BASIC PROBLEMS OF AGROPHYSICS

EDITED BY
DOROTA MATYKA-SARZYŃSKA and RYSZARD T. WALCZAK

Centre of Excellence for
Applied Physics in Sustainable
Agriculture AGROPHYSICS

Institute of Agrophysics Polish
Academy of Sciences

EU 5th Framework Program
QLAM-2001-00428

BASIC PROBLEMS OF AGROPHYSICS

MULTI AUTHORS WORK

EDITORS:

Dorota Matyka-Sarzyńska
Ryszard T. Walczak

SCIENTIFIC COMMITEE

Józef Horabik
Grzegorz Józefaciuk
Dorota Matyka-Sarzyńska
Zofia Sokołowska
Ryszard T. Walczak

Lublin 2004

ISBN 83-87385-87-5

Edition: 180 copies

Project of cover: Grzegorz Józefaciuk
Computer edition Dorota Matyka-Sarzyńska
Technical assistance Krzysztof Józefaciuk

Print: Drukarnia *ALF-GRAF*, ul. Kościuszki 4, 20-006 Lublin

Soil-plant-atmosphere system is influenced by the state and physical properties of three soil phases: solid, liquid and air, and by complex equilibria among them. Various biological, physical, physicochemical and chemical processes continuously affect this system, which thus exhibits an extreme degree of complicacy. This system is a base for our survival, providing our life space and food. To get the food in enough amount and quality, the system plant-machine-agricultural product should be well understood.

Studying of both above systems is the role of agrophysics, new branch of science established few tens years ago. Basic problems of agrophysics are physical and chemical properties of soils and processes significant for natural environment, sustainable agricultural production and processing of agricultural products.

The aim of this volume is to provide an overview on some basic physical, physico-chemical and biological problems of agrophysics. Emphasis is given on the possibility of application of different physicochemical and physical methods in studies of soil and plant materials.

The problems presented in this volume were lectured at the Training Course for Young Research Workers "Physicochemical and Physical Methods of Studies of Soil and Plant Materials. Theory and Practice" hold on 27th November-2nd December 2003, organized by Centre of Excellence AGROPHYSICS (WP 5), and the Institute of Agrophysics PAS in Lublin.

The main idea of publishing this issue was to provide a written background on basic agrophysical theories and problems for other young research workers and students who started their PhD courses in the Institute of Agrophysics this year, however the Editors will be glad if this may serve for other scientific purposes.

The Editors

CONTENTS:

CENTRE OF EXCELLENCE FOR APPLIED PHYSICS IN SUSTAINABLE AGRICULTURE

Walczak R.T., Skierucha W.

Information about the AGROPHYSICS Centre of Excellence is available in Internet at www.6pr.pl/coe/mini/data/5.html and on the IAPAS site www.ipan.lublin.pl

ABSTRACT

Research in the idea of sustainable agriculture cover different areas of science including physics, economy, social science, engineering and also politics. Implementation of sustainability in agriculture as the capability of maintaining agricultural productivity and usefulness to society indefinitely requires the cooperation of multidisciplinary specialists. The researchers from the Institute of Agrophysics Polish Academy of Sciences have been recognized by the European Community as specialists in applied physics and agriculture. The Institute has been honoured as an European "Centre of Excellence for Applied Physics in Sustainable Agriculture: with the acronym "AGROPHYSICS". The study presents the research and support objectives of the Centre and invites scientists to cooperate in the implementation of the idea of sustainable agriculture.

INTRODUCTION

Agriculture has changed dramatically, especially since the end of World War II. Food and fiber productivity soared due to new technologies, mechanization, increased chemical use, specialization and government policies that favored maximizing production. Although these changes have had many positive effects and reduced many risks in farming, there have also been significant costs. Prominent among these are topsoil depletion, groundwater contamination, the decline of family farms, continued neglect of the living and working conditions for farm laborers, increasing costs of production, and the disintegration of economic and social conditions in rural communities.

A growing movement has emerged during the past two decades, called sustainable agriculture integrates three main goals: environmental health, economic profitability, and social and economic equity. A variety of philosophies, policies and practices have contributed to these goals. People in many different capacities, from farmers to consumers, have shared this vision and contributed to it. Sustainability rests on the principle that we must meet the needs of the present without compromising the ability of future generations to meet their own needs. Sustainable agriculture can be achieved with systems perspective, from the individual farm, to the local ecosystem, and to communities affected by this farming system both locally and globally. A systems approach also implies interdisciplinary efforts in research and education.

AGROPHYSICS – CENTRE OF EXCELLENCE FOR APPLIED PHYSICS IN SUSTAINABLE AGRICULTURE

The Institute of Agrophysics Polish Academy of Sciences (IAPAS) has been honoured as an European “Centre of Excellence for Applied Physics in Sustainable Agriculture: with the acronym “AGROPHYSICS”. The Centre started in March 2003 and it will work in the period of three years. Centres of Excellence are units conducting scientific research, developing modern technologies in accordance with international standards and using the research facilities of cooperating institutions for joint projects. The status of the Centre of Excellence allows the Institute to receive funds from European Union and the Polish State Committee for Scientific Research to support the innovative activities of the Institute, promotion of its research aimed to further development of technologies and products both domestically and abroad.

The overall objectives of the Centre involve:

1) research activities financed from the budget of the Institute of Agrophysics: studies on various aspects of sustainable development of agricultural areas and the effective use of agricultural-food,
2) support activities financed by European Community:
    a) organization of research workgroups, conferences, summer schools, lectures,
    b) international cooperation: scientific exchange with other research Centres (trips, lectures), participation and creation of international research projects under 6th Framework Programme of EC,
    c) development of Agrophysics as a scientific discipline: exchange of experience, unification of research methods and terminology.

The research program of the Centre is focused on the:

1) physical, physico-chemical and biological processes of mass and energy transportation in the “soil-plant-atmosphere” system,
2) physical properties of agricultural materials and the processes influencing plant production,
3) processes related to the harvesting, transportation and storage of agricultural products.

The activity of the Centre is the composition of actions carried out by particular Work Packages (WP), which are the collections of specialized thematic areas selected on the base of the Institute of Agrophysics internal organization structure. They are presented below together with the names of persons responsible for planning, organization and execution of objectives specific for the particular WP.

WP1 **Title:** Hydro- and thermo-physical characteristics of porous media as parameters of mass and energy transport models
Leader: Prof. Ryszard Walczak (*rwalczak@demeter.ipan.lublin.pl*)
Objectives: Promotion of European cooperation in the field of determination of hydro- and thermo-physical characteristics of porous media.

WP2 **Title:** Electrical measurements methods of porous material properties
Leader: Prof. Marek Malicki (*mmal@demeter.ipan.lublin.pl*)
Objectives: Promotion of European cooperation in the field of electrical measurement of porous material properties.

WP3 **Title:** Soil-plant-atmosphere aeration problems
Leader: Prof. Jan Glinski (*jglinski@demeter.ipan.lublin.pl*)
Objectives: Measurements of macro- and microdiffusions of oxygen in soil profile. Influence of moisture tension on gas diffusion from soils to the atmosphere. Consequences of soil anoxia conditions on plants.

WP4 **Title:** Control measures against topsoil degradation due to erosion
Leader: Dr Jerzy Rejman (*rejman@demeter.ipan.lublin.pl*)
Objectives: Exchange and comparison of methods used to evaluate erosion risk to elaborate the common procedures and indices. Elaboration of recommendation for sustainable development of multifunctional landscapes.

WP5 **Title:** Surface physical chemistry of soil and plant
Leader: Assoc. Prof. Grzegorz Jozefaciuk (*jozefaci@demeter.ipan.lublin.pl*)
Objectives: Increase participation in 6th FP EU featuring new research fields in soil and plant physical chemistry. Attract new scientists to current, modern soil-plant topics.

WP6 **Title:** Relationships between soil physical characteristics and root and shoot growth and plant water use
Leader: Prof. Jerzy Lipiec (*lipiec@demeter.ipan.lublin.pl*)
Objectives: Widening knowledge of root and shoot growth. Exchange of experience on relation between soil conditions and plant growth.

WP7 **Title:** Mechanics and micro-structure of agricultural plant materials
Leader: Prof. Krystyna Konstankiewicz
(*konst@demeter.ipan.lublin.pl*)
Objectives: Attract young researchers in filed of mechanics and micro-structure studies of agriculture plant materials. Increase participation in 6th FP EU in the field of mechanics and micro-structure of agricultural plant materials.

WP8 **Title:** Characteristics of granular agro-materials and food powders for safe and efficient storage, handling and processing and on-line quality control
Leader: Prof. Józef Horabik (*jhorabik@demeter.ipan.lublin.pl*)
Objectives: Improve links with outstanding Centres in the field of mechanics of particulate solids. Unification of terminology, measurements methods and test procedures in the field of mechanics of particulate solids. Implementation of the European Standards for the testing of bulk solids to determine physical properties of agro- bulk materials and food powders.

WP9 **Title:** Physical methods of evaluation of fruits and vegetables quality
Leader: Assoc. Prof. Bohdan Dobrzanski
(*bdob@demeter.ipan.lublin.pl*)
Objectives: Promote European co-operation in the field of evaluation of fruits and vegetables quality. Increase of staff professionalism

WP10 **Title:** Applied physics in assuring good quality of grains and seeds
Leader: Prof. Boguslaw Szot (*beszot@demeter.ipan.lublin.pl*)
Objectives: Growth of scientific potential of the Centre staff within assuring postharvest quality. Presentation of achievements and experience exchange with west specialists. Further development of measuring methods and knowledge of physical properties of grains and seeds.

WP11 **Title:** Validation and standardization of agrophysical measuring methods
Leader: Dr Andrzej Bieganowski (*biegan@demeter.ipan.lublin.pl*)
Objectives: Promotion of European cooperation in the field of validation and standardisations of agrophysical measuring methods. Training young researchers in validation procedures - „stocktaking” of the validation and standardisation of agrophysical measuring methods.

WP12 **Title:** Rules of participation in European research programmes – increasing active participation in ERA

Leader: Dr Andrzej Stepniewski (*astep@demeter.ipan.lublin.pl*)

Objectives: Improvement and distribution of knowledge on participation rules and current calls of European FP. Improvement of proposals prepared by Centre workers and collaborates. Encouragement for preparation more proposals to European FP. Training and information distribution to eastern partners of the Centre.

All scientists, young researchers and students interested in the research cooperation, exchange of experience, application of research work in practice, education in the fields presented above are invited to contact with the person responsible for the particular WP for information about the planned schedule of activities. Apart from lectures, workshops, training there are also possibilities to visit the Lublin, the agriculture as well as university centre in Poland.

We hope that the activity of "AGROPHYSICS" Centre Excellence for Applied Physics in Sustainable Agriculture will result in bilateral cooperation between IAPAS and other scientific organizations in the form of short and long-term visits and trainings as well as multilateral research cooperation finalized in generation the research projects of 6th FP of European Union.

SPECIFICITY OF AGROPHYSICAL MEASUREMENTS. PROBLEM OF STANDARDIZATION AND VALIDATION OF METHODS

Bieganowski A., Walczak R.T.

VALIDATION AND STANDARDIZATION OF AGROPHYSICAL MEASURING METHODS (WP 11)

The multitude of the research objects, with reference to which the research methods of the physical sciences are applied, caused the separation of the disciplines, such as: biophysics, geophysics or agrophysics. The prefix in the name of each of these disciplines usually shows the subject of the study.

Respectively, *agro-* in the name of *agrophysics* informs that the objects of the investigations can be soils, plants, plant and animal materials as well as the machines, used for the processing of the above mentioned objects.

Physical sciences are considered here as all the natural and technical sciences, which precisely define the investigated values, deal with their measurement/monitoring and undertake the analysis and interpretation of the results. The analysis and interpretation of the investigated dependencies between parameters values and the courses of the processes enables to elaborate simulation and prognostic models which with some approximation, conditioned by needs and possibilities, describe the studied phenomena. Monitoring and modelling are two main features of physical research work.

Agrophysics investigates the properties of the objects as such and their interactions with the surroundings (e.g. in the soil-plant-atmosphere or plant-machine-agricultural products systems). The results of these investigations can be used in sustainable plant and animal production as well as for implementation and improvement of modern processing technologies with special consideration of raw materials and food products.

An important area of activity for agrophysics is elaboration and/or improvement of the measuring methods.

The dynamical development of agrophysics during the last years reveals high demand of the consumers (agriculture with its surrounding in its broad sense and processing industry) for research methods and specific methods of analysis and interpretation of the results concerning differentiated objects, including the objects with biological activity.

The reason for popularity of agrophysics is its interdisciplinary character. A good example of this can be a broad spectrum of the specialists engaged in the Institute of Agrophysics, Polish Academy of Sciences in Lublin. The cooperation exists here between physicists, chemists, mathematicians, computer scientists, electronic engineers, biologists, geographers, agronomists and engineers of other disciplines. The reason that extracts the necessity of creation of multi-disciplinary teams is the specificity of agrophysical measurements.

SPECIFICITY OF AGROPHYSICAL MEASUREMENTS.

The specificity of agrophysical measurements refers to two fundamental aspects:

1. The multitude and high diversity of the studied objects, e.g.:
   - material objects
     - plants (mostly considered in the context of their behavior in the environment, as understood in broad sense),
     - soil as the environment of plant's growth and development,
     - environments in greenhouse production,
     - nutritive substances for plants,
     - plant pesticides,
     - plant materials,
     - animal materials,
   - processes
     - taking place in the environment of plant's growth and development,
     - of plant production,
     - of food production (from raw materials of plant and animal origin).
2. Space and time variability of the investigated objects.
   - agrophysical objects are characterized by natural space variability, e.g. spatial variability of parameters describing the soil status in the micro-scale (i.e. local status) and in the macro-scale (i.e. averaged for a chosen volume or area),
   - agrophysical objects also reveal time variability caused by the dynamics of the extorting processes (e.g. change of atmospheric conditions or biological activity, including micro-biological activity). Time variability caused by biological activity is one of the reasons that the difficulties occur when trying to select methods which follow one of the basic rules of metrology, i.e. not to disturb the properties of the investigated object.

The application of geostatistical methods (kryking, cokryking) and the analysis of the time-space series make it possible to determine the way of performing representative measurements, i.e. to localize in space the measuring points, the number of repetitions and the frequency of measurement.

It should be stressed, that the discussed earlier aspects of the specificity of agrophysical measurements can, in particular situations, occur in any combinations, causing additional difficulties with proper interpretation of obtained results.

PROBLEM OF STANDARDIZATION OF METHODS

The specificity of agrophysical measurements imposes other, than in classical measurements, attitude towards the issue of validation of the measuring methods and their standardization.

Before the further discussion will be undertaken, it is worth to answer the question what validation of the research/measuring method is. The ISO/IEC 17025 norm, describing "General requirements concerning the competence of the research and standardizing laboratories" defines that "validation is a confirmation, by the investigation and presentation of an objective proof, that the special requirements have been fulfilled, concerning a specific intended application". In other words, the validation has to answer the question, if the results obtained with a given method, really describe in a proper way the values which should be described. It is connected with inseparably with ability to interpret the obtained results.

Therefore, it is extremely important in any investigations (including agrophysical ones) to put forward a question, what the aim of the performed investigations is. Without answering it, the selection of a proper research/measuring method and correct interpretation of the results is not possible. Answering this question is also inevitable in the context of the method 's validation For example, the problem of the water content measurement in the soil can be solved only after precise defining of the aim of the conducted studies. The gravimetric method gives the information about the averaged water content for the whole sample, being in fact useless in the studies of the dynamics of water transport in the soil. Moreover, the gravimetric method requires collecting samples, and by this the investigated objects are disturbed. In case of the studies of the objects having small dimensions it can exclude this method's applicability. The solution of this problem can be the use of a non destructive method, such as Time Domain Reflectometry (TDR) technology. The additional advantage of this technique is that it enables to process the investigated physical value (water content) into the electrical value which can be easily transmitted, digitalized, registered and processed in computers.

The research/measuring methods applied by agrophysicists can be divided into normalized and not normalized ones (Fig. 1). In the group of the former methods, the ones can be selected which are described by the standards (international, European, domestic, etc.). The use of standardized methods in the form of standards is convenient because they can be regarded as fully validated and there is no necessity to perform individually the process of validation. The user, however, has to possess the proofs that he is able to use the given method according to the recommendation of the standard and give the evidence of a declared by himself uncertainty of the measurement.

The user of a standardized method has a right or even an obligation to resign from the recommendation of a standard and perform the modification of the method, if it is required by the common sense and a need resulting from a specific application of the method. In such a case, the premises leading to the decision of the method's modification should be documented as well as the criteria of choosing the way of method's modification and the proofs that the modification enabled better and closer to the expected goal use of the method.

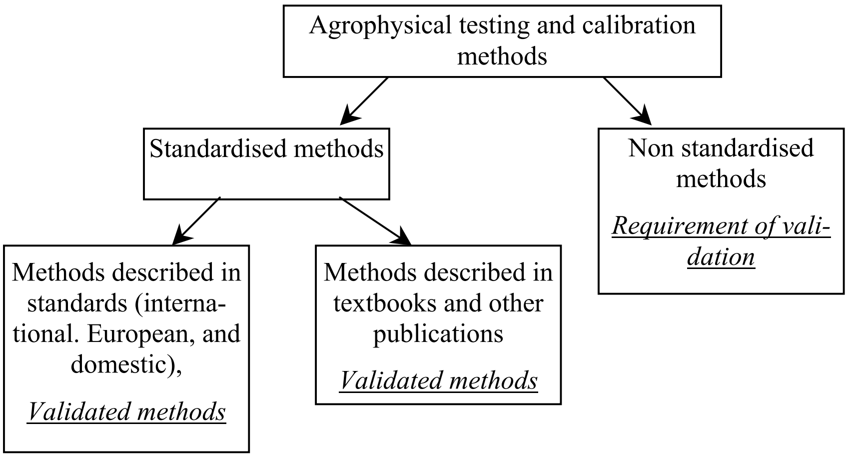


Fig. 1. *The division of agrophysical research/measuring methods in respect to the need of performing the validation by the laboratory which uses a given method*

The problem which should be discussed when considering the application of the standardized methods in agrophysics includes the answer to the question: Can a measuring method, described not in an international standard but in an academic book or in a publication be considered as a validated one?

There is no an unambiguous reply to this question. Everything depends on the proofs presented in the description of this method. However, it results from the experiences given by agrophysicists, representing different branches of agrophysics, that unfortunately, a large group of measuring methods has not been accurately validated. In spite of this fact, these methods are used and obtained results are interpreted, without taking into consideration the occurring doubts.

As an example we can consider the problem of the use of soil extracts as a nutrient medium for bacteria multiplication in microbiological investigations of the soil environment. There are no publications which would undertake the problem of the impact of the used extract (from which kind of soil it originates and in what concentration) on the obtained results, although it is an important parameter for this method. This gap, connected with the lack of validation of the method becomes even much serious when considering the fact of not giving in particular publications the information, which soil was the base for preparation of the extract what concentration/solution was used. Due to this, it is impossible to compare the results, obtained in various laboratories.

Another problem (which is independent on the fact if a given research/measuring method can be considered as validated or not) which can be noticed when revising agrophysical publications is inaccurate description of the environment, conditions and the way of performing the described research /measurements.

The example of this problem can be the studies of soil in respect to its aeration, in which the methods and the duration of storing the soil samples used in the investigations, are not presented. And in fact, they are extremely important, considering the microbiological activity and respectively, a possibility of changes (in time) of aeration of the studied samples.

