated with oxygen while deeper waters are anoxic. Thus in such a lake permanently covered with ice there is a full spectrum of conditions from completely oxic to anoxic.

LITHOSPHERIC OXYGENOLOGY

Oxygenology of lithosphere relates to the processes of distribution, supply, uptake, transport and the role of oxygen within the lithosphere and especially in the pedosphere being its most active part. Here we can define some special research fields such as:

- oxygenology of wetlands (natural, agricultural and constructed wetlands)
- oxygenology of drylands (natural and agricultural)
- oxygenology of anthropogenic systems (landfills, recultivated areas, waste water treatment plants, storages of agricultural materials etc.)

An example of oxygen distribution within a wetland is presented in Fig. 1. As it can be noticed oxygen concentration drops rapidly to zero at a depth of several centimetres below the soil – water interface. Examples of oxygen distribution in agricultural soil are shown in Fig. 2. In such a situation we deal with subatmospheric oxygen concentrations (usually between 10 and 20% by volume) and above – atmospheric carbon dioxide concentrations (usually between 0.1 and 10% by volume).

BIOOXYGENOLOGY

Biooxygenology has been defined as the oxygenology of living organisms i.e. oxygenology of biota. It is focused on the effect of oxygen availability in the environment on living organisms as well as on the studies of transport, absorption, and the role of oxygen within the organisms themselves. Within biooxygenology, such areas as microbial oxygenology, phytooxygenology (oxygenology of plants), and zoological oxygenology (zoo-oxygenology) have been distinguished.

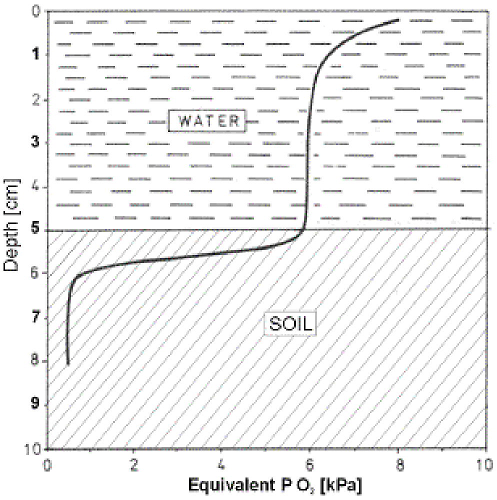

Fig. 1. *Oxygen distribution in a flooded soil (Modified from Patrick and Mikkelsen, 1971)*

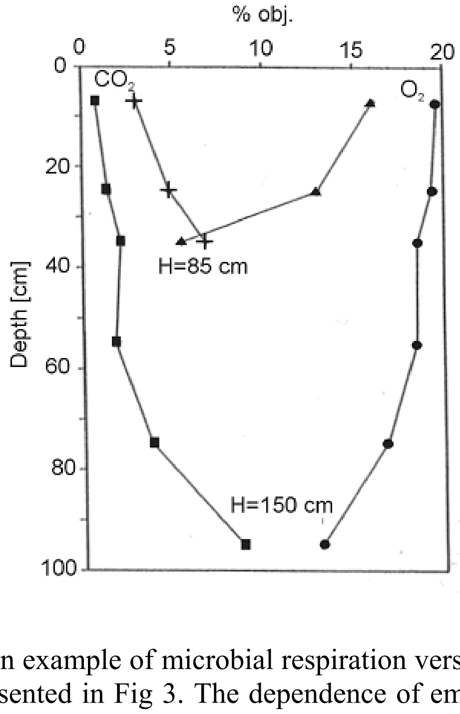

Fig. 2. *Oxygen and carbon dioxide distribution in a gley meadow soil (Garbów, near Lublin, Poland) at two groundwater levels on 1971.06.19 (ground water level H = 85 cm) and on 1971.09.04 (H = 150 cm). (Unpublished data of W. Stępniewski).*

An example of microbial respiration versus oxygen concentration in the soil air is presented in Fig 3. The dependence of emergence of oats seedlings versus oxygen availability (as measured by the indicator called oxygen diffusion rate ODR) is presented in Fig. 4. It can be noticed that the response has a typical character with limiting and critical value of ODR As an illustration of the issues of the zooxygenology is presented in Fig. 5. It shows the hatching percentages of *Centropages hamatus* eggs versus oxygen concentration in sea water.

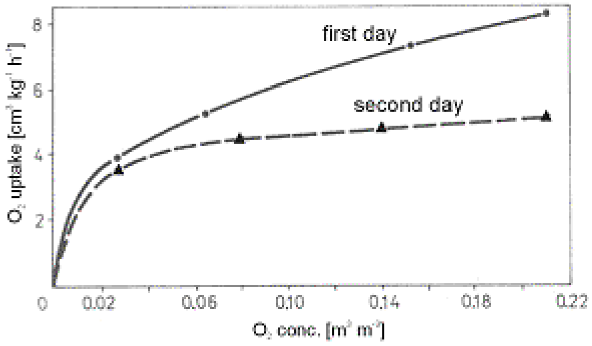

Fig. 3. *Soil microbial respiration versus oxygen concentration for a meadow loamy soil (3-7 cm clods) from a depth of 5-15 cm, at soil pore water pressure –11 kPa. 1 – first day after sampling, 2 – second day after sampling (from unpublished data of J. W. Bakker and W. Stępniewski).*

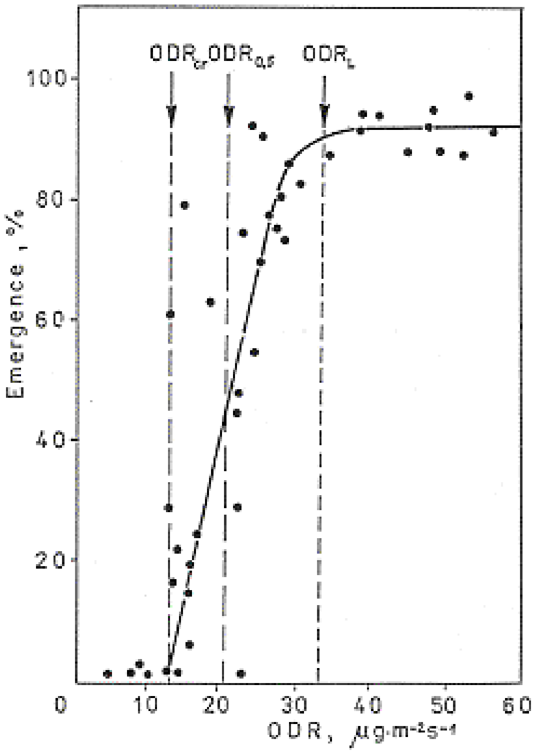

Fig. 4. *Final emergence of oats versus oxygen diffusion rate (ODR). Modified from Gliński, Stępniewski, Łabuda and Przywara, Roczn. Glebozn., 35, 3, 1984.*

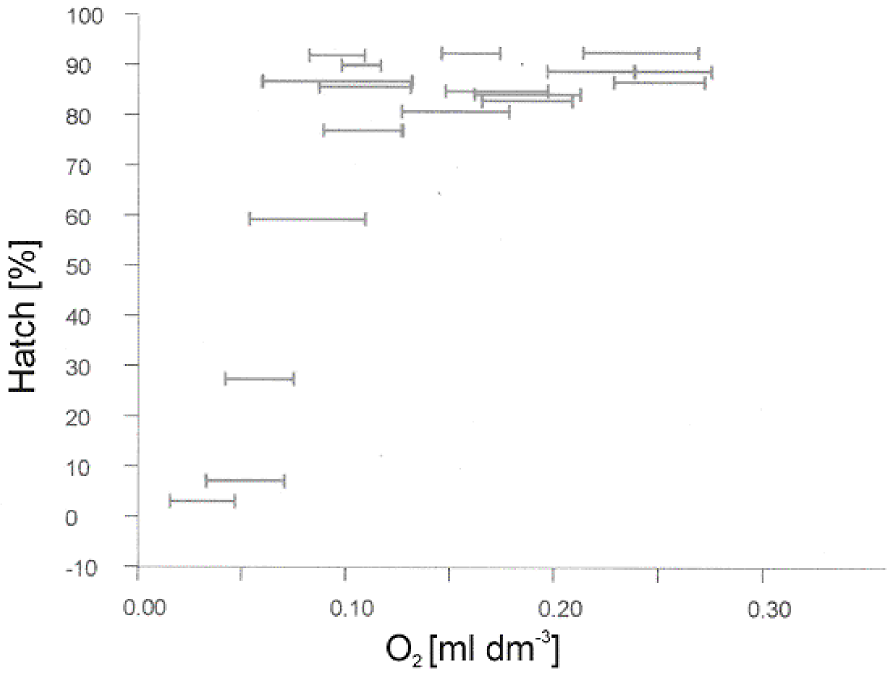

Fig. 5. *Hatching percentages of Centropages hamatus eggs versus oxygen concentration in sea water (The incubation was performed in sea water oxygenated for 11 days). Modified from Lutz et al. 1992.*

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NITROUS OXIDE EMISSION FROM SOILS

Włodarczyk T., Gliński J., Kotowska U.

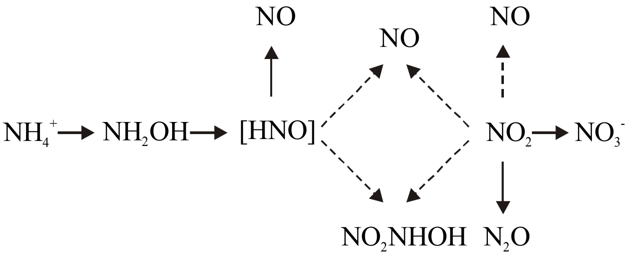
INTRODUCTION

Ambient concentration of N_2O have increased slowly from 288 ppb in 1750 until 1950 and then more rapidly to a current atmospheric 306 ppb (Duxbery et al., 1993). In general, most N_2O is formed from denitrification in oxygen deficient environment, although it can also be produced from chemolitotrophic nitrification in aerobic conditions (*Martikainen et al., 1993, Rice and Rogers 1993*)

N_2O production is affected by many physical and biochemical factors, such as nitrate and O_2 concentration, organic matter content, temperature, soil pH and soil moisture content (*Horn et al., 1994, Yu et al., 2001*).

NITRIFICATION

Nitrification is understood to be an aerobic process, however there is strong evidence that it can also occur under anaerobic conditions. Nitrifying bacteria have been shown to produce NO and N_2O.



According to *Groffman* (1991) two processes are responsible for N_2O formation from nitrification:

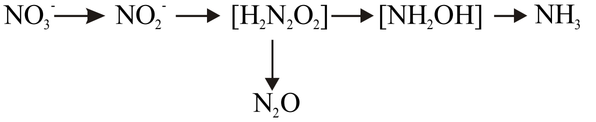
1. Ammonium oxidisers can use NO_2^- as an alternative electron acceptor when O_2 is limiting and produce N_2O. This process is called nitrfier denitrification.

2. Intermediates between NH_4^+ and NO_2^-, or NO_2^- itself, can chemically decompose to N_2O, especially under acidic conditions (a type of chemodenitrification).

Nitrification is often considered to be the dominant source of N_2O in "aerobic" soils (*Bremner and Blackmer, 1978*).

ASSIMILATORY REDUCTION OF NITRATE

In nitrate assimilation, the first step is the reduction to nitrite, which is accomplished by the enzyme nitrate reductase. Subsequently, the nitrite is reduced to hydroxylamine by the enzyme nitrite reductase to finally be reduced to ammonia (*Payne, 1973*). The net reaction is shown in the following equation:



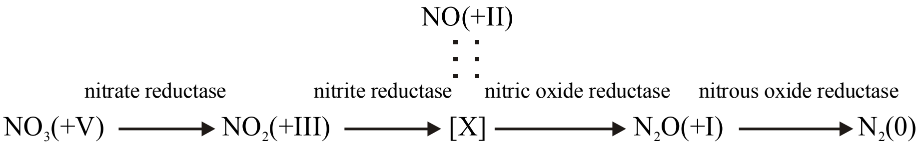
$$\begin{tikzcd} NO_3^- \arrow[r] & NO_2^- \arrow[r] & {[H_2N_2O_2]} \arrow[r] \arrow[d] & {[NH_2OH]} \arrow[r] & NH_3 \\ & & N_2O & & \end{tikzcd}$$

where N_2O rather than N_2 may be produced as a by-product from the indicated intermediate (hyponitrite). The reaction shown is essentially the same as that which occurs during NO_3^- reduction to NH_4^+ and involves the same precursor of N_2O, again probably hyponitrite (*Freney et al., 1979*; *Mosier et al., 1983*).

DISSIMILATORY REDUCTION OF NITRATE

When the dissimilative reduction produces the gaseous dinitrogen or nitrous oxide compounds, the process is termed **denitrification**.

Biological denitrification is the last step in the N-cycle, where N is returned to the atmospheric pool of N_2. It is an anaerobic process. Biological denitrification is a respiratory process in which N-oxides (electron acceptors) are enzymatically reduced under anaerobic conditions to nitrous oxide and dinitrogen for ATP production by organisms that normally use O_2 for respiration. The process of denitrification (including rhizobial denitrification) can be presented as follows: Conditions influencing nitrous oxide production in soils



$$\begin{tikzcd} & & NO(+II) \arrow[d, dotted, no head] & & \\ NO_3(+V) \arrow[r, "\text{nitrate reductase}"] & NO_2(+III) \arrow[r, "\text{nitrite reductase}"] & {[X]} \arrow[r, "\text{nitric oxide reductase}"] & N_2O(+I) \arrow[r, "\text{nitrous oxide reductase}"] & N_2(0) \end{tikzcd}$$

OXYGEN The oxygen status in soil, which is inversely, proportional to the amount of soil moisture, appears in many studies to be one of the key factors influencing nitrous oxide production (McKenney et al., 2001), (Fig. 1. Włodarczyk, 2000).

ORGANIC MATTER AVAILABILITY Denitrification is a respiratory process, which requires an easily oxidisable organic substrate. The presence of readily metabolized organic matter and the availability of water soluble organic matter are closely correlated with the rate of biological denitrification and hence with the potential production of N2O from soil. There is observed very high correlation between N2O emission and organic matter content (Fig. 2 Włodarczyk, 2000).

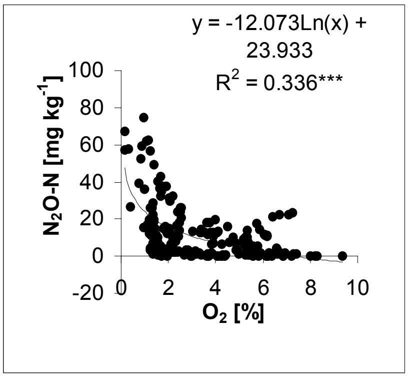


Fig. 1 *N_2O emission as a function of O_2 content for the day of maximum emission.*

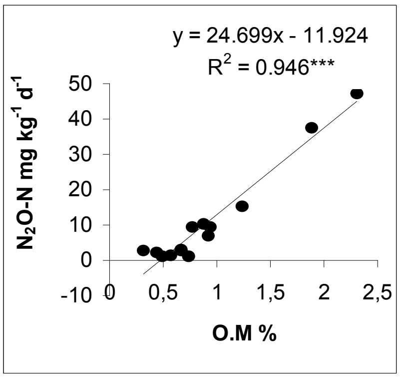


***Fig.2. N2O emission as a function of organic matter content**.*

DEHYDROGENASE ACTIVITY Dehydrogenases conduct a broad range of oxidative activities that are responsible for degradation (i.e. dehydrogenation) of organic matter. The amount of nitrous oxide formed due to denitrification showed high positive correlation with dehydrogenase activity (Fig. 3., Włodarczyk et al., 2001).

pH Under conditions where NO3- concentration does not limit potential denitrification, the overall rates of both denitrification and nitrification decline with decreasing pH from optimum of about pH 7.5 (Fig. 4 Włodarczyk 2000).

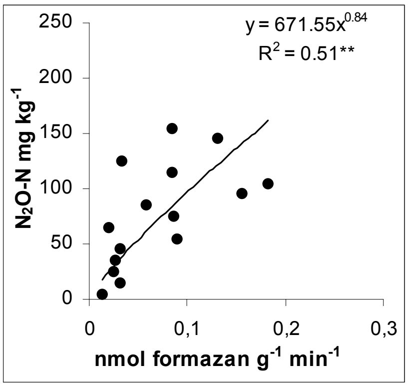


Fig.3. *N_2O emission as a function of dehydrogenase activity.*

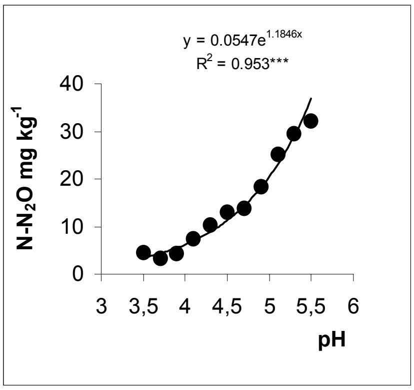


Fig.4. *Average N_2O emission as a function of pH for the day of maximum emission.*

NITRATE CONCENTRATION Total denitrification fluxes (N_2O plus N_2) are directly proportional to soil NO_3^- concentrations while the other important component, a readily metabolizable organic substrate, is also present and non rate-limiting. When a lack of metabolizable organic matter limits potential denitrification, N_2 plus N_2O fluxes do not increase with increasing NO_3^- concentration (*Sahrawat and Keeney, 1986*).

Nitrate reduction is now thought to be the major process involved in those gaseous emissions, for which NH_4^+ oxidation provides the denitrification electrons.

SOIL ***TEXTURE*** The soil texture and particle size distribution significantly affect the production of N_2O (Fig. 5). Nitrous oxide production from heavier-textured soils exceeds that from coarse-textured soils up to 6-times *(Włodarczyk, 2000).*

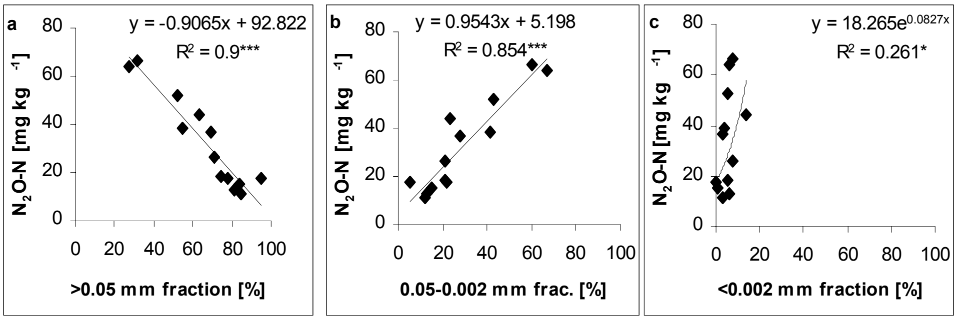


Fig. 5. *N_2O emission as a function of granulometric composition.*

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SOIL – PLANT – ATMOSPHERE AERATION AND ENVIRONMENTAL PROBLEMS

PART B: AERATION AND BIOLOGICAL ASPECTS

AERATION STATUS OF SOIL AND ENZYME ACTIVITY

Brzezińska M.

Soil is naturally exposed to the fluctuation of wet and dry cycles and to diurnal and seasonal temperature gradients. Thus, under field conditions, soil air-water status plays an important role in the regulation of the composition and metabolic activity of soil microorganisms. Moreover, air-water relations in soil are strongly effected by soil management. The kind of fertilization, the type and degree of tillage and other agricultural practices influence many physical characteristics such as aggregate stability, pores distribution, retention properties, and implicate alteration of numerous chemical and biological processes (Gliński and Stępniewski 1985; Lipiec and Stępniewski 1995; Kandeler et al., 1999; Walczak et al., 2002). Flooding the soil creates conditions markedly different from those of a well-drained, aerobic soil. In addition to retardation of gaseous exchange between soil and air, waterlogging results in the changes to microbial populations and in series of physico-chemical and biochemical transformations. Numerous permanently anaerobic aggregates and microhabitats occur also in well-aerated soils. In the absence of molecular oxygen, anaerobic microorganisms (facultative followed by obligatory) utilize oxidized soil components as terminal electron acceptors in processes involved in respiration metabolism. In the result, a stepwise reduction of soil system takes place, soil redox potential (Eh) decreases, pH alters, and concentrations of reduced forms increase (Gliński et al, 1996; Gliński and Stępniewski 1985; Ottow 1982).

This paper refers to the effect of the deterioration of soil aeration status on the activities of selected soil enzymes.

SOIL AERATION AND OXIDOREDUCTASES

Oxidoreductases are involved in respiration processes of all soil microorganisms. **Dehydrogenases** catalyze the transferring of hydrogen and electrons from oxidized substrates to acceptors. Thus, dehydrogenases take part in energy accumulation and are active in all soil microorganisms – aerobic as well as anaerobic. Many different intracellular enzymes or enzyme systems contribute to the total soil dehydrogenase activity. Assays for dehydrogenase activity in soil has often been used to achieve an index of total soil microbial activity.

Soil dehydrogenase activity increases under anaerobic conditions. This tendency has been observed in model experiments (with soils incubated at diminished oxygen concentration or under soil flooding) as well as under natural field conditions (Gliński et al., 1983; Okazaki et al, 1983; Pedrazzini and McKee, 1984; Tiwari et al., 1989). The anaerobic respiration is less efficient than aerobic (with utilization O_2 as terminal electron acceptor). Increased dehydrogenase activity under prolonged soil hypoxia suggests that the facultative and anaerobic members of the microbial community become more important in the total soil respiration. Soil sampled from natural sites, characterized by extremely different oxygenation conditions, varied in their dehydrogenase activity level. For example, a pseudegley meadow soil located in a terrain depression showed many-fold higher dehydrogenase activity, especially in wet springtime, than drained soil of a forest-covered slope site (Gliński et al., 1986). Dehydrogenase activity of loess soil incubated under controlled soil water potential, temperature and density, followed the changes in aeration status, and increased under soil hypoxia (14-day flooding at 30°C) more than 100-times as compare to aerated soil (pF 2.2, 10°C), (Brzezińska et al., 1998).

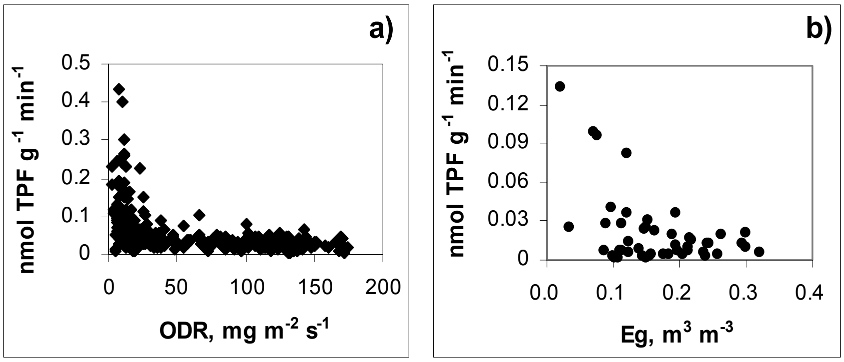

Fig. 1. *Relation between soil dehydrogenase activity and oxygen diffusion rate (a) and air-filled porosity (b) (from Brzezińska et al., 2001b, and Stępniewska et al., 2000)*

Soil dehydrogenase activity was shown to be negatively related to the air-filled porosity (Eg), oxygen diffusion rate (ODR) and redox potential (Eh), with threshold values at about 0.2 m^3 m^{-3}, 20-30 μg m^{-2} s^{-1}, and 200-300 mV, respectively. In turn, a positive relation to water content and concentration of reduced Fe was observed (Brzezińska et al., 2001b; Gliński et al., 1983; Gliński et al., 1986; Stępniewska et al, 1997; Stępniewska et al, 2000; Stępniewski et al., 2000; Włodarczyk et al., 2002). The electron activity of the soil solution (as reflected by redox potential) was shown to be more important for determining the conditions for enzyme activity, than the direct availability of O_2 (measured by Eg or ODR).

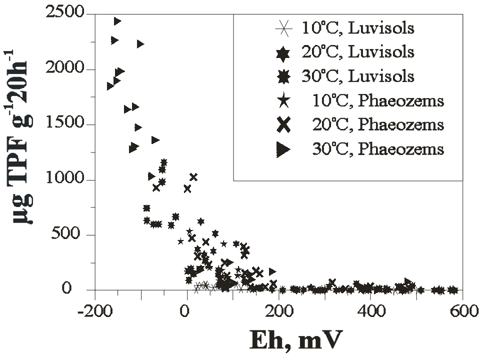

Fig. 2. *Dehydrogenase activity of five Luvisols and five Phaeozems in relation to redox potential (Eh) after pre-incubation at different soil water potential and temperature (from Brzezińska et al., 1998)*

Catalase is heme-containing enzyme that catalyses decomposition hydrogen peroxide to water and molecular oxygen. Reactive oxygen species, such as H_2O_2, formed during aerobic respiration as a by-product in a number of cellular systems, are the price, which aerobic organisms have to pay for the high efficiency of O_2-dependent respiration metabolism. Because of its extreme reactivity, H_2O_2 creates a risk of the irreversible damage of proteins by oxidising the SH-groups (Alef and Nannipieri, 1995). Thus, catalase plays an important role in protection of cell proteins and membranes. All aerobic and most of the facultative anaerobic microbes exhibit catalase activity. Deterioration of soil oxygen conditions, in contrary to dehydrogenases, results in inhibition of soil catalase activity. Catalase activity in soil showed positive correlations with air-filled porosity, oxygen diffusion rate and redox potential, but negative with water and Fe^{+2} content. (Gliński et al., 1986; Gliński et al., 1983; Gliński et al., 2000; Stępniewska et al., 2000).