Presented examples of not complete validation and not preserving the recurrence of the research/measuring procedure (standardization) should mobilize everyone to pay more attention to this problem. In any case, the actual aim of the study should be defined and then one or the combination of the following techniques [ISO/IEC 17025]should be used:

- normalization during application of the reference norms or the reference materials
- comparison of the results obtained by other methods
- comparison between laboratories
- systematic evaluation of the factors influencing the result
- evaluation of uncertainty of the results based on scientific understanding of theoretical foundations of the method and on practical experience

Underestimated and especially important problem in agrophysical studies is the method of taking representative samples. Uncertainty of the measurement connected with the method of collecting the samples frequently exceeds the uncertainty resulting from the method of measurement of a given property.

The majority of agrophysicists knows about the importance of validation and standardization problems, undertaking some actions in this field and then presenting their results in publications.

REFERENCES

1. Bieganowski A., Baranowski P., Walczak R.T.: Agrofizyczne systemy monitorowania procesu produkcji bezpiecznej żywności. Acta Agrophysica, 84, 21-29, 2003.
2. Walczak R.T., Bieganowski A.: Agrofizyczne monitorowanie i modelowanie procesów wytwarzania żywności. Acta Agrophysica (in printing).
3. ISO/IEC 17025:1999. „General requirements for the competence of testing and calibration laboratories”.
4. Guide to Expression of Uncertainty in Measurement, issued by BIPM, IEC, IFCC, ISO, IUPAC, IUPAP and OIML. ISO 1993.
5. Elandt R. Statystyka matematyczna w zastosowaniu do doświadczalnictwa rolniczego. PWN Warszawa, 1964.
6. Usowicz B., Paszczyk J., Walczak R. 1991 a. Description and analysis of the soil tempera-ture dynamics with ARIMA models. Part I. Theory and experiment. Zesz. Prob. Post. Nauk Rol., 396, 167-172.
7. Usowicz B., Paszczyk J., Walczak R. 1991 b. Description and analysis of the soil temperature dynamics with ARIMA models. Part II. Analysis. Zesz. Probl. Post. Nauk Rol., 396, 173-180.
8. Walczak R. Usowicz B. 1994. Variability of moisture, temperature and thermal properties in bare soil and in crop field. Int. Agrophysics, 8(1), 161-168.

INSTRUMENTAL MEASUREMENT OF SPECIFIC SURFACE AREA IN LIQUID NITROGEN TEMPERATURE

Bowanko G.

THEORETICAL PRINCIPLES

The process of adsorption of gas on a solid surface, whether active or not, consists of an accumulation of a fluid phase on the surface of the solid. Such a phenomenon is characterized by the energy of interaction between the gas (adsorbate) and the solid (adsorbent).

These interactions fall, broadly speaking, into two categories:

- where the energy of adsorption is determined by weak Van der Waals forces (c. 10 $kJmol^{-1}$) corresponding to the heat of the adsorbed fluid (Ar, He, CO, Kr, N_2,). In this case the adsorption process is a physical adsorption (or **Physisorption**) and is always exothermic.
- where the energy of adsorption corresponds to the heat of reaction (80 - 300 $kJmol^{-1}$), The adsorption process is a chemical adsorption (or **Chemisorption**) and need not necessarily be exothermic.

For physical adsorption a minimum in potential energy, between 2-15 $kJmol^{-1}$, exists at a distance corresponding to the Van der Waals radius (c. 6Å). In the case of the Chemisorption, however, the minimum occurs at a distance less than 3Å corresponding to the length of a covalent bond. Moreover, the minimum in potential energy is much better defined due to the greater bonding energy involved. With physical adsorption, the quantity of the fluid phase adsorbed decreases with increasing temperature. At a constant temperature, the quantity adsorbed corresponds to the relative pressure P/P_0, where P is actual gas pressure and P_0 the saturated vapor pressure of the adsorbate. Generally, a monolayer of physisorbed molecules is obtained at relative pressures of around 0,1. Above this pressure various multilayers are formed.

The specific surface area and the pore size distribution are fundamental parameters for the characterization of solids. Properties such as porosity, strength, hardness, permeability, separation selectivity, corrosion, thermal stress resistance, etc. can be directly correlated to the porous structure of the material. These properties can be easily investigated by the Physisorption technique.

The quantity of gas adsorbed during chemisorption depends in an inversely proportional way on temperature. Moreover, with increasing pressure, up to a certain value, a plateau exists which corresponds to the volume of gas adsorbed as a monolayer.

Catalysts are an almost unique solution to many of the problems found not only in chemical industries and processes but also in our everyday life (i.e. pollution). The Chemisorption techniques provide information on the quality, activity and selectivity of a wide range of catalysts, including active sites specific surface, metal dispersion, metal aggregate (size), acid/basic sites concentration, strong/weak interactions distinction. The characterization of activated solids as catalysts, acid/basic materials, supported materials, oxides, active carbons, zeolites can be easily performed using reactive gases (i.e. hydrogen, carbon monoxide or ammonia, hydrocarbons, methane, water vapor, SO_2). Different ovens are available to perform the Chemisorption analyses from room temperature up to 450 or 1100 °C (using suitable holders).

PHYSICAL ADSORPTION

If a gas or vapor is in contact with an adsorbent, the molecules of the adsorbed material are distributed between the gaseous and the adsorbent phases. The atoms, or atomic groups, distributed on the surface of a solid do not entirely exchange their valence electrons with those nearby, as happens within the mass. These free electrons create some residual valences, which enable liquid or gaseous molecules coming into contact with the solid surface to combine with it by means of relatively weak interactions known as Van der Waals bonding. This occurs principally when the solid possesses a structure full of interstices and ultramicroscopic pores providing a greater area of irregular surfaces.

Substances formed by complex molecules and ions having a higher electrical charge are better adsorbed. In adsorption equilibrium is always achieved and the quantity adsorbed, under equilibrium conditions, is a function of temperature, pressure and properties of the adsorbent and adsorbed species.

At a constant pressure and temperature we have, therefore, dependence between the adsorbent and the nature of the adsorbed gas. If we name V_a the gas volume adsorbed at 0°C and 760 mm Hg per weight unit of adsorbent, it results that V_a is a function of pressure and temperature:

$$\mathbf{V_a = \mathit{f}(PT)}$$

Taking P as constant we have isobar adsorption represented by:

$$\mathbf{V_a = \mathit{f}(T)}$$

Isobar adsorption is remarkable at low temperature but decreases quickly with increasing temperature.

Taking T as constant the equation becomes:

$$\mathbf{V_a = \mathit{f}(P)}$$

Isothermal adsorption increases with pressure and decreases with temperature rise (exothermic process).

By using inert gases such as Nitrogen, it is possible to determine the specific surface and pore size distribution of a large number of solids and powders (catalysts, active carbons, charcoals, phamaceuticals, building materials, cements, glass, soils, mineral metal powders and sintered metals, oxides and salts, adsorbents, ceramics, pigments). In case of very low specific surfaces (non porous materials). Krypton can be easily used, while for some ultramicroporous solids, like some zeolites, Argon physisorption is a common technique applicable by the instrument. Common coolants for the analysis are liquid Nitrogen or Argon.

SPECIFIC SURFACE

The definition of specific surface is different for porous and non-porous solids. For a non-porous solid it represents the outer surface. For a porous solid it considers the outer surface similar to that of a non-porous solid plus an inside surface remarkably superior to the one which is formed by the surface total pores.

Generally only this latter concerns heterogeneous catalysis because it has been shown that the mass porosity hence the surface area, plays an important role in the determination of the catalytic activity of a substance.

METHODS OF SURFACE AREA MEASUREMENT

As mentioned above adsorption studies allow specific surface of the adsorbent to be evaluated. Emmet and Brunauer stated that if the gas is adsorbed at very low temperature, eg. at the gas boiling point, we can get at relatively high pressures either multimolecular adsorption or capillary condensation. In fact, a surface covered with a complete molecular layer is sometimes able to adsorb a second molecular layer. If the interactive forces between the adsorbed molecules and those in gaseous phase are sufficiently strong a second layer may easily be formed. It is quite difficult to state when the adsorption is complete in the first layer and when further layers are formed on the one already adsorbed. We should, therefore, always refer to multimolecular adsorption. In order to calculate the adsorbent surface area it is necessary to determine the gas volume relative to the monomolecular layer and to know the molecular section area of the gas adsorbed.

Brunauer and Emmet experimented with different gases adsorbed on an adsorbent and determined the volumes of the gases adsorbed at different points of the isotherm. They found that the values of surface area were approximately constant only when they considered the volumes corresponding to the starting point of the intermediate linear position of the isotherm.

INSTRUMENTAL MEASUREMENTS OF LOW TEMPERATURE ADSORPTION- DESORPTION ISOTHERMS

Sample pretreatment

To remove all species naturally present and adsorbed to the sample surface, i.e. O_2, N_2, CO_2, organics, etc., the sample is heated gently under vacuum for a few hours or overnight. To avoid possible attached to contamination the outgassing circuit is kept separated from the analytical circuits. This operation is carried out using the outgassing stations and the furnaces located on the front of the instrument.

The conditions of vacuum and temperature may vary from sample to sample according to their different nature and characteristics therefore refer to the technical literature about specific pre-treatment conditions about samples. Generally it is possible to reassume that:

- organic materials are usually treated at temperature not exceeding 60-70ºC

- soil samples are usually treated at temperature 105ºC
- samples as alumina/silica are usually treated between 150 and 180ºC
- coals and active carbons are usually treated between 200and 250ºC
- zeolites are usually treated at temperatures between 250-350ºC.

The outgassing time, that is the time necessary to remove the percentage of humidity present in a given sample, can vary from 1 hour up to 15-16 hours according to the sample characteristics. In substance this time is a function of the “difficult” to remove completely the humidity form the samples. The sample must be placed into a burette properly chosen according to the characteristics of the sample.

General design of the apparatus

The principal idea of the equipment used for low-temperature sorption measurements is illustrated in Fig. 1.

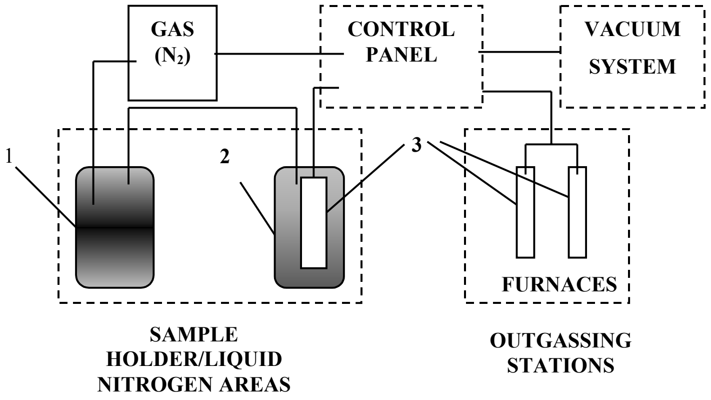


Fig.1. *Idea of the low-temperature sorption equipment. 1. Liquid nitrogen standard reservoir; 2. Cooling Dewar vessel; 3. Sample burettes*

Adsorption

In adsorption the micro dose delivery system of the adsorbate (nitrogen) is connected to the adsorbent chamber. The chamber is filled with gas until the automatically chosen loading pressure is reached. After equilibration, the procedure is repeated stepwise at higher pressures. The amount of gas adsorbed is authomatically measured knowing the amount of the gas dosed and the gas equilibrium pressure in the adsorbent chamber.

Desorption

During desorption the chamber is connected with the vacuum system. The measuring gas is coming out from the sample holder (that is desorbing from the sample). After reaching an equilibrium the next amount of gas is desorbing from the sample holder.

EXEMPLARY ANALYTICAL RESULTS

For analysing samples of small porosity, exhibiting not well developed hysteresis loops (Fig. 2.), one uses the Dollimore – Hill approach along with the BET (Brunauer et. al. 1938, Gregg and Sing 1967). The exemplary results for the illustrated sample are presented in the Table 1.

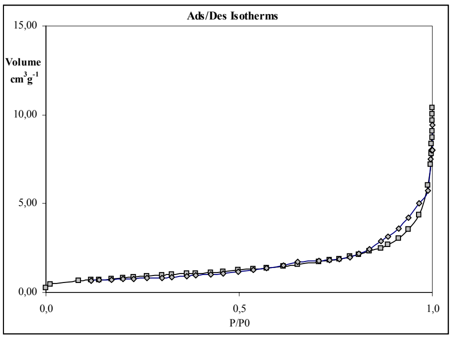


Fig.2. *Small porosity sample isotherms.*

Table. 1. Surface and pore parameters for small porosity sample.

Init. P/P_0 for BET :	0,05
Final P/P_0 for BET :	0,33
Monolayer volume (cm^3g^{-1})	0,689003
Specific surface area (m^2g^{-1})	3,001096
C value of BET Equation	65,0842
Correlation factor	0,9999688
Pore specific volume (cm^3g^{-1})	1,551439 E-02 (at $P/P_0 = 0,9999$)
Total Adsorbed volume (cm^3g^{-1})	10,37264

Similar approach is used for analysing samples of medium porosity (Fig. 3.). The exemplary results for the illustrated sample are presented in Table 2.

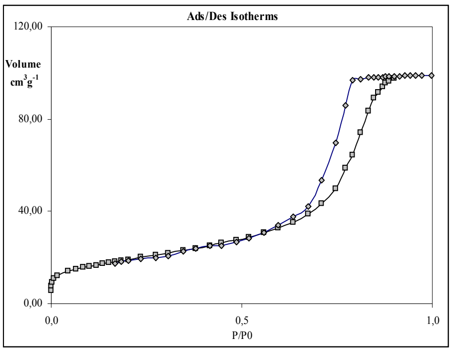


Fig.3. *Medium porosity sample isotherms.*

Table. 2. Surface and pore parameters for medium porosity sample.

Init. P/P_0 for BET :	0,0242
Final P/P_0 for BET :	0,2787
Monolayer volume (cm^3g^{-1})	15,79084
Specific surface area (m^2g^{-1})	68,74065
C value of BET Equation	114,8095
Correlation factor	0,9999448
Pore specific volume (cm^3g^{-1})	0,1537804 (at $P/P_0 = 0,9975$)
Total Adsorbed volume (cm^3g^{-1})	102,1861

For analysing samples of large porosity (Fig. 4.) one usually applies Horvath-Kawazoe (1983) along with Dubinin (1955) methods. The exemplary results for the illustrated sample are presented in Table 3.

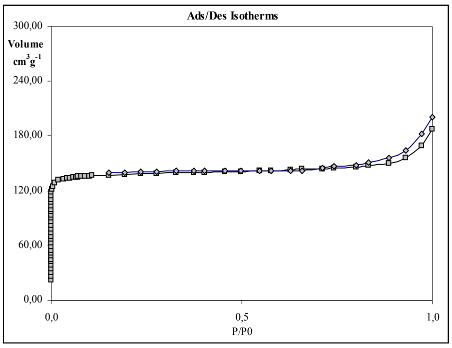


Fig.3. *High porosity sample isotherms.*

Table. 2. Surface and pore parameters for high porosity sample.

Init. Log2 (P_0/P) :	1,5366
Final Log2 (P_0/P) :	12,389
Monolayer volume (cm^3g^{-1})	137,7137
Specific surface area (m^2g^{-1})	599,4954
Correlation factor	-0,9990602
Micropore volume (cm^3g^{-1})	0,2128322
Total Adsorbed volume (cm^3g^{-1})	221,9524

REFERENCES

1. Barret E.P., Joyner L.G. and Halenda P.P., Journal American. Chemestry, Society, vol. 73, 373 (1951).
2. Brunauer S., Emmet P.H. and Teller E., J. Am. Chem. Soc., vol. 60, p. 309 (1938).
3. Dubinin M. M., Quart. Rev. Chem. Soc. vol. 9, p. 101 (1955).
4. Gregg, S.J., Sing, K.S.W. 1967. Adsorption, Surface Area and Porosity. Academic Press, London and New York.
5. Horwath G. and Kawazoe K., J. Chem. Rng. Jap. Vol. 16, p. 6, 470 (1983).

SOIL MICROBIOTA AND ENZYME ACTIVITY IN RELATION TO ORGANIC MATTER TRANSFORMATIONS

Brzezińska M.

The primary functions of the soil are directly related to its biomass, which is, as a continually cycled pool of nutrients, the prerequisite for the growth of plants. For the nutrients to be taken up, organic matter entering the soil has to be degraded to inorganic components. This degradation is brought about by the indigenous microbiological activity of soil. During the decomposition and synthesis of organic substances in the soil, the metabolism and energy exchange proceed with the participation of the enzymes. Consequently, the development of soil fertility is closely associated with microbial and enzymatic processes (Galstian 1974; Stevenson 1986). 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.

SOIL MICROBIOTA

Soil microorganisms can be grouped into three categories (Bolton 1993):

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 (Jones et al. 1994). 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 1993).

Microbial diversity in soil ecosystem exceeds that of eucaryotic organisms. Microorganisms in soil occur in huge numbers and display an enormous diversity of forms and functions. Major microbial groups in soil are bacteria, actinomycetes, fungi, algae and protozoa. Because of their extremely small cell size, enormous number of soil microbes can occupy a relatively small volume; hence space is rarely a constraint on soil microbes.

Bacteria are the most numerous of the microbial group in soil, but because of its small size, it is estimated that they account for less than half of the total biomass in agricultural soils. Fungi are probably of equal or greater importance in many soils as indicated by their biomass, associations with roots and saprophytic competence. Soil microbes are very diverse metabolically and use many different sources of C and N (phototrophs, chemotrophs, autotrophs, heterotrophs, lithotrophs). Most of soil organisms are organotrophs, transforming soil organic matter.

Microorganisms play also an important role in the formation of soil structure (Lynch and Bragg 1985). Actinomycetes produce hyphal treads that bind soil particle together. Extracellular polysaccharides produced by bacteria bind soil particles together, assisting in building soil structure. Humic materials from bacterial action form organic matter/clay complexes and help aggregate stability in soil. This action reduces erosion, allows good water infiltration and maintains adequate aeration for the soil (Kennedy 1999).

The special role for soil microbes plays plant root. The rhizosphere stimulates the microbial growth surrounding the root due to the release of a wide variety of organic compounds (exudates - low molecular weight compounds, sugars, amino acids, that leak from intact cells; secretions - compounds that are actively released from root cells; mucigel - gelatinous material on the root surface composed of plant mucilage, bacterial cells, metabolic products, colloidal organic and minerals; lysates - material released through the lysis of older epidermal cells). Thus, both higher populations and a greater diversity of microbes were found closer to the plant roots, and there can be considerable differences in the relative abundance of various taxonomic and nutritional groups of microbes between rhizosphere and non-rhizosphere soil (Bolton et al. 1993).

MICROBIOTA LIVING SPACE

The oligotrophic - non-rhizosphere bulk soil - includes numerous microhabitats within which microbial activity is ephemeral and responsive to fluctuating substrate availability as well as physical and chemical micro-environmental conditions (Metting 1993). Microhabitats, variable in dimension and containing single cells, small colonies or mixed communities, occur on or near particulate surfaces as well as within soil aggregates.

Recent researches have demonstrated that bacterial communities are not randomly distributed in soil. Spatial patterns have been identified in the distribution of bacteria and bacterial function at scales from several millimeters to several meters. It has been suggested that microscale patterns may have a regulatory effect on bacterial activity, as a result of the diffusive delivery of substrate to, and the dispersion of product from bacterial cells, which may have rate-limiting or stimulatory effects on microbially mediated processes. Furthermore, there is increasing evidence that bacteria can release chemical signals, the environmental concentration of which is related to cell density, that modulate bacterial function once a critical concentration of chemical is reached (Nunan et al. 2003).

The conditions of a microsite in one soil pore may be quite different from adjacent microsite, leading to the development of microsite-specific communities and thus increasing the diversity of a given soil. Soil texture and percent pore space can directly affect 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 in soils subjected to different fertilization treatments, more than 80% of the bacteria were located in micropores of stable soil microaggregates. This is consistent with the findings of Foster (1988) and Kilbertus (1980) who illustrated with electron micrographs that bacteria were more abundant within aggregates than in larger pores between aggregates. Such microhabitats offer the most favorable conditions for microbial growth with respect to water and substrate availability, gas diffusion and protection against predation (Ranjard and Richaume 2001).

Soil physical phases (solids, water, gases) determine the size and topography of pore networks and distribution of water in pores of different size, as well as modify the gas diffusion and soil aeration status (Gliński and Stępniewski 1985; Gliński et al. 2000; Lipiec and Hatano 2003; Walczak et al. 2002; Witkowska-Walczak and Walczak 1999). Thus, strongly influence the distribution of microbial cells and indirectly regulate interactions among organisms and their access to oxygen, substrate, and water. In drier soil, because of water requirements, cells will tend to be located in smaller pores, as soil water also serves as the transport medium through which many nutrients and organic compounds diffuse to the microbial cell, and through which metabolic waste products are removed (Young and Ritz 1998; Young and Ritz 2000; Ranjard and Richaume 2001; Nunan et al. 2003; Foster 1988).

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 Young and Ritz 2000). 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 soil, in its natural environment, is exposed to fluctuating wet and dry cycles and to diurnal and seasonal temperature gradients. Soil microbiota possess different adaptive mechanisms. Even if one population of microorganisms is destroyed as a result of unfavorable effects, the free niche is rapidly colonized by the invasion of the next, competitive population.

The biomass in soil porous media is there contained in two phases: the aqueous phase and the solid-associated biofilm phase. 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). Cells within biofilms adhere to surfaces through interaction of London – van der Waals attractive forces and electrostatic forces arising from the physical properties of the diffuse double layer. 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).

MICROBIAL MOBILITY

Microbial mobility 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 subject 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). 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). However, because the geometry of macropores in the field may change frequently due to wetting, drying, freezing, thawing or burrowing of invertebrate animals, movement of microorganisms through the soil matrix may be necessary, to, for example, reach substrate (Gannon et al. 1991). This movement is controlled by mechanical filtration and adsorption on clay particles. Thus, the influence of soil type on microbial transport will be due to both its physical structure (relative proportion of sand, silt, clay and organic matter) and to variation in adsorptive capacity of its colloidal material. 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; Madsen et al. 1982). 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 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. Such adsorption, at time, may even enhance the transport because it retards adsorption on bigger particles. It is also possible for microorganisms to be trapped in pore that is too small to allow passage (Gannon 1991).

The speed and distance of dispersal of soil microbes depend also on soil management practices. The movement of soil during cultivation can disperse microorganisms within 20-30 cm of the plough depth and several meters horizontally. Moreover, ploughing increase porosity, but heavy traffic compact the soil and destroys macropores, thus influencing mobility of microbes. It seems that, besides of sub-surface water flow, the surface water erosion may affect transport of microbes in soil.

Gerba et al. (1991) considered five key factors that determine the physical transport of microorganisms through soil:

1. Advection – the process of transport in bulk motion of flowing water with carriage at a rate equal to the average velocity of the water flow;
2. Dispersion – spreading of the organisms as they pass through the subsurface medium. This is a function of the variation in *actual* pore water velocity compared with the *average* pore water velocity, and the effect of Brownian movement;
3. Adsorption – adhesion to soil particles;
4. Filtration – removal of organisms from the pore water by size exclusion;
5. Decay or die-off – inactivation by environmental stress, such as temperature or lack of nutrients (Dighton et al. 1997; Ginn et al. 2002).

Electrostatic and chemical interactions between microorganisms and solid surfaces may act at close separation distances (nanometers of microns), but ultimately determine how microorganisms adsorb and desorb from the negatively charged solid surface, and thus, affect microbial transport (Dighton 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). Bacterial dispersal by their 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 1997; Misaghi et al. 1992; Wong and Griffin 1976).

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 forces 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 ENZYMES

Soils harbor numerous organisms - bacteria, actinomycetes, fungi, microalgae, protozoa, nematodes, earthworms and other invertebrate microfauna - mostly arthropods (crustaceans and insects), ascari and mollusks (Metting 1993). Soil enzyme activity is produced primarily by microorganisms (e.g. bacteria, fungi), but also originated from animal and plant sources (e.g. roots, lysed plant residues, digestive tracts of small animals), (Ladd 1978). Some enzymes may originate in part from plant remains while others may be synthesised almost entirely by soil organisms. Macroscopic animals, including earthworms, arthropods and vertebrates are important in soil biology as well, but are on the scale larger than the microhabitat and their contribution to overall soil enzyme activity is difficult to estimate (Curl and Harper 1990).

The endoenzymes may exist in living cells in different cellular compartments, such as the cytoplasm or periplasm, or they may be associated with the cell membrane and/or cell wall. Extracellular enzymes are produced and secreted by living cells and operate at a distance from the parent cell, either as free enzymes in the liquid phase, or as enzymes still associated with the external surface of root epidermal or microbial cell wall (i.e. partially attached to or trapped within a viscous network of homo- and heteropolysaccharides secreted by several cells which still allow the passage of substrate and products (Gianfreda and Bollag 1996). Components of the enzyme activity of soil were classified first by Kiss et al. (1975) and subsequently by Skujins (1978). Burns (1982) divided the overall enzymatic activity of soil into 10 reasonably distinct categories and this clear and precise classification includes that of Kiss and Skujins. In fact, individual enzymes may belong to more than one category and may change from one to another with time. Some of the enzymes (e.g. urease and β-glucosidase) catalyse reactions both inside and outside of the organisms that synthesised them; some of the cellulases and proteinases can only function outside of the producing cells because of their large size of their target substrate; and others (e.g. dehydrogenases and nitrate reductase), being involved in the central aspect of metabolism, do not function extracellularly (Gianfreda and Bollag 1996).

Free enzymes are believed to be short-lived in soils, being vulnerable to degradation and to immobilization on the surfaces of soil clay and organic colloids. Immobilization, being the norm in the soil environment (Burns 1978; Burns 1982; Ladd 1978; Ladd et al. 1996; Ruggiero et al. 1996), protect enzymes against degradation and denaturation, and retain their activity for a long time, usually at the cost of some loss of activity. These stabilized enzymes can be active also in the absence of proliferating and nonproliferating microorganisms. Thus, the overall activity of any enzyme in soil is the result of activities associated with enzymes at different sites (Dilly and Nannipieri 1998).

ENZYME SPECIES

Soil organic matter transformation is strongly effected by the activities of soil microorganisms, which use many enzymes in their metabolic pathways. Result of many experiments show the relations between particular enzyme activity and different soil properties (Alef and Nannipieri 1995; Bandick and Dick 1999; Frankenberger and Dick 1983; Gostkowska and Furczak 1983; Kandeler et al. 1999; Kiss et al. 1975; Kobus et al. 1988; Kucharski and Niklewska 1991; Kuprevich and Shcherbakova 1971; Megharaj et al. 1999; Myśków et al. 1996; Nannipieri et al. 1990; Ruggiero and Bollag 1996; Skujins 1976).

Assays have been devised for a wide range of soil enzymes that are representative most of the enzyme classes. Oxidoreductases and hydrolases have been the most studied because of their role in organic matter degradation and release of nutrients. Few studies have been concerned with the activities of transferases (e.g. transaminase, rhodanese) and lyases (e.g. decarboxylases), (Skujins 1978).

Oxidoreductases

Dehydrogenases catalyse a broad range of reactions of degradation (dehydrogenation) of organic matter. Numerous soil dehydrogenases are assumed to function only intracellularly, exclusively associated with live, intact cells. Dehydrogenase activity has been used as a general index of biological activity because of the involvement of these enzymes in the oxidative energy-transfer sequences (Ladd et al. 1996). Numerous studies reveal correlations of the activity with several biomass parameters such as microbial numbers, soil respiratory activity, ATP content, other enzyme activities, carbon and nitrogen cycling, organic matter content (Bandick and Dick 1999; Curl and Harper 1990; Nannipieri et al. 1990; Schäffer 1993).

Catalase catalyse decomposition of hydrogen peroxide, formed during aerobic respiration as a by-product, thus playing an important detoxifying role because of the extreme reactivity of H_2O_2 and possibility of irreversible damage of biomolecules. Catalase is produced by aerobes and most of the facultative anaerobes (Guwy et al. 1999; Trasar-Cepeda et al. 1999).

Peroxidases, catalysing the oxidation of substrates in the presence of H_2O_2, are involved in the degradation of lignin and phenols (Kirk and Farrell 1987; Russel 1972).

Phenoloxidases oxidise phenols, generated during degradation of lignin or microbial synthesis (Kirk and Farrell 1987). The group includes o-diphenol oxidase (tyrosinase), p-diphenol oxidase (laccases) and polyphenol oxidases. These enzymes are apparently involved in humification processes (Skujins 1978).

Hydrolases

Amidases (acylamide amidohydrolases), catalyse the hydrolysis of amides (C-N bonds) to ammonia and the corresponding carboxylic acid. Amidases are common enzymes, accumulated in soil (Deng and Tabatabai 1996).

Amylases (α- and β-amylases) hydrolyse starch and related oligo- and polysaccharides containing glucose units. β-Amylases are more active. Both the forms are accumulated in the soil. Starch (consisting of two glucose polymer, amylose and amylopectin) is the major food reserve of plants. α-Amylase degrades both amylose and amylopectin to units consisting of several glucose molecules. β-Amylase reduces amylose to maltose. Amylopectin is degraded to a mixture of maltose and dextrin. Many bacteria and fungi degrade starch (Paul and Clark 1996).

L-Asparginase and L-Glutaminase hydrolyses L-asparagine and L-glutamine to L-aspartic and L-glutamic acids, respectively, and NH_3. These intra- and exracellular enzymes are widely distributed in nature and have an important role in nitrogen mineralization in soils (Frankenberger and Tabatabai 1991a ; Frankenberger and Tabatabai 1991b; Frankenberger and Tabatabai 1995).

Cellulases catalyse the hydrolysis of the β-1,4-glucan bonds of cellulose to D-glucose. This biochemical activity is an interaction of three enzyme groups: endo-β-1,4- glucanases, exo-β-1,4-glucanases (cellobiohydrolases) and β-glucosidases (cellobiases) (Alef and Nannipieri 1995; Eriksson and Wood 1985; Ladd 1978;

Paul and Clark 1996). Extracellular cellulases bind to the crystalline substrate and cleave celluloligosaccharides from the non-reducing ends, intracellular enzymes cleave glucosidic linkage along non-crystalline parts of cellulose substrate, while β-glucosidases release glucose from cellulolgosaccharides and aryl-β-glucosides. Cellulose, the most abundant structural polysaccharide of plant cell walls, is nearly always associated with hemicellulose and lignin. The degradation of cellulose in soils is a slow process, depending on environmental factors and activity of soil microorganisms. Soil cellulases are mainly produced by fungi, but also by a few species of actinomycetes and some anaerobic *Clostridium* (Clark and Stone 1965). Hemicelluloses are the heterogeneous group of compounds – polymers of hexoses and pentoses. In nature hemicelluloses are complexed with other substances that make the breakdown difficult. The process involves the action of pectinases. Fungi appear to initiate the degradation of hemicelluloses and actinomycetes can maintain the attack over a prolonged period. Hemicelluloses are generally considered to be degraded faster than cellulose, probably as a result of a grater number of microorganisms using these compounds as a substrate (Haider 1992; Paul and Clark 1996).

Chitinase and chitobiase catalyse the hydrolysis of chitin to acetyl glucosamine. Chitin, one of the major contributors of amino sugars in soil, is the components of fungal cell walls (Alef and Nannipieri 1995).

Glucanase (β-1,3-glucan glucanohydrolase, laminarinase), present as exo- and endocellular enzyme, hydrolyses β-glucan component of cell wall (Schäffer 1993).

Glucosidases. β-glucosidases (called as cellobiases, gentobiase, emulsin) exist in extra- and intracellular forms and are the rate limiting enzymes in the microbial degradation of cellulose to glucose. α-Glucosidase (maltase), β-galactosidase (lactase) and α-galactosidase (melibiase) are also included among glucosidases (Alef and Nannipieri 1995; Skujins 1978; Burns 1978).

Ligninase. Lignin is slowly catabolised to CO_2, but very little lignin C is found in microbial biomass, whereas 70 % or more was being stabilised in the soil (Stott et al. 1983). The biodegradation of lignin, with its phenylpropanoid units irregularly connected by C-O-C and C-C linkages, is less understood than that of cellulose. Lignin is formed as an encrusting material on the cellulose and hemicellulose matrix and does not show a specific order (Haider 1992; Paul and Clark 1996). The most active biodegraders of lignin belong to the white-rot fungi, present mostly in forest, not arable, soils. In arable soils, lignocelluloses are probably degraded by synergistic consortia of microbes (Fungi Imperfecti, the actinomycetes and bacteria). None of the organisms yet isolated can use lignin as a sole C source (Haider 1992). The enzymes involved in lignin degradation are lignin peroxidases (ligninase), manganese peroxidases, lignase, laccases, and glucose oxidases (Martin et al. 1980; Stott et al. 1983; Schoemaker et al. 1985).

Lipase (triacylglicerol acylhydrolase, classified also as carboxylic ester hydrolase, aryl esterase, glycerol ester hydrolase) hydrolyses the initial step of degradation of lipids to fatty acids and glycerol (Alef and Nannipieri 1995; Kirk and Farrell 1987).

Phosphatases represent a broad range of intracellular as well as extracellular enzymes that catalyse the hydrolysis of phosphate esters (Schäffer 1993). These enzymes exhibit rather broad specificity, capable of acting on a numerous of different structurally related substrates at different rates. They include phosphoric monoester hydrolases (i.e. nucleotidases, phytase, sugar phosphatases and glycerophosphatase), phosphoric diester hydrolases (nucleases, phospholipases), triphosphoric monoester hydrolases, and enzymes hydrolyzing P-N bonds, such as phosphoamidases. Phosphomonoesterases are enzymes extensively studied because of their role in hydrolysing of organic phosphomonoester to inorganic phosphorus, which can be taken up by plants. According to the optimum pH, phosphomonoesterases are classified as acid, neutral and alkaline phosphatases (Alef et al. 1995; Bandick and Dick 1999; Schäffer 1993).

Proteases catalyse the hydrolysis of proteins to polypeptides and oligopeptides to amino acids, which are further transformed to ammonium and nitrate. The first step of protein degradation is extracellular because of the high molecular weight of proteins. Proteolytic activity in soil is an important part of the N cycle. Proteins, amino acids, amino sugars, amides and nucleic acids (from plant residues and dead microbial cells) are generally readily degraded by many soil microorganisms via proteolytic enzymes that hydrolyze the peptide links (pronase, proteases, peptidases, amidohydrolases). In soil, proteases are present in living, active cells, in dead cells, as free enzymes and adsorbed to organic, inorganic and organo-mineral particles (Alef and Nannipieri 1995; Schäffer 1993; Schinner and von Mersi 1990).

Saccharase (β-fructosidase, invertase) catalyses the hydrolysis of sucrose to D-glucose and D-fructose (Ross 1965).

Sulphatases include enzymes of the mineralization of organic sulphate esters in soil. There are numerous sulphatases, bound to the cell walls or present in the periplasm. Production of arylsulphatases and choline sulphatase is repressed in the presence of available SO_4^{2-} (Bandick and Dick 1999; Paul and Clark 1996; Schäffer 1993).

Urease catalyses the hydrolysis of urea to CO_2 and NH_3. This enzyme is very widely distributed in nature. Urease is accumulated in soil to a significant extent and is tightly bound to soil organic matter and soil minerals. Because of the agricultural importance of urease as a decomposing agent for urea, which is used as a fertiliser, urease has been widely studied. Urease activity of soil is considered to be due mainly to enzyme located extracellularly (Deng and Tabatabai 1996; Ladd 1978; Schäffer 1993).

Xylanase, acts on β-1,4-xylans present as cell wall constituents of plants. Activity of xylanase includes endoxylanases, which catalyse the hydrolysis of xylans to oligosaccharides, and exoxylanases, catalysing hydrolysis of oligosaccharides to reduced monomers (Alef and Nannipieri 1995; Schäffer 1993; Schinner and von Mersi 1990).

MICROBIALTRANSFORMATION OF SOIL ORGANIC MATTER

The dynamic nature and complex chemistry of soil organic matter makes it a major source of plant nutrients in terrestrial ecosystems. SOM contents range from less than 0.2 % in desert soils to over 80 % in peat soils. With 95 % of soil nitrogen (N), 40 % of soil phosphorus (P) and 90 % of soil sulfur (S) being associated with the SOM fraction, decomposition and turnover can supply most macronutrients needed for plant growth. During decomposition, heterotrophic microorganisms assimilate complex organic substances for energy and carbon (C) and release inorganic nutrients. The special role in nutrient cycling play autotrophic microorganisms which, like higher plants, assimilate CO_2 as well as N_2-fixing bacteria. The processes of soil organic matter transformation are controlled by temperature, moisture, soil disturbance, as well as by the quality of SOM as a microbial substrate (Smith et al. 1993). The close relationships between C availability, activity of soil biomass and nutrient transformations have been established in both laboratory and field experiments. Specific ^{14}C-, ^{15}N-, ^{32}P- and ^{18}O-labelled compounds (including that in plant residues) have been used to describe the degradation of added materials to the soil (Nannipieri et al. 1990).

Plants contain 15-60 % cellulose, 10-30 % hemicellulose, 5-30 % lignin, 2-15 % protein and up to 10 % soluble materials (such as sugars, amino sugars, organic acids and amino acids), (Haider 1992; Paul 1976). Plant residues, freshly incorporated into topsoils, are quickly colonised by a variety of microorganisms. In addition to rhizospheres, decomposing organic particles represent concentrations of biological activity in the soil matrix (“hot spots” of activity), (Ladd et al. 1996). Under suitable conditions of pH, temperature, and moisture content, plant residues are extensively degraded within a few months (Foster 1988; Jenkinson 1981). Most of the plant residue is decomposed in the first year, releasing a significant amount of plant nutrients, and C as CO_2. The remainder decomposes more and more slowly with time and becomes steadily incorporated into soil humus.

During plant matter decomposition, complex compounds are broken down to simpler compounds that can be utilised by the microorganisms. A part of the polysaccharides is depolymerised to disaccharides and then hydrolysed to simple sugars. The more chemically complex compounds undergo a series of catalysed reactions, performed by more than one microbial species. The humified SOM is slow decomposable material that is complexed, to various degrees, with the mineral fraction of the soil. The composition of humic substances depends on plant vegetation (Turski and Flis-Bujak 1982). The active SOM pool consists of readily decomposable C compounds rich in N, P, and S. Microbial biomass pool is central to this model and transforms each component to CO_2, cell biomass and microbial products (Smith et al. 1993).

The uniqueness of nitrogen consists in the fact that the major N forms in organisms (proteins - including enzymes, nucleic acids and cell wall constituents - chitin and peptidoglycan) are very important for the overall vital activity. Transformations of N in soils include mineralization of organic N, N_2-assimilation, nitrification, denitrification and ammonification. (Włodarczyk 2002).

Phosphorus and Sulfur Transformation

It is assumed that uptake of P by microorganisms often exceeds that of the higher plants. However, this short-term bacterial immobilization protects some soil P from long-term fixation in soil minerals. Soil microorganisms are involved in the solubilization of insoluble or poorly soluble inorganic forms as well as in the mineralization of organic P. Thus, soil biota facilitates the availability of P to plants and thus takes part in the soil P cycling. Phosphatases, the enzymes involved in P transformation, have been detected on root surfaces, in the rhizosphere soil, and in soil without plant root influence (Joner et al. 1995; Paul and Clark 1996). Many plants (for instance clover, soybean, tomato and cereals) are known to exude acid phosphomonoesterases from their roots to soil, especially when the plants are grown in phosphorus deficient nutrient solutions (Vuorinen and Saharinen 1996). It has been shown, that fractions of soil organic phosphorus, a product of microbial activity, are transformed rather rapidly in the rhizosphere, where both soil and root phosphatases are active (Helal and Sauerbeck 1991).