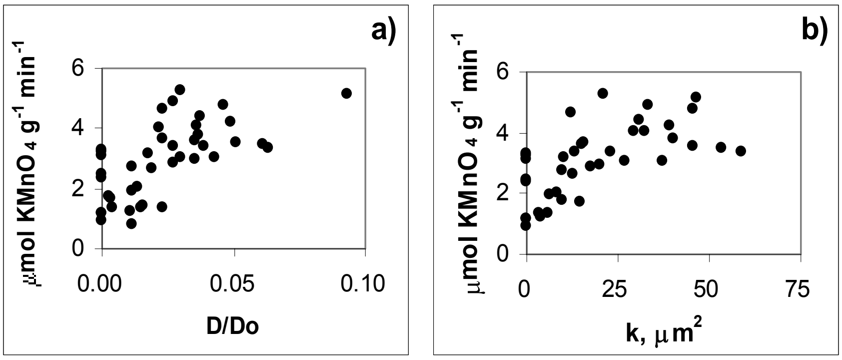

Fig. 3. Soil catalase activity versus gas diffusion coefficient (a) and air permeability (b) (From Stępniewska et al., 2000)

Catalase activity of loess soil was found to be depressed under soil hypoxia only by 16% (Brzezińska et al., in preparation). This incomplete enzyme inhibition may result from the activity of facultative and microaerophilic microorganisms, equipped with this defensive mechanism. Moreover, the action of enzymes still active outside living cells may contribute to the estimated activity, as catalase is known to be very stable in soil (Alef and Nannipieri, 1995). Extracellular enzyme activity is not related to microbial activity and, therefore, not subjected to repression or induction and probably not sensitive to environmental conditions affecting the physiological state of the microorganisms (Nannipieri et al., 1996).

Irrigation with wastewaterchanges soil aeration status. Additionally, nutrients and toxic substances present in wastewater create the special conditions for soil biota. The experiment with *Eutric Histosol* periodically irrigated with treated wastewater showed an elevation of soil dehydrogenase activity on average by 44% and 27% for the low (750mm per year) and high (1500mm) wastewater doses, but reduction of catalase activity on average by 12% (Brzezińska et al., 2001a).

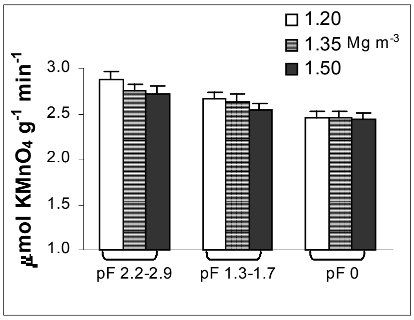

Fig. 4. *Combined effect of soil compaction and water potential on catalase activity in Orthic Luvisol (Brzezińska et al., in preparation)*

SOIL AERATION AND HYDROLASES

Pulford and Tabatabai (1988) studied the effect of soil redox potential on the activity of eight **hydrolases** involved in C, N, P and S cycling in soil. Hydrolysis of native soil organic P and pyrophosphate added to soil are significantly affected by waterlogging. Mostly decreases in phosphatase activities were found, especially in acid and alkaline phosphatases and pyrophosphatases. Some soils showed the increase in phosphodiesterase activity. The activity of arylsulphatase diminished and the change in activity of β-glucosidase depended on the soil. Urease activity decreased but amidase activities increased after soil waterlogging. Flooded rice soils showed higher urease activity than upland rice soils (Baruah and Mishra, 1984). Invertase activity was retarded by soil flooding (Chendrayan et al., 1980).

Deng and Dick (1990) reported that the response of rhodanese activity (**transferase** converting $S_2O_3^{2-}$ to SO_3^{2-}) to change in water potential depended on soil. Similarly, Ray et al. (1985) showed a 2.5-6-fold increase in rhodanese activity in a pokkali (acid sulphate) soil after flooding but no changes in a flooded alluvial soil.

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MAPPING OF SOIL AERATION PROPERTIES

Gliński J., Stępniewska Z., Ostrowski J., Stępniewski W.

REDOX PROCESSES IN SOILS

Soil aeration is closely connected with the relations of air-water conditions in soils. This relations affect biological activity of soil organisms mainly microorganisms which are very sensitive to oxidation or reduction processes (Gliński and Stępniewski, 1985).

For the environment the most important are reduction processes. Redox status is a base for understanding soil properties, such as composition of soil solution, soil reaction, availability of water, gases emission to the atmosphere, stability of metal-organic compounds, electrokinetic properties, surface charge, biological activity and others (Carter, 1980; Engler and Patrick, 1974; Gliński and Stępniewski, 1985; Hesse, 1971; Jeffrey, 1960; Kauncher *et al.*, 1974; Patrick and Jugusjinda, 1992; Ponnamperuma, 1986; Van Cleemput *et al.*,1976; Yu, 1985; Gliński *et al.*, 2000).

The reduced forms of elements, often toxic for plants and other living organisms, pollute environment and increase greenhouse gases concentration in the atmosphere.

The status of soil redox processes is expressed by the redox potential (Eh). The ability of the soil to maintain its redox potential is a measure of soil resistance to reduction (Gliński and Stępniewski, 1986; Stępniewska, 1988).

Soil can counteract changes in its redox potential (redox buffering). Soil redox buffering capacity is a result of microbial activity, carbon availability, temperature, and of the oxidizing forms of nitrogen, manganese, iron, sulphur and phosphorus. It is defined as a time during which soil redox potential, under flood conditions at a definite temperature, drops to the value of 400 mV corresponding to nitrate decomposition (t_{400}) or to the value of 300 mV corresponding to the reduction of manganese and iron (t_{300}).

The determination of soil resistance to reduction consists of flooding of the air dry soil samples with distilled water (soil : water = 1:1 w/w ratio), one time mixing and placing quiet in a thermostat. During the incubation a drop of Eh is measured. From the plots of the relation between Eh and time, t_{400} and t_{300} values are found.

The above mentioned determinations were used to analyse around 900 soil samples stored in the Bank of Soil Samples of the Institute of Agrophysics of the Polish Academy of Science in Lublin (Gliński *et al.*, 1991).

BANK OF SOIL SAMPLES

The samples of the Bank were taken from the representative soil profiles characterizing main units of the arable mineral soils of the entire soil cover of Poland (Table 1).

The number of profiles representing particular units (from 7 to 169) was proportional to the area occupied by a given unit in the territory of Poland that allowed statistical elaboration of the data and guarantied credible results.

Table 1. Soil units under study, their area in Poland and number of the profiles representing particular units

No. of soil unit	Soil unit	Area thousand ha	No. of soil samples
1	Rendzic Leptosols IB la	190	8
2	Rendzic Leptosols IB lb	45	8
3	Haplic Phaeozems	236	10
4	Haplic Luvisols and Dystric Cambisols - loose sands	4098	169
5	Haplic Luvisols and Dystric Cambisols - light loamy sands	163	18
6	Haplic Luvisols and Eutric Cambisols - loamy sands	605	10
7	Eutric Cambisols - loamy sands over loams		26
7a	Haplic Podsols - loamy sands	1858	47
8	Eutric Cambisols - light loams		34
8a	Haplic Podzols - light loams	1897	43
9	Eutric Cambisols - medium loams		27
9a	Haplic Podzols - medium loams	937	13
10	Eutric Cambisols and Haplic Luvisols - heavy loams	121	9
11	Eutric Cambisols and Haplic Luvisols - non uniform loams	570	11
12	Haplic Luvisols and Distric Cambisols - gravels	88	23
13	Eutric Cambisols - hydrogenic silts		8
13a	Haplic Podzols - hydrogenic silts	739	13
14	Haplic Luvisols and Eutric Cambisols - loess	1056	23
15	Haplic Luvisols and Eutric Cambisols - clays	50	9
16	Haplic Luvisols and Eutric Cambisols - loams and skeleton loams	168	10
17	Haplic Luvisols and Eutric Cambisols - loams	192	34
18	Haplic Luvisols and Eutric Cambisols - calys	38	7
19	Haplic Luvisols and Eutric Cambisols - silts	201	13
20	Eutric Fluvisols - loams and silts	505	10
21	Distric Fluvisols - sands	211	13
22	Eutric Fluvisols - light lilty loam	70	7
23	Mollic Gleysols - dev. from loams and silts	660	31
24	Mollic Gleysols - dev. from sands	394	27
25	Terric Histosols	114	11
Total		15779	672

MAPS

The obtained results introduced to the Soil Cartographic Data Base were, after computer processing with the use of statistical methods, converted to the spatial characteristic of the soil units that allowed to generate computer maps (Ostrowski *et al.*, 1998). A set of such maps of arable soils in Poland was compiled to the scale of 1:2.5 M. The purpose of these maps was to give specialists in ecology, environment protection and agriculture an opportunity to gain knowledge on soil redox properties, and also with their spatial and seasonal variability.

The colour maps in the amount of 33 were gathered in the **Atlas of the Redox Properties of Arable Soils in Poland** (Stępniewska *et al.*, 1997).

These maps show:

- soil redox resistance t_{300} and t_{400} of upper and 2 deeper horizons at the temperatures of 4, 10, 15 and 20°C for t_{300}, and 4, 7 and 20°C for t_{400};
- standardized redox potential (Eh and pH 7) for 3 soil horizons at 2 temperatures 4 and 20°C.

Percentages of particular t_{300} and t_{400} values and Eh and pH 7 classes at different temperatures in the total surface of the investigated soils are presented in the diagrams.

Two examples of such maps are shown (Map 1 and 2).

The maps may be used for:

- evaluation of hazards and agricultural damage (e.g., crop yield losses) connected with temporal soil water saturation;
- estimation of ecological damage connected with nitrogen losses due to denitrification and the emission of nitrous oxide (strong greenhouse gas) to the atmosphere;
- prediction of negative ecological and agricultural effect of climate change;
- use t_{300} and t_{400} values for land reclamation design, and as an environmental parameter for hydrological calculations (admission time of soil waterlogging.

The other expression of soil redox conditions was a map of potential denitrification (PD) of Polish soils in the scale 1:2,500,000 (Gliński *et al.*, 2000). It is based on the knowledge that about 80% of N_2O emission originates from soil and land use practices (Mosier and Bouwmann, 1993; Pedrazzini and Moore, 1983; Speir *et al.*, 1995). This map was elaborated on soil material gathered in the Bank of Soil Sample of the Institute of Agrophysics (Gliński *et al.*, 1991) and constructed in the same manner like those on soil redox resistance (Stępniewska *et al.*, 1997). It shows the areas of soil surface horizons having different potential denitrification (PD, kg N ha^{-1} d^{-1}) at the temperature of 20°C. This map comprises 6 units of PD: <5, 5-15, 15-25, 25-40, 40-80 and >80 kg N ha^{-1} d^{-1}. The construction of the map was based on the knowledge of soil nitrate pool and the soil redox buffering capacity (t_{300}-t_{400}):

$$PD = 10\Delta Hd \frac{C(NO_3 - N)}{t_{300} - t_{400}}$$

where: PD – kg ha^{-1} day^{-1} N;
d – soil bulk density, Mg m^{-3};
ΔH – thickness of the soil plough layer, m;
$C(NO_3\text{-}N)$ – nitrate – nitrogen content, g $(Mg\ soil)^{-1}$ = mg $(kg\ soil)^{-1}$;
10 – results of division of 10 000 m^2 per ha by 1000 g per kg;
$t_{300} - t_{400}$ – nitrate buffer period.

Recently it has also appeared a new idea concerning the classification of oxidoreduction resistance evaluation of Polish arable soils and their spatial characteristics (Stępniewski *et al.*, in press). On the basis of analysis of t_{300} values determined in 4 temperatures (4, 10, 15 and 20°C) for 3 subsequent soil horizons, 4 homogenic soil groups were distinguished and mapped for the whole country: soils with inconsiderable (<4 days), limited (<8 days), differentiated (5-20 days) and prolonged (till 50 days) resistance.

Moreover, the relation between soil redox resistance and its ability to self oxygenation through outflow of gravitational water from soil profile allowed to create a new term "hydrooxygenic degradation of soil" (Ostrowski *et al.*, in press).

Except of mapping of soil aeration properties based on the Bank of Polish Soils, other soil properties were mapped, as well. For the territory of the whole Poland maps of specific surface area of soils (total and external), maps of static and dynamic hydrophysical characteristics of soils (water retention and water permeability in saturated and unsaturated zones) were published (Stawiński *et al.*, 2000; Walczak *et al.*, 2002).

GENERAL CONCLUSION

Maps of soil aeration and other physical properties of Polish soils together with the knowledge of weather conditions create a base for prediction of various scenarios of processes in soil environment in the large areas.

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MICROBIAL ECOLOGY OF SOIL POROUS MEDIUM

Gliński J., Brzezińska M., Włodarczyk T.

Soil is heterogeneous, porous medium containing solids, liquids and gases. It is open system, exchanging both mass and energy with the surrounding atmosphere and hydrosphere. There is a functional connection between abiotic and biotic soil components. Lavelle et al. (1993) proposed a hierarchical model in which the physical environment, the resources quality and the living organisms (in that order) become increasingly important in determining soil processes at decreasing spatial and time scale.

MICROBIAL DIVERSITY

Soil organisms can be grouped into three categories:

1) 'Root biota' – the organisms living in association with the living plant, either beneficially (symbiosis) or detrimentally (diseases and pests);

2) 'The decomposers' – microflora and micro-/mesofauna acting as regulators of numbers and activities of microorganisms and microbial feeders. They occur in the bulk soil, in the rhizosphere where root-derived materials form their substrate, and in 'hot-spot' where concentrations of dead organic matter form their substrate;

3) 'Ecosystem engineers' – meso-/macrofauna that create microhabitats for other soil biota by reworking the soil. Earthworms and termites can be considered the most important here because of their far-reaching and lasting effects by modulating soil physical and chemical properties (Bolton et al., 1993; Brussard, 1998).

Soil microorganisms occur in huge numbers and display an enormous diversity of forms and functions. Major microbial groups in soil are bacteria, actinomycetes, fungi, and algae. Because of their extremely small cell size (volume of unicellular bacteria is about 1 μm^3), enormous number of soil microbes can occupy a relatively small volume. Prokaryotic bacteria, the most numerous - more than 10^9 bacteria per gram - account for almost half of the total biomass in agricultural soils. Soil fungi are probably of equal or even greater importance in many soils, as indicated by their biomass, associations with roots and saprophytic competence. Actinomycetes are known for producing various chemicals that can promote or inhibit the growth of other organisms (antibiotics, vitamin). Soil microorganisms, diversed metabolically, both autotrophs and heterotrophs, are able to use many different C and N sources. Most of them are organotrophs. The number of organisms and their collective biomass vary within and among soils, and decrease with depth (Metting, 1993). Soils inhabit microfauna (protozoa, nematodes, etc.), mesofauna (enchytraeids, microarthropods, etc.) and macrofauna (earthworms, macroinvertebrates).

Soil microorganisms play an important role in the processes of soil structure formation and maintain aggregate stability. Actinomycetes produce hyphal treads that bind soil particle together. Extracellular polysaccharides synthesized by bacteria bind soil particles together, assisting in building soil structure. Humic materials from bacterial action form organic matter/clay complexes (Lynch and Bragg, 1985; Ranjard and Richaume, 2001).

HABITABLE PORE SPACE

The structural organisation of the soil creates a mosaic of microenvironments, differing in terms of their physico-chemical and structural characteristics, representing many different habitats for the biotic components (Ranjard and Richaume, 2001). Microbial activity within microhabitats is unstable and responsive to fluctuating substrate availability and physical and chemical conditions. Microhabitats, variable in dimension, and containing single cells, small colonies or mixed communities, occur in soil pores - on or near particulate surfaces as well as within soil aggregates.

Physical conditions of one microsite may be quite different from the adjacent, leading to the development of microsite-specific communities and thus increasing the diversity of a given soil. Soil texture and percent pore space directly affect microbial community composition. Microorganisms adapt to microhabitats and live in consortia with more or less sharp boundaries, interacting with each other.

It has been shown that more than 80% of the bacteria are located in micropores of stable soil micro-aggregates <6 μm (Foster 1988; Young and Ritz, 2000). Mean diameter of pores colonised mainly by bacteria is estimated to be 2 μm, while no bacteria could be observed in pores below 0.8 μm in diameter (Kilbertus 1980). A positive correlation between the quantity of bacterial biomass and the volume of pores of the mean diameter 1.2 μm in different soils was observed (Hassink et al., 1993). The maximum diameter of the pores most frequently colonised by bacteria was estimated to range from 2.5 μm to 9 μm for fine and coarse texture soils, respectively (Hattori, 1988; Ranjard and Richaume, 2001).

Separation of microhabitats by physical fractionation of the soil showed that, independent on tillage treatment, 80-95% of the N biomass was located in the fractions smaller than 63 μm - in the clay (2-0.1 μm) and silt fraction (63-2 μm). Long-term organic amendments increased the capacity of the small-size fractions to protect soil microorganisms (Kandeler et al., 1999). More than 50% of the microbial biomass C content of the total soil and 37% of the soil organic C content, as well as 40-70% of total soil bacteria were associated with the aggregated structures (20-2 μm) and the clay-size (<2 μm) fraction (Ranjard and Richaume, 2001).

Microhabitats offer the most favourable conditions for microbial growth with respect to water and substrate availability, gas diffusion and protection against protozoan predation. Clay particles and organic colloids ensure microbial growth and survival in soils by their capacity to buffer the nutrient supply to microorganisms closely associated with their surfaces, and determine in this way also the spatial distribution of microbial biomass in the soil structure (van Gestel et al., 1996; Nunan et al., 2003).

The bulk of non-rhizosphere soil is oligotrophic, thus plant roots create the special space in the soil. The rhizosphere stimulates the microbial growth surrounding the root due to the release of a wide variety of organic compounds (leaking or actively released from root cells). Thus, significant differences in taxonomic and nutritional groups between rhizosphere and bulk soil are observed (Metting, 1993).

Plant residues, freshly incorporated into topsoils, are quickly colonized by a variety of microorganisms, creating ‘hot-spots’ of soil biological activity. Under suitable conditions of pH, temperature, and moisture content, plant residues are extensively decomposed within a few months (Metting, 1993, Sessitsch et al., 2001). It can be expected, that substrate located in pores below a threshold size is unavailable to organisms since they cannot gain physical access to it. Nevertheless extracellular enzymes may be able to penetrate pores down to extremely small dimensions (Young and Ritz, 2000).

The biomass in soil porous media may be considered as being located within one of two phases: the aqueous phase and the solid-associated biofilm phase (Ginn et al., 2002). The aqueous-phase biomass is commonly treated as a dilute suspension of ‘free-living’ (i.e., aqueous) cells. Three different conceptual models have been used for solid-phase biomass: continuous biofilm, discontinuous patchy biofilm, and unstructured biophase. The first two are physically structured models that consider the influence of biofilm geometry on mass transfer, while the unstructured model treats the biomass as a suspended but kinetically sorbing/desorbing species (Ginn et al., 2002).

The surface biofilm may be the principal site of microbial activity in soil (Burns 1989; Metting 1993). Cells within biofilms adhere to surfaces due to the balance of van der Waals attractive forces and electrostatic forces. Factors that influence the relative importance of these forces include properties of the colloidal component, system pH, properties of water phase, temperature as well as properties of bacterial cells (Metting, 1993).

Soil aeration status is an effect of dynamic interaction between processes of O_2 consumption combined with CO_2 production, and physical processes of gas transport between soil and atmosphere. It is evident that gas transport depends directly on the diffusion coefficient in the soil which is determined by the amount, size and continuity of the air-filled pores, i.e. by water content and physical arrangement of soil particles and, indirectly, by all the modifying factors (compaction, tillage, irrigation, drainage etc.) (Gliński and Lipiec, 1990; Gliński and Stępniewski, 1985; Lipiec and Hatano, 2003; Stępniewska et al., 2000; Stępniewski et al., 1994; Walczak et al., 2002). Aerobic and anaerobic sites exist in close proximity. Depending on the spatial arrangement of soil-water films, the diffusion of O_2 to the centre of a well-aerated aggregate may be decreased significantly. Centres of artificial aggregates were shown to be abundant with anaerobic and denitrifying microorganisms while outer layers of aggregates were occupied by aerobes (Horn et al., 1994). The existence of the microaerophilic and anaerobic microsites in soil is vital to biogeochemical cycling of mineral nutrients. Soil aggregates are specific porous media within which biological activities are present on the levels of enzyme molecules, DNA fragments, microbial cells and populations. The quality and intensity of these activities (including genetic exchange and organisms survival) is interrelated to the physical microstructure, chemical composition as well as water and oxygen availability (Gliński and Stępniewski, 1985; Nannipieri et al., 2001; Pietramellara et al., 1997).

MICROBIAL TRANSPORT

Microbial transport in the subsurface involves many complex and interacting reactions. Because microbes are living organisms, their transport is more complex than is the case for abiotic colloids. Not only are they subjected to the same physicochemical phenomena as are colloids, but there are also a number of strictly biological processes that affect their transport (e.g., temporal changes in surface properties due to changes in metabolic state) (Ginn et al., 2002).

Gerba et al. (1991), Dighton et al., (1997) and Ginn et al. (2002) reviewed models developed to describe the movement of organisms in soil. Macropore flow may be a major mechanism of bacterial transport in soil. There is a greater potential for microbial movement in coarse than fine soils; relatively free movement has been observed in sandy soil (Dighton et al., 1997). It was demonstrated that transport of bacteria through soil was not detectable in the absence of a transporting agent such as water and movement through the soil column stopped when the water content was at or below field capacity (Gannon et al, 1991). Migration across a relatively large pore space lined only with a thin film of moisture would require a longer passage and utilization of more energy compared to a direct route made permissible by the pore being filled with water. The effective diameter of microbes in relation to the pore neck radius also may affect its ability to move. There is little bacterial dispersion below a pore neck radius of 1.5 μm for bacterial cells of 0.5 μm diameter (Dighton et al., 1997). It is speculated that bacteria adsorbed on particles smaller than the cells may move to some extent together with the particles on which they are adsorbed. It is also possible for microorganisms to be trapped in pore that is too small to allow passage (Gannon et al., 1991).

Electrostatic and chemical interactions between microorganisms and solid surfaces may act at close separation distances (nanometers or microns), but these ultimately determine how microorganisms adsorb and desorb from the negatively charged solid surface, and thus affect microbial transport (Dighton et al., 1997; Ginn et al., 2002; Metting 1993). Biological processes, involved in microbial movement, may be response to local nutrient availability, survival mechanism and growth. Chemotaxis is the natural ability to move in response to a chemical gradient (i.e. nutrient supply). This process requires energy (Ginn et al., 2002). Bacterial dispersion by its own motility in soil water films will be very restricted. The largest recorded distance moved by self-propulsion was 60 mm day^{-1}, but generally it is below 10 mm day^{-1} (Dighton et al., 1997; Misaghi et al., 1992).

RELATIONS

The relations between soil organisms (especially competition and predator:prey interactions) are of great importance for microbial community structure and diversity, as well as for the decomposition of natural substrates and thus for biogeochemistry of ecosystems (Mamilov et al., 1001; Torsvik and Øvreås 2002). There are some mechanisms by which the soil microbiota and their predators are able to coexist in soil. These mechanisms include location of the soil microorganisms in pores of sufficiently small neck diameters to prevent access of larger predators (mainly protozoa and nematodes) and critical prey densities (cell numbers or biomass per unit of soil pore volume) below which too little energy is obtained by the predator to maintain its active search for food (Ladd et al., 1996). Crawford et al. (1993) calculated that about half of the potential habitable area for a bacterium of 5 μm diameter would be accessible to a predator of 30 μm (for example amoebal pseudopodia can penetrate pores to gain access to bacteria). It has been generally accepted that bacteria are protected from flagellates, nematodes, and ciliates in pores with entry neck sizes <3 μm, <20 μm, and <30 μm respectively (Darbyshire 1976; Kuikman 1991; Wallace 1958). Moreover, a positive correlation between pores in the size class 0.2-1.2 μm with bacterial biomass and between pores in the size class 30-90 μm with nematode biomass was found in grassland (Brussaard 1998).

THE ROLE OF MICROBES IN GAS FORMATION IN SOIL

The existence of organisms in soil porous medium entirely depends on actual soil status. Three soil phases (solid, liquid and gaseous) determine the physiology and mobility of soil biota by physical, chemical and physicochemical effects. On the other hand, soil microorganisms react against these effects by the use of different functions that are involved in complex mechanisms regulating the cell metabolism. Due to the action of various metabolites as well as extracellular enzymes released outside the cells, impact of soil biota extends to the external medium, thus taking part in formation of the soil ecosystem. Soil acts as a source and a sink of gaseous compounds that are involved in the biogeochemical cycles. The composition of the soil atmosphere directly refers to the metabolic activity of soil microorganisms. Soil aeration controls the levels of oxygen and carbon dioxide, involved in both respiration and photosynthesis, as well as determines the formation and fate of nitrous oxide and volatile organic compounds such as methane and ethylene (Gliński and Stępniewski, 1985).

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REDOX RELATIONS IN A LOESS SOIL ON ERODED HILL SLOPE

Gliński P., Stępniewska Z.

INTRODUCTION

Loess soils are among the group of silty formations with a chemical composition differentiated with relation to the intensity of erosion processes [Boardmann et.al., 1994; Gliński and Dębicki, 2000 a, b; Mazur et. al., 1972; Ziemnicki and Łoś, 1979]. They contain clay minerals from the montmorillonite group, or mixed montmorillonite-illite structures. Loess soils are characterized by a high level of water retention (Haplic Luvisos and Eutric Combisols) [Michalczyk, 1998]. Typologically, they are classified among the grey-brown podzolic (lessive) soils and the brown soils [Turski et.al, 1993]. Topside gleying that is sometimes encountered in lessive soils indicates periodic disturbances in the water-air relations in the soils.