Sulfur plays a special role in the stabilization of the biologically active structure of proteins. Sulphatases are enzymes involved in mineralization of sulphate esters in soil. Elemental sulfur (So) must first be converted to sulphate by oxidation before it can be taken up by plants. Nor and Tabatabai (1975) detected thiosulphate as one of the intermediates during So oxidation. Since rhodanese (thiosulphate sulfurtransferase) converts $S_2O_3^{2-}$ to SO_3^{2-}, they hypothesised that it has a role in S^o oxidation in soil. Deng and Dick (1990) suggested that there are other enzyme systems and alternative pathways which are more influential on S^o oxidation than rhodanese.

EFFECT OF SOIL AERATION ON ENZYME ACTIVITY

Soil air-water status plays primary role in the regulation of the composition and metabolic activity of soil microorganisms. Under natural conditions, soil is naturally exposed to the fluctuation of wet and dry cycles and to diurnal and seasonal temperature gradients. 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). Waterlogging or 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 transformations. Well-aerated soils also include numerous permanently anaerobic aggregates and microhabitats. The existence of microaerophilic and anaerobic microsites in soil is vital to biogeochemical cycling of mineral nutrients, including N, C, S, Fe (Gliński and Stępniewski 1985; Metting 1993; Pulford and Tabatabai 1988).

In the absence of molecular oxygen, anaerobic microorganisms (facultative followed by obligatory) utilize oxidised soil components such as NO_3^-, Mn(IV), Fe(III), SO_4^{2-}, CO_2 and dissimilatory products of organic matter as terminal electron acceptors in their respiration (Gliński and Stępniewski 1985; Gunnison et al. 1985; Ottow 1982).

Thus, decomposition of soil organic matter still occurs in O_2 free systems and CO_2 is also formed by anaerobic respiration. The respiration pathways are initiated by action of intracellular dehydrogenases and are terminated (due to the action of different enzymes, e.g. reductases) in the extracellular medium (soil solution). In the result of anaerobic respiration, the stepwise reduction of soil system takes place, soil redox potential (Eh) decreases, pH alters, and concentrations of reduced N-forms, Mn^{2+}, Fe^{2+}, S^{2-} and CH_4 increase (Gliński et al. 1991; Gliński et al. 1996; Gunnison et al. 1985).

It has been observed that dehydrogenase activity is higher in flooded than in well-aerated soil (Baruah and Mishra 1984; Tiwari et al. 1989), and an increase of this activity is accompanied by a decrease of redox potential (Okazaki et al. 1983; Pedrazzini and McKee 1984). Studies of soil in its natural sites, as well as under controlled air-water conditions, showed the close relationship between soil dehydrogenase activity and aeration status (Brzezińska et al. 1998; Brzezińska et al. 2001; Gliński et al. 1986; Gliński et al. 1983; Gliński et al. 2000; Stępniewska et al. 2000; et al. 1997; Stępniewski et al. 2000; Stępniewski et al. 1993). This fact results probably from the much more energetic efficiency of an aerobic respiration (with utilization O_2 as terminal electron acceptor) than that of an anaerobic one. It has been shown that dehydrogenase activity varied during preincubation of the soil under different aeration conditions and was negatively correlated with air-filled porosity (Eg), oxygen diffusion rate (ODR) and redox potential, but positively with water content and concentration of reduced Fe (Stępniewska et al. 2000; Stępniewska et al. 1997). Brzezińska et al. (1998) observed that the modification of the soil physical properties such as water content and temperature, caused changes of the dehydrogenase activity value of loess soils up to 150-fold. They showed that the electron activity of the soil solution (reflected by Eh) is more important for the activity of soil dehydrogenases than the direct availability of O_2 (measured by ODR). Studies of catalase activity showed its dependence on soil aeration status expressed as ODR and Eh (Brzezińska et al. 1998; Stępniewska 2000).

Pulford and Tabatabai (1988) studied the effect of redox potential on the activity of eight enzymes involved in C, N, P and S cycling on soil. They observed that the hydrolysis of native soil organic P and pyrophosphate added to soil is significantly affected by waterlogging. Mostly decreases in phosphatase activities were found, especially in acid and alkaline phosphatase and pyrophosphatase activities. 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. The increase in enzyme activities was perhaps due to inhibition by the reduced metal ions produced upon soil flooding. The increase of enzyme activity resulted probably from the activation of these enzymes by the released metal ions or an increase in the concentration of the enzymes due to microbial adaptation to the reduced environment (Pulford and Tabatabai 1988).

Well aerated soils always have a marked ligninolytic activity with an appropriate microflora and it is possible that this microflora is also active in the degradation of humic compounds, once their intimate association with an inorganic or a structural matrix has been disturbed (Haider 1992; Martin et al. 1980).

Soil is an extremely heterogeneous environmental system in which different physical phases (e.g., solid, liquid, and gaseous) and numerous biotic (e.g., microorganisms, small animals, plant roots, enzymes) and abiotic (e.g., clay minerals, humus material, organomineral aggregates) components are involved in physical, chemical and biological processes. Enzymes ensure the movement of materials among the biotic and abiotic portions of soil environment - all biochemical transformations in soil are dependent on, or related to the presence of enzymes (Burns and Dick 2002; Gianfreda and Bollag 1996; Nannipieri et al. 2002).

REFERENCES

1. Alef K., Nannipier P., Trazar-Cepeda C.: Phosphatase activity. In: Methods in Applied Soil Microbiology and Biochemistry (K. Alef, P. Nannipieri Eds). Academic Press, Harcourt Brace & Company, Publishers, London, 335-344, 1995.
2. Alef K., Nannipieri P.: Enzyme activities. In: Methods in Applied Soil Microbiology and Biochemistry (K. Alef, P. Nannipieri Eds). Academic Press, Harcourt Brace & Company Publishers, London, 311-373, 1995.
3. Bandick A.K., Dick R.P.: Field management effects on soil enzyme activities. Soil Biol. Biochem. 31, 1471-1479, 1999.
4. Baruah M., Mishra R. R.: Dehydrogenase and urease activities in rice field soils. Soil Biology & Biochemistry 16, 423-424, 1984.
5. Bolton H.Jr., Fredrickson J.K., Elliott L.F.: Microbial Ecology of the Rhizosphere. In: Soil Microbial Ecology (Metting F.B.Jr. Ed.) Marcel Dekker, Inc., New York, Basel, Hong Kong. Chapter 2, 27-63, 1993.
6. Brzezińska M., Stępniewska M., Stępniewski W.: Soil oxygen status and dehydrogenase activity. Soil Biol. Biochem. 30, 1783-1790, 1998.
7. Brzezińska M., Stępniewska Z., Stępniewski W., Włodarczyk T., Przywara G., Bennicelli R.: Effect of oxygen deficiency on soil dehydrogenase activity (pot experiment with barley). Int. Agrophysics 15, 3-7, 2001.
8. Burns R.G., Dick R.P.: Enzymes in the Environment. Activity, Ecology and Applications. Marcel Dekker, Inc. New York, Basel, 2002.
9. Burns R.G.: Enzyme activity in soil: Location and possible role in microbial ecology. Soil Biol. Biochem. 14, 423-427, 1982.
10. Burns R.G.: Enzyme activity in soils: some theoretical and practical considerations. In: Soil Enzymes, (R.G. Burns Ed.). Academic Press, London, Chapter 8, 295-326, 1978.
11. Clark A.E., Stone B.A.: Properties of a β-1,4-glucan hydrolase from *Aspergillus niger*. Biochem. J. 96, 802-807, 1965.

12. Curl E.A., Harper J.D. Fauna-microflora interactions. In: The Rhizosphere (J.M. Lynch Ed.). Wiley-Interscience, New York, 369-388, 1990.
13. Deng S., Dick R.P.: Sulfur oxidation and rhodanese activity in soils. Soil Sci. 150, 552-560, 1990.
14. Deng S.P., Tabatabai M.A.: Effect of tillage and residue management on enzyme activities in soils. I. Amidohydrolases. Biol. Fertil. Soils. 22, 202-207, 1996.
15. Dighton J., Jones H.E., Robinson C.H., Beckett J.: The role of abiotic factors, cultivation practices and soil fauna in the dispersal of genetically modified microorganisms in soil. Applied Soil Ecology 5, 109-131, 1997.
16. Dilly O., Nannipieri P.: Intracellular and extracellular enzyme activity in soil with reference to elemental cycling. Z. Pflanzenernähr. Bodenk. 161, 243-248, 1998.
17. Eriksson K.E., Wood T.M.: Biodegradation of cellulose. In: Biosynthesis and biodegradation of wood components (T. Higuchi Ed.). Academic Press, New York, 469-503, 1985.
18. Foster R.C.: Microenvironments of soil microorganisms. Biol. Fertil. Soils 6, 189-203, 1988.
19. Frankenberger W.T.Jr., Dick W.A.: Relationships between enzyme activities and microbial growth and activity indices in soil. Soil Sci. Soc. Am. J. 47, 945-951, 1983.
20. Frankenberger W.T.Jr, Tabatabai M.A.: Factors affecting L-asparaginase activity in soils. Biol. Fertil. Soils 11, 1-5, 1991a.
21. Frankenberger W.T.Jr., Tabatabai M.A.: L-Glutaminase activity if soils. Soil Biol. Biochem. 23, 869-874, 1991b.
22. Frankenberger W.T.Jr., Tabatabai M.A.: Enzyme activity of soils. In: Methods in Applied Soil Microbiology and Biochemistry (K. Alef, P. Nannipieri Eds). Academic Press, Harcourt Brace & Company Publishers, London, 321 -330, 1995.
23. Galstian A.Sh.: Enzymatic activity of soils. Geoderma 12, 43-48, 1974.
24. Gannon J.T., Mingelgrin U., Alexander M. and Wagenet R.J.: Bacterial transport through homogenous soil. Soil Biol. Biochem. 23, 1155-1160, 1991.
25. Gerba C.P., Yates M.V., Yates S.R.: Quantitation of factors controlling viral and bacterial transport in the subsurface. In: Modelling the Environmental Fate of Microorganisms (C.J. Hurst Ed.).. Washington, DC, American Society for Microbiology, 1991.
26. Gianfreda L., Bollag J.M.: Influence of natural and anthropogenic factors on enzyme activity in soil. In: Soil Biochemistry, Vol. 9 (G. Stocky, J.M. Bollag Eds,). Marcel Dekker Inc, New York, Basel, Hong Kong, Chapter 4, 122-193, 1996.
27. Ginn T.R., Wood B.D., Nelson K.E., Scheibe T.D., Murphy E.M. and Clement T.P.: Processes in microbial transport in the natural subsurface. Advances in Water Resources 25, 1017-1042, 2002.
28. Gliński J., Stahr K., Stępniewska Z., Brzezińska M.: Changes of redox and pH conditions in a flooded soil amended with glucose and nitrate under laboratory conditions. Z. Pflanzenernähr. Bodenk. 155, 13-17, 1991.
29. Gliński J., Stahr K., Stępniewska Z., Brzezińska M.: Changes of redox and pH conditions in a flooded soil amended with glucose and manganese oxide under laboratory conditions. Z. Pflanzenernähr. Bodenk., 159, 297-304, 1996.
30. Gliński J., Stępniewska Z., Brzezińska M.: Characterization of the dehydrogenase and catalase activity of the soils of two natural sites with respect to the soil oxygenation status. Pol. J. Soil Sci. 19, 47-52, 1986.

31. Gliński J., Stępniewska Z., Kasiak A.: Changes of soil enzyme activity at different water and oxygen content (in Polish). Roczn. Glebozn. 34, 53-59, 1983.
32. Gliński J., Stępniewski W.: Soil Aeration and its Role for Plants. CRC Press, Boca Raton, Florida, 1985.
33. Gliński J., Stępniewski W., Stępniewska Z., Włodarczyk T. i Brzezińska M.: Characteristics of aeration properties of selected soil profiles from Central Europe. Int. Agrophysics 14, 17-31, 2000.
34. Gostkowska K., Furczak J.: The effect of the cultivation system used on the microbiological activity of loess soil. Pol. J. Soil Sci. 16, 1, 39-45, 1983.
35. Gunnison D., Engler R. M., Patrick W.H.Jr.: Chemistry and microbiology of newly flooded soils: relationship to reservoir - water quality. In: Microbial Processes in Reservoirs (D. Gunnison Ed.). Dr W. Junk Publishers, Dordrecht, Boston, Lancaster, 39-57, 1985.
36. Guwy A.J., Martin S.R., Hawkes F.R., Hawkes D.L.: Catalase activity measurements in suspended aerobic biomass and soil samples. Enz. Microb. Techn. 25, 669-676, 1999.
37. Haider K.: Problems related to the humification process in soils of temperate climates. In: Soil Biochemistry Vol. 7 (G. Stocky, J.M. Bollag Eds). Marcel Dekker Inc, New York, Basel, Hong Kong, Chapter 2, 55-94, 1992.
38. Helal H.M., Sauerbeck D.: Soil and root phosphatase activity and the utilization of inositol phosphates as dependent on phosphorus supply. In: Plant Roots and their Environment (B.L. McMichael, H. Persson Eds). Elsevier Science Publishers B.V., 1991.
39. Jenkinson D.S.: The fate of plant and animal residues in soil. In: The Chemistry of Soil Processes (D.J. Greenland, M.H.B Hayes Eds). John Wiley & Sons, New York, 506-561, 1981.
40. Joner E.J., Magid J., Gahoonia T.S., Jakobsen I.: P depletion and activity of phosphatases in the rhizosphere of mycorrhizal and non-mycorrhizal cucumber (*Cucumis sativus L.*). Soil Biol. Biochem. 327, 1145-1151, 1995.
41. Jones C.G., Lawton J.H., Shachak M.: Organisms as ecosystem engineers. Oikos 69, 373-386, 1994
42. Kandeler E., Tscherko D., Spiegel H.: Long-term monitoring of microbial biomass, N mineralization and enzyme activities of a Chernozem under different tillage *management. Biol. Fertil. Soils* 28, 343-351, 1999.
43. Kennedy A.C.: Bacterial diversity in agroecosystems. Agriculture, Ecosystems and Environment 74, 65-76, 1999.
44. Kilbertus G.: Study of microhabitats in soil aggregates – Relation to bacterial biomass and size of prokaryotes. Rev. Ecol. Biol. Sol 17, 543-557, 1980.
45. Kirk T.K., Farrell L.: Enzymatic "combustion": the microbial degradation of lignin. Annu. Rev. Microbiol. 41, 465-505, 1987.
46. Kiss S., Dragan-Bularda M., Radulescu D.: Biological significance of enzymes accumulated in soil. Adv. Agronom. 27, 25-87, 1975.
47. Kobus J., Kurek E., Józefaciuk C.: The influence of organic fertilization on the biological.
48. Kucharski J., Niklewska T.: The effect of manuring with straw on microbial properties of light soil (In Polish). Pol. J. Soil Sci. 24, 2, 171-177, 1991.
49. Kuprevich V.F., Shcherbakova T.A.: Comparative enzymatic activity in diverse types of soil. In: Soil Biochemistry Vol. 2 (A.D. McLaren, J. Skujins Eds). Marcel Dekker Inc, New York, 167-201, 1971.

50. Ladd J.N.: Origin and range of enzymes in soil. In: Soil Enzymes (R.G. Burns Eds). Academic Press, London, Chapter 2, 51-96, 1978.
51. Ladd J.N., Foster R.C., Nannipieri P., Oades J.M.: Soil structure and biological activity. In: Soil Biochemistry, Vol. 9 (G. Stocky, J.M. Bollag Eds). Marcel Dekker Inc, New York, Basel, Hong Kong, Chapter 2, 23-78, 1996.
52. Lavelle P., Blanchart E., Martin A., Spain A.V., Toutain F., Barois I., Schaefer R.: A hierarchical model for decomposition in terrestrial ecosystems: application to soils of the humid tropics. Biotropica 25, 130-150, 1993.
53. Lipiec J., Hatano R.: Quantification of compaction effects on soil physical properties and crop growth. Geoderma 116, 107-136, 2003.
54. Lipiec, J., Stępniewski, W.: Effect of soil compaction and tillage systems on uptake and losses of nutrients. Soil Tillage Res. 35, 37-52, 1995.
55. Lynch J.M., Bragg E. Microorganisms and soil aggregate stability. Adv. Soil Sci. 2, 133-171, 1985.
56. Madsen L.E., Alexander M.: Transport of *Rhuzobium* and *Pseudomonas* through the soil. Soil Sci. Soc. Am. J. 46, 557-560, 1982.
57. Martin J.P., Haider K. Kassim G.: Biodegradation and stabilization after 2 years of specific crop, lignin, and polysaccharide carbons in soils. Soil Sci. Soc. Am. J. 44, 1250-1255, 1980.
58. Megharaj M., Singleton I., Kookana R., Naidu R.: Persistence and effects of fenamiphos on native algal populations and enzymatic activities in soil. Soil Biol. Biochem. 31,1549-1553, 1999.
59. Metting F.B.Jr.: Structure and Physiological Ecology of Soil Microbial Communities. In: Soil Microbial Ecology (Metting F.B.Jr. Ed.) Marcel Dekker, Inc., New York, Basel, Hong Kong. Chapter 1, pp. 3-25, 1993.
60. Misaghi I.J., Olsen M.W., Billotte J.M., Sonoda R.M.: The importance of rhizobacterial motility in biocontrol of bacterial wilt of tomato. Soil Biol. Biochem. 24, 287-293, 1992.
61. Myśków W., Stachyra A., Zięba S., Masiak D.: Biological activity as index of soil fertility (In Polish). Roczn. Gleb. 47, 1/2, 88-99, 1996.
62. Nannipieri P., Grego S., Ceccanti B.: Ecological significance of the biological activity in soil. In: Soil Biochemistry, Vol. 6 (J.M. Bollag, G. Stocky Eds). Marcel Dekker Inc, New York, Basel, Hong Kong, Chapter 6, 293-355, 1990.
63. Nannipieri P., Kandeler E., Ruggiero P.: Enzyme activities and microbiological and biochemical processes in soil. In: Enzymes in the Environment. Activity, Ecology and Applications (R.G. Burns and R.P. Dick Eds) Marcel Dekker, Inc. New York, Basel, 2002.
64. Nor Y.M., Tabatabai M.A.: Colorimetric determination of microgram quantities of thiosulfate and tetrathionate. Anal. Lett. 8, 537-547, 1975.
65. Nunan N., Wu K., Young I.M., Crawford J.W., Ritz K.: Spatial distribution of bacterial communities and their relationships with the micro-architecture of soil. FEMS Microbiology Ecology 44, 203-215, 2003.
66. Okazaki M., Hirata E., Tensho K.: TTC reduction in submerged soils. Soil Sci. Plant Nutr. 29, 489-497, 1983.
67. Ottow J.C.G.: Bedeutung des Redoxpotentials für die Reduktion von Nitrat und Fe(III)-Oxiden in Böden. Z. Pflanzenernäh. Bodenk. 145, 91-93, 1982.

68. Paul E.A., Clark F.E.: Soil Microbiology and Biochemistry (Eds E.A. Paul, F.E. Clark). Academic Press, Inc., 129-179, and 289-313, 1996.
69. Paul E.A.: Dynamics of organic matter in soils. Plant Soil 76, 275-285, 1976.
70. Pedrazzini F.R., McKee K.L.: Effect of flooding on activities of soil dehydrogenases in rice (*Oryza sativa L.*) roots. Soil Sci. Plant Nutr. 30, 359-366, 1984.
71. Pulford I.D., Tabatabai M.A.: Effect of waterlogging on enzyme activities on soils. Soil Biol. Biochem. 20, 215-219, 1988.
72. Ranjard L., Richaume A.: Quantitative and qualitative microscale distribution of bacteria in soil. Res. Microbiol. 152, 707-716, 2001.
73. Ross D.J.: A seasonal study of oxygen uptake of some pasture soils and activities of enzymes hydrolysing sucrose and starch. J. Soil Sci. 16, 73-85, 1965.
74. Ruggiero P., Dec J., Bollag J.M.: Soil as a catalytic system. In: Soil Biochemistry, Vol. 9. (G. Stocky, J.M. Bollag Eds). Marcel Dekker Inc, New York, Basel, Hong Kong, Chapter 3, 79-122, 1996.
75. Russel S.: Methods of soil enzymes deterimation (In Polish). PTG. Komisja Biologii Gleby. Warszawa 1972.
76. Schäffer A.: Pesticide effects on enzyme activities in the soil ecosystem. In: Soil Biochemistry, Vol. 8. (J.M. Bollag, G. Stocky Eds). Marcel Dekker Inc, New York, Basel, Hong Kong, Chapter 8, 273-340, 1993.
77. Schinner F., von Mersi W.: Xylanase-, cellulase- and invertase activity in soil: an improved method. Soil Biol. Biochem. 22, 511, 515, 1990.
78. Schoemaker H.E., Harvey P.J., Bowen R.M., Palmer J.M.: On the mechanism of enzymatic lignin break-down. Fed. Eur. Biochem. Soc. 183, 7-12, 1985.
79. Sessitsch A., Weilharter A., Gerzabek M.H., Kirchmann H., Kandeler E.: Microbial population structures in soil particle size fractions of a long-term fertilizer field experiment. Appl. Environ. Microbiol. 67, 4215-4224, 2001.
80. Skujins J.: Extracellular enzymes in soil. CRC Crit. Rev. Microbiol. 4, 383-421, 1976.
81. Skujins J.: History of abiontic soil enzymes research In: Soil Enzymes (R.G. Burns Ed.). Academic Press, London, Chapter 1, 1-49, 1978.
82. Smith J.L., Papendick R.I., Bezdicek D.F., Lynch J.M.: Soil organic matter dynamics and crop residue management. In: Soil Microbial Ecology (F.B.Jr. Metting Ed.). Marcel Dekker, Inc., New York, Basel, Hong Kong, Chapter 3, 65-94, 1993.
83. Stępniewska Z., Brzezińska M., Gliński J., Stępniewski W., Włodarczyk T., Čurlik J., Houšková B.: Aeration status of some Slovakian soils. Int. Agrophysics 14, 327-339, 2000.
84. Stępniewska Z., Gliński J., Włodarczyk T., Brzezińska M., Blum W.E.H., Rampazzo N., Wimmer B.: Soil aeration status of some Austrian soils. Int. Agrophysics 11, 199-206, 1997.
85. Stępniewski W., Stępniewska Z., Gliński J., Brzezińska M., Włodarczyk T., Przywara G., Várallayay G., Rajkai K.: Dehydrogenase activity of some Hungarian soils as related to their water and aeration status. Int. Agrophysics 14, 341-354, 2000.
86. Stępniewski W., Stępniewska Z., Włodarczyk T., Dąbek-Szreniawska M., Brzezińska M., Słowińska-Jurkiewicz A., Przywara G.: Aeration related properties and their influence on soil biological parameters. Int. Agrophysics, 7, 163-173, 1993.
87. Stevenson F.J.: Cycles of soil: carbon, nitrogen, phosphorus, sulphur, micronutrients. John Wiley & Sons, New York, 1986.

88. Stott D.E., Kassim G., Jarrel W.M., Martin J.P., Haider K.: Stabilization and incorporation into biomass of specific plant carbon during biodegradation in soil. Plant Soil 70, 15-26, 1983.
89. Tiwari M. B., Tiwari B. K., Mishra R. R.: Enzyme activity and carbon dioxide evolution from upland and wetland rice soils under three agricultural practices in hilly regions. Biol. Fertil. Soils 7, 359-364, 1989.
90. Trasar-Cepeda, C., Camina, F., Leirós, M.C., Gil-Sotres, F.: An improved method to measure catalase activity in soils. Soil Biol. Biochem. 31, 483-485, 1999.
91. Turski R., Flis-Bujak M.: The influence of crop rotation on the composition of humic compounds in loess soils. Pam. Puł. 77, 33-47, 1982.
92. Vuorinen A.H., Saharinen M.H.: Effects of soil organic matter extracted from soil on acid phosphomonoesterase. Soil Biol. Biochem. 10/11, 1477-1481, 1996.
93. Walczak R., Rovdan E., Witkowska-Walczak B.: Water retention characteristics of peat and sand mixtures. Int. Agrophysics 16, 161-165, 2002.
94. Witkowska-Walczak B., Walczak R.: Water characteristics and evaporation of soil aggregates formed from the different soils. J. Hydrol. Hydromech. 47, 417-429, 1999.
95. Włodarczyk T.: Nitrogen transformations and their circumstances in soils. Acta Agrophysica 61, 2002.
96. Wong P.T.W., Griffin D.M.: Bacterial movement at high matrix potentials, part II. In fungal colonies. Soil Biol. Biochem. 8, 219-223, 1976.
97. Young I.M. and Ritz K.: Can there be a contemporary ecological dimension to soil biology without a habitat? Discussion. Soil Biol. Biochem. 30, 1229-1232, 1998.
98. Young I.M. and Ritz K.: Tillage, habitat space and function of soil microbes. Soil and Tillage Research 53, 201-213, 2000.

EXPERIMENTAL VERIFICATION OF THE AGROPHYSICAL MODELS

Fernández J.E., Slawinski C., Moreno F., Lamorski K.,
Walczak R.T., Vanclooster M.

INTRODUCTION

Mathematical and physical models are useful tools in agriculture research and engineering. They may be used for many different applications, from pure modelling of transport phenomena in soil medium to application such as yield prediction. Even models which are describing in a proper way physical processes in modelled object, may not give accurate results, when good values of physical parameters of modelled object are not known.

Generally model have to be first calibrated for application in which when will be used. Even if the model have been widely used, uncertainties still arise when they are applied to conditions different than those for which the model was previously tested. Some precautions should be considered, and the procedures could be followed to evaluate the performance of a leaching simulation mode, in view of a management application. Basically, it is recommended that the model must be correctly tested using high quality data sets for which the model is intended to be used. Special care should be paid to the estimation of the model inputs. A clear distinction must be made between model calibration, which is an inverse modelling parameter estimation, and model prediction evaluation. It is suggested to use independent modelling data sets for each of these phases. The appropriateness of the model predictions must be objectively assessed by simulation graphics or using statistical model indicators.

EXAMPLE: WAVE & ACCESS

As an example we consider calibration and validation of two models used for crop prediction and hydrological modelling.

WAVE 2.1 (Vanclooster et al., 1996), from now on referred to as WAVE, and EURO-ACCESS-II (Armstrong et al., 1996), from now on referred to as ACCESS, are comprehensive deterministic integrated models simulating the fate of water, heat and solutes in the soil-crop system.

The water component of the WAVE model has been used for the analysis of flow behaviour in controlled laboratory experiments, field experiments, and regional scale assessments. The model has further successfully been used for modelling fate of nutrients and agro-chemicals, and crop production in the soil-crop environment at different scales.

In contrary to the WAVE model, the water component of the ACCESS model considers explicitly a horizontal flow model (Slawinsky et al., 1996). It is also conceived to take into account bypass flow through cracks and macro-pores (Walczak et al., 1996). Apart from simulations of water fluxes in the soil, ACCESS has also been used for yield prediction .

Both models were calibrated and validated with two different field data sets. The experimental field was near Seville, southwest Spain, situated in a semi-arid Mediterranean area. Simulation graphics and modelling statistics were used to assess the validity of the results predicted by the models. Sensitivity analysis was carried out to identify the crucial input parameters of both models. The possible influence of the spatial and temporal variability of the main soil characteristics on the modelling results is further discussed.

CALIBRATION DATA SET

Basically, maize was grown consecutively from 1991 to 1996 under Mediterranean management practices in the Guadalquivir River Valley. The experiments were carried out in the experimental farm La Hampa, of the Instituto de Recursos Naturales y Agrobiología, Spanish Council for Scientific Research (southwest Spain, 37º 17’ N, 6º 3’ W, elevation 30 m). The average rainfall (P, mm) for the period 1971-1999 is 494 mm. Rain falls mainly from October to May, being dry and hot for the rest of the year. About 625 mm of water was supplied by furrow irrigation during each crop season (end of March – middle of August) to cover the crop water needs. The physical and chemical properties within the field were studied in detail by sampling and analysing the soil at a 5 x 5 m grid scale. The soil showed to be highly uniform with depth and was classified as a sandy loam Xerochrept. Measurements of soil water content (q, m3 m-3; neutron probe and gravimetric), soil matric potential (h, MPa; mercury tensiometers) and hydraulic conductivity (K, mm h-1; the internal drainage method) were taken at three locations within the field. The sampling locations were defined in terms of the results of the spatial variability study. Crop height (h_c, m) was measured five times during the crop period of 1992, and every week in 1993. These measurement were done on one plant of each 5 x 5 m grid. Leaf area index (LAI) was determined for the fully mature crop in 1992, and every 7-10 days in 1993, on three plants of a representative size. Root depth (z_r, m) and crop yield (Y, kg ha-1) were determined at the end of both crop periods. The water lost through drainage (D, mm) was estimated using Darcy’s law and the $K(q)$ relationships determined in the field. The crop evapotranspiration (ET_c, mm) was determined from the water balance equation. The values of ET_r needed for determining K_c were calculated from the data recorded at the automatic weather station of the farm, some 120 m from the experimental plot. Weekly averages of ET_c and ET_r were calculated for the whole crop periods.

MODEL TESTING

The WAVE and the ACCESS models were tested following the two-phases protocol. In a first phase – the calibration phase - the values of the model input parameters were taken from the measurements carried out in the experimental field during the 1993 crop period. Parameters like the saturated hydraulic conductivity which in the model are considered as being static, exhibited important temporal variations. In these cases, a mean value for the whole calibration period was considered as initial parameter set. The model parameters were calibrated by the trial and error method, minimising thereby the difference between the simulated and measured data. The parameter perturbation was made within the range of physical possible values. In a subsequent phase – the validation phase - an independent data set was used to test the model's prediction capacity. For this data set was used data of the 1992 crop period, and no adjustments of the model parameters was thereby done.

CALIBRATION

The ET_c and D values simulated by both models during the calibration phase, corresponding to the 1993 crop period, agreed well with the values determined from the field measurements (Figure 1). The seasonal time courses of both variables were better described by the WAVE model, although the simulations of the ACCESS model were also reasonably good. The values of ET_c and D for the whole crop season inferred from simple mass balance calculations (ET_c = 640 mm; D = 58 mm) were very similar to the simulated values by WAVE (ET_c = 626 mm; D = 71 mm) and ACCESS (ET_c = 629 mm; D = 78 mm). Figure 2 shows the measured and simulated values of q at five different depths for the 1993 cropping season. These graphical calibration results are completed with the statistical model indicators calculated for the same period (Table 2). Lower values of RMSE were obtained with WAVE than with ACCESS, except for the 0.2-0.4 m and 0.4-0.6 m soil layers. The inability of the model to reconstitute the soil moisture correctly at the 0.4-0.6 m soil depth is a well known problem in the WAVE 2.1 version which is attributed to a poor performing root uptake mechanism in the subsoil. The RMSE suggests that WAVE was slightly better in predicting q than ACCESS. The same conclusion can be drawn when analysing the values of EF. In fact, the EF values of WAVE were closer to one than those of ACCESS, except when considering the total soil moisture storage in the profile. In this case both models yielded similar EF values. The results of Figure 2 and Table 2 show that, in general, any of the two models can be used with confidence for simulating the total soil moisture storage in the profile, but that caution should be taken when simulating moisture contents at different soil layers.

In addition to quantifying the modelling error, considerable attention must be paid to the origin of the modelling error when assessing the model performance. A substantial part of this modelling error is due to scale problems in the data collection and parameter identification phase. Actually, parameters governing in situ water flow are well known to be subjected to important spatio-temporal variations. Any spatial or temporal variation in the soil texture or soil compaction, for instance, will have a significant impact on the lack of agreement between the predicted and the measured results, if it is not well reflected in the modelling structure.

As expected, the prediction of the crop water consumption by both models depended very much on the input values of *LAI*, as well as on K_c for WAVE . This is well reflected in the results from the sensitivity analysis made for WAVE and ACCESS (Table 2). Therefore the user of any of these models should pay special attention to the accuracy of the input *LAI* values, and take into account the quick variations of this variable in certain periods of the crop development. In the WAVE model just a reduced number of K_c values can be input for the whole crop period, which can be the reason for part of the disagreement between the observed and the predicted results. It is well known that the actual K_c values may vary markedly in short periods of time. In this work was used as input three K_c values for each of the studied crop periods.

The values of q_{init} and K_{sat} resulted to be less crucial than those of *LAI* and K_c (Table 2). However, the model user should be aware of possible errors coming from spatial variations of q_{init} and K_{sat}. In addition, the temporal variation of K_{sat}, due mainly to soil compaction throughout the crop period, is not taken into account by the models, since just a single average K_{sat} value can be input for each considered soil layer.

VALIDATION

The validation exercise, carried out for the 1992 cropping period, gave satisfactory results for both models (Figure 3). As in the calibration exercise, the ET_c and D values predicted by WAVE (ET_c = 589 mm; D = 144 mm) were closer to the values calculated from a simple field water balance (ET_c = 610 mm; D = 167 mm) than those predicted by ACCESS (ET_c = 664 mm; D = 82 mm). Both models can be considered, in fact, as useful tools for predicting crop water consumption and water losses by drainage in areas under similar conditions to our experimental plots. This is of particular importance for optimising water use in the vast areas of Mediterranean climate where irrigated maize is cropped. The use of the models may not only improve water saving, but may also minimise groundwater contamination by fertilisers and pesticides. Reasonably good results were also obtained in the q values predicted for the five considered soil layers. The graphical simulation shown in Figure 4 is completed with the statistical evaluation of the results shown in Table 2. Both analysis of the deviations between the predicted and observed q results show a performance for both models as good as during the calibration phase, in some cases even better. It can therefore be assumed that both the WAVE and the ACCESS models are reliable engineering tools for predicting water dynamics in the soil-plant system of an irrigated cropped plot of sandy loam soil under semi-arid Mediterranean conditions.

SUMMARY & CONCLUSIONS

Our results shows that good predictions of the soil moisture status can be expected when using any of the two evaluated models, provided they have been previously calibrated for the conditions in which they are used. If the model calibration phase is not correctly made, the predicted results by both models may be far away from reality.

Special care has to be paid to the errors in the input values coming from spatial and temporal variability. The user must be aware that scale discrepancies exist between the experimental techniques with which system variables can be monitored and/or system parameters be identified and the system variables considered in the models. This scale discrepancy justifies the calibration phase. As such, calibration can be considered as stage in which a-priori modelling data, inferred from a set of local scale experiments, are corrected to estimate the effective field parameters which match the ‘observed’ field system. It is obvious that the ‘effective’ parameter sets obtained from calibration will be conditioned to the quality of the data with which system variables can be mapped, and are therefore subjected to the spatio-temporal resolution of the adopted sampling scheme.

This training material is based on publication [2].

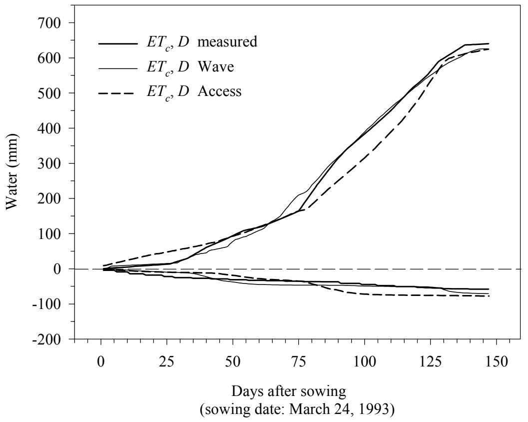


Fig. 1. *Results on the time course of the crop evapotranspiration (ET_c) and drainage (D) simulated with the WAVE and the ACCESS models during the calibration test, corresponding to the crop period of 1993. The ET_c and D results from the field measurements are also shown*

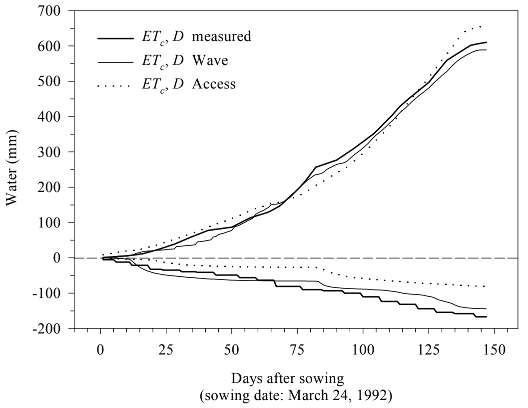


Fig. 2. *Results on the time course of the crop evapotranspiration (ET_c) and drainage (D) simulated with the WAVE and the ACCESS models during the calibration test, corresponding to the crop period of 1993. The ET_c and D results from the field measurements are also shown.*

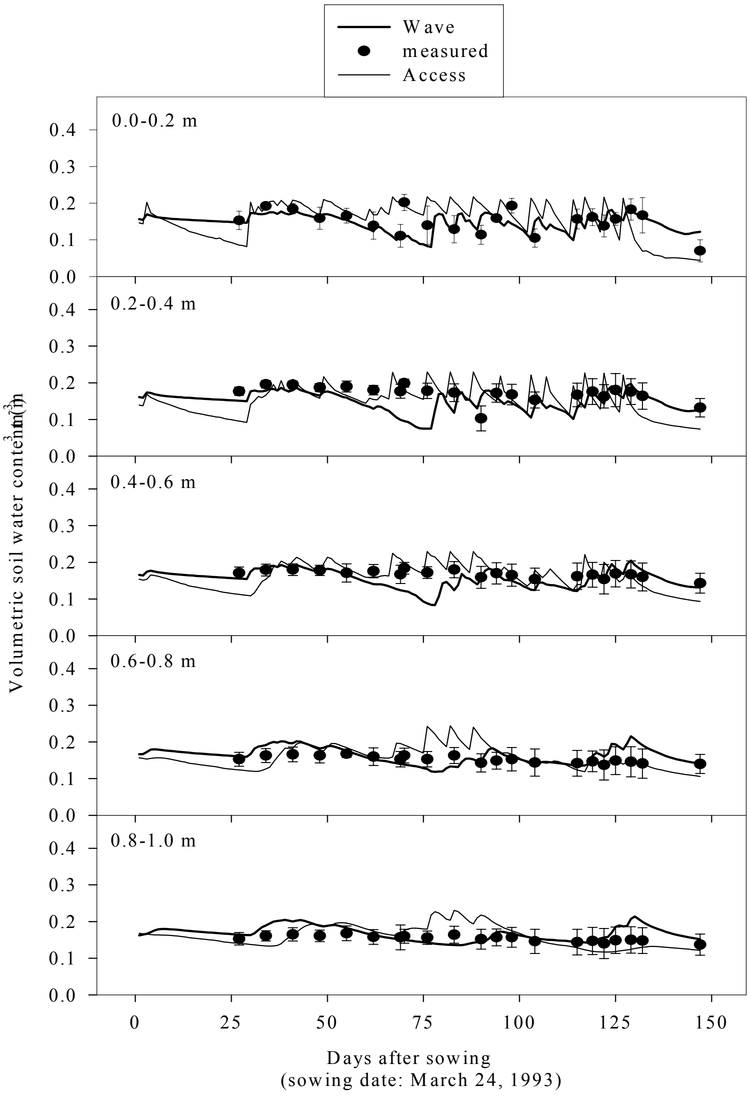


Fig. 3. *Results on the time course of the volumetric soil water content in the five soil layers considered in the evaluation of the WAVE and ACCESS models during the calibration test. The data correspond to the crop period of 1993. Each point represents the average of three values measured in representative locations of the experimental plot. The vertical bars represent the 95 % confidence interval.*

Table 1. Statistical performance criteria for the simulated volumetric water content in the different soil layers and complete soil profile during the model calibration (1993 crop period) and the model validation (1992 crop period) phase. n = number of observations or predictions; RMSE = Root mean square error; EF = model efficiency. Details on the statistical indicators are given in the text.