Soil redox relations, expressed by means of the Eh index (mV), determine the stage of processes of the reduction or oxidation of soil components [Carter,1980; Gliński and Stępniewska 1986; Gliński et. al.,2000].

Under the conditions of insufficient oxygenation of soil, caused by eg. excessive soil moisture content, reduction of oxidized forms takes place, successively, of nitrates, manganese oxides, iron and sulfur, in the course of which the Eh index may even assume negative values [Patrick, 1981; Patrick and Jugsujinda].

Soils developed from loess formations are among the most susceptible to the lowering of Eh value under the conditions of insufficient oxygenation [Stępniewska, 1996], and therefore to rapid reduction of the oxidized forms of their components. The process, in the case of eroded areas, may result, under specific weather conditions, in the migration of such components downhill and on to the water course. Water economy in basins in agricultural regions is one of the current problems related to the phenomenon of recurring floods [Mioduszewski, 1997, 1998; Walczak et. al., 1998].

The objective of the study was to investigate predicted changes in the Eh of soils on an eroded loess hill slope, under assumed moisture and temperature conditions. The results presented herein constitute a fraction of a larger work concerned with predicted changes in the redox processes and their effects, studied on the example of a small basin under intensive agricultural use, characteristic for the loess areas of the Lublin Upland region.

OBJECT AND METHOD OF THE STUDY

The object of the study was an eroded loess hill slope at the locality of Baszki near Lublin, located in the Ciemięga river basin in the north-east part of the Nałęczów Plateau, a sub-region of the Lublin Upland.

The hill slope, with an angle of slope of about 4°, is covered with grey-brown podzolic and brown soils (Tab. 1) with the granulometric composition of loamy silts. The content of C_{org} in the humus horizons varies from 1.4 to 2.72%, with the lowest value in the middle part of the eroded hill slope. In that part of the slope, the sub-humus horizon is characterized by a similar content of C_{org} (2.04%), as opposed to the sub-humus horizons in the upper (0.35%) and the lower (1.16%) parts of the slope. The total specific surface area, characterizing jointly the granulometric composition and the humus content, indicates a certain differentiation – higher values (40.44 i 39.78 m^2g^{-1}) were observed in the soil on the slope, and lower values in the soil on the upper and the lower parts of the slope (27.6-37.3 m^2g^{-1}). The values of the external specific surface area tend to decrease in the soils from the upper part of the slope (15.31 m^2g^{-1}), through the middle part (10.88 m^2g^{-1}) towards the lower part of the slope (8.97 m^2g^{-1}). The reaction of the soils studied is neutral, and even alkaline in the soils on the upper part of the slope.

Table 1. Basic soil properties

Location		granulometric composition (% of fraction in mm)						Corg.	S H_2O	S N_2	pH H_20
		1–0.1	0.1–0.05	0.05–0.02	0.02–0.005	0.005–0.002	< 0.002	%	m^2g^{-1}	m^2g^{-1}	
1	A	6	9	53	21	3	8	2.28	36.78	15.31	8.11
	B	2	10	50	23	6	9	0.35	37.30	14.92	8.14
2	A	4	13	50	20	5	8	1.94	40.44	10.88	7.06
	B	4	10	50	21	6	9	2.04	39.78	12.55	7.01
3	A	8	14	58	13	2	5	2.72	35.36	8.97	7.60
	B	3	13	54	19	4	7	1.16	27.60	9.44	7.91
4	A	6	17	58	6	8	5	2.28	34.02	6.40	7.88

The moisture relations of the soils on the hill slope under study [Orlik, 1979] are affected by atmospheric precipitation, the average annual sum of which is 570 mm with a predominance in the summer season (Gliński and Dębicki, 2000b) when daily precipitation of up to 30 mm are a frequent occurrence. This causes surface runoff of the soil, the infiltration coefficient of which is much higher in the upper (2.30 cm h^{-1}) than in the lower part of the slope (1.66 cm h^{-1}) [Gliński and Dębicki, 2000a].

In 2003, soil samples for laboratory analyses were taken from three places on the slope studied (upper part -1, middle part -2 and lower part -3 and 4) from the humus horizon (A 0-20 cm) and the sub-humus horizon (B 20-40 cm). The soil samples were flooded with distilled water (at the ratio of 1:1) and incubated at 5, 10 and 20° C. In the course of the incubation, at different time intervals depending on the incubation temperature, Eh was measured in the soil suspension by means of PIONer meter made by Radiometer.

Values obtained from the measurements (n = 20) permitted the determination of the dynamics of Eh in the course of the incubation process, and the determination of indexes indicating the limits below which manganese and iron oxides (index t_{300}) and nitrates (index t_{400}) are reduced [Gliński and Stępniewska, 1986].

Measurements of the basic properties of the soils were performed as follows: granulometric composition acc. to the areometric method, content of C_{org} acc. to Tiurins method, total specific surface area acc. to the water vapour adsorption method, and the external specific surface area acc. to the nitrogen adsorption method.

RESULTS

Results of the analyses are presented in Tables 2-4 and in Fig. 1. At the beginning of the incubation, Eh values in all 7 soil samples fall within the narrow range of 386-455 mV. Afterwards, the values decrease in the course of the incubation process, the rate and degree of the decrease being related to the incubation temperature and the place of sampling on the hill slope.

The initial Eh values on the first day of incubation of samples at 20°C were usually somewhat higher than in the case of incubation at 10 and 5°C which resulted from the much faster rates of the redox reactions at that temperature.

At 5°C, during the first 40 days of incubation, a systematic lowering in the Eh values was observed in all the soil samples, with a highly varies extent of the lowering – the most extensive reduction in Eh values was found in the samples of soils 4A and 3A (by 277 and 239 mV) which were characteristic for the lower part of the hill slope, a less pronounced lowering in the Eh value in the sample of soil 2A (by 151 mV) characteristic for the middle part of the slope, and the least extensive- in the sample of soil 1A (by 77 mV) characteristic for the upper part of the slope. The downward inflexion point of the curves occurred on the 20th day of incubation.

Table 2. Changes of Eh during the incubation of soil at different temperatures

Location		Day of incubation							Mean
		1	10	20	30	40	50	60	
1	A	394	373	381	364	317	299	178	329
	B	388	378	377	360	356	323	368	364
2	A	417	411	391	336	266	283	274	340
	B	424	410	371	333	258	224	282	329
3	A	399	359	305	234	160	218	280	279
	B	386	366	361	310	284	302	313	332
4	A	394	354	297	160	117	189	284	256
Mean	A	401	374	344	274	215	247	254	301
	B	399	385	370	334	299	283	321	342

Table 2. Continued

Location		Day of incubation							Mean
		1	7	14	21	28	35	42	
1	A	394	362	356	347	347	292	282	340
	B	388	354	356	336	308	284	318	335
2	A	417	373	309	297	293	224	225	305
	B	424	375	338	293	331	261	226	321
3	A	399	318	226	171	230	181	360	269
	B	386	320	296	276	270	239	294	297
4	A	394	315	184	146	265	256	134	242
Mean	A	401	342	269	240	284	238	250	289
	B	399	350	330	302	303	261	279	318

Location		Day of incubation						Mean
		1	2	3	5	10	13	
1	A	390	333	302	315	267	191	300
	B	447	366	300	344	308	269	339
2	A	455	357	313	281	187	180	296
	B	433	386	332	353	216	188	318
3	A	430	350	295	205	198	206	281
	B	418	368	313	291	265	282	323
4	A	397	311	230	171	140	162	235
Mean	A	418	338	285	243	198	185	278
	B	433	373	315	329	263	246	327

Explanations: 1-4 sampling position from the upper (1) to the lower (4) part of the slope
A – surface horizon, B – subsurface horizon.

Table 3. Eh at the 7-10 day of incubation

T^{o}C	A		B		T^{o}C	A		B	
5	1	373	1	378	20	1	267	1	308
	2	411	2	410		2	187	2	216
	3	359	3	366		3	198	3	265
	4	354				4	140		
10	1	362	1	354	Mean	1	334	1	347
	2	373	2	375		2	324	2	334
	3	318	3	320		3	292	3	317
	4	315				4	270		

During subsequent 20 days of continued incubation, the Eh values in most of the soil samples increased, reaching – on the 60th day of the process – values from 254 to 368 mV, i.e. values much closer to the initial ones (368-455 mV). A notable exception was the sample of soil 1A, in which the value of Eh decreased systematically throughout incubation period, reaching 178 mV at the end of the process.

Table 4. Soil aeration indicators at different temperatures

Location		5°C		10°C		20°C	
		t_{300}	t_{400}	t_{300}	t_{400}	t_{300}	t_{400}
1	A	49.5	0.1	34	0.1	5.5	0.1
1	B	>60	0.1	30	0.1	2	0.5
2	A	35	15	19	3.5	3	0.5
2	B	34.5	12.5	20	4	6	0.5
3	A	21	0.125	8	1	1.75	0.25
3	B	34	0.1	13	0.1	3	0.25
4	A	19.5	0.1	8	0.1	1.25	0.1

At the incubation temperature of 10°C, the course of changes in the Eh of the soils during the initial 21 days of incubation was similar to that at 5°C, though at 10°C the changes in Eh occurred at a faster rate. The lowering in the Eh value was the greatest in the humus horizons of samples 3A (by 228 mV) and 4A (by 248 mV), less pronounced in sample 2A (by 120 mV) and the smallest in sample 1A (by 47 mV). An exception here is the sample 4A, in which throughout the incubation process the value of Eh decreased systematically, reaching 134 mV at the end of the incubation process, on day 42.

At 20°C, the course of the redox processes during the incubation of the soils studied was the fastest (till day 12) when compared to the changes occurring at 10 and 5°C. Lowering of Eh to the value of 150 mV in the characteristic sample 2A occurred on the 9th day of incubation. The courses of the curves of the changes were gentle, and the differences among the particular samples were the smallest.

In the characteristic days of incubation, the 7th and 10th, which were comparable for the courses of all the incubation temperatures, both the surface horizons (A) and the deeper horizons (B) did not differ with respect to the Eh values at the lower temperatures of 5 and 10°C, while at 20°C the differences in soils samples from all the three sampling sites were considerable, from 29 to 67 mV, in favor of the surface horizons. Considerable differences between horizons A and B occurred also at the smallest decreases in the value of Eh on the 40th day, 21st day, and in the period of days 4-9, at incubation temperatures of 5, 10 and 20°C, respectively.

There is a noticeable overall tendency for Eh to decrease in the soils from the upper towards the lower parts of the hill slope, the strongest effects of such changes being observable at the incubation temperature of 20°C. In the soils from the deeper horizons (B), however, the changes were not as clear cut as in the soils from the humus horizons (A).

Values obtained from the measurements (n = 20) permitted the determination of the dynamics of Eh in the course of the incubation process, and the determination of indexes indicating the limits below which manganese and iron oxides (index t_{300}) and nitrates (index t_{400}) are reduced (Table 4).

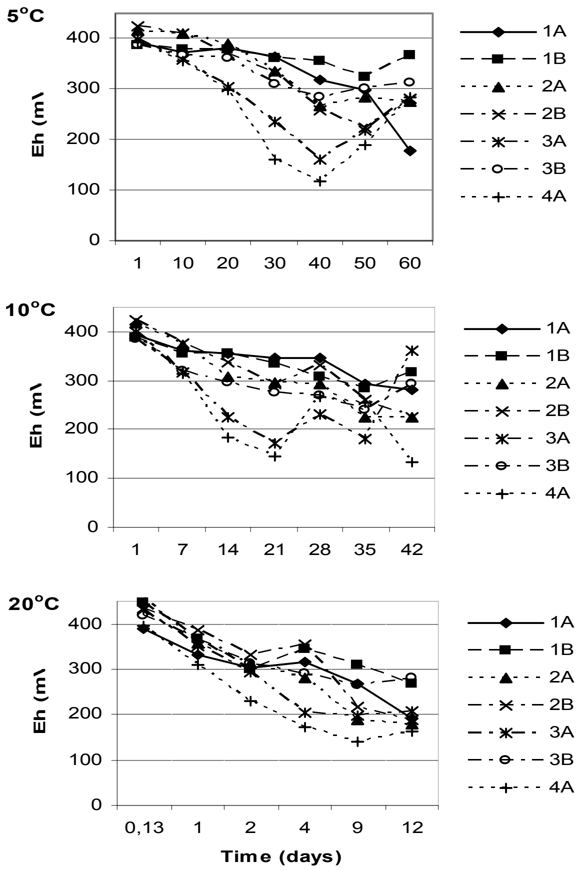

Fig. 1. Eh changes during the incubation of soil samples at different temperatures

CONCLUSIONS

1. The model studies carried out permit the prediction of changes in the redox potential in soils on an loess eroded hill slope under extreme moisture conditions at various temperatures corresponding to the three seasons of spring (5°C), summer (20°C) and autumn (10°C). The results refer to homogeneous loess soils under intensive agricultural use, with a low redox resistance as compared to soils developed from other formations. Their resistance to reduction at 20°C, as expressed by the t300 and t400 indexes, is several days and less than a day, respectively.

2. Under anaerobic conditions, the soils reached the lowest Eh values on the 40th day of incubation at 5°C, on the 21st day of incubation at 10°C, and on the 9th day of incubation at 20°C.

3. The soils situated on the lower parts of the hill slope proved to be more susceptible to changes in Eh value, while those from the upper part of the slope were the most resistant.

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STRUCTURE FORMATION AND ITS CONSEQUENCES ON GAS AND WATER TRANSPORT IN UNSATURATED ARABLE AND FOREST SOILS

Horn R.

INTRODUCTION

The aim of this paper is to clarify the effect of soil aggregation on soil physical and chemical properties of structured soils both on a bulk soil scale, for single aggregates, as well as for homogenized material. Aggregate formation and aggregate strength depend on swelling and shrinkage processes and on biological activity and kinds of organic exudates as well as on the intensity, number and time of swelling and drying events. Soil aggregates are, most of all, more dense than the bulk soil. The intraagregate pore distribution consists not only of finer pores but these are also more tortuous. Thus, water fluxes in aggregated soils are mostly multidimensional and the corresponding water fluxes in the intra-aggregate pore system are much smaller. Furthermore, ion transport by mass flow as well as by diffusion are delayed, whereby the length of the follow path in such tortuous finer pores further retards chemical exchange processes. The rearrangement of particles by aggregate formation also induces an increased apparent thermal diffusivity as compared with the homogenized material. The aggregate formation also affects the aeration and the gaseous composition of the intra-aggregate pore space. Depending on the kind and intensity of aggregation, the intra-aggregate pores can be completely anoxic, while the inter-aggregate pores are already completely aerated. The higher the amount of dissolved organic carbon in the percolating soil solution, the more pronounced is the difference between the gaseous composition in the inter- and in the intra-aggregate pore system.

PROCESSES OF AGGREGATE FORMATION

In soils containing more than 15% clay (< 2 μm) the mineral particles (sand, silt, and clay) tend to form aggregates. Usually the process occurs when soils dry and swell, and it is further enhanced by biological activities. Aggregates may show great variation in size from crumbs (diameter < 2mm) to polyhedres or subangular blocks of 0.005-0.02 m, or even to prisms or columns of more than 0.1 m.

During the first period of shrinkage, mineral particles are tied together by capillary forces which increase the number of points of contact and result in a higher bulk density. The initial aggregates always have rectangular-shaped edges because, under these conditions, stress release would occur perpendicular to initial crack and stress would remain parallel to the crack (strain-induced fracturing). However, due to the increased mechanical strength, the mobility of particles in the Terzaghi (cited by Horn, 1989), nonrectangular shear plains are also created which after repeated swelling and shrinking processes result in fractures in which the value of the angle of internal friction determines the deviation from a 90° angle.

In newly formed aggregates, the number of contact points depend on the range of moisture potential and on the distribution of particle sizes as well as on their mobility (i.e., state of dispersion, flocculation, and cementation). Soil shrinkage, including crack formation, increases bulk density of aggregates. The increase in bulk density with the initial watering and drying of the soil permits the aggregates to withstand structural collapse. The increase of the strength of single aggregates is further enhanced by a more pronounced particle rearrangement, if the soil is nearly saturated with water increasing the mobility of clay particles due to dispersion and greater menisci forces of water. (Horn and Dexter, 1989). Drying causes enhanced cohesion by capillary forces. Consequently, in order to carry the same soil load the bulk density of aggregates and thus the number of contact points decreases. With increasing intensity of drying of the moulded soil, its ability to perform reversible volume changes decreases. In wetter soils, the smaller proportion of residual to normal shrinkage (i.e., the greater reversibility during swelling) causes more intensive particle mobility and rearrangement in order to reach a state of minimum free energy. Although swelling may lead to partial expansion of contracted particles following rewetting of aggregated soils, a complete disaggregation is not possible if there is no additional input of kinetic energy, as has been demonstrated also by the puddling or kneading of rice soils (Horn, 1976). Thus, aggregate strength will depend on (i) capillary forces, (ii) intensity of shrinkage (normal/residual), (iii) number of swelling and shrinkage cycles, (iv) mineral particle mobility (i.e., rearrangement of particles to reach the status of lowest free energy), and (v) bonding energy between particles and/or between aggregates, or in the bulk soil.

HYDRAULIC ASPECTS

A. Water Retention Curve

Aggregation due to swelling and shrinking is affected by hydraulic properties of the soil. With an increase in the number of drying cycles the total porosity first decreases. Later it may increase again (Horn and Dexter, 1989). The volume of fine pores (i.e., the volumetric water content at pF > 4,2) is enhanced by decreasing drying intensity. In addition, the amount of water available to plants (i.e., water content at pF 1,8-4.2) is reduced with more intensive soil drying. Only at more negative water potentials is the air entry value exceeded depending how wet the soil had been kept. The latter effect is determined by the correspondingly steep slope of the pF/water content curve at pF 1.8.

B. Darcy Law: Hydraulic Conductivity

Given a laminar flow and a homogeneous pore system, the water flux in soils can be described and quantified by the Darcian law. Generally, the values of the hydraulic gradient vary only by half an order of magnitude depending on water potential, grain, and pore size distribution. If the soil-plant interaction is also taken into account, values of hydraulic gradients of up to 9 kPa $\cdot$ m^{-1} can be calculated when water content differences are expressed as pF at a given time and assuming a constant water content/pF curve. The values of the hydraulic conductivity of soils range between 10^{-4} and 10^{-13} $m \cdot s^{-1}$ depending on water potential, texture, and structure. Under saturated conditions, hydraulic conductivities range between 10^{-4} and 10^{-5} $m \cdot s^{-1}$ in a sandy soil and between 10^{-6} and 10^{-9} $m \cdot s^{-1}$ in a clay. Hydraulic conductivity is affected by structure and texture. It is high when the soil is highly porous, fractured, or aggregated and low when it is tightly compacted and dense. The hydraulic conductivity depends not only on the pore volume but also on the continuity of conducting pores. In structured soils with very large cracks the hydraulic conductivity for the bulk soil increases while flow velocity is strongly reduced inside the aggregates due to shrinkage (Table 1).

Table 1. Saturated Hydraulic Conductivity kf ($m\ s^{-1}$) for structured Bulk Soil Samples and Single Aggregates

Structure	Texture	kf ($m\ s^{-1}$)	
		Bulk Soil	Aggregates
Subangular-blocky	Loamy clay	1.1×10^{-4}	$3.5 \times 10^{-8} \pm 2.2 \times 10^{-8}$
Blocky	Loamy clay	1.6×10^{-5}	$4.8 \times 10^{-8} \pm 2.7 \times 10^{-8}$
Prismatic-blocky	Loamy-clay	2.6×10^{-7}	$6.0 \times 10^{-8} \pm 2.5 \times 10^{-8}$
Prismatic-blocky	Loamy-clay	3.8×10^{-5}	$3.4 \times 10^{-8} \pm 2.4 \times 10^{-5}$

The hydraulic conductivity may decrease by 4 orders of magnitude in single aggregates compared to the bulk soil unless the aggregates contain more sand than silt and clay, in which case there would be no difference compared to the bulk soil. The effects of structure on hydraulic conductivity persist under unsaturated conditions. Also, changes in structure directly affect the degree of variation in the hydraulic conductivity. At less-negative values of water potential, the unsaturated hydraulic conductivity of single aggregates decreases with the compaction of the structural elements (prisms less than polyhedres or subangular blocks) compared to fluxes in bulk soils. Only in weak aggregates are differences and ranges smaller. After exceeding the crossover potential values at very negative potentials, higher values of hydraulic conductivity are obtained in aggregates as compared to the bulk soil.

This heterogenization of the flow paths in aggregates compared to the bulk soil is further enhanced, since the outer skin of aggregates contains more clay than the center and the latter has more coarse pores than the outer part. Consequently, water and air flow in single aggregates is reduced further, which can also be linked to the increasing tortuosity of the pore system at different positions in the aggregate.

C. Darcy Law: Hydraulic Gradient

With respect to the water transport out of single aggregates and the effect of pore continuity, a retarded change in water potentials between different positions in the aggregates and a delayed water flux from the center to the surface could be proved.

Even when single aggregates are placed in a completely homogenized loess soil material at the same bulk density, the increases in water potential inside the single aggregate and in the bulk soil are not identical. Differences increase with drying of the soil. Therefore, it can be concluded that aggregate formation always induces a multidimensional water flux even if the aggregates are rather soft and coarse.

SOIL AERATION

In general, soil aeration is governed by two processes, namely (a) transport of oxygen from the atmosphere into the soil (atmospheric air contains, by volume, 20.5% O_2 and soil air 0%-20%), and (b) consumption of oxygen by biological respiration or by chemical reactions. Enhancement of gas transport in the soil occurs both as a mass flow along a pressure gradient and as a diffusional flow with a concentration gradient in air-filled pores. As for water, gas transport phenomena in soils also include the problem of pore size distribution, pore continuity and water saturation (Scheffer and Schachtschabel 2002). Currie (1965) described gas transport in aggregated soils and dealt with the problem of a bimodal pore system on gas exchange processes in soils. He pointed out that soils with a highly developed natural aggregation should have distinct zones of aggregated or crumb pores, separated by a more continuous system of inter-aggregate pores.

Gas transport in soil profiles will occur preferentially through this inter-aggregate pore system formed by macropores. Additionally, oxygen diffusion to sinks (respiration by soil microorganisms) in the intra-aggregate pores is induced by the concentration gradient.

Besides diffusion, diurnal pressure and temperature changes allow an exchange of soil macropore air by mass flow processes. However, the transported gas volume is rather small and exchanged gas volumes are mainly in the top 20 cm of the soil (Glinski and Stepniewski, 1985). Oxygen diffusion to sinks (respiration by soil microorganisms) takes place in the interaggregate pores and is induced by the concentration gradient resulting from respiration.

When the oxygen demand within soil aggregates is high and O_2 diffusion is limited by partial or even complete water saturation (oxygen diffusion will be reduced by a factor of 10.000 in water saturated pores) and low pore continuity, anoxic sites may develop even if the interaggregate pore space contains sufficient oxygen. These conditions often have been described in the field with respect to denitrification and root growth conditions. Thus, in well-structured soils research on aeration should focus on oxygen transport within aggregates and on oxygen consumption. Greenwood and Goodmann (1967) were the first to determine the oxygen distribution within single aggregates saturated with KCl. Using platinum electrodes they measured anoxic zones in aggregates of only 8-mm diameter. Sextone et al. (1985) used shielded microelectrodes with a tip diameter of 30-50 μm to determine the oxygen distribution within water-saturated aggregates. Both authors stated that O_2 gradients inside single aggregates appeared to be steeper in artificial or disturbed aggregates.

A. Effect of Texture on Gas Transport

Studies of the effects of soil texture on gas transport and on the composition of soil air in artificial aggregates reveal a strong correlation between the pore size distribution and the air entry value. The air entry value is the soil water potential at which gas diffusion to the aggregate centre increases because water menisci are removed from continuous pores.

In prisms of sandy-loamy texture the increase in O_2 partial pressure occurred at a soil water potential of about – 15 kPa while polyhedrons with loamy-clay became aerated at more negative water potentials of < - 60 kPa (Zausig et al., 1990). According to Fick's law, gas flow depends on the diffusion coefficient and concentration gradient. Assuming an oxygen content of the air surrounding the aggregate of 20%, O_2 transport within the aggregate would require additional time. If chemical and microbial oxygen demand inside the aggregate exceeds oxygen supply, zones of low oxygen partial pressure or even anoxic microsites may develop. Stepnieweski et al. (1991) described a method where O_2-sensitive microelectrodes were pushed through soil aggregates at a constant speed of 0,00166 mm $\cdot$ s^{-1}. By this procedure continuous radial profiles of oxygen partial pressure could be measured. The method was used to compare the internal oxygen status of artificially formed spherical aggregates (diameter of 24 mm) of six different soil samples at soil water potentials ranging from – 1 to – 6 kPa (Zausig et al. 1993). It was found that the intensity of anoxia and the diameter of anoxic centres would be controlled not only by microbial and chemical oxygen demand but also by parameters such as aggregate hydraulic conductivity and pore size distribution, i.e., by the soil texture.

B. Effect of Soil Structure on Aeration

Aggregated soils always include secondary large interaggregate pores (coarse pores > 50 μm) and small intraaggregate pores (finer pores < 0.2 μm). This results in a heterogenization of the pores system and of the texture within the aggregates which strongly affects transport phenomena. The smaller the biological activity and the smaller the degree of organization of soil particles the smaller the intraaggregate pores which in turn restrict gas diffusion. A large reduction in O_2 partial pressure or even anoxia within aggregates under in situ conditions results from restricted pore space (diameter and continuity) as well as a source of reduced carbon, provided O_2 consumption by microbes is the main factor causing anoxia. Thus, natural soil aggregates should have an anoxic or less-aerated centre if the soil water potential is > - 60 kPa.

Significant amounts of organic substances may induce large decreases in redox potential soon after saturation with water. Thus, in humic A horizons redox potentials should drop rapidly upon wetting while in subsurface horizons with low contents of organic substances only small redox potential changes occur.

The intensity and speed of changes of redox potential may depend on more than the content of organic matter. The chemistry of the mineral soil components appears to be important as well. Soils containing clay show less-intensive changes of redox potential than silty soils. In aggregates with sandy texture, the largest decreases of redox potential occurred. Thus, fine-textured soils seem to contain more substances that function as a redox buffer, whereas the quartz fraction of sandy soils is more or less inert and does not affect chemical processes. One of the first substances used as an electron acceptor by anaerobic microorganisms is nitrate-N. Only 12 h after watering of aggregates from N- and C-enriched soil material to –0.5 kPa soil water potential denitrification was observed even in aggregates of 2 mm diameter. Larger aggregates had bigger anoxic volumes and thus the amount of denitrified N increased. Also, the type of microorganisms differed between the inner and the outer part of the aggregates. In the outer skin aerobes did exist while in the centre denitrifiers dominated.

Table 2. Processes of aggregation and changes in functions

Stage	Process	Aggregate type	Consequences	Hydraulic effects	Aeration effects
I. Mechanical effects Early	Rectangular cracks	Singular Coherent Prism column	-Increasing number of contact points -Increasing aggregate bulk density -Formation of inter- and intra-aggregate pores	-Decreased intra-aggregate pore volume and saturated hydraulic conductivity -Increased macropore flux	-Reduced intra-aggregate aeration -Increased differentiation of aerobic and anaerobic zones
Increased number of drying cycles or drying intensity	-Crack formation by shear forces -Oblique shear planes	Polyhedre	-Rearrangement of particles inside aggregates -Clay skins -Accumulation of coarser particles in aggregate centre -Increased intra-aggregate tortuosity	-Decreased hydraulic conductivity as compared with bulk soil -Smaller decline of the k/ψ curve of aggregates	-Differentiation of gaseous composition -Steeper decline of pO_2 at a given water potential
Final	Reaching smallest free entropy	Natural Aggregate Density sphere	-Reduced aggregate bulk density -Increased aggregate strength	-Increased plant available water -Steeper slope of k/ψ curve	-Improved aeration
II. Biological effects	Biological activity	Crumb	-Homogenization by mixing processes -a reduced bulk density -Increased strength	-Increased saturated hydraulic conductivity -Steeper slope of the k/ψ curve	-Increased aeration -Increased oxygen consumption -Decreased redox potential

CONCLUSIONS

Soil structure is defined as the arrangement of single mineral particles and organic substances to greater units known as aggregates and the corresponding inter-aggregate pore system. In dependence of the external as well as internal forces and strength of the already existing structure unit, several more general but detailed accounts are available in the international literature, which has also been dealt with in the present paper. The presented results found in the literature verify the idea that processes of aggregation do affect the availability of water for plant uptake and the accessibility of water-filled pores for roots, which is reduced owing to the formation of finer pores where water is available only at more negative pore water pressures. If the processes of aggregate formation under mechanical and biological conditions are combined with the corresponding effects on hydraulic and aeration properties, it can be in general concluded that there is never constancy at the beginning of soil structure formation but it is only reached after a longer period, i.e. at the smallest free entropy (Table 2).

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FATE OF DNA IN SOIL

Nannipieri P.

The engineering of genetically modified plants (GMPs) has great potential for future agriculture, but asks for well-defined risk assessment. As it concerns the cultivation of these plants above ground effects have received more attention than below ground effects. Among the below ground effects, one possible risk is the persistence of transgenic DNA and the possible incorporation of this DNA in the genome of soil microflora. This could happen if transgenic DNA persist in soil after its release by plant cells. Of the three Horizontal Gene Transfer processes, the transformation only involves extracellular DNA. Two aspects have been, or are presently being studied by several groups to address natural transformation in the environment: i) How long does free DNA persist in soil and is DNA still available for natural transformation? ii) How frequently do different bacterial species under environmental conditions reach a state of being able to take free DNA? My presentation will focus on the persistence of DNA in soil and the possible incorporation of transgenic DNA in the microbial genome of soil.

Soil colloids can adsorb important biological molecules such as proteins and nucleic acids. For this reasons adsorption and binding of nucleic acids have been extensively studied in the last 10-15 years. Nucleic acids adsorbed and bound to clay minerals, sand particles and humic substances are partially protected against degradation by nucleases and other degradative enzymes, and retain their capacity to transform competent bacterial cells (Ardema et al. 1983; Lorenz et al. 1988; Khanna and Stotzky 1992; Gallori et al. 1994; Stotzky et al. 1996; Vettori et al. 1996; Crecchio and Stotzky 1998). Adsorption of nucleic acids by clay minerals depends on pH (Khanna and Stotzky, 1992). It has been proposed that cations forms bridges between phosphate groups of the DNA molecules and the negatively charged sites of clays and sand (Lorenz and Wackernagel 1987; Khanna and Stotzky 1992). DNA adsorption has been found to increase by increasing the concentration and valence of the charge-compensating cations on the surface of clay minerals (Paget et al. 1992). Electron microscopy analysis of DNA-clay complexes showed that DNA was mainly bound on the edges of the clays, with a minor proportion bound on the planar surface (Paget and Simonet 1994; Khanna et al. 1998). Adsorption or binding of DNA by montmorillonite or kaolinite, homoionic to Ca^{2+}, was not affected by base composition, blunt or cohesive ends (Pietramellara et al. 2001). The amount of lower molecular mass DNA adsorbed or bound to clay minerals was higher than that of the higher molecular mass DNA. However, the latter could interact with a larger number of binding sites on the external surface of clay mineral than the lower molecular mass DNA (Pietramellara et al. 2001).

DNA can be also protected in dead cells and this DNA can still have transforming activity. Nielsen et al (2000) showed that cell lysates of *Pseudomonas fluorescens, Burkholderia cepacia* and *Acinetobacter spp* were available as a source of transforming DNA for *Acinetobacter spp* populations in sterile and non sterile soil for a few days and that cell debris protected DNA from inactivation in soil. Cell wall may protect DNA after cell death (Paget and Simonet, 1997).

During processes such as leaf senescence, pathogen attack or decaying plant tissues, transplastomic (chloroplast genome containing the transgene) tobacco plant DNA is degraded but sufficient DNA persist to be released into soil (Ceccherini et al 2003). The quality and quantity of plant DNA and the transgene were evaluated by direct visualization of DNA on agarose gel, gene extraction yield (the number of amplifiable *aadA* sequence in extracted DNA), and the frequency that recipient bacteria could be transformed by plant DNA.

Until recently it was unclear if bacteria could be transformed by plant DNA at all. The high content of non-bacterial DNA and the much higher mthylation rate were supposed to prevent a transfer of antibiotic resistance genes from transgenic DNA to bacteria. However, *Acinetobacter sp* BD413 pFG4Δ*npt*II was capable of capturing and integrating transgenic plant DNA based on homologous recombination under optimal laboratory conditions (Gebhard and Smalla 1998). De Vries and Wackernagel (1998) reported that transformation of competent *Acinetobacter sp* BD413 cells containing an *npt*II-gene with 10 bp deletion with DNA from various transgenic plants (*Solanum tuberosum*, *Nicotiana tabacum, Beta vulgaris*, *Brassica napus*, *Lycopersicon esculentum*) carrying *npt*II as marker gene resulted in restoration of the deleted *npt*II gene. Both studies had in common that *Acinetobacter sp* BD413 was transformed and that a deleted *npt*II gene served for sequence homology and as a detection system (restoration of the *npt*II gene resulted in kanamycin resistance phenotype).

The persistence of transgenic (rizomania-resistant) sugar beet DNA has been studied in the field. To detect transgenic DNA, total community DNA was extracted from soil and amplified with three different primer sets specific transgenic DNA. Parts of the construct were detectable for up to 2 years and long-term persistence could be shown also in microcosms with introduced free DNA (Gebhard and Smalla, 1999).

Presently, we think that horizontal gene transfer from plants to bacteria are rare events. In addition, since antibiotic resistance genes are located on mobile genetic elements and are widespread in bacterial populations, and horizontal gene transfer events from transgenic plants to bacteria are rare under field conditions, it is unlikely that antibiotic resistance genes used as markers in transgenic crops will contribute significantly to the spread of antibiotic resistance in bacterial populations (Smalla, personal communication).

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THE BIOCHEMISTRY OF THE RHIZOSPHERE SOILS

Nannipieri P.

Extended summary mostly from the book by Pinton et al (2001)
and the paper by Falchini et al. (2003)

RHIZOSPHERE AND RHIZODEPOSITION

The term rhizosphere was first used by Hiltner in 1904 to indicate the zone of soil where root exudates released from plant roots can stimulate, inhibit, or have no effect on microbial activities (Pinton et al 2001a). The importance of the topic is testimonied by an extensive bibliography including several reviews and five entire books dedicated to the matter (Scott Russsell 1977; Harley and Scott Russell 1979; Curl and Truelove 1985; Lynch 1990; Keiser and Cregan 1991; Pinton et al 2001b).

The rhizosphere is divided in two parts: ectorhizosphere and endorhizosphere. The former includes the soil layer surrounding roots where the effect of the plant is manifested, whereas the second part includes the root layer colonised or potentially colonised by microorganisms (Pinton et al 2001a). The two areas are separated by the root surface, that is the rhizoplane.

The organic compounds released from roots are called rhizodeposition and have been classified according to: 1) their chemical properties, such as stability (e.g., hydrolysis and oxidation), solubility in water, volatility, molecular weight; 2) the modality of their release (exudates, secretions, or lysates); c) the way of utilization by microorganisms (low molecular weight compounds are readily taken up by microbes whereas high molecular weight compounds are first hydrolysed by extracellular enzymes and then the hydrolytic products can be taken up by microbes); 4) their function (phytohormones, ctoenzymes, phytoalexins, etc).

Root exudation depends on the root area considered, plant species, the physiological state of the plant and microbial species inhabiting rhizosphere soil. Usually release of the high molecular weight substrates is localised in the apical root zones and is higher when the plants are in the vegetative growth (Pinton et al 2001a). Annual species release much less organic C than perennials, probably because the latter have to invest more of their assimilates to survive the year around (Brimecombe et al (2001). The quantity of both proteins and carbohydrates released by herbaceous plants decrease with age (Brimecombe et al 2001), whereas metabolites from *Pseudomonas aeruginosa* and not from *Arthrobacter* species stimulated the release of ^{14}C-labeled exudates by perennial ryegrass (Meharg and Killham 1995).

Root diffusates include sugars, organic acids, amino acids, water, inorganic ions, etc, whereas secretions generally include compounds with specific functions such as enzymes, mucilage, siderophores, allelochemicals, etc (Uren 2001). Excretions include carbon dioxide, bicarbonate ions, protons, electrons, etc. Root debris represent the other root product released into soil.

Usually 50% of the net fixed C is released from roots of young plants and it decreases with the age of the plant (Brimecombe et al 2001) whereas N rhizodeposition can amount to 20% of the total plant N at maturity (Jensen 1996).

ROOT EXUDATES WITH SPECIFIC FUNCTIONS: MICROBIAL SIGNALS AND PHYTOSIDEROPHORES

Usually root secretions have a specific functions (Uren 2001). Molecular signals released from roots can promote the infection of beneficial microorganisms such as N_2-fixing microorganisms and mycorrhizal fungi (Martin et al 2001; Pinton et al 2001a; Werner 2001). Indeed signals and receptor molecules are involved in the molecular cross talk between a plant root and a specific microorganism; generally, it involves a continuous exchange of diffusible signal molecules which, once recognized by specific receptors, elict transductional processes, leading to a rapid activation of gene expression. Usually flavonoids, released from roots, act are molecular signals and are involved in the initiation and development of rhizobia and mycorrhizal infection (Pinton et al 2001a). These compounds are species-specific (Hungria and Stacey 1997).

Phytosiderophores, another class of compounds released by roots, have been studied not only for their role in Fe nutrition, but also for their importance in plant disease suppression by mediating nutritional competition for Fe and in phytoremediation of heavy metals by facilitating heavy metal uptake and food chain transfer of metals (Crowley 2001). Generally they are non-proteinaceous amino acids released by strategy II plants (graminaceous plants) in response to Fe deficiency and are highly effective Fe chelators; their release generally occurs in subapical root zones (Neumann and Romheld 2001).

MICROBIAL DIVERSITY, MICROBIAL PROCESSES AND ENZYME ACTIVITIES

The rhizodeposition markedly affects the size and the activity of soil microflora (Pinton et al 2001a). Plant-microbe interactions may be considered beneficial, neutral or harmful to the plant, depending on the specific microorganisms and plants involved and on the prevailing environmental conditions. Microbes can be beneficial to plants because they increase the supply of nutrients (dinitrogen-fixing bacteria, mycorrhizal fungi, etc), they prevent the activity and growth of plant pathogens (biocontrol agents) and they stimulate plant activity by producing phytohormones (plant growth-promoting rhizobacteria). Harmful interactions are due to the presence of plant pathogens.

The determination of microbial diversity in soil has been problematic because classical techniques such as plate counts only detected microbial species capable of growing in culture media. The problem has been solved by fatty acids analysis or by using molecular techniques based on DNA extraction (Crowley 2001). The bacterial diversity was greater in older than younger barley roots, as shown by the PCR-DGGE technique with universal primers for eubacteria (Crowley 2001). Under field conditions r-strategists dominated in the rhizosphere of young wheat roots, whereas K-strategists dominated in mature roots (De Leij et al 1993).

Enzyme activities of rhizosphre soil are higher than the respective enzyme activities of the bulk soil because of the presence of root-derived enzymes and enhanced microbial activity. Both acid and alkaline phosphomonoesterases were higher closer to the rhizoplane of *Brassica oleracea, Allium cepa, Triticum aestivum* and *Trifolium alexandrinum* than in the bulk soil; on the contrary the content of organic P decreased closer to the rhizoplane (Tarafdar and Jungk 1987).

Since the C/N ratio of the root released material is higher than that of soil microflora, microbial N immobilization prevails over N mineralization (Badalucco and Kuikman 2001). Thus, the stimulation of microbial activity by growing and decomposing roots may result in a temporary reduction of available N. However, according to Clarholm (1985), the microbial N immobilization through growth on root-released organic C seems to be balanced by N mineralization promoted by protozoan grazing, with the release of NH_4^+ after bacterial cell digestion. Indeed the C/N ratio of bacteria is lower than that of protozoa. The increase in both histidinase and casein-hydrolysing activities, associated to higher bacterial populations and associated grazing bacteria in the rhizosphere soil, seems to prove this hypothesis (Badalucco et al 1996; Badalucco and Kuikman 2001).

It is difficult to study biochemical and microbiological phenomena in the rhizosphere soil in situ due to the presence of a complex mixture of organic compounds and the difficulty of sampling soil at distinct and known distances from the root surface (Sorensen 1997). Falchini et al (2003) have solved both problems by considering the effect of each compound added to soil and by using a suitable system (firstly described by Badalucco and Kuikman 2001) allowing the formation of a concentration gradient with soil sampling at various distances from the rhizoplane. They studied the mineralization and the diffusion of ^{14}C-labeled glucose, oxalic acid, or glutamic acid from the cellulose filter placed on top of a sandy loam core. Glucose and glutamic acid showed a positive priming effect whereas the mineralization of oxalic acid was delayed probably because only a few microbial species were capable of oxisidising it. The composition of the bacterial community, as showed by DGGE analysis, showed some changes in the glutamic acid or oxalic acid treated soils, with appearance of new DNA bands in the 0-2 mm soil layer.

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SOIL AERATION AND PESTICIDE DECOMPOSITION

Stępniewska Z., Fornal E., Kosiorowska I., Charytoniuk P.

ABSTRACT

The behaviour of two pesticides (glyphosate and fonofos) was investigated under different oxygen conditions in *Haplic Phaeozem.* Soil samples were incubated in glass columns 20 cm high and 3 cm in diameter at three glyphosate and fonofos treatments (control, 0.63 mg kg^{-1}, and 6.3 mg kg^{-1}) and two moisture regimes (flooded and non-flooded) for 4 weeks, with weekly elution with 7 mm of water. After 4 weeks of incubation, the effect of glyphosate and fonofos amendment on dehydrogenase and phosphomonoesterase activity was tested.

It was found that acid phosphomonoesterase activity was positively and linearly correlated with the redox potetial, while the alkaline phosphomonoesterase activity increased when Eh dropped to negative values, not significantly except for the acid phosphatase under flood conditions.

INTRODUCTION

Herbicide is usually applied under aerated soil conditions, but as a result of transport processes in the landscape it can be transferred to anaerobic conditions occurring in lowlands and sediments. Due to this, its fate and environmental effects, both under aerobic and anoxic conditions, are of scientific interest.

N-(Phosphonomethyl)glycine (glyphosate), one of the most frequently used herbicides, is an active substance of many popular concoctions. In soil it is degraded at a moderate rate, and one of the degradation reactions involves the carbon-phosphorus bond cleavage by soil bacteria enzymes. On the other hand, glyphosate can inhibit biosynthesis of aromatic amino-acids of some bacteria, thus affecting protein synthesis in bacteria cells and consequently also the synthesis of enzymes of the xenobiotics degradation pathways (Schäffer 1993, Wiersema *et al.* 2000).

Fonofos (Methylphenylsulphone) is a very popular insecticide well-bound to soils, with a field half-life of ~ 40 days (Wauchope et al.1992). Fonofos can be transported in runoff (water solubility: 13 mg dm-3); in ground water it was detected on the level of 0.01-0.03 µg·dm-3 (Panshin et al. 1998).

A general inhibitory effect (from 5% to 98%) was observed for phosphatase in the presence of glyphosate (Sannino and Gianfreda, 2001). One of the factors affecting microbiological activity in soil, and thus the rate and pathways of biodegradation of introduced organic substances, is the aeration status of soil (Ponnamperuma 1972, Gliński and Stępniewski 1985, Picek *et al.* 2000) which can be characterized by redox potential (Eh). Under natural conditions, Eh values of soils vary from –0.4 V (anaerobic conditions) to +0.8 V (aerobic conditions). Several relationships between O_2 availability (and thus the Eh value) in soil and the xenobiotics behavior have been published (Katayama and Kuwatsuka 1991, Hekstra 1995, Gisi *et al.* 1997, Vink *et al.* 1997, Singh *et al.* 1999, D'Angelo and Reddy 2000, Picek *et al.* 2000, Accinelli *et al.* 2001).

Soil phosphatases are enzymes which are responsible for hydrolytic decomposition of the esters and anhydrides of phosphoric acid. This class includes phosphomonoesterases which catalyse the hydrolysis of organic phosphomonoesters to inorganic phosphorus. Depending on their optimal pH, acid and alkaline phosphomonoesterases can be distinguished (Alef and Nannipieri, 1995). These enzymes are intracellularly and extracellularly active in soils where they can be secreted by microbial and plant root cells. They are important for plant nutrition as they hydrolyze organic phosphates, which amount to 20-85% of the total soil P, to phosphates easily uptaken by plant roots (Alef and Nannipieri 1995; Marzadori *et al.* 1998; Hayes *et al.* 2000; Schneider *et al.* 2001; Yadav and Tarafdar 2001). The phosphomonoesterase activity is strongly influenced by soil depth and soil properties, such as aeration status (Alef and Nannipieri 1995; Hýsek and Šarapatka 1998).

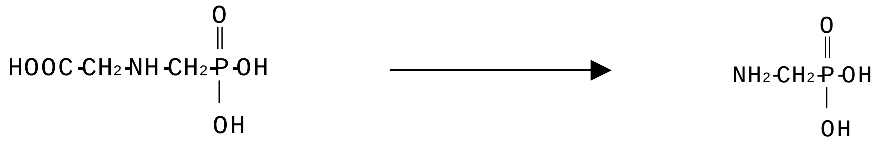
The aim of this work was to establish how two different doses of fonofos and glyphosate treatment influence the dehydrogenase and phosphomonoesterase activity under different soil aeration conditions in *Haplic Phaeozem*.

MATERIAL AND METHODS

Thirty grams of fresh *Haplic Phaeozem* (2.12 % organic carbon, pH 7.4; 38% sand, 25% silt, 37% clay) containing 21% water, taken from the Ap horizon of a meadow of the Tyśmienica river (Poland), was sieved (through a 2 mm sieve) and (198 g) placed in glass columns (20 cm high and 3 cm in diameter), moistened to full water capacity and allowed to drain the free water for two days. Then the soil surface was sprayed with a 0.5 % water solution of glyphosate (Sigma-Aldrich) or with a water solution of fonofos (Riedel-de-Haen). The amounts of glyphosate and fonofos solution applied were 0 (control), 20 μl (as a normal dose, recommended for weed treatment) and 200 μl (18.9 and 15 kg ha^{-1} for glyphosate and fonofos respectively). Nine columns were incubated under flood conditions with one cm water stagnating on the soil surface. The second group of nine columns was incubated at water content corresponding to water holding capacity after the free water was drained off. In each column 3 platinum electrodes (at three depths: 5, 10 and 15 cm) were installed for redox potential measurements. The incubation lasted 4 weeks at a temperature of 24°C. Once a week all the columns were eluted with 4.87 ml of water (corresponding to 7 mm of water head) to simulate average rainfall of 360 mm per year. During the incubation, a Eh/pH was performed using Pt electrodes/glass electrode. Both Eh and pH measurements were carried out with pH/Eh-meter (type CPI-551, Elmetron, Poland). As a reference, a saturated calomel electrode was used. Each treatment was triplicated.

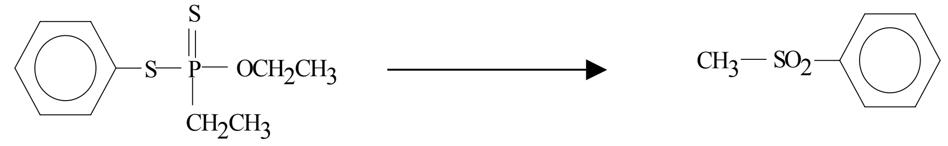
In eluted waters, the concentration of used pesticides and their metabolites were tested by the HPLC method.

Glyphosate (G) **Aminomethylphosphoic acid (AMPA)**



$$HOOC\text{-}CH_2\text{-}NH\text{-}CH_2\text{-}\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle OH}{|}}{P}}\text{-}OH \longrightarrow NH_2\text{-}CH_2\text{-}\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle OH}{|}}{P}}\text{-}OH$$

Fonofos (F) **Methylphenylsulphone (MFS)**



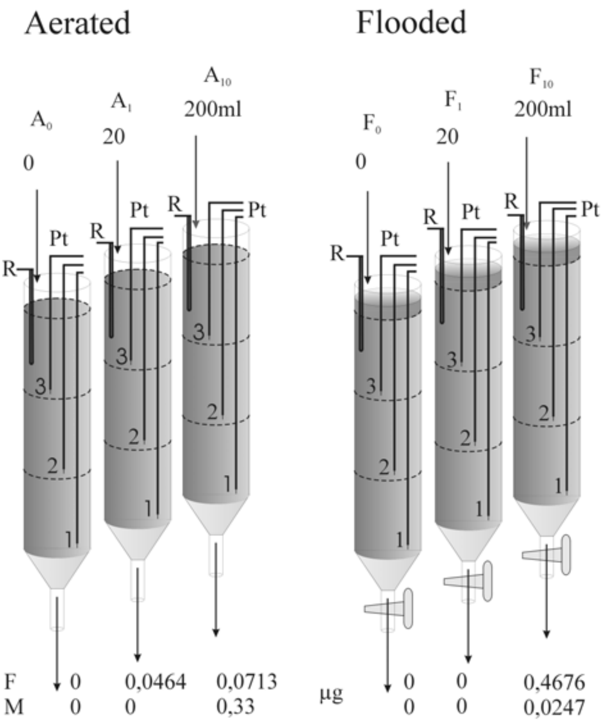


Fig.1. *Experimental set and doses of added pesticides and its leaching metabolites*

Immediately after the incubation, the soil from each column was divided into 4 segments and analyzed for redox potential (Eh), pH *in situ,* dehydrogenase, as well as acid and alkaline phosphomonoesterase activity.

Activity of dehydrogenase (DHA) was determined after incubation with TTC at 30°C for 24 h according to Casida *et al.* (1964). Dehydrogenase activity was expressed in mg TPF g^{-1} dry soil min^{-1}.

Acid and alkaline phosphomonoesterase activities were assayed according to Tabatabai and Bremner (1969) and expressed in ng of *p*-nitrophenol g^{-1} dry soil min^{-1}. All the measurements were replicated three times.

RESULTS

Figures 2 and 3 present mean redox potential values of the entire 4 weeks incubation period (A) as well as its final values (B) at different soil depths for glyphosate and fonofos treatment. The general mean value of Eh (in the entire soil depth) was >400 mV for non- flooded columns. The final Eh values were much more differentiated (from –240 mV to +480 mV) as compared to the dose and type of pesticides. In the case of the flooded treatments, Eh values were around – 200 mV and those for non-flooded treatments ranged from +50 mV (10 fold glyphosate dose) to about 480 mV for the treatment with the low herbicide dose. The differentiation of pH values did not exceed 0.2 units.