		1993 crop period			
		WAVE		ACCESS	
Depth (m)	n	RMSE	EF	RMSE	EF
0.0-0.2	21	21.96	-0.08	35.97	-1.89
0.2-0.4	21	26.16	-1.34	24.08	-2.77
0.4-0.6	21	19.56	-1.91	18.72	-8.97
0.6-0.8	21	17.99	-7.61	22.63	-12.71
0.8-1.0	21	15.90	-7.42	18.94	-11.95
0.0-1.0	105	15.58	0.96	20.49	0.96
		1992 crop period			
		WAVE		ACCESS	
Depth (m)	n	RMSE	EF	RMSE	EF
0.0-0.2	21	18.21	-4.69	19.18	-0.25
0.2-0.4	21	16.38	-0.57	24.41	-3.93
0.4-0.6	21	20.33	-0.27	21.66	-7.06
0.6-0.8	21	26.37	-0.18	19.41	-6.17
0.8-1.0	21	31.20	-0.88	18.90	-6.80
0.0-1.0	105	15.62	0.96	16.09	0.96

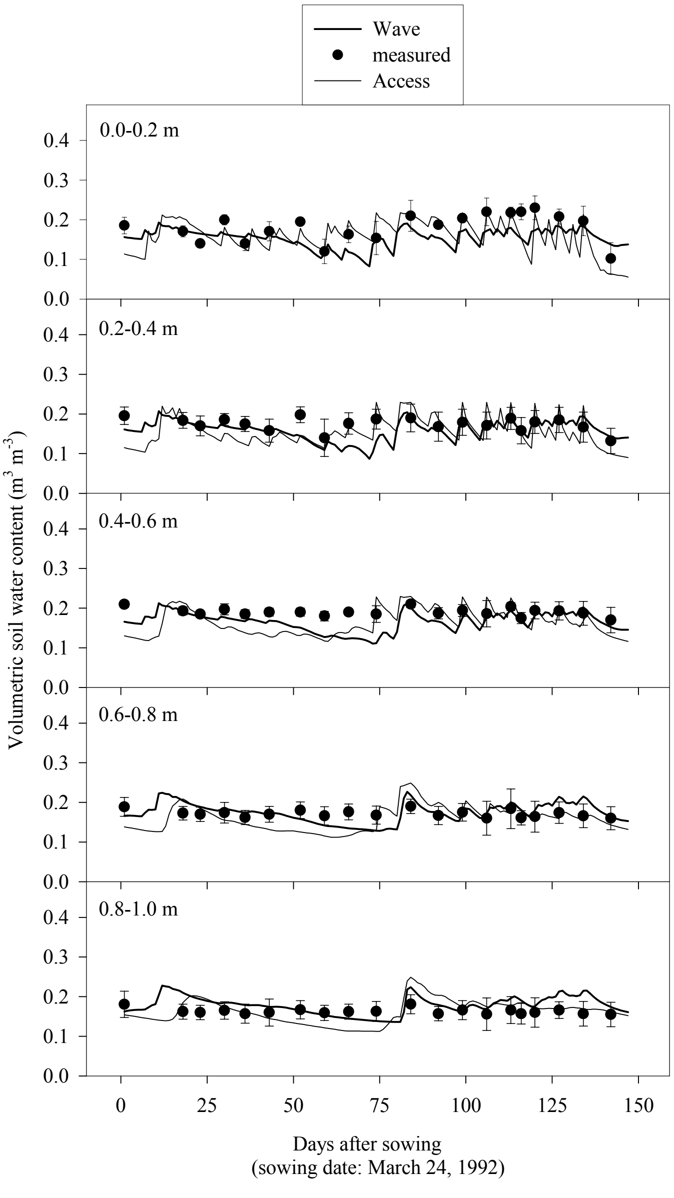


Fig. 4. *Results on the time course of the volumetric soil water content in the five soil layers considered in the evaluation of the WAVE and ACCESS models during the calibration test. The data correspond to the crop period of 1993. Each point represents the average of three values measured in representative locations of the experimental plot. The vertical bars represent the 95 % confidence interval.*

Table 2. Sensitivity analysis for the WAVE and ACCESS models in which the influence of key input parameters (K_{sat} = hydraulic conductivity in the range near saturation; $\theta_{initial}$ = volumetric soil water content at the beginning of the simulation period; LAI = leaf area index; K_c = crop coefficient) on the crop evapotranspiration (ET_c), drainage (D) and volumetric soil water content (θ) has been determined. The analysis shown here was made with the results of the 1993 crop period.

	Sensitivity coefficient for		
Parameter	ET_c	D	θ
WAVE			
K_{sat}	0.005	0.014	-0.017
$\theta_{initial}$	0.006	0.394	0.026
LAI	0.035	-0.183	-0.026
K_c	0.174	-1.0	-0.130
ACCESS			
K_{sat}	0.016	0.337	-0.060
$\theta_{initial}$	0.004	-0.060	0.034
LAI	-0.034	-0.121	0.115

REFERENCES

1. Armstrong, A. C., Legros, J. P., Voltz, M.: „ACCESS-II: detailed model for crop growth and water conditions." Int. Agrophysics. Vol. 10 (1996), No 3, 171-184.
2. Fernandez J.E., Slawinski C., Moreno F., et al.: „Simulating the fate of water in a soil-crop system of a semi-arid Mediterranean area with the WAVE 2.1 and the EURO-ACCESS-II models", AGR WATER MANAGE 56 (2): 113-129 JUL 30 2002
3. Slawinski C., Sobczuk, H. Walczak, R. T.: „Submodel of bypass flow in cracking soils. Part 1 – Theory.", Int. Agrophysics. Vol. 10 (1996), No 3, 189-195.
4. Vanclooster, M., Viaene, P., Christiaens, K., Ducheyne, S.: "WAVE, release 2.1, Instruction Manual." Institute for Land and Water Management, Katholieke Universiteit Leuven, Vital Decosterstraat 102, B-3000 Leuve, Belgium, 1996
5. Walczak, R. T., Sobczuk, H., Sławinski C. „Submodel of bypass flow in cracking soils. Part 2 – Experimental validation.", Int. Agrophysics. Vol. 10 (1996), No 3, 197-207

POROUS STRUCTURE OF NATURAL BODIES

Hajnos M.

INTRODUCTION

Porosity is one of more important parameters characterizing porous bodies. The solid phase of a given body may be either nonporous (cast, monolyte) or may contain pores - spaces filled by liquid or gas phases. The pores may be open and/or closed, may have different shape, may be available or nonavailable from the surface of the body, may have very different sizes. So, the **porosity** is defined as the occurrence of internal spaces in solid body.

A measure of the porosity is a volumetric ratio of all free spaces to the bulk of the body. The latter value is called **absolute porosity** (m^3/m^3). The other definition, **relative porosity** (m^3/m^3), is a ratio of a volume of available (open) pores only to the bulk volume of the body.

Both porosity values may be expressed also as percentage or, which is frequently used, as volume of pores in a mass unit of the body (m^3/kg).

Porous structures may be formed in several ways:

- As a result of connection of smaller nonporous units (grains) into larger aggregates. The porous structure is thus formed from internal spaces between the grains and the grains themselves form the structure skeleton. Such materials have **granular structure**.
- As a result of the removal of some part of the solid from monolytic body (e.g. leaching, dissolution). Such materials have a **sponge structure.**
- As a result of both processes together.

For most porous materials one can distinguish the **intergranular porosity** (between the grains) which is called bed porosity and **intragranular porosity** (inside the individual grains). Solid bodies may have also a geometrically irregular surface, which is difficult to distinguish from “real” pores. The pore is thus defined by a convention as the surface cavity having larger depth than the half of its average size (e.g. the radius for cylindrical pore).

The pores may be classified according to different criteria:

According to their availability from outside (Fig. 1) one distinguishes:

Unavailable pores (totally closed, isolated) – having any connection with surface of the solid body (e.g. occluded gas or liquid bubbles in rocks). Such pores are not detected by most porosimetric methods, however they influence among others the measurements of solid phase density, shear stresses under high pressures and may be responsible for a collapse of a solid under high external forces.

Available pores – connected with the surface either indirectly or via other pores (channels). These pores are subdivided on several groups:

- **pores available from one side** (one-side open)
- **pores available from two sides** (two-side open),
- **connected pores**,

- **pore nets or clusters** – systems of interconnected pores (channels, voids, cavities).

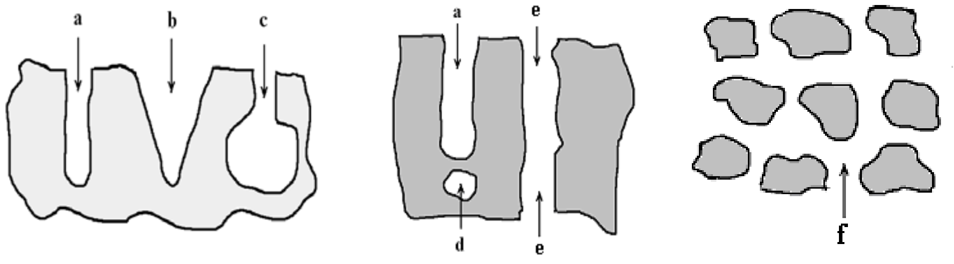


Fig. 1 *Pore types. One-side open pores: cylindrical - a, conical - b, bottle - c. Unavailable pore- d. Two-side open pore - e. Pore net - f.*

The shape of natural pores is usually nonuniform. Their complicated build-up for calculation purposes is usually approximated by selected geometrical models. Among many models (slit-like, ink-bottle, conical, globular etc.) the most frequently used is a cylindrical pore model.

According to the dimension of pores, that is connected with the method of their measurement, one distinguishes:

From point of view of capillary condensation process, **Dubinin** proposed the following classification:

- macropores – more than 200 nm in radius; in such pores no capillary condensation occurs but they may be important in diffusion transport of molecules,
- mesopores - 2 - 200 nm in radius; in these pores capillary condensation takes place,
- micropores – less than 2 nm in radius; in these pores no capillary condensation occurs, but a volumetric filling with adsorbate vapor Dubinin – Radushkevich theory).

A popular soil science classification (**Luxmoore**) is based on water retention (pF curve) in soils and is related to plant water availability. One distinguishes capillary and noncapillary (aeration) pores. The boundary between the above is 20 μm in diameter (pF = 2,2). In pores larger than 20 μm (macropores) the water is passed through with gravitational force.

Less than 20 μm, capillary pores are divided on criteria of water availability for plants:

- storing easily available water, d = 20 - 3 μm (pF = 2,2 - 3)
- storing difficult available water, d = 3 - 0,2 μm (pF = 3 - 4,2)
- storing unavailable water, microcapilary pores, d < 0,2 μm (pF > 4,2).

Smart classified pores according to image resolution:

- for an eye - larger than 200 μm
- for microphotography – larger than 6 μm

- for optical microscopy – larger than 0,2 μm.

Geenland had distinguished:

- bonding pores (<5 nm), important for menisci forces connecting primary soil aggregates;
- residual pores (5 - 500 nm), important for soil reactions on molecular level;
- water storage pores (0,5 - 50 μm), storing water available for soil organisms;
- transmission pores (50 - 500 μm), important for water movement and roots penetration

These nonuniform classification systems lead to misinterpretations of porosity. Therefore the International Union of Pure and Apllied Chemistry (**IUPAC**) reccommends use of the following terms:

- micropores – of radii less than 2,0 nm
- mesopores - between 2,0 and 50 nm
- macropores – larger than 50 nm.

Various pore size classification systems presented above are summarized in Fig. 2.

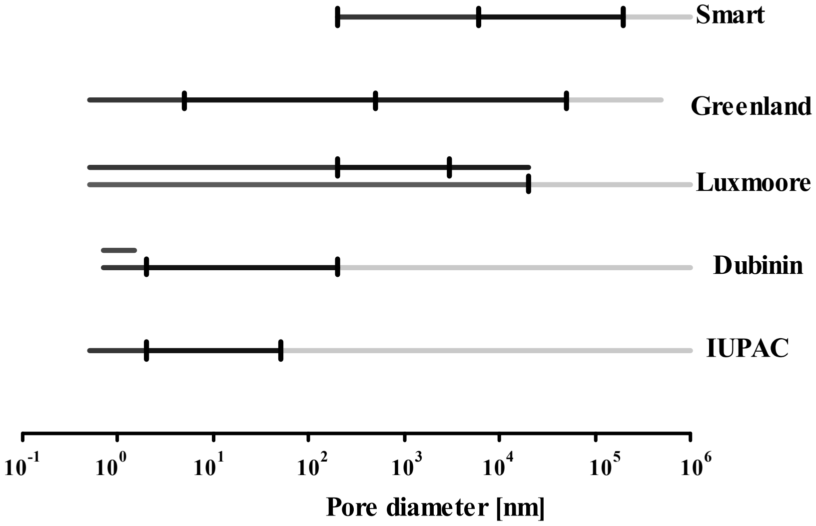


Fig. 2. *Comparison of pore classifications according to their sizes (explanations in the text).*

MEASUREMENT OF ABSOLUTE AND RELATIVE POROSITY

Total (absolute and/or relative) porosity may be estimated from measurements of the bedvolume (or bulk density) and the solid phase density. The open pores volume may be estimated pycnometrically basing on Boyle-Mariotte gas law.

Total porosity value is of less importance for characteristic of porous materials because provides no information on pore dimensions and number. The same total porosity can result from small number of large pores and large number of small ones despite both above materials have quite different properties. More important pore characteristic is than a function relating pore volume and dimensions within defined pore size class (pore size distribution).

MEASUREMENT OF PORE SIZE DISTRIBUTION

The pore size distribution is determined using so called direct and indirect methods.

Direct methods are usually used for investigation of larger than 30 μm pores and indirect methods for studying of smaller pores. Direct methods are based on an analyze of cross sections of porous bodies: nontransparent sections in reflected light and transparent ones in transmitted light microscopy. Soil cross sections are useful for determination of pore shapes. Image analyze of XRD and NMR scanning photographs is used, as well.

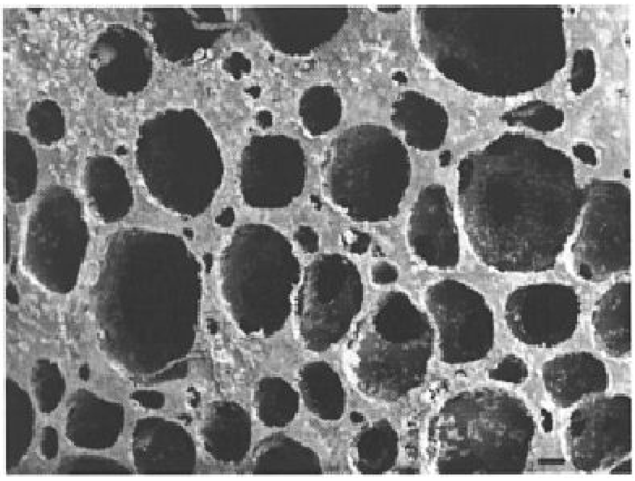


***Fig. 3.** The example of the microscopic picture to the analysis in the direct method.*

Indirect methods determine pore size distributions basing on measurements of other physicochemical parameters related to pore sizes and volumes as for example gas, vapor or liquid volume and pressure present within and over the sample of porous body in equilibrium. The gas or vapor condensed in a pore or liquid filling the pore form a lens-shaped surface, called meniscus. The pressure difference across the meniscus (inside and outside the pore), ΔP, is related with the curvature of the meniscus r (and so the pore dimension) according to Young-Laplace equation:

$$\Delta P = \frac{2\gamma}{r}$$

where γ is a surface tension of the liquid (condensate) present in a pore.

The curvature of the meniscus is dependent somehow with the pore dimension. One relates these two values using any convenient pore model, which is selected either operationally or basing on a knowledge of the sample structure. As far as the model pore shape may not reflect the real pore shape, the pore dimensions calculated using models are called equivalent dimensions. The pore size distributions coming from indirect measuring methods do not include closed, nonavailable pores.

Among most frequently used indirect porosimetric methods one can list mercury intrusion, nitrogen or water vapor sorption and water retention. The ranges of (equivalent – cylindrical model) pores detected by the above methods are:

- from water vapor desorption isotherms: 1,6 to 60 nm;
- from mercury intrusion porosimetry: 3,7 to 7500 nm;
- from water retention (pF) curves: 95 to 150000 nm.

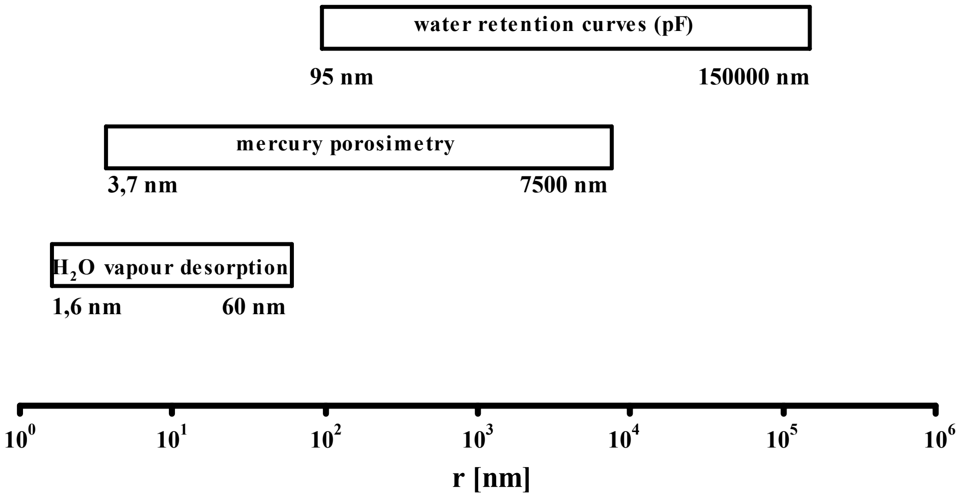


Fig. 4. *The ranges of pores detected by the above methods.*

MERCURY INTRUSION POROSIMETRY TECHNIQUE

The mercury intrusion porosimetry involves forcing of mercury into soil samples at increasing hydraulic pressure. Because mercury does not adhere to most of solids (the contact angle is higher than 90 degs), it enters the pores only when an external pressure (p_m) is applied (for example water of contact angle close to 0 degs enters the pores spontaneously). The higher the pressure, the mercury is force to narrower pores. The pores should be empty at the beginning and so the sample is outgassed at a vacuum prior to the mercury intrusion. The mercury intrusion porosimetry apparatus registers the volume V of the mercury forced into the sample against the intrusion pressure $V = V(p_m)$.

The volume V of the mercury forced into the pores is related directly to the pore volume and the intrusion pressure may be related to the (equivalent) pore radius using Washburn equation:

$$r_0 = -2\gamma_m \cos\theta_m / p_m$$

where: γ_m - is a mercury surface tension, θ_m - is mercury – solid contact angle (for soils this equals to 141,3 degs).