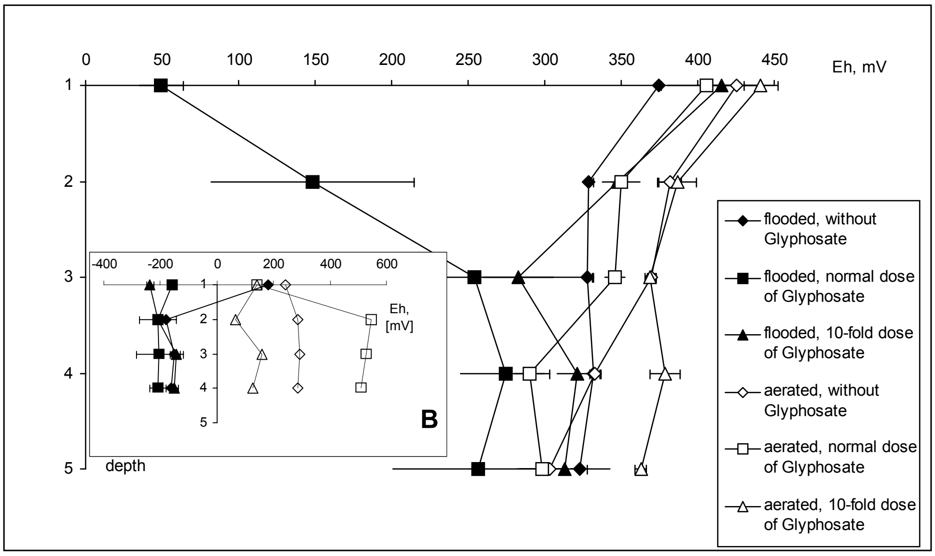


Fig.2. *Redox potential (Eh) at different depths: mean values for the whole period (A) of 24 days incubation accompanied by Eh measured on the last day (B) of incubation (inset) in glyphosate treatment.*

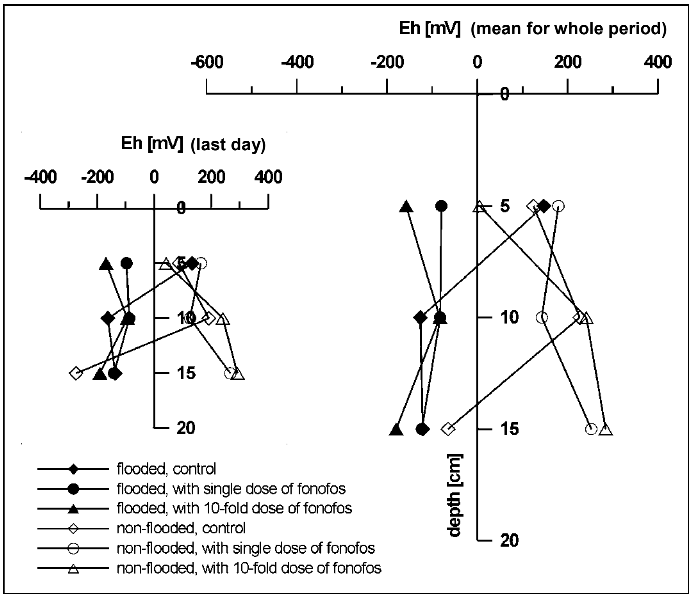


Fig. 3. *Redox potential (Eh) at different depths: mean values for the whole period (A) of 24 days incubation accompanied by Eh measured on the last day (B) of incubation (inset) in fonofos treatment*

Concentrations of pesticides and their metabolites in leaching solution, obtained during 4 weeks of experiment with glyphosate and fonofos at different aeration conditions, are presented in Tab. 1.

A crucial role in the transport and movement of pesticides is played by their sorption affinity to soil particles and the rate of decomposition by soil microorganisms. The behavior of tested pesticides indicates their different rate of transformation in aerated and flooded conditions.

Table 1. Concentrations of pesticides and their metabolites in leaching solution

Treatment	[µg per column]			
	Aerated		Flooded	
	A_1	A_{10}	F_1	F_{10}
Fonofos introduced	0.1	1	0.1	1
Fonofos leached	0.0464	0.0713	0.0382	0.4676
MFS leached	0	0.33	0	0.0247
% of leaching F+MFS	46.4	40.1	38.2	49.2
Glyphosate introduced	0.1	1	0.1	1
Glyphosate leached	0.0414	0.7283	0.0572	0.1686
AMPA leached	0	0.0202	0	0.0976
% of leaching G+AMPA	41.4	74.8	57.2	26.6

The rather small concentration of AMPA in the leaching solution testifies that glyphosate is characterized by great stability in aerated conditions and indicates small affinity to sorption (presence of 72.8% in water solution after 4 weeks after amendment). Opposite to aerated conditions, where G+AMPA content was 74.8% of introduced Glyphosate, only 26.6% of G+AMPA was found in the solution in flooded treatments, of which 57% was detected as the MPA form.

On the contrary, the higher concentration of MFS in leaching solution indicates fast transformation of fonofos in the aerated treatment. At low-oxygen incubation it is decomposed rather slowly, which indicates the proportion between F and MFS as 95% and 5% in leaching solution. In the anaerobic treatment with the 10-fold dose of fonofos, about half (49.2%) of the pesticide introduced was found in the leaching solution, while 40% of the metabolites was found in aerobic conditions. At smaller doses of pesticide introduced, no presence of MFS was identified after 4 weeks of incubation. Figs 4 and 5 present the dehydrogenase and acid and alkaline phosphomonoesterase activity changes as modified by aeration conditions and dosage of pesticides.

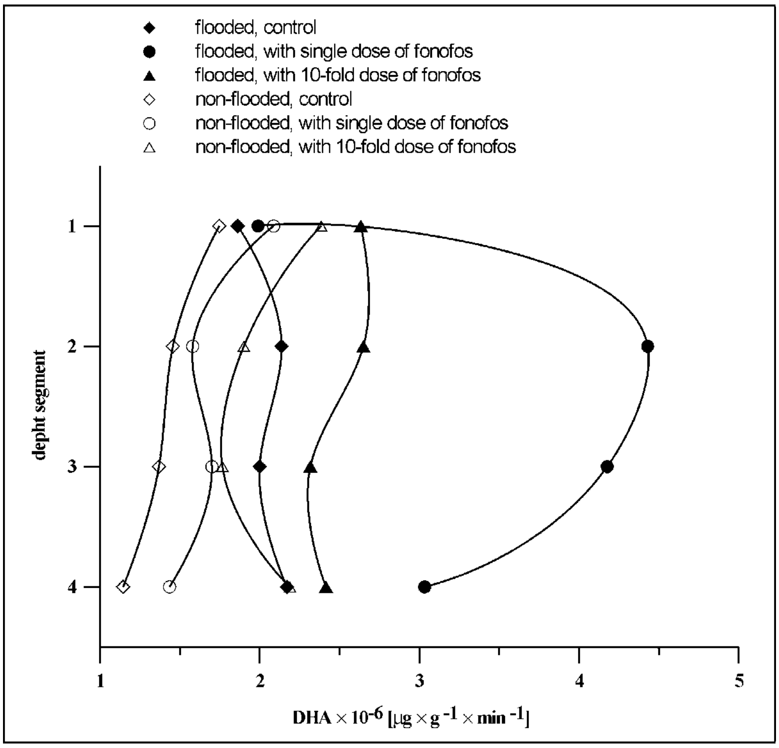


Fig.4. *Dehydrogenase activity in soil column after different doses of glyphosate (A) and fonofos (B) amendments after 4 weeks of incubation*

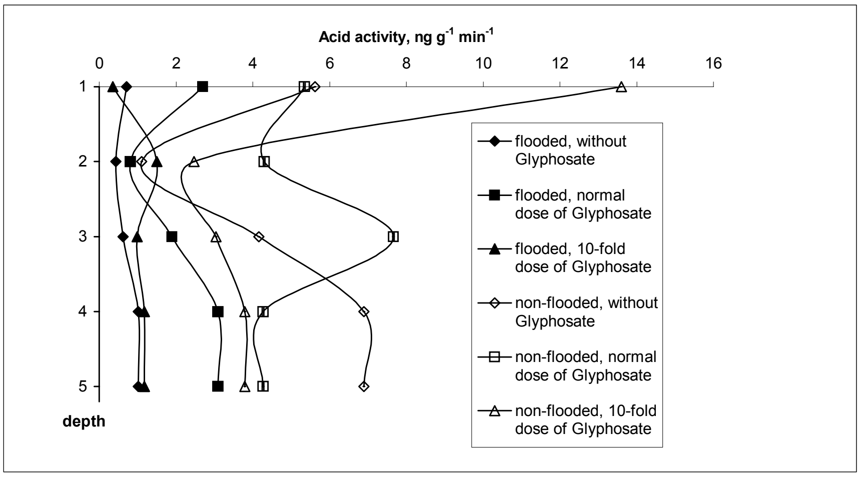


Fig.5. Acid and alkaline phosphomonoesterase in soil column after different doses of glyphosate (A) and fonofos (B) amendments after 4 weeks of incubation

The effect of oxygen on the dehydrogenase activity is presented in Fig. 6. While the transformation of glyphosate was dependent on the aeration conditions and the dosage of pesticide, the Eh value had a much stronger effect on the dehydrogenase activity. The presence of the pesticide was rather indirect as a new carbon source for microorganisms.

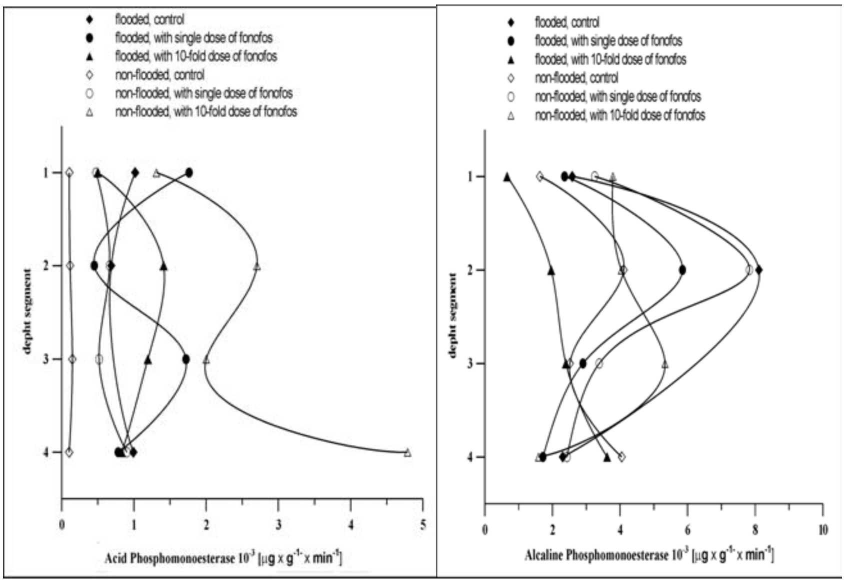


Fig.6. *Acid and alkaline phosphomonoesterase activity in soil column after different doses of fonofos amendments*

The effect of the pesticide dosage (6.3 mg $kg^{-1} \cong 18.9$ kg $ha^{-1}$of glyphosate) after 4 weeks of incubation appeared to be significant for acid phosphomonoesterase both under flood and non-flooded conditions, where significantly higher values occurred at the higher glyphosate and fonofos doses. Alkaline phosphomonoesterase activity in flooded soil columns was significantly higher than in aerated ones, indicating an inhibitory effect of glyphosate and fonofos.

The above differs from the results discussed by Schaffer (1993) who stated that glyphosate as well as paraquat, trifluralin and atrazine at levels of 5.4, 2.2, 3.4, and 1.2 kg ha^{-1} did not change the phosphatase activity of soil. Similarly, Davies and Greaves (1981) stated that the activities of phosphatase and urease were unchanged by glyphosate at 21.6 kg ha^{-1}.

Phosphatases, like dehydrogenases, are often used as a test for the toxicity of metals or organic pollutants, e.g. pesticides (Tam, 1998). According to this author, phosphatases are less sensitive to variations in the soil moisture content. He found that alkaline phosphatase activity increased more than three-fold after 2-4 weeks of flooding. Our studies confirmed that under flood conditions the activity of akaline phosphomonoesterase increased up to three times. They also showed the existence of opposite functional relationships for acid and alkaline phosphomonoesterase activities with redox potential.

CONCLUSIONS

During incubation, in a model experiment, of *Haplic Phaeozem* samples enriched with two doses of glyphosate at different redox conditions the following results were found:

- redox potentials in flooded soil after 4 weeks of incubation were more lower by over 450 mV compared to water holding capacity treatment,
- flooding the soil differentiated significantly the dehydrogenase activity and both acid and alkaline phosphomonoesterase activity.
- the dehydrogenase activity was negatively correlated with redox potential
- the application of glyphosate and fonofos (doses of 1.89 and 1.5 kg ha^{-1} and 10 times higher for glyphosate and fonofos respectively) caused significant changes in its activity
- at flooded conditions, the decomposition of tested pesticides is going rather slowly, which possibly indicates decomposition of the leaching solution.

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METHANOTROPHIC ACTIVITY OF COAL MINE ROCKS

Stępniewska Z., Stefaniak E., Szmagara A.

INTRODUCTION

Atmospheric methane concentration almost twice as high as it was a hundred years ago, and as much as 22 times more effective in potentially warming the Earth's surface than each additional gram of carbon dioxide, can have a dramatic impact on atmospheric climate changes. One of the most important sources of methane are landfills, where emission is estimated at around 40 Tg/year [1], and underground coal mines which liberate – worldwide – about 41-57 Tg/year, out of which only 3.2 Tg/year is used as fuel [Bibler], the remaining part being lost and not used as an energy resource. Ten largest coal producers in the world are responsible for 90% of global methane emission from coal mines. China is the largest emitter of coal methane, followed by the Commonwealth of Independent States (particularly Russia, Ukraine and Kazakhstan), the United States, Poland, Germany, South Africa, the United Kingdom, Australia and the Czech Republic. In some of these countries methane is used for a variety of purposes, like heating, coal drying, or electric power generation. But there are some technical barriers to coal mine methane use, such as lack of infrastructure or low permeability of coals, as well as low gas quality or low natural gas prices.

Table 1. The ten largest coal producing countries and methane emission (Bibler)

Country	Coal production $[10^6 \text{ t yr}^{-1}]$	Methane Emission $[\text{Tg yr}^{-1}]$
China	1200	16.1
Former Soviet Union	438	10.5
United States	264	7.5
Germany	54	2.6
South Africa	98	1.86
United Kingdom	43	1.86
Poland	16.3	3.0
Australia	53	1.0
India	64	1.0
Former Czechoslovakia	127.2	0.57
Total	2303.5	46.1

Although some projects on gas recovery as a source of energy seem reliable [2], there are still lots of landfills where utilisation of methane is not profitable. In such cases, the way to reduce methane emission is its removal *in situ* by microorganisms from the group of methanotrophs, which seems to be very promising. It has been known that bacteria living in various types of soil can oxidise methane

[3], but there is also another environment advantageous for methanotrophs – the coal mine tailing wastes, usually deposited as hills or dumps, being no more than a burden for the natural environment. The aim of this work was to estimate the methanotrophic activity of coal mine dump rock with respect to different time of storage, temperature and water content as well as concentration of substrates.

MATERIALS AND METHODS

The rock material for the studies was taken from the Lublin Coal Basin (east part of Poland).

Samples of coal mine rock at different times of exposure to weathering on earth surface (fresh material, 1, 2/3, 5 and 10 years) were ground in a roller mill (Testchem, Poland) up to 1 mm of grain diameter and the materials obtained were characterized by the following grain-size distribution:

Table 2. Grain-size distribution of tested material

mm	%
1 - 0.1	68
0.1 - 0.05	6
0.05 - 0.02	8
0.02 - 0.005	7
0.005 – 0.002	5
< 0.002	6

XRD analysis showed that all the rock samples consisted mainly of kaolinite, illite, coal and quartz. The content of pyrite did not exceed 1.5% w/w, however the content of total sulphur varied significantly among the samples.

The chemical composition of each sample was measured by the INAA, ICP-AES and ICP-MS methods.

Water capacity and pH of the collected dump rock samples at different times of weathering are presented in Table 3. Acidity of the samples was measured according to the EPA SW-846 method 9045.

Table 3. Total water capacity and acidity of the dump rock samples

SAMPLE	TIME OF DUMPING [YEARS]	TOTAL WATER CONTENT [ml/g of dry mass]	pH
S1	0 (fresh rock)	0.306	6.30 (SD 0.47)
S2	ca 1	0.320	6.45 (SD 0.40)
S3	ca 2/3	0.314	6.85 (SD 0.28)
S4	ca 5	0.371	4.32 (SD 0.25)
S5	ca 10	0.386	2.73 (SD 0.10)

GC TESTS

Air-tight bottles (60 ml) sealed with a rubber septa for gas sampling were filled with 15g of each rock and brought to a moisture content of 50%, 100% and 200% of the total water capacity. The bottles were incubated at 5, 10, 20 and 30oC with different methane concentration levels (from 0% to 30% v/v). The concentration of methane, carbon dioxide and oxygen in the headspace were measured by gas chromatography technique. Simultaneously, control samples with the same methane concentrations (containing purified sand instead of the rock under examination) were included. The experiment was continued until the rate of oxidation stabilised.

RESULTS

The dynamics of methane oxidation is shown in Fig. 1. The concentration of oxygen decreases exponentially, while the curve of methane concentration has a sigmoidal shape. Carbon dioxide concentration rises up to a maximum value. Three additional curves reflect the changes of the examined gases in the control samples. Incubation of 5%v/v methane over the inert medium (i.e. purified sand) proved no changes of methane concentration during the whole time of incubation. The decrease of O_2 concentration and increase of CO_2 content in the sample without methane indicated aerobic decomposition of organic mater. No changes in methane concentration in the control combination show that the observed methane oxidation process occurred only in the presence of coal mine rocks.

The efficiency of methane oxidation at different initial methane concentrations (from 0.5 up to 30 % v/v) and at 50%, 100% and 200% of total water capacity of tested materials at 20^{o}C is presented in Table 4.

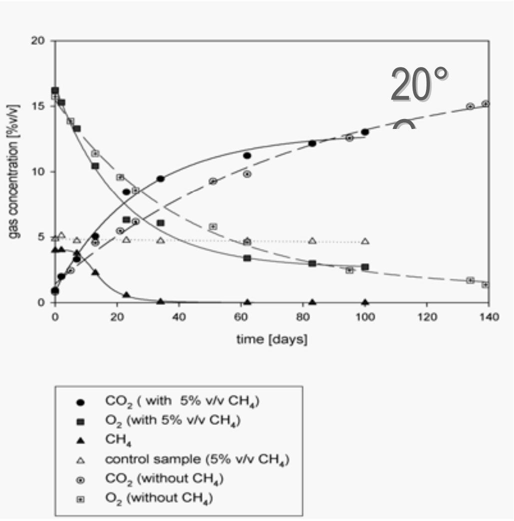

Fig. 1. *Kinetics of atmosphere composition changes during the incubation of fresh rock samples (S1) with and without methane addition (at 50% of total water capacity)*

Table 4. Methane oxidation efficiency with respect to all examined parameters

Initial methane concentration [%v/v]	% of methane oxidised (sample moisture: 50% of a total water capacity)				
	S1	S2	S3	S4	S5
0.5	100.0	100.0	100.0	21.3	0
1	100.0	100.0	100.0	46.0	0
2	100.0	100.0	100.0	48.4	0
5	100.0	100.0	100.0	44.9	0
10	94.0	72.0	100.0	13.0	0
15	32.8	32.4	19.1	9.5	0
30	1.2	0.1	3.4	0.0	0
Initial methane concentration [%v/v]	% of methane oxidised (sample moisture: 100% of a total water capacity)				
	S1	S2	S3	S4	S5
0.5	100.0	100.0	100.0	100.0	0
1	100.0	100.0	100.0	100.0	0
2	100.0	100.0	100.0	100.0	0
5	100.0	100.0	100.0	100.0	0
10	99.2	92.5	100.0	83.0	0
15	48.1	39.7	47.8	40.7	0
30	1.3	2.1	4.3	7.1	0
Initial methane concentration [%v/v]	% of methane oxidised (sample moisture: 200% of a total water capacity)				
	S1	S2	S3	S4	S5
0.5	100.0	100.0	100.0	100.0	8.9
1	100.0	100.0	100.0	100.0	30.4
2	100.0	100.0	100.0	100.0	23.9
5	100.0	100.0	100.0	100.0	29.2
10	86.8	95.2	99.2	95.2	13.1
15	14.1	9.3	24.0	39.1	9.2
30	1.4	1.3	1.6	14.9	1.6

The amounts of consumed substrate calculated per gram of dry rock in relation to environmental factors, such as moisture content and initial methane concentration, are shown in Fig. 2.

The rate of methane oxidation is governed both by the level of initial methane concentration and by the water content. The maximum of the oxidation rate occurs at about 10% v/v of methane in the atmosphere at 50% of water content, and rapidly decreases with higher methane concentrations. Moreover, the oxidation rate is lower for higher water content levels. Sample moisture content equal to the total water capacity or twice as high makes the oxidation rate 2-3 fold lower. It is probably caused by worse diffusion of substrates inside the rock pores and - therefore - worse availability of substrates for the microorganisms. On the other hand, this relationship is true for relatively fresh samples, up to 3 years of dumping. For older rock samples, after longer exposure to weathering, the higher water content facilitates(?) the oxidation of methane and does not reach maximum values even at 30% of methane in the atmosphere. In any case, the efficiency of methane consumption remains on the level of 100% independently from the water content at methane concentrations not higher than 5%.

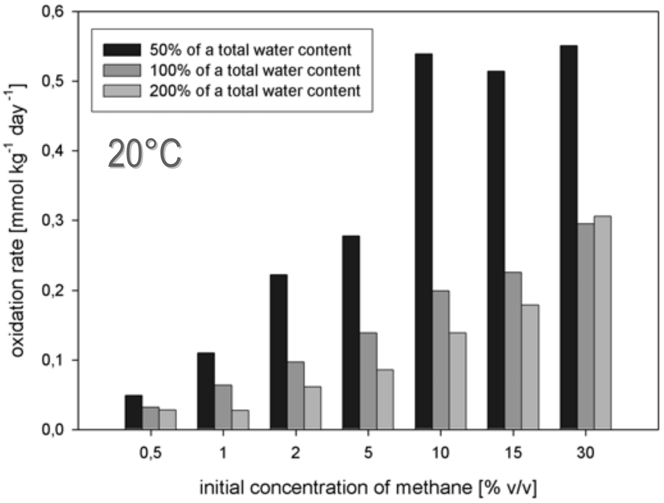

***Fig. 2.** The effect of water content and methane concentration on the methane oxidation rate*

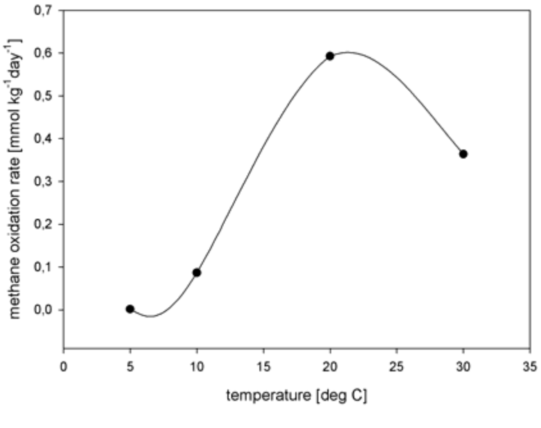

***Fig. 3.** The influence of temperature on the methane oxidation rate (50% of total water capacity and 10% (v/v) CH_4)*

The influence of temperature on methane oxidation rate at a moisture content of 50% of total water capacity and at 10% (v/v) CH_4 is presented in Fig. 3. The methane oxidation rate increases very sharply from about 0 at 5°C to 0.6 mmol $kg^{-1}day^{-1}$ in the temperature range of 10-20 °C, reaching a maximum at 20 °C, then rapidly decreases at higher temperatures. The optimum temperature and slope of the plot represent an energy hump (activation energy) that must be overcome for the reaction to proceed. Therefore, it is not surprising that the observed process of methane oxidation is dependent on microbial activity and that specific organisms providing this process grow at moderate temperature.

The presence of methanotrophic bacteria in coal mine rocks can reduce methane level in mines, organic waste deposits and other localities from where methane is volatised to atmosphere.

Methanotrophic bacteria are strict aerobes and they are dependent on the presence of molecular oxygen.

CONCLUSIONS

Waste rock from the Bogdanka coal mine near Lublin (Poland) is capable of oxidising methane as a favourable environment for the group of methanotrophs. It keeps these properties for ca 5 years of storage in the open air, i.e. exposure to weathering.

Methane oxidation rate is governed by 3 major factors: methane (and oxygen) concentration, water content and pH. The highest rate occurs for 10%v/v of methane initial concentration at sample moisture equal to 50% of total water capacity under pH conditions close to neutral. The lower the pH values, the higher the water content necessary to keep methanotrophs active. Methanotrophic activity of coal mine tailing rocks decreases with time and becomes extremely low after 10 years of weathering, which is probably due to the high acidity brought by oxidation of pyrites generating sulphuric acid.

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SOIL – PLANT – ATMOSPHERE AERATION AND ENVIRONMENTAL PROBLEMS

PART C: POROUS ENVIRONMENT

DETERMINATION OF ENERGETIC STATUS AND EVAPORATION FROM POROUS BODIES ON THE BASE OF INFRARED IMAGING

Baranowski P., Lamorski K., Mazurek W., Walczak R.T.

INTRODUCTION

Determination of heat and water properties of agrophysical objects is closely connected with their composition. Frequently, the objects of agrophysical studies (e.g. plants tissues, seed material, soil matrix, etc.) are characterized by cellular or granular composition. In natural conditions these physical bodies are situated in complicated systems and many various factors influence the transport of energy and mass in them. The energetic status of these porous bodies, which is expressed by the heat balance equation, can be indirectly evaluated by the measurement of the radiation temperature of their surface providing the knowledge of other agro-meteorological parameters (Baranowski et al. 1996, 1998, 2001).

In case of limited availability of soil water for the rooting system, the transpiration intensity decreases and canopy temperature becomes higher. The application of radiation temperature measurement of plant cover with thermography makes possible to evaluate actual evapotranspiration because plant itself is the best sensor of the physiological processes taking place in it. The main factors influencing transpiration intensity are: water potential in the soil and in plants, water vapour pressure deficit in the air and stability conditions of the near surface atmosphere.

Radiation temperature of canopy can be used to evaluate evaporation from soil surface and transpiration from plants (jointly evapotranspiration). The quantitative determination of evapotranspiration rate is essential in the investigations of water balance. Thermal images of agricultural areas, available from airborne or satellite levels, contain information about physical status of cultivated fields. However, their proper interpretation requires the basic studies, to obtain the knowledge of interactions between different soil and meteorological factors, affecting the actual value of crop radiation temperature.

Recently, some trials have been undertaken to use thermography for the detection of inhomogeneity of heat properties within the soil on the base of temperature distribution on surface of the soil or plant cover. These studies are based on the assumption that heat transfer under the temperature gradient in a body with the intrusion is strongly modified if the intrusion's thermal properties are different than the rest of the medium. The detection of military intrusions in the soil (e.g. mines) has an important practical aspect.

FACTORS INFLUENCING RADIATION TEMPERATURE OF PLANT COVER AND BARE SOIL

Numerous factors influence radiation temperature of plant surface. They can be divided into three groups:

- properties of plant surface and canopy (emissivity ε, albedo α_s, i.e. fraction of global radiation reflected by the surface, aerodynamic roughness z_0, soil cover expressed by the leaf area index (LAI), position of the canopy surface in relation to the incident solar radiation);
- physical status of the boundary layer of atmosphere and the processes taking place in it (shortwave R_s and longwave R_l solar radiation fluxes, air temperature T_a, air pressure p_a, water vapour pressure in the air e_a, wind speed u) and in the soil (soil water potential Ψ_g, soil water content θ, temperature in the soil profile T_g, soil water characteristics $K(\theta)$ and $\Psi_g(\theta)$, soil heat properties, i.e. thermal conductivity λ, thermal diffusivity α, heat capacity c_v, content of chemical substances, soil pollution);
- physical status and physiological processes in plant, (variety, phase of physiological development, depth of the rooting system, diseases, etc.).

All these factors influence the transport of water and energy in plants, expressed by the heat balance equation, in which the conditions of the stability of the atmosphere just above the crop should be included.

Plant temperature is nearly always different from the ambient temperature or from the soil temperature and it depends on a number of agro-meteorological factors as well as physiological processes. The actual value of plant temperature is mainly affected by the intensity of transpiration, which depends on the availability of soil water for the rooting system and meteorological conditions while to smaller extent on the thermal conditions in the soil and its surface (Mazurek et al, 1996, 1998). Plants that suffer from the water stress caused by a limited availability of soil water for the root system, during the hours of the high solar radiation intensity, have the radiation temperature several degrees higher than the plants growing in the comfortable soil water conditions.

It should be noticed that for the relative air humidity values above 75% and for the air temperature below 15^0C the differences of radiation temperature are close to zero.

During the measurements in the open air the influence of wind speed on measured radiation temperature should be considered. It is not recommended to perform measurements of radiation temperature of terrestrial bodies under the wind speed higher than 8 m/s. In some cases it is necessary to apply a correction coefficient, which would make possible to recalculate the values of the radiation temperature obtained for different wind speed values to the values corresponding to wind speed 1 m/s.

The measurement with thermographic device embraces a two-dimensional surface, which cannot be easily defined because it creates a complicated dynamical system composed of various parts of plants having intricate geometry and in case of incomplete soil cover also of the bare soil, shining through the canopy. In each plant some physiological mechanisms exist, which enable to modify the characteristics of the surface under the impact of external factors (e.g. heliotropism). Therefore, the measured value of radiation temperature depends significantly on the angle of inclination of the thermal camera towards the surface and on its position in respect to the direction of sunbeams.

The studies of the inclination angle of the radiation thermometer (8-14 μm) axis in relation to the canopy surface were performed by Hatfield, 1979 and Nielsen et al., 1984. Making the measurements from the height of 1 m, he situated the radiation thermometer perpendicularly to the studied surface and at the angle of 45^0 from the main directions (N, S, E, W). He stated that in case of incomplete soil cover the lower values of radiation temperature are obtained for the angle of 45^0 than for 90^0 because in the first case less energy incoming to the detector comes from the bare soil.

THERMAL IMAGERY OF THE AREAS WITH PLANT COVER

In case of incomplete soil cover with plants, the total temperature of the surface T_{sf}, measured remotely, is a function of soil temperature and plants temperature multiplied by respective fractions of their surfaces in relation to the total surface. The energy balance equation of the surface is as follows (Heilman et al. 1981 and Kustas et al. 1990):

$$\left[\varepsilon_c f_c + \varepsilon_s \left(1 - f_c\right)\right] \sigma T_{sf}^4 = f_c \varepsilon_c \sigma T_c^4 + \left(1 - f_c\right) \varepsilon_s \sigma T_s^4 + f_c \left(1 - \varepsilon_c\right) R_l + \left(1 - f_c\right)\left(1 - \varepsilon_s\right) R_l \tag{1}$$

where: f_c – the ratio of the surface covered with plants to the total surface; T_{sf} – the total temperature of the surface [K]; T_s – soil temperature [K]; T_c – plant temperature [K]; ε_c – emissivity of plants; ε_s – emissivity of soil; σ - Stefan-Boltzman constant [$W \cdot m^{-2} \cdot K^{-4}$]; R_l – flux density of longwave surrounding radiation reaching the studied surface [$W \cdot m^{-2}$].

The quantity of R_l is determined on the base of the measurement of air temperature T_a and the knowledge of air emissivity ε_{α}:

$$R_l = \varepsilon_a \sigma T_a^4 \tag{2}$$

Under some simplifications resulting from the assumptions of the conditions of measurement, the terms of the longwave reflected radiation could be omitted in equation (1). Thus:

$$T_{sf}^4 = f_c T_c^4 + \left(1 - f_c\right) T_s^4 \tag{3}$$

The values of T_{sf} obtained by Kustas et al., 1990 from this simple model for the cotton canopy differed from the values obtained from ground measurements by 2^0C, on average. These authors stated that in case of incomplete soil cover with plants, the differentiation of soil temperature, resulting from its non-uniform illumination, should be considered.The problem formulated this way requires a modification of equation (3):

$$T_{sf}^4 = f_c T_c^4 + f_{sl} T_{sl}^4 + f_{sh} T_{sh}^4 \tag{4}$$

where: f_{sl} and f_{sh} are the fractions of illuminated and shaded soil surfaces to the total surface; T_{sl} and T_{sh} are the temperatures of illuminated and shaded soil surfaces [K].

EVALUATION OF PLANT WATER STRESS AND ACTUAL EVAPOTRANSPIRATION

The aim of the investigation performed in our Institute, was the quantitative evaluation of hourly and daily values of actual evapotranspiration of grass cover under different soil moisture and meteorological conditions on the base of thermographic measurements.

In the study actual evapotranspiration was calculated from energy balance equation:

$$L \cdot E + H + R_n + G = 0 \tag{5}$$

in which radiation temperature of plant cover is a component of the sensible heat flux, expressing the transport of heat energy from evaporating surface to the atmosphere:

$$H = \rho \cdot c_p \frac{T_c - T_a}{r_{ah}} \tag{6}$$

where: $L\cdot E$ - the latent heat flux [$W\cdot m^{-2}$] (energetic equivalent of the evapotranspiration flux); L - the latent heat of vaporisation of water per unit mass (L=2,45· 106 $J\cdot kg^{-1}$); E - evapotranspiration flux [$kg\cdot m^{-2}\cdot s^{-1}$]; H -the sensible heat flux [$W\cdot m^{-2}$]; R_n -the net radiation flux [$W\cdot m^{-2}$]; G - the heat flux into the soil [$W\cdot m^{-2}$], T_c - the crop surface temperature [K]; T_a - the air temperature [K] measured at reference height; *rah* - the diffusion resistance for transport of heat [$s\cdot m^{-1}$]; *r*- the density of air [$kg\cdot m^{-3}$]; c_p - the air specific heat [$J\cdot kg^{-1}\cdot K^{-1}$].

The experiment was performed in lysimetric station of the Institute for Land Reclamation and Grassland Farming in Sosnowica. Thermal images of plant cover in lysimeters were taken with AGEMA 880 LWB. The whole day registration of meteorological data was performed with the use of the automatic data acquisition system elaborated in IA PAS, Lublin.

On the base of temperature differences between crop surface and the air, the stability conditions in boundary layer of the atmosphere were determined. Using the appropriate equations for calculation of the components of the heat balance equation, the hourly and daily values of actual evapotranspiration were obtained. High differences in the course of sensible and latent heat fluxes for the lysimeters with different soil moisture levels were noticed. Daily courses of potential evapotranspiration calculated with different methods were compared with actual evapotranspiration under comfort soil water conditions. It was stated that the hourly values of actual evapotranspiration in lysimeters with comfortable water conditions follow best the evapotranspiration calculated according to the 63-Penman and Kimberly-Penman formulae. Considering daily values of potential and actual evapotranspiration the meaningful differences were noticed between lysimeters with stress and comfort conditions and between lysimeters with organic and mineral soils.

DETECTION OF LOCAL DISTURBANCE OF HEAT PROPERTIES IN THE SOIL PROFILE

The main factor influencing the radiation temperature of plants is the intensity of transpiration. This process, which consists of movement of water from a soil reservoir to the atmosphere through plants, mainly depends on availability of soil water for the rooting system. Plants react to any limitations in soil water availability, which reveal through high absolute values of soil potential, with the increase of their temperature. The increase of plant temperature as a result of water stress occurs under specific meteorological conditions, i.e. high intensity of solar radiation, low values of relative air humidity, high temperature of the air in plants surrounding and low wind speed.

The soil structure disturbance, e.g. buried stones or mines, cause changes of heat characteristics distribution in the soil, what in specific conditions can have its representation in a form of heat signature on the soil surface. In the conditions of dense soil surface cover, such a surface disturbance of the soil temperature is strongly attenuated by the plant cover and the turbulence transport of energy in the boundary layer of the atmosphere. Therefore, only in case of high values of the sensible heat flux in the soil surface – air interface, it is possible to assume the influence of soil surface temperature on the temperature of the plant cover. Such investigations were performed by Mateos et al., 1991. They used a two-layer model of the heat balance for the soil-plant atmosphere system, which took into account the heat balance on the surface of plant cover and the heat balance on the soil surface. These authors stated that only in case of incomplete soil cover (wheat canopy – LAI from 1 to 3), the temperature of the soil surface had influence on radiation temperature of plants in situation of the lack of any symptoms of plant water stress.

In case of a soil surface thermal signature of an underground object, the presented model seems to be important for the determination of the surface representation of this disturbance for various densities of the soil cover with plants. In the studies of this kind it seems to be necessary to take into account the angle of incidence of the sunbeams on the investigated surface because it can have an impact on the temperature of the translucent soil through variations of the ratio of illuminated to shaded surfaces. In this case, the most suitable would be the angle of 90^0 between the optical axis of the thermographic device and the investigated surface because it would give the largest area of the soil represented in the thermographic image (Kimes, 1983).

Considering a possibility of detection of the structural disturbances in the soil, e.g. military mines, it is necessary to take into account the following cases:

- the heat intrusion put into the soil shortly before the beginning of the thermographic observation; the damage of the rooting system disturbs the physiological processes in plants, the water consumption by plants is limited, the intensity of evapotransiration decreases; under convenient meteorological conditions the temperature of plants above the buried mines differs from the temperature of surrounding plants.
- the heat intrusion, e.g. a mine has been buried in the soil in the early stage of phenological development of plants or in previous vegetation season; under complete soil cover, a dominant factor modifying the value of radiation temperature of plant cover is the transport of water in plants and transpiration. In this case, the detection of heat intrusion in the soil through the measurement of the temperature of soil cover seems to be impossible.
- the heat intrusion, e.g. a mine has been situated just beneath the soil surface with incomplete plant cover; the thermal signature of the intrusion can have its representation in the total temperature distribution of canopy, however not only meteorological conditions during the measurement should be considered but also the fractions of illuminated and shaded soil surfaces.

In first two of the considered cases if the time from the installation of the heat intrusion to the thermal imaging is respectively long, the development and position of the rooting system cause, that plants have unlimited access to the water resources in the soil and the intrusion cannot be detected in the thermographic image of the canopy.

Generally, thermal properties such as heat capacity and heat conductivity of the soil and buried objects have different values. In natural meteorological conditions, the temperature within the soil profile varies in time and is not homogeneous. Due to this, the temperature of the soil surface is not homogeneous, too. Temperature differences of the soil surface may be detected using infrared techniques (Pręgowski et al. 2000). In a laboratory experiment with a antitank mine buried in sand, five centimeters below the soil surface the infrared lamps heated the surface for one hour, then the system was cooled. It was observed that the temperature of the soil surface was nearly uniform at the beginning of the experiment. After one hour of heating, a thermal signature of a buried mine was noticed at the soil surface and high differentiation of the soil surface temperature in the studied area was evident.

Temperature differences achieved in natural conditions are not as big as in this experiment, therefore other methods of thermographic observation have to be used. The temperature of the soil surface varies in a diurnal cycle. The visibility of a buried object changes in time, too. Thermal visibility is defined as a soil surface temperature difference between the center of a buried object, and a point at the soil surface far away from a buried object. The dynamical thermography may be used in this case. Dynamical thermography consists in making several infrared pictures of the investigated object at different times. Then, the pictures of this set are transformed, using images processing techniques, to improve the detection probability of a buried object. Dynamical thermography may be supported by numerical methods of thermal transfer modelling. Physical modelling of the daily soil temperature changes, allows improving probability of buried object detection, by estimating times in which infrared pictures should be taken.

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SURFACE PROPERTIES OF SOILS AND THEIR BEHAVIOR IN SOIL DEGRADATION PROCESSES

Jozefaciuk G.

SURFACE PROPERTIES OF SOILS AND THEIR ESTIMATION

Soil surface is extremely complex due to diversified mineral, organic and ionic composition of soil constituents. Among its specific physicochemical properties, researchers place particular attention on surface charge, area and energy.

Surface charge origins from isomorphic substitution of higher valence cations by lower valence cations in the crystal lattice of clay minerals during genetic processes (permanent charge) and from dissociation and association of hydrogen ions (protons) from/to surface functional groups of organic matter, edges of clay minerals, aluminum, iron and silicon oxides (variable charge). Contrary to the permanent charge, the magnitude of the variable charge depends on pH and composition of the soil solution. The easiest and most convenient method to study surface charge properties is back titration (Duquette and Hendershot 1993, Jozefaciuk and Shin 1996). In this method the titration is performed separately for soil suspension and for its equilibrium solution (supernatant), starting from low pH upwards. Hydroxylic ions of the base added to the suspension are consumed by acids present in the equilibrium solution and by acids present on the surface of the suspended solid. Therefore after subtraction of the titration curve of the equilibrium solution from this of the whole suspension, one obtains the titration curve of the solid. Titration of the solid leads to the neutralization of the active protons of surface acidic functional groups thus they become negatively charged, so the titration curve of the solid gives the dependence of the variable charge of the solid phase versus pH. To find the dependence of total soil charge vs. pH one shifts the variable charge vs. pH curve against the charge axis to meet any point (pH) for which the value of the total charge is known (e.g. CEC at pH 8.2, from the standard Mehlich's method).

Acidic functional groups of soil constituents have very different strengths, depending not only on the kind of the group, but also on its locality. Surface groups of stronger acidic character (higher values of dissociation constants K) are neutralized at lower pH values. The weaker acidic is the group (lower K), its neutralization requires higher pH value. If one assumes that surface acidity is composed from large number of small increments of various acidic groups having different pK values, than pK may be approximated by pH of the titration. Thus the solid phase charge vs. pH curve gives variable charge vs. pK dependence. From the latter curve fractions of charge generating groups having pK values in a defined range may be easily found from charge difference at two given pK values divided by total amount of variable charge measured in the experimental window.

For studies of surface areas and their energetic properties adsorption isotherm is used most frequently (Gregg and Sing 1967). The adsorption isotherm is a function relating the amount of adsorbed gas (vapor) to its equilibrium pressure during the pressure increase at a constant temperature. Soil surface area i.e. the overall area of all soil solid phase components which is available for molecules of soil liquid and gas phases (specific surface), is easily estimated from adsorption data. The idea of this estimation is to find a number of adsorbate molecules that cover the adsorbing surface as a monolayer, and to multiply this number by the area occupied by a single molecule. Surface area measured from nitrogen adsorption data is interpreted as an "external" surface, and the surface area measured from water adsorption data as a "total" one, including internal (e.g. mineral interlayer) surfaces.

Different surface sites bind adsorbate molecules with different energies thus influencing adsorption pathways (Jaroniec and Brauer 1986). Knowing that at the equilibrium the free energy is constant throughout the system, the energy of adsorbate at a given pressure is associated with adsorption energy on a given site, while the number of given adsorption sites is estimated from the amount adsorbed. Knowing both above values, one can easily derive an average adsorption energy that characterizes global energetic character of the surface.

SOIL SURFACE PROPERTIES IN DEGRADATION PROCESSES

Surface charge, area and energetic parameters become increasingly used for description and modeling of soil physical, chemical and biological processes (e.g. ion exchange, accumulation of uncharged species, water retention, microbial life, catalysis) as well as for quantitative analysis of soil typological and genetic properties (Balard et al. 1997, Chiou at al. 1990, Hajnos et al. 2003, Hernandez 2000, Hoffmann at al. 1999, Sequi and Aringhieri 1977, Sokolowska et al. 1993a,b, 1999, 2000, Tombacz et al. 1998, Wilczynski et al. 1993). Surface properties depend on clay, organic matter and exchangeable cations content (Petersen et al. 1996). They have been used as highly sensitive indicators of soil degradation processes: acidification and alkalization, soil organic matter leaching and oxidation, soil pollution etc. (Jozefaciuk et al.1996, Pachepsky et al. 1995). Among these processes, due to the limited space of the paper, particular attention will be placed on acidification and alkalization, as far as several mechanisms involved here may illustrate other degradation processes, as well.

SURFACE CHARGE

Acidification processes generally lead to a decrease in permanent charge and an increase in variable charge of soil clay minerals (Jozefaciuk and Bowanko 2002). This is due to destruction of the crystal lattice of the minerals and a simultaneous formation of variably charged destruction products, mainly silica. Entering of aluminum into clay minerals interlayers during acidification may block a part of the permanent charge. This charge is unblocked by Al neutralization during pH increase that is equivalent to an apparent increase of the variable charge. In acidified soils these processes are accompanied by dissolution of variably charged amorphous oxides of iron and aluminum (Jozefaciuk et al. 2000). In soils poor in clay content the latter processes prevail therefore the decrease in both charge types occur. In clay rich soils, frequently the variable charge rises. Surfaces of silica oxides are very weakly acidic while soil iron and aluminum oxides have surfaces of medium acidity thus usually the acidic character of soils decreases after acidification. Production of higher amounts of variable charge in soil mineral phases may partially counteract the decrease in soil CEC due to acidificaction.

However, other acidification effects have been observed, as well. Natural (slightly acidic) weathering of an illite-smectite produced an increase in CEC due to dissolution of illite-smectite and appearance of smectite as a separate phase (Sucha et al., 2001). Sun Kou et al. (2000) observed a dramatical increase in strong acidity after Al pillaring of a montmorillonite that can occur in acidic environments. A sharp increase of the biotite permanent charge was observed on acidification due to a formation of expanded lattice smectite-like (14Å) structures (Jozefaciuk and Bowanko (2002). The expanded spaces are available for exchange ions. Srasra and Trabelsi-Ayedi (2000) postulated generation of the strong acidic sites due to acid treatment of a glauconite.

During alkalization the dissolution of the crystal lattice of the minerals occurs also that leads to their permanent charge decrease. However, opposite behavior of surface charge is frequently observed due to zeolitization of clay minerals and precipitation of new phases (Baccouche et al. 1998, Ruiz et al. 1997, Shin et al., 1998). Alkalization of clay minerals increases generally the amount of variable charge. Opposite to the acidification, an increase of surface groups of intermediate acidity and decrease in low acidity groups occurs. Fraction of weakly acidic surface functional groups decreases due to strong silica dissolution in alkaline media or increases only slightly. The amount of the surface groups of intermediate acidity rises due to removal of outer silica sheets from mineral lattices leading to an exposure of aluminum (hydroxylated) layers of medium acidity.

Alkalization processes in soils are strongly affected by dissolution of soil organic matter (Jozefaciuk et al. 2000). While the effect of the acid treatment on the amount of organic matter is low, the organic material is easily removed under alkaline conditions. Organic matter carries huge amount of variable charge, tens times more (per unit mass) than soil mineral components. Therefore due to soil organic matter depletion, alkalization of clay poor soils leads to the decrease of variable charge. Clay rich soils may exhibit the opposite trends, due to a new formation of mineral variable charge surfaces under alkaline conditions.

The alkali-soluble fraction of organic matter has more fulvic character than the insoluble fraction (Wilczynski et al. 1993) thus having higher charge per unit mass and stronger acidic character. Removal of soluble organic matter may explain that the fraction of strongly acidic groups remaining in clay poor soils after alkali treatment is reduced to large extent that causes weakening of surface acidity and decrease in soil buffering properties in low range of soil pH's, which can be particularly important in natural acidic environments. For clay rich soils the alkali treatment can cause an increase in strongly acidic groups due to the cleaning of Al and Fe oxides from organic matter coatings as well as to the alkali effects on clay minerals. The latter mechanisms may enable exchange adsorption of excess basic cations in natural clay rich alkali soils.

SURFACE AREA

Production of amorphous silicon oxides during acidic destruction of clay minerals lattices leads to significant increase of surface areas and the external surface area increases faster than the total one. Therefore the treatment of minerals with inorganic acids, referred to as 'acid activation', is commonly used for production of sorbents or catalysts of large surface areas (white carbon blacks) used in industry or environmental protection measures (Breen et al. 1995). The rise in surface area under alkaline conditions is usually much lower than under acidic conditions.

Contrary to the behavior of pure minerals, a decrease in surface area occurs most frequently in acidified and alkalized soils. This is due to a decrease in the clay fraction content. At high pH values, leaching of organic matter markedly contributes to this effect (Jozefaciuk et al., 2000). Small and easily mobile (fulvic) organic matter particles of high charge and polarity have much higher surface areas than more hydrophobic, larger organic particles which are leached in lower extent. The drop of the surface area is also connected with the dissolution of amorphous and very finely dispersed soil solid phase components, having very high surface areas. The decrease in surface areas indicates a drop in soil water holding capacity. The rise in the surface area of clay rich soils may occur, that is connected with the acid activation of the minerals and production of amorphous silica oxides from destruction of mineral lattices that may prevail over the dissolution ones. Removal of organic matter sometimes increases surface area of mineral soils, most probably due to opening of the fine pores plugged by organic material (Sokolowska et al., 1993).

SURFACE ENERGY

Average adsorption energy of clay minerals under acidification and alkalization depends on their individual features. The observed increase in adsorption energy may be due to the formation of cracks and voids on the attacked surfaces. The decrease in adsorption energy may be due to the removal of surface impurities. Silicon oxides, products of mineral lattice destruction, have also low adsorption energy (Gregg and Sing, 1967). Acid treated minerals are generally less polar than these treated with alkali, due to formation of low energetic silica from mineral lattice destruction. Alkali treated minerals are more polar due to formation of finely dispersed and highly energetic Mg or Fe oxide precipitates and/or removal of outer silica sheets from mineral lattices leaving alumina sheets, more polar than silica.

In acidified and alkalized soils the average adsorption energy usually decreases that indicates that water binding forces become lower. Therefore soil water may be more available for plants, despite its amount decrease. Decrease in amount of high and medium energy centers, and increase in fraction of low energy centers is observed. The decrease of adsorption energy under acid treatment may be addressed to new silica oxide surfaces, having large but low energetic surface. However, under alkaline treatment the silica oxides are better soluble. The adsorption energy decrease under alkaline conditions is due to the fact that during the consecutive removal of organic matter the remaining organic material has more hydrophobic character and less adsorption energy (Jozefaciuk et al., 1996). For clay rich soils an increase of average adsorption energy may occur under alkali treatment. Cleaning of iron oxide surfaces and their peptization in alkali may be responsible for both surface area and adsorption energy increase. The rise of salinity and sodicity in natural saline soils may also decrease adsorption energy due to lower hydratation energy of sodium than the other ions (Toth and Jozefaciuk 2002).

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COMPACTION EFFECTS ON SOIL PHYSICAL PROPERTIES AND ROOT AND SHOOT GROWTH

Lipiec J.

INTRODUCTION

Soil compaction is an increasingly challenging worldwide problem for agricultural production and environment (Van Ouwerkerk and Soane, 1994). Most of soil compaction results from vehicular traffic being an essential component of the soil management system. Compactive stresses and displacements are largely influenced by wheel or axle load that rise with still increasing size of agricultural implements. A significant part of soil displacement is shearing, which jointly with compaction influences soil deformation (Horn, 2003). Alterations in the aggregate and pore structure influence many properties of the soil such as strength, water, air, heat, biological activity which in turn affect root and shoot growth and functions. In this paper responses of soil physical properties and plant to soil compaction are discussed.

SOIL PHYSICAL PROPERTIES

Accurate evaluation of alterations in soil structure induced by compaction cannot be done using only bulk density and should incorporate other measurements that influence the soil quality and sustainability of the soil. The measurements include structure parameters, strength, hydraulic, air and thermal properties.