The volume of pores having radii less than say r_0 is calculated as:

$$V(r < r_0) = V_0 - V_S - V(p_m)$$

where: V_S - is a volume of sthe solid phase of the porous body, V_0 - is a volume of all pores before the intrusion of mercury and $V(p_m)$-the volume of the intruded mercury at a pressure p_m.

Measurement:

1. Placing sample in dilatometer.
2. Evacuating sample for 30 - 60 min to remove air.
3. Filling with mercury.
4. Apply pressure for meso and fine pores.

The idea of the mercury intrusion measurements is briefly illustrated in Fig. 5.

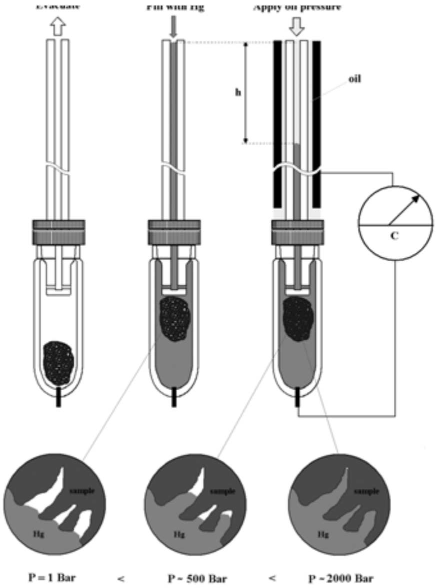


Fig. 5. *An idea of mercury intrusion porosimetry.*

Mercury intrusion data are plotted either in a form of cumulative curve showing total pore volume vs. pore size (Fig. 6.) or in a form of a derivative curve (Fig 7.) showing volumetric fractions of pores of different sizes.

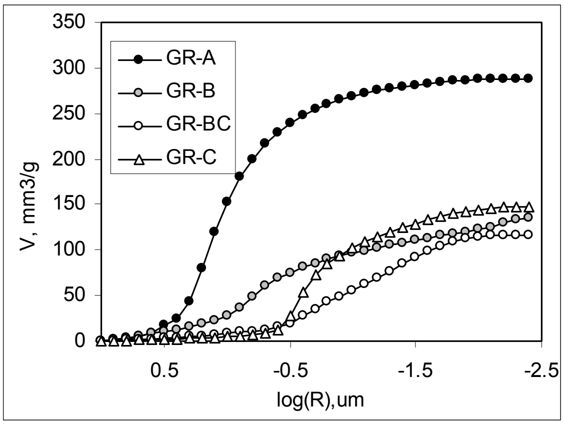


Fig.6. *Cumulative porosimetric curves for exemplary soil samples. V - pore volume, R – pore radius*

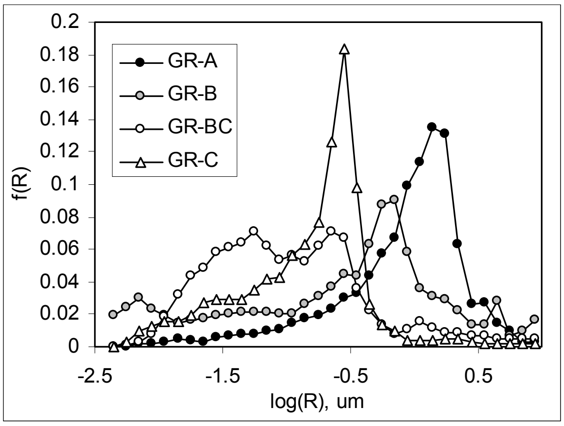


***Fig.** 7. Differential porosimetric curves exemplary soil samples*. f(R) *fraction of pores of radii - R*

Mercury intrusion porosimetry is widely used for characterizing mesopore structure of various porous materials: soils, minerals, sorbents, ceramics, building materials, as well as for plants and food products.

MECHANICAL PROPERTIES OF AGRO- BULK MATERIALS

Horabik J., Molenda M.

ABSTRACT

This work addresses the mechanical properties of agro- bulk materials important for storage, handling and processing technologies. The influence of the properties of individual particles and the geometrical structure of the bedding on the mechanical characteristics of the material was discussed. Examples of the anisotropy of the grain bedding and the swelling pressure of wetted grain were used to indicate the need for precise characterization of agricultural granular materials and food powders.

Keywords: granular materials, mechanical properties

INTRODUCTION

Storage and processing of granular materials are employed in numerous industries and are of interest to various branches of science and technology such as physics, chemistry, mechanics, agriculture and engineering. Agriculture and the food industry are, next to chemical and pharmaceutical industries largest producers and users of granular materials. Two basic conditions have to be fulfilled by equipment for storage and processing of granular materials: predictable and safe operations and obtaining high quality of final products.

Granular materials are distinctly different than typical forms of matter: gases, liquids and solids. Sometimes the statement is made that granular materials should be treated as an additional state of matter. Three types of effects typical for granular materials make them different from the other forms of matter: static friction between particles, non-elastic collisions and approximately zero energy of thermal movements as compared to potential energy due to the gravity. Faced with this mixture of known and unknown physical laws governing behaviour of granular materials engineering practices have been developed to solve practical problems.

In recent decades increases in the number of processes and operations involving granular materials have resulted in a growing need for new theory and technology. This was accompanied with growing interest in investigations of physical properties of granular materials. Elaboration of effective design methods of technological processes requires detailed knowledge of physical properties of the processed material as well as proper understanding of their interrelations with construction materials. Development and refinement of methods for determination of physical properties of granular materials is becoming particularly important. Despite unquestionable progress in development of measurement methods mechanical properties of granular materials measured in various laboratories can vary greatly. A significant source of the wide range of results is due to the large number of measurement methods and a lack of standard experimental procedures. Unification of terminology and standardization of measuring methods and test procedures in the field of mechanics of particulate solids currently undertaken in EU countries help in understanding and comparison of results from different, cross-disciplinary laboratories. Moreover some influencing factors such as moisture content, bulk density, packing structure and load history remain out of control that contribute to observed variability.

Granular materials of biological origin constitute a coherent group of materials distinguished by large deformability of particles and strong dependence of their mechanical properties on moisture content. Contrary to materials of mineral origin, moisture penetrates inside grain, leading in some cases to qualitative changes in physical properties.

The results presented in this paper were selected from several different completed projects and concern the: characterization of physical properties of agro-bulk materials and food powders, and the influence on pressure distribution in the silo during storage and handling.

WALL FRICTION

Friction of grain against construction materials depends on numerous factors, which the most important are: type of material, moisture content of grain, normal pressure, sliding path, orientation of grain against direction of sliding, air temperature and relative humidity and grain genus and variety. Coefficients of friction of various grain differ sometimes distinctly. One of the reasons for this variability are differences in roughness and texture of grains surfaces. Grain moisture content is also considered as one of the main reasons for variability in grain coefficient of friction. Coefficient of friction of cereal grains increases with an increase in moisture content, particularly above 13% [3].

Frictional interaction between grain and the bin material may change the value of coefficient of friction. During prolonged sliding, cutin a wax-like substance from the grain seed coat accumulates on the smooth contact surface [6].

INTERNAL FRICTION

The angle of internal friction depends on the properties of individual particles and on the geometrical structure of the bedding [3]. In the case of cereal grains factors that influence physical properties of kernels are: moisture content, genus, variety, state of maturity and conditions of cultivation. Factors that effect density of packing and spatial structure of arrangement of grains are: bedding formation, moisture content, pressure and time of storage. Dry cereal grain is in general considered cohesionless, and should be considered free-flowing. Cohesion arises for high moisture contents and long storage time.

MECHANICAL CHARACTERISTICS

Angle of internal friction is based on the stress-strain relationship obtained from experiments as e.g. direct shear test. Investigations of granular materials have traditionally used a procedure proposed by Jenike [4] with his direct shear apparatus. Stress-strain shearing curves for particular materials can differ substantially. Fig. 1 shows smooth curve that represented shearing of wheat flour, the curve with irregular oscillations illustrated shearing of salt, and the shearing curve of agglomerated milk, fine milk and potato starch showed very regular oscillations. This sawtooth pattern resulted in large variation in the shear stress for very small displacements. The amplitude of the oscillation was found to be proportional to the normal stress. The pitch of oscillation was determined to increase for an increase in normal stress. The pitch of oscillation was the highest for the agglomerated milk (approx. 0.5 mm) and the lowest for the potato starch (approx. 0.1 mm). The pitch of oscillation is a fraction of the mean grain diameter (0.2 and 0.16) in the case of the agglomerated milk and the fine milk and equals to approx. 3 grain diameter in the case of the potato starch. Therefore, it is probable that for this two group of powders two different mechanisms of the shear stress oscillation take place.

Cycles of hardening and weakening of the material in the narrow regions of shear zones are considered to be the source of the observed oscillations [1]. Maksimovic [5] indicated four components related to the angle of maximum shearing strength: the angle of physical friction, the angle of degradation, the angle of reorientation, and the angle of dilation. All four components are of different significance for different types of granular solids. The angle of physical friction depends on the material. This value is recorded only as combined with the values of angles of degradation and reorientation. It seems the most probable that in the case of the agglomerated milk and the powder milk grain degradation contributes the strongest the shear strength oscillation while in the case of the potato starch a component related to the grain reorientation is the strongest.

Molenda *et al.* [8] indicated that a probable reason of the stress oscillation during shearing of the soybean meal was the high compressibility of the material. Oscillation can be considered as part of a sequence of compaction-dilation events occurring around the area of shear zones developing in the material. Compaction of the particulate material resulted in an increase in material strength and the ability to withstand higher shear loads. When the maximum strength of the particulate material is exceeded dilation in the shear zone occurs resulting in a sharp decrease in the shear load. This leads to limiting mechanisms of slow dilatant plastic shear deformation. The extra angle of shearing of dense powders can be related to the rate of dilation and hence to the relative density and mean effective stress.

ANISOTROPY OF GRAIN BEDDING

Determination of the angle of internal friction with a triaxial shear test and a direct shear test have shown that the angle of internal friction increased with an increase in the angle between direction of preferred orientation of grains and the direction of sliding. Cereal grains are clearly non-spherical. In the case of wheat, the length of grain is approximately twice its width. When grains are oriented in random and packed with uniform density the bedding is isotropic and homogeneous. When longest axes of grains are oriented along certain directions the bedding shows anisotropic properties. Its strength is different in different directions. Slow rolling of grains along the cone of natural repose is an easy way to observe an example of formation of anisotropic bedding. (Fig. 2).

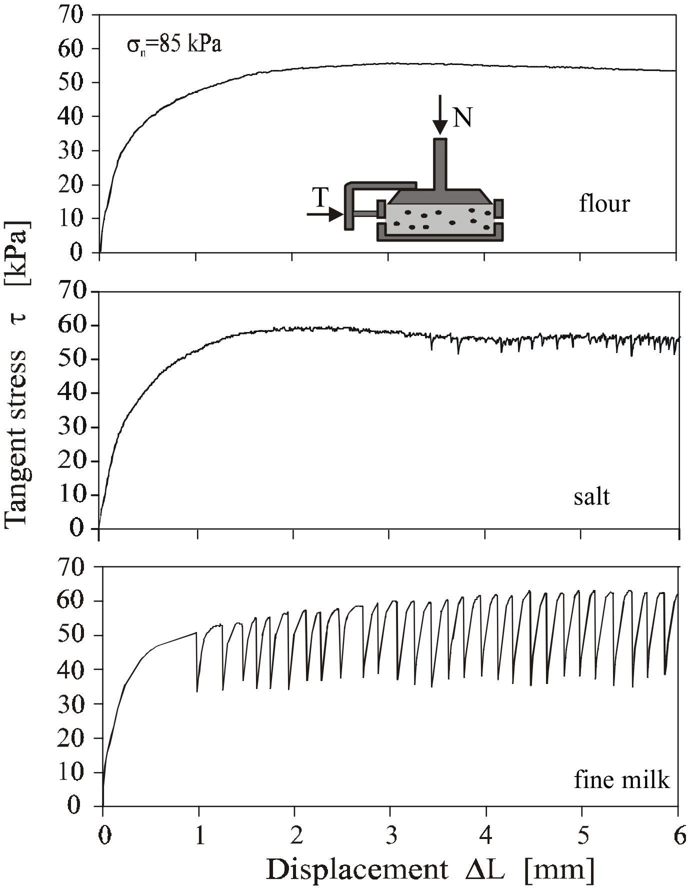


Fig. 1. *Comparison of the tangent stress-displacement relationships: smooth curve for wheat flour; irregular vibration for NaCl salt, and saw blade curve for fine milk [1].*

SWELLING OF GRAIN BEDDING

The uncontrolled increase of moisture content may take place in stored grain due to grain respiration or as a result of wetting with ambient air during aeration. Increased grain moisture content leads to an increase in volume. Walls of the silo confine deformation of the grain in the horizontal direction that may lead to an increased lateral pressure.

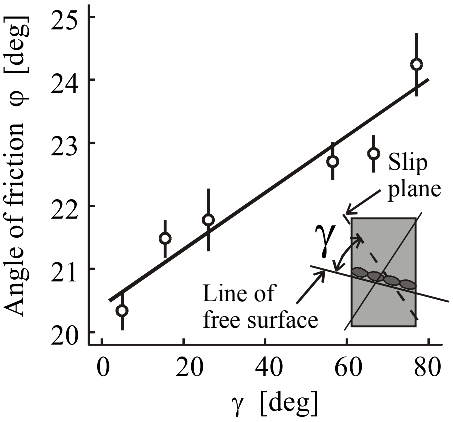


Fig. 2. *The influence of the angle of preferred grain orientation γ on the angle of internal friction φ [6].*

The mean lateral pressure σ_n on the wall of the model silo of 0.6 m in diameter and height as influenced by the moisture content increase for two values of initial moisture content was presented in Fig. 3. The swelling pressure increased linearly with the moisture content increase with the rate of 125 kPa*kg/kg. Comparison of two experimental relations for very close values of the initial moisture content indicates that swelling pressure is strongly influenced by the initial moisture content of grain. Another factor influencing value of the swelling pressure was a bedding structure of grain created during the filling procedure. The bedding structure influences the pore structure and distribution and, ultimately, the permeability of the layer of grain. Although the filling procedure was exactly the same in each replication of the experiment, the bedding structure may have differed considerably among replications. This is the most probable reason of relatively large variation of the swelling pressure values among replications of the test. The initial bulk density was a major factor influencing swelling pressure.

INVESTIGATIONS ON SILO MODELS

Investigations on model silos have been conducted in the Granular Mechanics Laboratory of the Department of Biosystems and Agricultural Engineering at the University of Kentucky, USA [7]. The tests were performed on smooth and corrugated-walled model silos 2.4 m in diameter and 7.3 m high. The wall and floor of the silo were each supported independently on three load cells to isolate the wall and floor loads. Such an experimental configuration allowed for determination of vertical wall and floor loads, and of the resultant moment exerted by grain on the wall and floor of the silo. Moment of force was a global measure of the asymmetry of pressure distribution. The silos were filled to a height to diameter ratio (H/D) of 2.75 and next discharged through the centric or eccentric orifice.

Eccentric discharge of the silo generates strong asymmetry of loads (Fig. 4). As suggested by silo users, such loads asymmetry may lead to ovalization of the wall, and after a longer period of operation or in the case particularly high loads may cause silo failure. The wall bending moment was found to be the highest for the discharge orifice located at half the radius of the silo floor. Smoother silo wall resulted in larger asymmetry of load distribution.

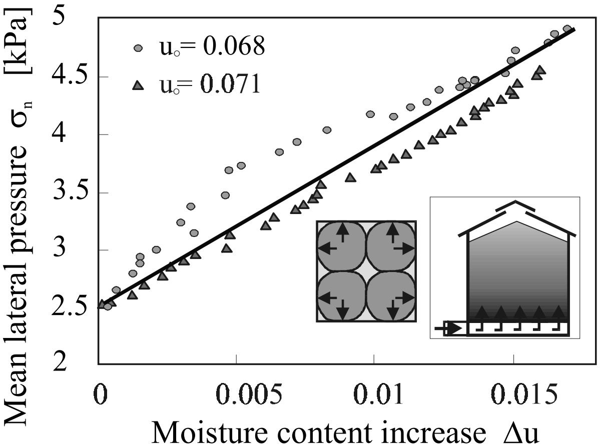


Fig. 3. *Mean lateral pressure σ_n on the silo wall as influenced by the moisture content increase Δu [2].*

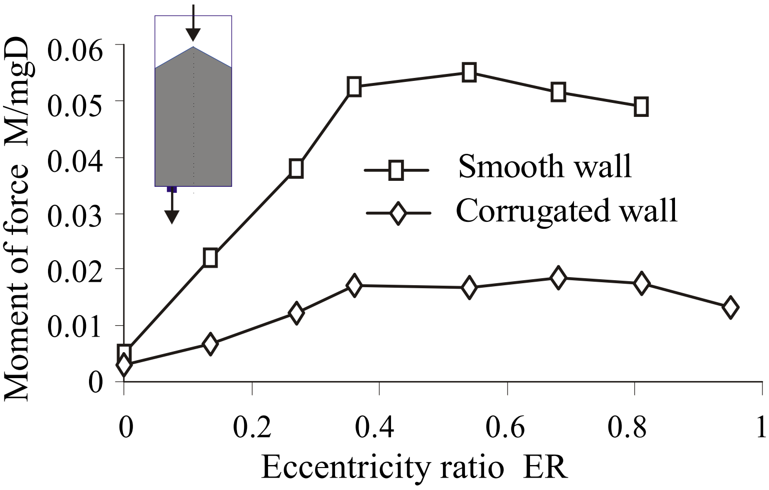


Fig. 4. *Dimensionless moment of force exerted by grain on the bin wall during eccentric discharge of the corrugated and smooth wall bin [7].*

CONCLUSION

There is a need for precise characterization of agricultural granular materials and food powders. A wide range of variability of material parameters has to be accepted as an inherent feature of the material because of the considerable number of factors which can influence these types of materials. Development and refinement of methods for determination of physical properties of granular materials is still important.

REFERENCES

1. J. Horabik, M. Grochowicz. Strength and dilatation of food powders. International Agrophysics, 16(3), (2002), 183-189.
2. J. Horabik, M. Molenda. Grain pressure in a model silo as affected by moisture content increase. International Agrophysics, 14(4), (2000), 385-392.
3. J. Horabik, M. Molenda, R. Rusinek, M. Stasiak. Influence of selected parameters on friction of cereals grain. Acta Scientiarum Polonorum - Technica Agraria, 1(2), (2002), 81-87 (in Polish).
4. A.W. Jenike. Storage and flow of solids. Bull. 123, Eng. Expt. Sta., Utah State Univ., (1964)
5. M. Maksimovic. A family of nonlinear failure envelopes for non-cemented soils and rock discontinuities. Electronic Journal of Geotechnical Engineering, 1, (1996), 1-15.
6. M. Molenda, J. Horabik, M. Grochowicz, B. Szot. Friction of wheat grain. Acta Agrophysica 4, (1995) (in Polish)
7. M. Molenda, J. Horabik, I.J. Ross. Comparison of loads on smooth- and corrugated-wall model grain bins. International Agrophysics, 15(2), (2001), 95-100.
8. M. Molenda, M.D. Montross, J. Horabik, I.J. Ross. Mechanical properties of corn and soybean meal. Transactions of the ASAE, 45(6), (2002), 1929-1936.

SURFACE CHARGE OF SOILS

Józefaciuk G.

Except of organogenic elements (carbon, hydrogen and oxygen), being the basic tissue material, the plants need also mineral elements taken from soils via their root system. Mineral elements may occur in soils as soluble salts in the soil solution, as hardly soluble precipitates, and as ions electrostatically bound to charged soil components.

Electric charge of soil components may be divided onto two general types: permanent charge and variable charge.