Pore structure

Image of resin-impregnated soil revealed that soil compaction reduced total pore space and contribution of large pores (e.g. Słowińska-Jurkiewicz and Domżał, 1991; Lipiec et al., 1998) including transmission pores (50 to 500 μm) and to lesser extent those smaller than 50 μm (Pagliai et al., 2000), and in sandy soils packing pores corresponding to the fabric of the elementary particles (Coulon and Bruand, 1989). The rubber-tracked compared to wheeled tractor reduced more volume of the transmission pores (Pagliai et al., 2000). As a consequence the structure of larger pores become less variable in compacted than in loose soil and the opposite is true for cluster or grain scales owing to shearing effect (Warkentin, 2000).

Soil strength

Frequently used strength parameters to characterize structure of compacted soil include penetrometer resistance, shear strength, precompression stress and aggregate strength (Lipiec and Tarkiewicz, 1986; Horn and Rostek, 2000).

Measurements of penetrometer resistance are relatively easy and thus useful for rapid evaluation of strength and structural changes related to wheel tracks and structural discontinuity (Lowery and Morrison, 2002). Strength discontinuities in soil profile often occur at the interface of aggregated seedbed and compacted soil below and of tilled layer and untilled subsoil (Gliński and Lipiec, 1990). This parameter well reflected spatial distribution of mechanical impedance under crawler rut and inter-rut areas in sloping vineyard (Fig. 1.). The effect of tractor traffic on the soil penetrometer resistance was more pronounced under the lower ruts due to greater loading associated with the tractor's tilt and thus on bulk density and higher soil water content at traffic.

New developments for simultaneous measurements of penetrometer resistance and volumetric soil water content with TDR using one probe allow to minimize soil disturbance and prevent complications due to soil heterogeneity (Vaz et al., 2001).

Precompression stress well characterizes mechanical stability and soil vulnerability to compaction and its values decrease with increasing soil moisture (Horn and Fleige, 2000; Keller et al., 2004) and coarseness of soil texture (Peng et al., 2004). At the same soil moisture precompression stress increases with increasing soil aggregation (Horn and Baumgartl, 1999). Greater tensile strength was reported for smaller than larger single aggregates (Lipiec and Tarkiewicz, 1986).

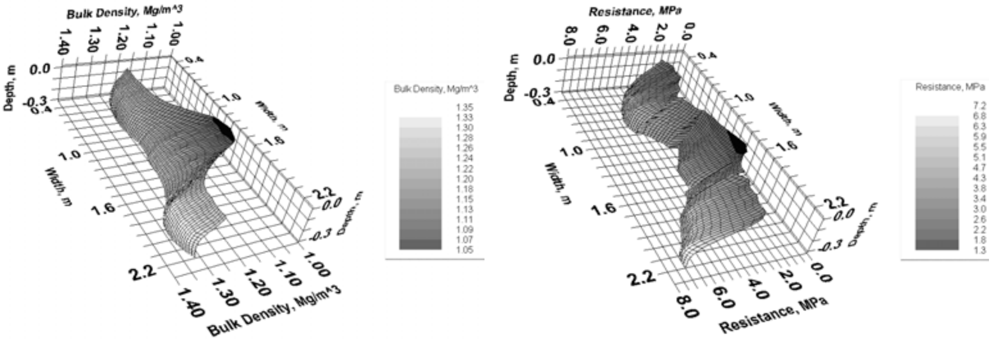

Fig. 1. *3 D maps of soil bulk density and penetration resistance in the sloping vineyard interrow (after Lipiec et al., 2003).*

Hydraulic properties

Reduced porosity and altered pore shapes and size distributions by compaction affect the soil water retention curve (SRWC) and hydraulic properties. It was shown that soil compaction leads to lower volumetric water content at high matric potentials range (from 0 to -10 kPa) and somewhat higher – at low potentials range (from - 250 to - 1550 kPa) (Walczak 1977; Ferrero and Lipiec, 2000). At the intermediate potential range this effect was small. At the potential -100 MPa volumetric water content in the compacted soils is slightly lower owing to somewhat lower reduced potential of surfaces whereas at the range of -100 and -1500 MPa compacted soil holds extra water with its films absorbed to particle surfaces (Assouline et al., 1997). Green et al. (2003) reported that under semi-arid conditions wheel tracks did not cause a significant effect on the average water retention. Thay stated that spatial and temporal variability that often overshadowed any measured differences between management treatments. Since measurements of the SWRC are time consuming and expensive regression-based pedotransfer functions (PTF) were developed to predict the SWRC from more easily measurable and more readily available parameters as particle-size distribution, organic matter and bulk density (Ahuja et al., 1998; Wösten, 2000). Most PTFs predict moisture content well near saturation and permanent wilting point whereas relatively high prediction errors were at field capacity due to principally altered morphology of pore volume (Cornelis et al., 2001). Using pedotransfer functions and the hydraulic data of European soils (12 countries) the database (HYPRES) was developed (Wösten, 2000). Neural networks were also useful to estimate soil water retention (Pachepsky et al. (1996) and Koekkoek and Booltink (1999) and the results compared well with those of regression-based PTFs when van Genuchten's equation was fitted and parameters of this equation were derived from texture and bulk density.

Effect of soil compaction on water flow is characterised by measurements of saturated hydraulic conductivity and water infiltration. Reduction of both parameters due to compaction can be from few (Young and Voorhees, 1982) to hundreds times (Arvidsson, 1997; Guerif et al., 2001) mostly due to decline of large pores. In case of dynamic loading by wheeling on wet soil total pore volume and macroporosity may rise but their conductivity is restricted by poor continuity (Weisskopf et al., 2000). Therefore volume of stained continuous macropores (hydraulically active) better reflected transmission functions of variously compacted (Lipiec and Hakansson, 2000) or tilled soil (Lipiec et al., 2003). Fig. 2 illustrates effect of tillage on stained porosity and infiltration rate. Reduced infiltration will increase runoff and soil erosion (Young and Voorhees, 1982; Fleige and Horn, 2000) but in very permeable sandy soils may get better water storage and diminish nutrient leaching (Agraval, 1991).

Using regression models (e.g. Guerif et al., 2001) saturated hydraulic conductivity of the compacted soil can be predicted by means of water retention curves, inherent properties and bulk density and incorporating the macro-pore flow may get better their efficiency in predicting water and chemical movement (Walczak et al., 1996; Borah and Kalita, 1999).

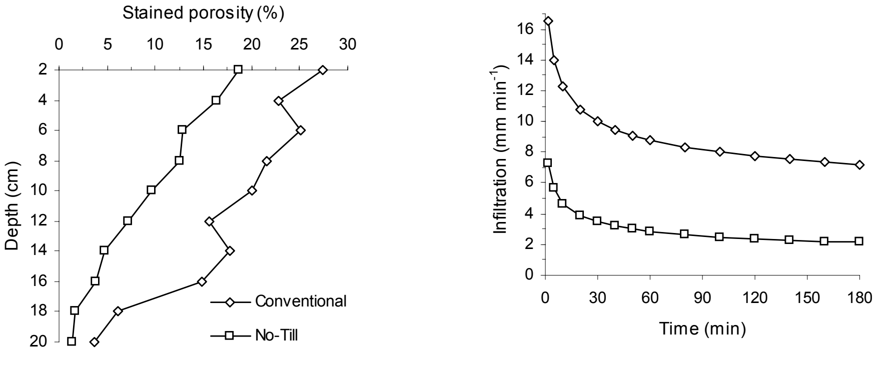

Fig. 2. *Percent of stained areal porosity relative to total area and infiltration rate under conventionally tilled and no-tilled soil (after Lipiec et al., 2003).*

The effect of soil compaction on unsaturated flow was not intensively studied. Some studies show (Walczak et al., 1993; Horton et al., 1994; Richard et al., 2001) that hydraulic conductivity as a function of soil water content or potential decreases with compaction. This can be enhanced by increased disconnection of pore spaces tortuosity of pores due to slipping traction devices (Horn, 2003) and the formation of relict structural pores (accessible only through the necks of the lacunar pores) during compaction Sillon et al. (2003). But at some compaction levels and low water potentials it can be higher compacted than non-compacted soil due to increasing the contact surface between soil aggregates if they are not damaged by compaction (Sillon et al., 2003). Unsaturated hydraulic conductivity together with root length density is a major factor affecting hydraulic resistance in unsaturated compacted soil (Lipiec and Tarkiewicz, 1988).

Important factors affecting soil water relations are unsaturated hydraulic conductivity and sorptivity of soil aggregates. Horn et al., 1994 reported that in more compacted single aggregates compared with bulk soil unsaturated hydraulic conductivity at low negative pore water pressure range (from 0 to –800 hPa) is decreased. Also the aggregate sorptivity was lower for aggregates from compacted than uncompacted soil (Lipiec et al., 2002a).

Aeration

Air-filled porosity, oxygen diffusion rate (ODR), redox potential and air permeability are frequently used to characterise response of soil aeration to compaction (Stępniewski et al., 1994). The value of air-filled porosity <10% (v/v) is often considered as critical for plant growth, but at a comparable air-filled porosity the equivalent pore diameter can be smaller in compacted than in uncompacted soil (Simojoki et al., 1991) that consequently results in different air permeability (as being related to the square of the diameter of the air-filled pores) (Stępniewski et al., 1994). For this reason transmission characteristics better reflect aeration status of compacted soil. At the same bulk density the air permeability was larger for coarse (4-8 mm peds) than fine structure (< 2 mm peds) (Lipiec, 1992). To characterise continuity and tortuosity of the pores in compacted soil relative gas diffusion coefficient (D/D_o) is used. In general, this coefficient diminishes with soil compaction (Stępniewski et al., 1994). Increasing effect of soil compaction and moisture on decreasing the oxygen diffusion rate (ODR) influencing oxygen supply to the roots is well documented in the literature (Stępniewski et al., 1994; Dexter and Czyż, 2000; Whalley et al., 2000).

Thermal properties

In general soil compaction leads to increased thermal conductivity, heat capacity and thermal diffusivity and this effect is ascribed to better contact between soil particles (e.g. Usowicz et al., 1996). In compacted soil the thermal properties were less variable than in the loose soil (Usowicz et al., 1996). Changes in the thermal properties affect soil temperature and its variability. Soil compaction resulted in lower rate of warming and cooling, smaller fluctuations of the daily temperature in surface soil and higher temperature in deeper soil (Lipiec et al., 1991; Abu-Hamdeh, 2000).

CROP RESPONSE

Roots

A characteristic response of root system to increased compaction level is a decreased root size, retarded root penetration and smaller rooting depth (Gliński and Lipiec, 1990; Whalley et al., 2000; Lipiec et al., 2003). This results in greater distances between the neighbouring roots and affects water and nutrient uptake. Table 1 shows that half distance between the neighbouring spring barley roots on horizontal planes till depth of 30 cm in loamy sand was less than 3.7 mm for loose soil and increased to 64 mm in the most compacted soil. However, absorption of water and nutrients takes place commonly in the soil adjacent to the root surface from 2 to 8 mm depending on soil and nutrient types. This implies that larger distances between the roots may increase leaching and ground water contamination. However, lower root size and uneven spatial distribution in compacted soil may favor groundwater contamination through leaching due to increased distances between the nearest roots.

Table 1. Half distances (mm) between the neighbouring roots at the heading growth of spring barley grown on loamy sand (after Lipiec and Hatano, 2003).

Depth, cm	Tractor passes			
	0	1	3	8
0-10	1.3	1.4	1.1	0.9
10-20	2.5	3.0	4.5	9.1
20-30	3.7	4.9	31.8	64
30-40	16	21.2	-	-
40-50	64	-	-	-
50-60	64	-	-	-

Root growth conditions in compacted soil can be improved by macropores formed by soil fauna or aggregate structure if not destroyed by compaction. The macropores allow roots by pass the zones of high mechanical impedance (Gliński and Lipiec, 1990). Preferential growth of roots into macropores is more pronounced in deeper and stronger layers (Goss, 1991) where the macropores can be the only possible pathways for root growth. The preferential root growth into macro-pores results in greater critical limits of soil strength measured by large penetrometer cones (Ehlers et al., 1983) which are relatively insensitive to pores having diameter greater than the roots and to heterogeneity in the soil at the scale of root tip (Whalley et al., 2000). The relationship between the distribution of macropores and roots in loose and moderately compacted soil can be described numerically using fractal analysis (Hatano and Sakuma, 1990; Lipiec et al., 1998).

Recent developments based on computer-assisted tomography (CAT) and magnetic resonance imaging (MRI) provide potential to non-destructive measurements of spatial distribution of bulk density and the dynamics of plant root systems and water uptake (Asseng et al., 2000).

Water uptake and stomatal diffusive resistance

Experiments performed in growth chamber allowed controlling soil physical conditions and precise measurements of water uptake and eliminating the effects of different weather conditions. Under conditions of sufficient water supply, total water use decreased with increasing soil compaction level while root water uptake rate was highest in moderately compacted soil owing to higher unsaturated hydraulic conductivity and greater water movement towards the roots and better root-soil contact area. However, increased water uptake rate was insufficient to entirely compensate the reduction in total root length and resulted in reduced total water uptake.

Water uptake depends on spatial distribution of soil compaction. Split root experiment showed that in treatment with root system of wheat seedlings split to loose and strongly compacted (vertically divided by plastic wall) reduced water uptake in compacted compartment was partly compensated for by greater water use in loose compartment (Fig. 3.).

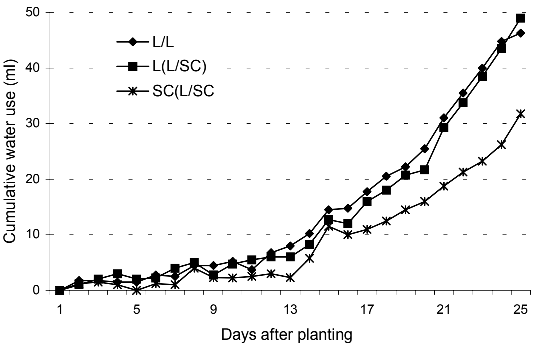

Fig. 3. *Cumulative water use from loose and strongly compacted soil compartments (after Lipiec et al. 2002).*

In treatment with loose and moderately compacted soil compartments the compensatory effect was less pronounced. Root water use efficiency was higher from compartments with moderately compacted than loose and strongly compacted soil. This indicates plasticity of root water absorption in response to localized soil compaction. The alterations in the root water use efficiency are of great importance in modelling plant water use (Novak, 1995; Walczak. et al., 1997).

Stomatal resistance responses to soil compaction relate to soil water status. In growth chamber with transient wetting the stomatal resistance and its variation over the growth period were markely higher in severely compacted soil than in low or medium compacted soil. Substantial increase of stomatal resistance in most compacted soil occurred when soil matric potential increased from approximately 400hPa (increasing soil moisture) (Lipiec et al., 1996). The highest stomatal diffusive resistance in most compacted soil has also been reported in dry period (Lipiec, Gliński, 1997). Some authors (Tardieu, 1994) stated that abscissic acis increase in plants grown in compacted soil is a result of root dehydration due to a limited water supply to the roots. Ali et al. (1999) reported that the increased leaf stomatal resistance occurred even before a measurable change in leaf water potential.

CONCLUSIONS

Alterations in the aggregate and pore structure affect the most important behavioural (strength, water, aeration and thermal) properties influencing root and shoot growth and functions, and the soil quality. Recent developments for combined measurements of penetrometer resistance and water conent will allow minimising disturbance of soil and preventing difficulties due to spatial soil heterogeneity. Decline of pore size, stained porosity (active pores) and continuity in compacted soil resulted in reduced transmission functions of soil as characterised by infiltration and air permeability. A characteristic response of root system to increasing soil compaction level is a decreased root size, retarded root penetration and shallower rooting depth. Root growth distribution in response to soil compaction is related to distribution pattern of pores. Total water and nutrient uptake in most compacted soil is considerably reduced. Under moderate compactaion greater uptake rate (per unit of root) alleviates a reduction in total water and nutrient uptake. Stomatal diffusive resistance was increased in most compacted soil under wet and dry soil conditions. Several mechanisms are suggested for stomatal response to soil compaction.

Computer-assisted tomography (CAT) and magnetic resonance imaging (MRI) provide potential to non destructive measurements of spatial distribution of bulk density and the dynamics of plant root systems and water uptake.

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MONITORING OF POROUS MEDIA PROCESSES WITH THE APPLICATION OF PHYSICAL AND CHEMICAL SENSORS

Skierucha W., Walczak R.T., Malicki M.A., Wilczek A.

INTRODUCTION

Monitoring is a systematic and purposeful observation and recording of an object, process or program activity. The registered data are necessary for decision making or for research purposes. Agrophysical objects are particularly difficult for monitoring because of their spatial and temporal diversity, different dimensional and temporal scale of appearance. The process of monitoring can be successful only when it is considered together with modelling and simulation to give predictive measures of the observed processes and objects.

The development of technology in the recent years increased the number of monitoring tools for the application in agrophysics. There are smart sensors integrating different technologies in one structure and sensor networks communicating together and with the management units in global way incorporating wireless communication and Internet. Concerning agrophysical porous materials, the most promising and needed are moisture sensors based on TDR technique. They can be easily enhanced by the simultaneous measurement of electrical conductivity and temperature from the same sample material. Also promising is the application of ion selective electrodes, that are presently used for the measurement of selected ion concentration in liquids, in porous media.

MONITORING AS AN ELEMENT OF GLOBAL EVALUATION OF AGROPHYSICAL PROCESSES AND OBJECTS

Collection of information on the objects and processes, including agrophysical porous objects and the related processes, is a complementary activity consisting of monitoring and modelling (Montanarella, 2002).

Fig. 1. *Monitoring and modelling as complementary activities of agrophysical processes and objects analysis*

The both elements treated together show the complete view of the object or process for the decision making, e.g. defining the direction of further research or drawing conclusions (McKenzie et al., 2002). Monitoring is used for validation purposes and as a source of input data for the models. Modelling determines whether the trends in specific attributes can be successfully detected with monitoring and identifies key components of system behaviour that can be measured in a monitoring program.

Modelling refers to the process or object in artificial and limited conditions, where research tools can be successfully applied, but still close enough to the real process or object under consideration. Modelling is applied when the analysed object is too small or too big, the process is too fast or too slow or it is impossible to conduct research because of technical or economical reasons. The biggest advantage of model research is that they can be accomplished as material, statistical and the mostly used mathematical-physical models (Walczak, 1984). The examples of mathematical-physical models applied to porous materials are: the movement of water in capillary-porous body with the driving force, described by Richard's equation; simultaneous transport of water, heat and salt in the soil profile; description of water movement in the soil as a heterogenic medium or dielectric mixing models describing a 4-phase medium.

QUANTITATIVE EVALUATION OF AGROPHYSICAL PROCESSES

The example of quantitative evaluation of agrophysical processes will be discussed on the example of the soil solid phase. Similar discussion can be done for other porous media and related processes in agrophysics.

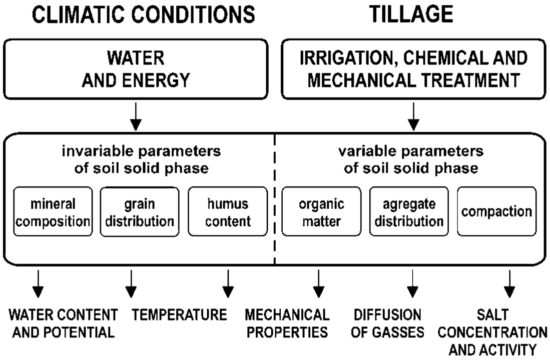


Fig. 2. *Factors influencing invariable and variable parameters of soil solid phase and physical quantitative indicators of soil solid phase*

Soil physical parameters change continuously for climatic reasons and human activity as well. Mineral composition, grain distribution and humus content are practically not affected by spatial and temporal change. Human activity: organic and chemical fertilization, as well as mechanical influence modify the variable parameters of the soil solid phase including: organic matter content, aggregate distribution and soil compaction. The basic quantities describing the soil physical status in the quantitative way are: soil water content and potential, soil temperature, mechanical properties: texture and porosity, gas diffusion, salt concentration and ions activity. The field sensors used to determine the physical indicators of soil solid phase are:

- water content and potential: TDR moisture probes, capacitive probes, neutron scattering probes, gypsum blocks, tensiometers, thermocouple psychrometers;

- temperature: semiconductor, thermocouple and mercury thermometers, heat flux sensors (soil thermal conductivity measurement);
- mechanical properties: penetrometers, density and texture measurement require laboratory equipment;
- diffusion of gases: redox potential meter, ODR – platinum electrodes;

salt concentration and ions activity: soil electrical conductivity sensors, ion selective electrodes.

The most important soil physical property for the monitoring, directly influencing the others is soil water content. Also the concentration of selected ions in the soil giving the information about its fertility and/or intoxication seems to be of major concern as a chemical sensor.

REFLECTOMETRIC POROUS MEDIA MOISTURE SENSOR

Traditional and the most widely used method for porous media moisture determination is the direct standardized gravimetric method (ISO 16586, 2003). It has many disadvantages: needs laboratory equipment, is laborious and time-consuming (24 hours for soil samples drying at 105°C) and cannot be automatized. These are reasons for researchers to look for an indirect method for water content determination. The parameter that is the most selective for water is its dielectric constant. For porous material consisting of three phases (or four if bound water phase is included) the liquid phase has the dielectric constant significantly bigger than the others (dielectric constant of water in room temperature is 81, for air is 1, for solid phase is less than 5). This phenomenon is caused by the appearance of a permanent dipole in a water molecule. From the measurement of the bulk dielectric constant, ε_b, of a porous material one can determine the amount of water in it by the use of dielectric mixing models (Dirksen & Dasberg, 1993) of the empirical calibration (Topp et al., 1980; Malicki & Skierucha, 1989, Malicki et al., 1996). The time domain refletometry (TDR) equipment for porous materials moisture determination has been developed in the Institute of Agrophysics, Lublin,, Poland since mid eighties (Malicki & Skierucha, 1989; Malicki et al., 1996; Malicki & Walczak, 1999; Skierucha & Malicki, 2000; Skierucha, 2002). Now it is widely used by numerous researchers all around the world because of its advantages: simplicity of operation, accuracy and rapid response, usually does not need calibration, is non-destructive, portable systems are available, ability to automatize and multiplex probes. There are efforts to standardize it as a soil moisture measurement method.

The empirical calibration for typical mineral and organic soils and laboratory prepared mixtures of sand and peat (to achieve soil samples with evenly spread bulk densities) of TDR method to measure soil moisture is presented in Fig. 3.

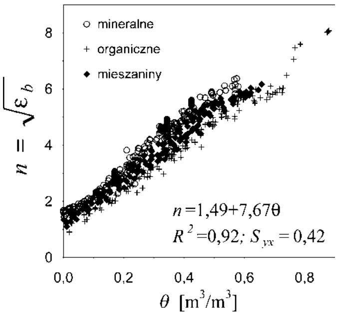
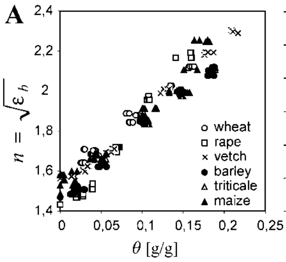


Fig. 3. *Empirical calibration of TDR soil moisture meter, θ is gravimetric soil moisture, R is correlation coefficient, S_{yx} is a standard deviation from the trend line, $n = \sqrt{\varepsilon_b}$ is the soil refractive index*

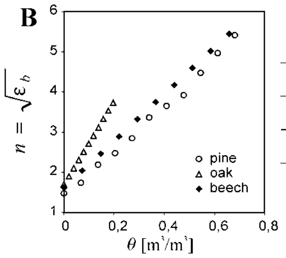
The TDR moisture measurement method applied for soil as a porous material should be effective in measurement of other biological materials of less than soil differentiated structure, i.e. plant or building materials. In Fig. 4 there is a relation between the refractive index, n, and moisture, θ, for some varieties of cereal grain and wood (Malicki, 1999).

A



	R^2	S_{yx}
wheat n=1,56+3,36θ	0,99	0,02
rape n=1,37+5,11θ	0,99	0,04
vetch n=1,52+3,67θ	0,99	0,03
barley n=1,44+3,68θ	0,99	0,02
triticale N=1,46+3,55θ	0,99	0,02
maize n=1,52+3,61θ	0,98	0,05

B



	R^2	S_{yx}
pine n=1,36+5,75θ	0,99	0,09
oak n=1,70+10,3θ	0,98	0,08
beech n=1,62+5,80θ	0,99	0,06

Fig. 4. *Empirical calibration of TDR moisture measurement for cereal grain* (**A**)*, and wood* (**B**) *and corresponding regression parameters*

ION SELECTIVE ELECTRODES (ISE)

The efforts to use ISEs for soil/ground tests are limited mainly to the tests of soil solution extract or a mixture (in different ratios) of distilled water or other solvent with soil (Birrel & Hummel, 2001; Wang & Scott, 2001). Measurements performed on such a sample although quite precise, are not practical in the application with automatic acquisition systems or mobile devices connected with GPS systems used in precision agriculture. However there are experiments (Snakin & Prisyazhnaya, 2001) showing the possibility to monitor the electrolyte concentration with ISEs in field condition.

The most important part of ISE is the polymeric membrane containing compounds (known as ionophores) that are able to form complexes with ions in a fast and reversible mode. The presence of ionophores and other active additives within the membrane phase determines the membrane selectivity and its working characteristics such as linear range of the calibration curve, response time, life-time, etc.

This is the reason why the optimisation of the composition of the ion-selective membrane is such an important matter.

The potentiometric method with the application of ISEs seems to be ideal due to the fact that the concentration ranges of ions (e.g., K^+, Ca^{++}, NO_3^- or pH) that exist in the soil fit nicely to the linear response ranges of respective ISEs. However, soils are very difficult analytical objects and the composition of polymeric membranes and the construction of indicator as well as reference electrodes must be chosen very carefully to make it compatible with a measuring system.

The scientists from the Institute of Agrophysics PAS and Technical University, Warsaw, specializing in ISE development, started a project for the monitoring system of selected ion concentration in field condition.

SUMMARY

Important issues of porous media monitoring, still left for discussion, are: selection criteria of porous media indicators for monitoring, new technical solutions of smart sensors incorporating MEMS (Micro-Electro-Mechanical Systems) technology, global networks of smart sensors, existing and planned monitoring systems in Europe, especially concerning soil, smart transducer interface presented by IEEE 1451 standard, wireless communication between sensors, and many others. Technical means coming from military and telecommunication industries, which are the driving forces of the sensors development, can be utilized in environmental research, also in monitoring of porous media processes and objects to contribute in the sustainable agriculture.

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CONCEPTS AND MORPHOLOGY OF HYDROMORPHISM IN SOILS

Stahr K.

The concept of gleysation related with the influence of groundwater is as old as modern soil science. However, soon it was evident, that a simple uniform concept will not be able to explain all morphological features that appear with hydromorphism or reductomorphism. Therefore Kubiena in his visionary approach for a natural soil system in Central Europe used the water regime for the subdivision of soils at the highest level. He separated submerged soils under the influence of full time or part time flooding from the semiterrestric or ground water influenced soils and the most important division of terrestrial soils. Within the terrestrial soils, he included soils with stagnant meteoric water. The later decision caused many problems and was criticized by quite a few scientists. However, the modern approach for example by WRB combining gleyic and stagnic properties, does cause even more confusion and hinders the separation of two major different groups of pedogenic processes.

Using iron and manganese oxides as colouring and diagnostic features, it was elaborated, that with ground water influence these oxides are generally precipitated on the walls of macropores that is on the external site of aggregates. On the other hand, stagnant water pushes the same oxides into the internal matrix of the aggregates, resulting in mottling and the formation of concretions. This concept is world-wide applicable, however it has its limits. One limit, which has also significant ecological consequences, is the wet or reduction bleaching, which may occur with ground water in the subsoil or with stagnant water in the topsoil and results in the export of the iron and manganese compounds from the whole horizon or even the soils. Other limitations do occur in the morphology, if very sandy or heavy clay texture is present or under saline, carbonatic or sulfidic conditions. For all these conditions, the concept has to be modified, if not totally reassessed.

There are at least two more cases, which have to be taken into account, when hydromorphism/ reductomorphism should be covered by soil science in full. The one case existing mainly in lowland situation is the overlapping of ground water influence from below and stagnant water from above. In those cases often an impermeable soil layer or soil horizon separates those regimes, but at least is semi-permeable allowing to combine the features. Another very complicated situation is envisaged, if stagnant or ground water influence is combined in sloping areas with a dominant lateral water flow and consequently the expression of morphological features along the slope more than within the profile.

These approaches will be discussed systematically in the forthcoming paper.

HYDROPHYSICAL CHARACTERISTICS OF POROUS BODY AS INPUT DATA FOR WATER TRANSPORT MODELS

Walczak R. T., Sławiński C., Witkowska-Walczak B.

ABSTRACT

The water retention, saturated and unsaturated hydraulic conductivity coefficients are the basic hydrophysical characteristics of the soil. The correct determination of those characteristics is indispensable to obtain the required accuracy of the used models of water transport in soil profile. Therefore, the methods of measurement and estimation of these characteristics are extensively developed.

DETERMINATION OF STATIC WATER RETENTION CURVE

The dependence between soil water potential and soil water content, called the soil water retention curve (Fig.1), is a basic hydrophysical soil property. The static soil water retention curve is determined in Richards chambers or on the sandy-gypsum blocks. It is determined for the state of thermodynamic equilibrium which is obtained after the specific time.

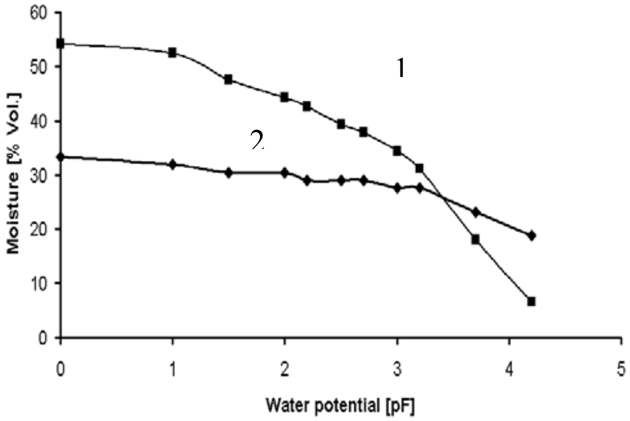


Fig. 1. *An exemplary of static water retention curve for loamy (1) and sandy (2) soils.*

DETERMINATION OF HYDRAULIC CONDUCTIVITY COEFFICIENT AND DYNAMIC RETENTION CURVE

Unsaturated hydraulic conductivity is one of the most important physical soil characteristics. Applying TDR techniques [2, 3, 6] and the instantaneous profile method (IPM) the measurement of hydraulic conductivity coefficient $k(\psi)$ and also dynamic retention curve $\theta(\psi)$ has become much faster and effective. It was demonstrated, that this method gives accurate results for various initial and boundary conditions applied to the soil sample. The instantaneous profile method (IPM) rest on simultaneously measurements of water content and water potential dynamic in the process of drying or wetting the soil column (Fig. 2, 3).

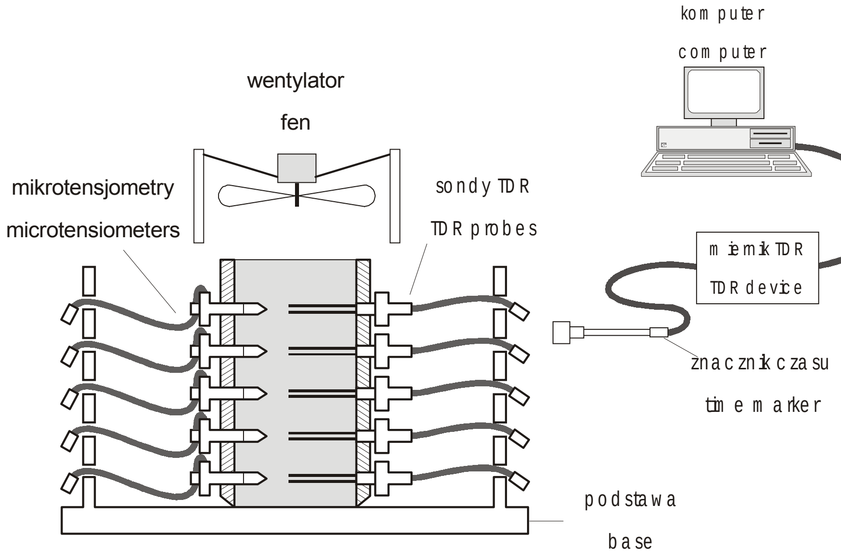


Fig. 2. *TDR set-up for water content and water potential dynamic measurements in evaporation process*

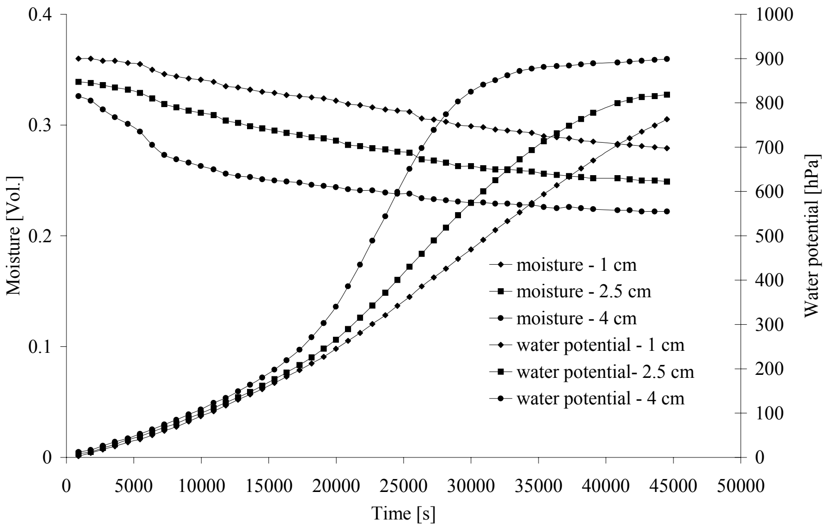


Fig. 3. *Water content and water potential dynamic in soil column*

Assuming that the process of water transport takes place under isothermal conditions and is one-dimensional, the Darcy's low is valid for the proposed experimental conditions. The water flow can be described with the use of the following equation:

$$q(z,t) = -k(\psi)\left(\frac{\partial \psi(z,t)}{\partial z} - 1\right) \tag{1}$$

Alternatively the flux can be calculated from the equation:

$$q(z,t) = -\int_{z=z_0}^{z} \frac{\partial \theta(z,t)}{\partial t} dz \tag{2}$$

Comparing these equations it is possible to calculate the hydraulic conductivity k(ψ) from the equation:

$$k(\psi) = \frac{\int_{z=z_0}^{z} \frac{\partial \theta(z,t)}{\partial t} dz}{\left(\frac{\partial \psi(z,t)}{\partial z} - 1\right)} \tag{3}$$

Using this method it is possible to determine relationship between hydraulic conductivity coefficient and water potential (see fig. 4) and so called dynamic retention curve (see fig. 5).

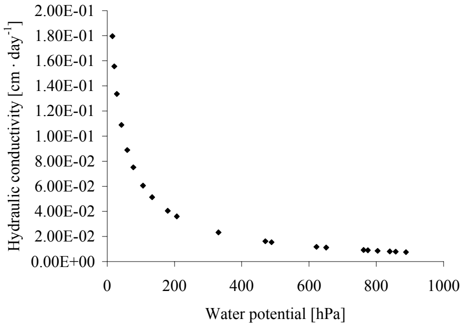


Fig.4. *Hydraulic conductivity coefficient as a function of water potential*

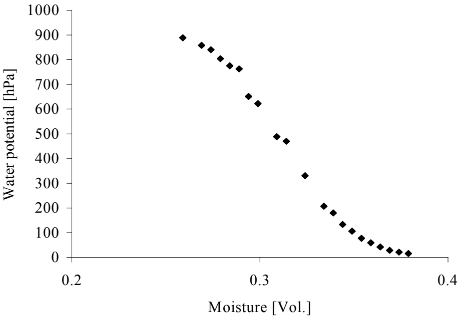


Fig. 5. *Dynamic retention curve*

ESTIMATION OF THE HYDROPHYSICAL CHARACTERISTICS ON THE BASE OF PHYSICAL PARAMETERS OF SOIL STRUCTURE

In the Institute of Agrophysics, Polish Academy of Sciences, a database of hydrophysical properties of Polish arable soils was created [11], containing, among others, the information about physical properties of the soils, the water retention curves and the values of water conductivity coefficients under different values of soil water potential. Therefore, a possibility was created to study the impact of chosen soil physical parameters on the value of the water content and water conductivity coefficient under chosen soil water potential values.

The measurements of the water retention curve and the water conductivity coefficient in saturated and unsaturated zones are time and labor consuming and require a specific instrumentation. Therefore, a general tendency exists to evaluate those characteristics with acceptable accuracy with the use of elaborated physical, mathematical and statistical models and algorithms. The investigations, performed in this direction have resulted in creation of numerous models and algorithms, which enable to evaluate the water retention curve and the values of the coefficient of water conductivity. A large group of these models are pedotransfer functions. Therefore in the Institute of Agrophysics PAS in Lublin, the model of retention curve was elaborated, based on the following equations of multiple regression [10, 12]:

$$\theta_p = b_0 + b_1 Y_1 + b_2 Y_2 + b_3 Y_3 \qquad (4)$$

for water potential values in the range from pF 0 to pF 2.7 (0.98-490 hPa) and

$$\theta_p = b_0 + b_1 Y_1 \qquad (5)$$

for the water potential values higher then pF 2.7 (490 hPa), where: θp is the predicted water content [g g^{-1}], Y_1 - the specific surface area [$m^2 g^{-1}$], Y_2 - the mean weight diameter of particles [mm], Y_3 - the bulk density [g cm^{-3}] and the parameters b_0, b_1, b_2, b_3 are the regression coefficients. The obtained correlation coefficients for this model were in the range $0.94 < R < 0.98$.

The impact of chosen soil physical parameters on the value of the water conductivity coefficient under chosen soil water potential values was investigated [5]. The following values of the soil water potential were taken for the statistical analysis and the respective pF values: pF 0 (0.98 hPa); pF 1 (9.8 hPa); pF 1.5 (31 hPa); pF 2 (98 hPa); pF 2.2 (155 hPa); pF 2.5 (310 hPa); pF 2.7 (490 hPa); pF 3 (980 hPa).

The investigations were performed for 290 soil profiles selected from the Bank of Samples of the Mineral Arable Polish Soils.The performed analysis of the segmental regression for the logarithms of the coefficient of water conductivity showed that for the regression equations with the following set of parameters: the percentage content of clay – F_{clay}, the percentage content of sand – F_{sand}, the specific surface area- S_{BET}, the percentage content of organic carbon - C_{org}, the content of gravitational water – W_G and the water content under the potential corresponding with the field water capacity - FWC, the values of correlation coefficient 0.81 ≤ R ≤ 0.85 were obtained. The relatively high correlation coefficients caused that this model was used for particular soil textures. The correlation coefficient values within the range 0.86 ≤ R ≤ 0.96 were obtained for the following set of parameters: the percentage content of clay- F_{clay}, the percentage content of sand – F_{sand}, the specific surface - S_{BET}, the percentage content of organic carbon - C_{org}, the content of gravitational water – W_G and the water content under the potential corresponding with the field water capacity – FWC. The general form of this model's equation is:

$$\begin{aligned} LogK \ &= A(a_0 + a_1 F_{clay} + a_2 F_{sand} + a_3 S_{BET} \\ &+ a_4 C_{org} + a_5 W_G + a_6 FWC) + \\ &B(b_0 + b_1 F_{clay} + b_2 F_{sand} + b_3 S_{BET} \\ &+ b_4 C_{org} + b_5 W_G + b_6 FWC \end{aligned} \tag{6}$$

where: A=1and B=0 for LogK≤ PP as well as A=0 and B=1 for LogK > PP, PP is the point of break.

The soil hydrophysical characteristics obtained by measurements or/and modeling can be use as input data for water transport models.

In the frame of EURO-ACCESS (AgroClimatic Change and European Soil Suitability) project [1, 4, 6, 7, 9] (Fig. 6.) the model of crop growth and yield prediction was elaborated. Hydrological part of this model is based on one-dimensional Richard's equation. For the purpose of heterogeneity of the soil profile, in the Institute of Agrophysics PAS, the model of bypass flow was elaborated and included into the hydrological part of EURO-ACCESS model.

Main assumptions of bypass flow submodel:

Heterogeneous soil profile is divided into homogeneous compartments.

Vertical water flow in soil matrix is described by Richard's equation (one-dimensional flow model).

Part of water is flowing directly in macropores (proportionally to relative cracks area).

Part of water which can not vertically infiltrate in soil profile (runoff) is flowing into the macropores.

Water fills crack (Fig. 7.), giving the hydrostatic pressure distribution at the crack wall which is used as the boundary condition for the water infiltration into the soil.

Initial moisture for each time step of horizontal infiltration is assumed to be constant in space.

The Green-Ampt approach is use for the horizontal infiltration description.

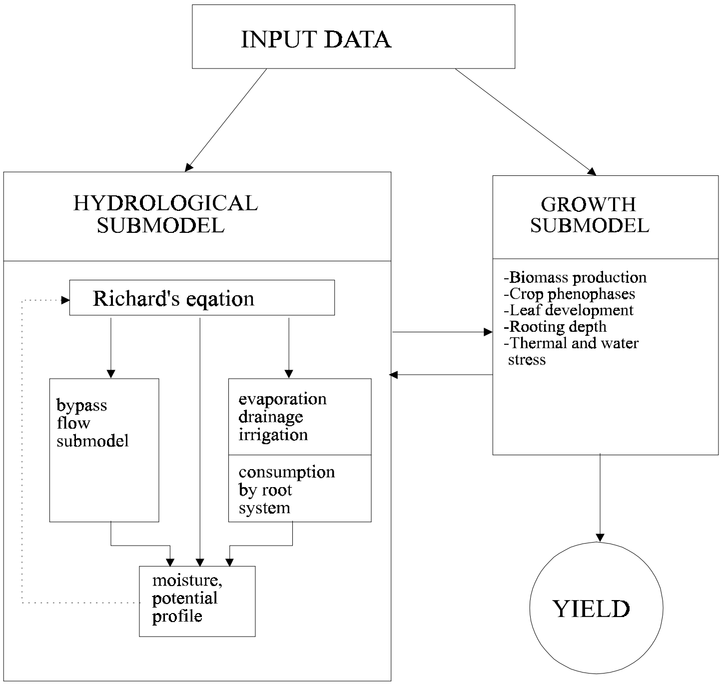


Fig. 6. *Scheme of EURO-ACCESS-II model [4]*

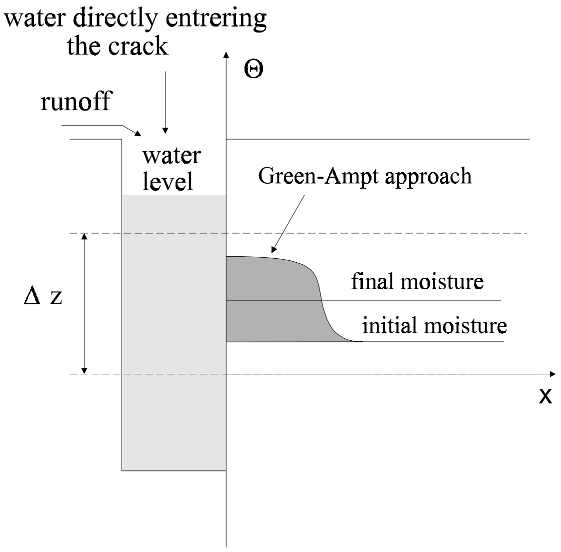
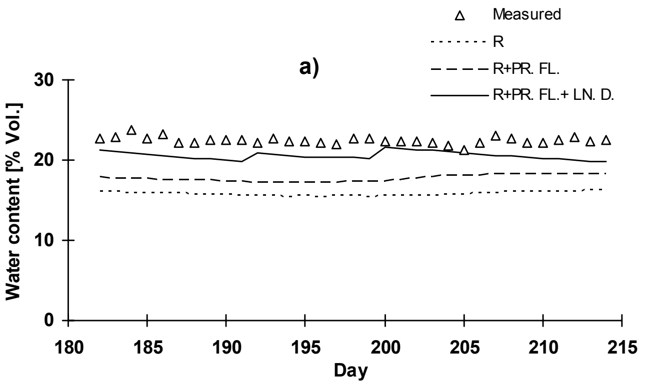


Fig. 7. *Scheme of macropore [4]*



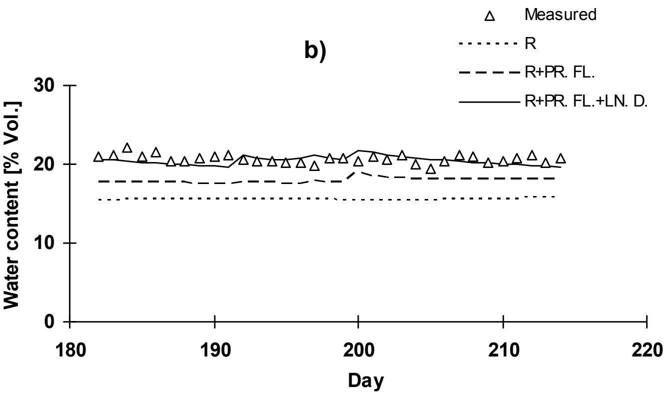


Fig. 8. *Results of experimental verification (Grabów-Poland) of importance of precipitation intensity in dynamic modelling of exampled profiles compartments (a - 85 cm, b - 135 cm) for three versions:*
R. - soil profile is composed of homogeneous layers; rainfall intensity is approximated as daily average value;
R.+PR. FL. - soil profile is composed of homogeneous layers with vertical macropores; intensity is approximated as daily average value;
R.+PR. FL.+LN. D. - soil profile is composed of homogeneous layers with vertical macropores; rainfall intensity is approximated by distribution estimated from pluviographic data collected for a given place and period of year.

The experimental validation of elaborated model was done using data gathered at Grabów site. The research area Grabów is located in the southern part of the Mazovian Plain, constituting a part of the greater physiographic subprovince called Middle Polish Lowlands. The soil is classified as Stagnogleic Luvisols. The profile is at a site characterized by intensive farming and belongs to a state-run farm - Agricultural Experimental Station of the Institute of Soil Sciences and Plant Cultivation.

The experimental field is located about 100 meters far from the agrometeorological station, where the following climatic data are collected: precipitation, max/min temperature, wind velocity and direction, total and net radiation, and cloudiness. The collected meteorological data were used for modelling. The water content dynamics in the soil profile was measured using TDR equipment [2, 3] everyday on 2 PM. There was measurements for winter wheat.

The relative crack cover was fit to the data in order to minimize the difference to measured water content. The best fit gives the value σ = 1.0% for the relative crack area. We checked the values between 0.0% and 20.0% which cover the whole range of variability of this parameter.

The experimental verification showed (Fig. 8) that for a good description of soil water profile in case of the existence of vertical macropores (even if they take 1% of the soil surface only) it is necessary to use simultaneously:

-hydrological submodels with preferential flow procedures

-estimation of rainfall intensity using a procedure giving more precise distribution for its description than daily average value, e.g. log-normal distribution, characteristic for a given place and period of the year.

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AUTHORS

Baranowski Piotr	Institute of Agrophysics PAS, Lublin, Poland Piotr.Baranowski@demeter.ipan.lublin.pl
Brzezińska Małgorzata	Institute of Agrophysics PAS, Lublin, Poland mbrzezin@demeter.ipan.lublin.pl
Charytoniuk Piotr	Catholic University of Lublin, Poland stepniews@demeter.ipan.lublin.pl
Fornal Emilia	Catholic University of Lublin, Poland Emilia.2.Fornal@kul.lublin.pl
Gliński Jan	Institute of Agrophysics PAS, Lublin, Poland Jan.Gliński @demeter.ipan.lublin.pl
Gliński Piotr	University of Technology, Lublin, Poland PIOTRG@akropolis.pol.lublin.pl
Hatano Ryusuke	Soil Science Laboratory, Graduate School of Agriculture, Hokkaido University, Sapporo, Japan hatano@chem.agr.hokudai.ac.jp
Horn Rainer	Institute for Plant Nutrition and Soil Science, Kiel, Germany rhorn.@soils.uni-kiel.de
Jaakkola Antti	Department of Applied Chemistry and Microbiology, University of Helsinki, Finland antti.jaakkola@helsinki.fi
Józefaciuk Grzegorz	Institute of Agrophysics PAS, Lublin, Poland jozefaci@demeter.ipan.lublin.pl
Kotowska Urszula	Institute of Agrophysics PAS, Lublin, Poland ukot@ demeter.ipan.lublin.pl
Kosiorowska Izabela	Catholic University of Lublin, Poland IKosiorowska@kul.lublin.pl
Lamorski Krzysztof	Institute of Agrophysics PAS, Lublin, Poland Krzysztof.Lamorski@demeter.ipan.lublin.pl
Lipiec Jerzy	Institute of Agrophysics PAS, Lublin, Poland Jerzy.Lipiec@demeter.ipan.lublin.pl
Malicki Marek	Institute of Agrophysics PAS, Lublin, Poland Marek.Malicki@demeter.ipan.lublin.pl
Mazurek Wojciech	Institute of Agrophysics PAS, Lublin, Poland Wojciech.Mazurek.@demeter.ipan.lublin.pl

Nannipieri Paolo	Dipartimento della Scienza del Suolo e Nutrizione della Pinta, Università degli Studi di Firenze, Italy paolo.nannipieri@unifi.it
Ostrowska Aneta	Institute of Agrophysics PAS, Lublin, Poland Aneta.Ostrowska@ demeter.ipan.lublin.pl
Ostrowski Janusz	Institute for Land Reclamation and Grassland Farming, Falenty, Poland e.lipinska@imuz.edu.pl
Skierucha Wojciech	Institute of Agrophysics PAS, Lublin, Poland skieruch@demeter.ipan.lublin.pl
Sławiński Cezary	Institute of Agrophysics PAS, Lublin, Poland cslawin@demeter.ipan.lublin.pl
Stahr Karl	Department of Soil Science of the Hohenheim University, Stuttgart, Germany kstahr@uni-hohenheim.de
Stefaniak Elżbieta	Catholic University of Lublin, Poland Elżbieta.Stefaniak@kul.lublin.pl
Stępniewska Zofia	Catholic University of Lublin, Poland stepniews@demeter.ipan.lublin.pl
Stępniewski Witold	University of Technology, Lublin, Poland stepw@fenix.pol.lublin.pl
Szmagara Agnieszka	Catholic University of Lublin, Poland Szmagara.Agnieszka@kul.lublin.pl
Walczak Ryszard T.	Institute of Agrophysics PAS, Lublin, Poland rwalczak@demeter.ipan.lublin.pl
Wilczek Andrzej	Institute of Agrophysics PAS, Lublin, Poland awilczek@demeter.ipan.lublin.pl
Witkowska-Walczak Barbara	Institute of Agrophysics PAS, Lublin, Poland bwitwal@demeter.ipan.lublin.pl
Włodarczyk Teresa	Institute of Agrophysics PAS, Lublin, Poland teresa@ demeter.ipan.lublin.pl