The permanent charge occurs mainly in clay minerals, which dominate in soil clay fraction. This fraction contains soil material of finest sizes (less than 2μm particles). Clay minerals, formed as secondary weathering minerals, are hydrated aluminum (or rarely magnesium) silicates of layer structure. They are built from couple of subsequent flat layers of silicon oxide and aluminum oxide. The permanent charge origins from imperfections of the crystal structure of the minerals. The most frequent phenomenon responsible for these imperfections is that higher valence cations in the crystal lattice (for example silicon in the silica layers) are substituted by lower valence cations (for example by aluminum) during the genetic processes. This results in the "unsaturation" of oxygen bonds and excess of the negative charge. The substituting cation should be of similar size to this being replaced, therefore this process is called isomorphic substitution, which is very schematically presented in Figure 1.

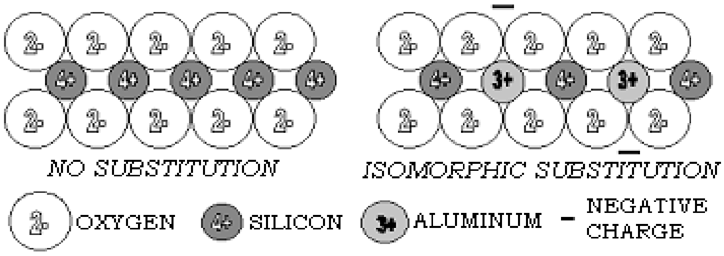


***Fig. 1**. Isomorphic substitution of silicon by aluminum in the clay lattice*

Frequently the summarical amount of the charge resulting from the isomorphic substitution is not equal to the permanent charge of the mineral. For example a part of the lattice charge may be neutralized by specifically bound cations inside the mineral particle structure (i.e. in the spaces between several subsequent structural layers – interlayers), as this frequently occurs in illites (binding of potassium cations) and is schematically presented in Figure 2.

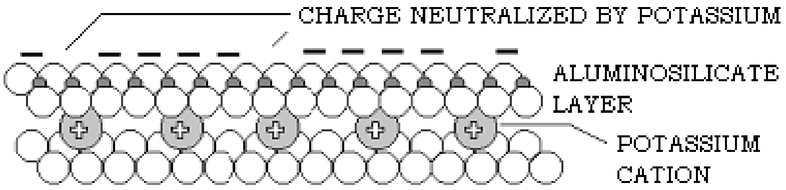


***Fig. 2**. Neutralization of the lattice charge by potassium cations.*

The amount of permanent charge is characteristic for the mineral and conditions of its genesis. For most frequently occurring clay minerals this charge amounts from a few (kaolin group) by few tens (mica group – illites) to hundreds (smectites, zeolites) of centimoles per kilogram of the mineral (1centimole = 965 Coulombs = $6{,}023 \times 10^{21}$ elementary charges).

Permanent charge minerals dominate in mineral soils of the temperate climatic zone, therefore soils of these regions are called permanent charge soils.

Variable charge occurs on surfaces of most soil solid phase constituents: organic matter, aluminum, iron and silicon oxides, edges of clay minerals (on their basal surfaces the permanent charge is exposed) and many more. Contrary to the permanent charge, the magnitude of the variable charge depends on the of the composition of the soil solution (pH, concentration, ionic composition). The variable charge origins from dissociation and association of hydrogen ions (protons) from/to surface functional groups.

On surfaces of soil organic matter functional groups of acidic character dominate. An increase of the pH of the soil solution leads to the neutralization of the active protons of these groups thus they become negatively charged, forming negative surface charge. Such reactions are similar to the reactions of neutralization e.g. simple organic acids, as this is illustrated below for acetic acid:

$$CH_3COOH + OH^- \longleftrightarrow CH_3COO^- + H_2O,$$

but in soil organic matter the acidic groups are bound to the surfaces of organic macromolecules of complicated composition and very high molecular weight:

$$\text{SURFACE-}CH_2COOH + OH^- \longleftrightarrow \text{SURFACE-}CH_2COO^- + H_2O,$$

Acidic functional groups of soil organic matter (aliphatic and aromatic carboxylic, phenolic etc.) have very different acidic strength, depending not only on the kind of the group, but also on its locality. Analogically, the carboxylic group has different acidity in simple aliphatic acids, depending on the chain length to which the group is connected: the formic acid HCOOH is rather strong, the acetic acid CH_3COOH is weaker, the propionic acid CH_3CH_2COOH is much weaker and so long. Surface groups of stronger acidic character (similarly as stronger acids) are neutralized at lower pH values. The weaker acidic is the group, its neutralization requires higher pH value. Therefore the higher is the soil pH, the larger surface charge occurs on organic matter surfaces.

These acidic surface groups, which are located closely to each other, create common electric field surrounding these groups and within this field their protons become delocalized (proximity effect). The delocalized protons behave as strong acids and so the neighboring groups are strongly acidic and the soil organic matter has some negative charge even at very low pH values. Above processes are illustrated in Figure 3.

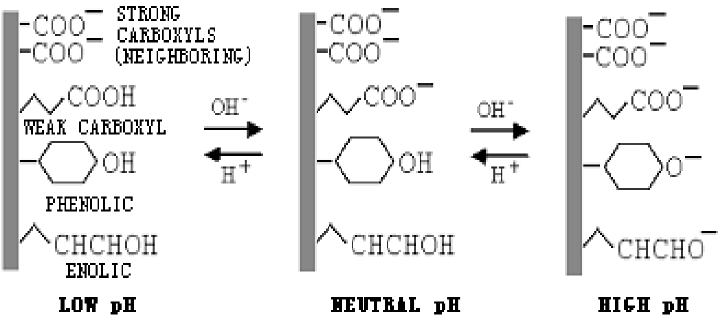


Fig. 3. Formation of negative variable charge on soil organic matter.

Depending on soil pH value, surfaces of some mineral soil constituents can have either positive, zero or negative charge. In relatively low pH range, surface hydroxylic groups (SURFACE-OH) of these constituents may associate protons from soil solution via hydrogen bonds thus the surface becomes positively charged. In relatively high pH range, these surface hydroxyls may also undergo acidic dissociation, resulting in formation of negative charge. At a defined pH value the surface hydroxyls neither associate the protons from the solution nor dissociate their own ones and the surface has no charge. The latter value of pH is called point of zero charge (PZC). One can imagine the above reactions are similar to these illustrated in Figure 4 for aluminum (or iron) oxide.

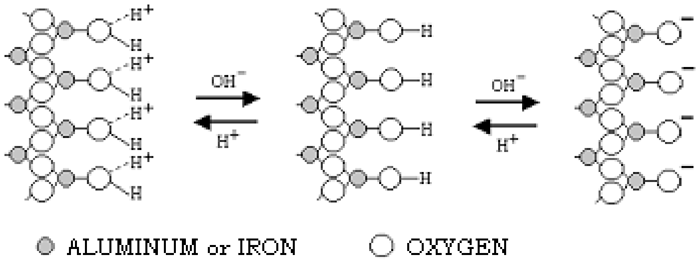


***Fig. 4.** Formation of variable charge on surface of aluminum and iron oxides.*

The point of zero charge for some most frequently occurring soil constituents is: 3-4 for silicon oxides, 5-8 for iron oxides, 6-10 for aluminum oxides. The PZC of edge surfaces of clay minerals is most frequently around 8,2.

Variable charged mineral constituents, mainly oxides and hydroxides of iron, aluminum and silicon and mixed aluminum-silicon oxides – allophanes and imogolites occur in large amounts in highly weathered soils of humid tropics and subtropics, therefore soils of these climatic zones are called variable charge soils.

The charged surface attracts ions of opposite sign of charge (counterions) from soil solution and repels ions of the same sign (coions). The tendency of the whole system to rich minimum potential energy would request the counterions to locate just near the surface and the coions to be repelled far away. The simultaneous tendency to rich maximum dissipation (entropy) would request an uniform distribution of both counter and coions in the solution. Thus, in the system, the potential energy factor is responsible for accumulation of most counterions close to the surface and repulsion of the coions while the entropy factor causes diffusion of some counterions out from the surface and of coions to the surface. As a result of these two opposite tendencies, the specific distribution of the ions near the surface occurs which meets the conditions of minimum free enthalpy. The ions balancing surface charge together with the charged surface are called diffuse double layer (DDL). The schematic build-up of this layer is shown in Figure 5. In this Figure, only counterions distribution is depicted.

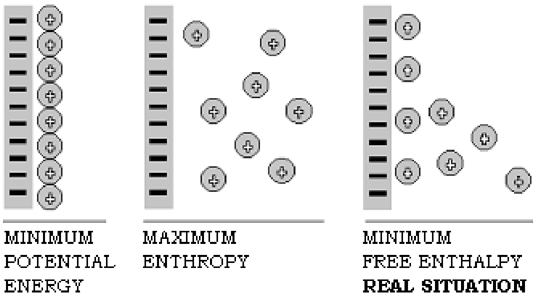


Fig.5. *Distribution of counterions near negatively charged surface.*

Prevalence of negatively charged surfaces in temperate climatic zone soils causes that they bound mainly cations. And so the troubles with anionic fertilization may arise. For example the negatively charged nitrate anions are repelled to the solution and they are easily washed out from the soil with the rainwater. Therefore this is better to apply the nitrate fertilizers in a few doses rather than in a single one, or to use foliar application. In mineral soils of humid tropics, having usually lower pH than the PZC, the deficit of cationic nutrients is a frequent phenomenon.

The counterions present in the DDL, as bound to the surface with rather low energies via electrostatic forces, may be easily exchanged with other ions being actually in an excess in soil solution as soluble salts. This process is called ion exchange and is schematically presented in Figure 6. The formal boundary between the DDL and the bulk solution is drawn as a dashed vertical line.

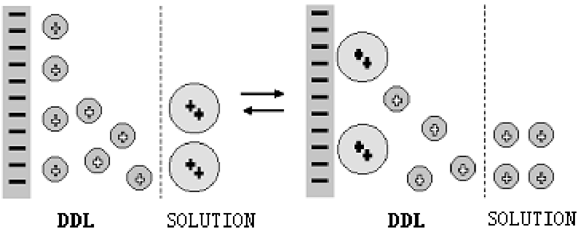


Fig.6. *Schematic view on cation exchange.*

The higher is the charge of the counterion and the higher is its mass, the higher is the force of its binding in the DDL and so this ion is more difficult to be exchanged by other ions. Therefore acidic soils may loose their ability to bind nutrient cations: trivalent aluminum cations or polymeric aluminum cations of large charge and mass may be so strongly bound that the soil charge becomes almost totally blocked. Deblocking of soil surface charge and renovation of exchange properties of the soil requests neutralization of aluminum and its precipitation as oxides, which can be performed by liming.

Cations adsorbed in the DDL (cations of soil exchange complex) are easily taken by plants. To fulfill the condition of an electric neutrality of the system, the plant should release the equivalent amount of cations to the soil. These ions are hydrogen ions, because the plant can not produce the other ones. This is one of the important mechanisms of soil acidification, and is more pronounced in agricultural areas from which the soil nutrients are removed from soils together with the taken biomass. Therefore the crops need the mineral nutrients supply. In natural environments the cations taken from soils, or at least their large part, may return to the soil after decomposition of the died plants. From this reason this is advantageous to leave the crop residues in the field after harvesting.

Taking into account a basic character of the presented material, this is obvious that this does not pretend to fulfill all scientific standards. Therefore I propose some nice books for further reading:

REFERENCES

1. Bolt G.H., Bruggenwert M.G.M., 1976, “Soil Chemistry A. Basic elements.” Elsevier, Amsterdam.
2. Bolt G.H., 1982, “Soil Chemistry B. Physicochemical models.” Elsevier, Amsterdam.
3. Dinauer R.C., ed. 1977, "Minerals in Soil Environments", SSSA, Madison Wisc. USA.

TRANSFORMATION OF SOIL ORGANIC MATTER

Księżopolska A.

THE ROLE OF ORGANIC MATTER AND SOIL FERTILITY

One of the fundamental tasks of contemporary agriculture is to maintain optimum soil fertility in the situation of increasing demand for plant and animal products. A basic requirement for this is to maintain in the soil a correct proportion between the content of organic mater and that of the mineral components. The soil organic matter consists of humus compounds proper and small organic parts with undisturbed tissue structure, whose separation from completely humified organic residue is practically impossible. Therefore it is assumed, in a broad and general sense, that organic matter is synonymous with humus. Humus, as a specific form of organic substance, gradually decomposing in the course of mineralization processes, is the source of numerous nutrients necessary for plant growth and development. Therefore, the content of humus in mineral soils is an index of their productivity. The role of humus is very important, due to the direct and indirect functions it has in the formation of the physical, chemical and biochemical properties of soils. The presence of humus in soils has a positive effect on the formation of the water-resistant structure of the soils, and on the development of favourable water-air and thermal relations. However, it should be emphasized that humus rich in fractions of durable humus-mineral compounds is better preserved in soils. Organic compounds are not only a source of nitrogen and carbon dioxide, but also play an important role in decontaminating the soil environment from various toxic substances, e.g. heavy metals.

TRANSFORMATION OF SOIL ORGANIC MATTER AND FACTORS AFFECTING ITS COURSE

All the processes affecting soil fertility are based primarily on the transformation of organic matter. Organic matter is composed of organic compounds of various origins, containing carbon, hydrogen, oxygen, nitrogen, and other elements. In the agricultural sense, these are organic fertilizers which, after their introduction to the soil, are defined as organic soil mater. The organic soil matter includes also post-harvest and animal residues, as well as products of the metabolism of various soil organisms, at varying degrees of decomposition and humification. Organic matter in the soil is in a state of dynamic equilibrium, as processes of mineralization and humification occur simultaneously. Organic matter introduced in the soil with organic fertilizers and that remaining in the fields in the post-harvest residue differ considerably in terms of their chemical composition. However, for the determination of the humus-forming value, the content of carbon and nitrogen in organic fertilizers is of the utmost importance. Under specific soil conditions, as a result of the processes of decomposition and synthesis, humus compounds of a concrete C:N ratio develop from the organic matter. In arable soils the C:N ratio most frequently varies from 8 to 12, with the average at 10. The first mathematical description of the transformation of organic matter in soil was that by Henin and Ddupuis. In subsequent years, mathematical functions and statistical simulation models of organic matter mineralization were developed by Jenkinson and Rayner , Russel , Veen and Paul, Janssen and others. Janssen and Noij, and Janssen, developed a simulation model for the calculation of the mineralization of carbon and nitrogen after a one-time introduction of organic matter in the soil. The model can be used to calculate the mineralization of carbon as well as of nitrogen, since the C:N ratio in the soil is relatively stable over multi-year periods. The model takes into account numerous factors determining the rate of organic matter mineralization in soils, such as the dosage of organic mater, the C and N content in the organic matter, the type of organic matter, the determined time of total mineralization of different organic matter in years, the duration of the period since the fertilization, and the temperature during the period studied. The time of total mineralization in years was determined as 1 for green fertilizers, 1 to 4 for straw, 2 to 4 for manure, and 4 to 13 for peats. The rate of transformation of organic matter depends also on such factors as the climatic conditions, the content of clay particles, the soil structure, and also on the abiotic factors of the environment and on the degree of its contamination.

BALANCE OF ORGANIC CARBON AND EMISSION OF CO_2

The problem of organic carbon balance in soils is currently a major subject of research. Since the beginning of the 1960's research scientists have been striving to quantify the balance of organic carbon in the biosphere. The balance of organic carbon is a value, expressed in percentages or weight units per a certain value of surface area, representing the ratio of the initial organic carbon content to its present content. Such changes, referenced to time periods, express the dynamics of quantitative changes which are often accompanied by qualitative changes in the organic matter. Organic carbon balance in the soil depends on a number of factors, most important of which are fertilization and the mass of post-harvest residue remaining on the field after the harvest of the crops. Less important in this respect is the mineral fertilization, as are the agrotechnical measures applied. The humus-forming effectiveness of these factors depends to a considerable extent on the properties of the soil environment, and especially on the biological activity of the soil. The anthropogenic emission of carbon compounds to the atmosphere amounts to 6.3 Gt C annually, and the concentration of CO_2 in the atmosphere, on the global scale, increases at the rate of about 1,5 ppm per year . This increase does not account for over a half of the carbon released to the atmosphere. According to the calculations by Sarmiento and Sundquist (1992), after taking into account the intake of carbon compounds by the oceans (2.2 Gt C per year), an amount of about 1.2 Gt C per year remains, this being probably accumulated in the form of organic matter somewhere on the land areas. The most commonly adopted hypothesis , ascribes such a function to the forest ecosystems of the moderate zone.

One of the methods for the study of the mineralization of carbon is the assessment of CO_2 diffusion from the soil. Diffusion of CO_2 is a measure of the intensity of all soil processes, both biological – the respiration of microorganisms, roots, and soil fauna, and non-biological (physico-chemical) – chemical oxygenation . Numerous calculation indicate that a thousand million cells, under field conditions, provide an emission of 0.004 mg CO_2 per hour. According to Alexander, arable soil emits 22 kg of the gas within a 24-hour period.

CO_2 –THE MOST IMPORTANT OF THE GREENHOUSE GASES

For many years carbon dioxide has been considered to be an neutral gas, as it is a natural component of atmospheric air and constitutes an important link in the carbon circulation cycle in the natural environment. Only the rapid increase in its concentration in the atmosphere brought about a change of the opinion. At present CO_2 is treated as other atmospheric contaminants and is considered to be the most important of the so-called greenhouse gases. CO_2 is absorbed by the biosphere in the processes of photosynthesis and deposited in the form of carbon. In the processes of respiration and decomposition of organic matter it is released again to the atmosphere. Carbon contained in plant residue is accumulated in the soil or washed out and deposited in the ocean. Moreover, CO_2 is absorbed directly from the atmosphere by the ocean, and then bound by plankton, marine plants and animals (crustaceans, anthozoa). It gets released to the atmosphere primarily due to volcanic activity, biosphere respiration, and processes of combustion. Approximately 4 % of CO_2 emitted to the atmosphere originates from artificial sources, of which about $6.5*10^9$ t C/year from the burning of power-generation fuels, and about $2.5*10^9$t C/year from changes in soil utilization (deforestation, among other things). Approximately $2*10^9$ t C/year is absorbed by the ocean, $2.4*10^9$ t C/year by the biosphere, and $3,4*10^9$ t C/year by the atmosphere. Whatever happens to the rest of it remains an unknown.

FORECASTING THE EFFECTS OF EXCESSIVE CO_2 CONTENT IN THE ATMOSPHERE

The current excessive concentration of CO_2 in the atmosphere is due mainly to increased anthropogenization, and primarily to the combustion of enormous amounts of fossil fuels (oil, coal, gas), which may lead to still further increase in CO_2 concentration in the atmosphere with disastrous consequences for the environment (greenhouse effect, i.e. a mechanism by which greenhouse gases affect the energy balance of the Earth through increasing temperature). This dangerous process is intensified by – among other things - greenhouse gases, such as carbon dioxide, methane, nitrogen monoxide, and by hydrocarbon halogen derivatives (freons and halons) originating from anthropogenic sources in their entirety. The greatest part in the process of global warming is attributed to increasing concentration of CO_2. Among the existing models of global climate change due to increased concentration of greenhouse gases in the atmosphere, most model indicate that doubling the concentration of CO_2 will cause an increase in the global temperature by 1.7- 5.3ºC, the most frequently given value being 2.3ºC (the increase to be different over the different parts of the globe).

The global warming will bring its consequences for agriculture. There will be indirect or direct effects on the species and varietal composition of crop plants grown. There may be a reduction in the amount of nitrogen accumulated in the plant tissue. There will be an increase in the intensity of plant affection by pathogens and pests, an increase in weed growth in crops, a decrease in farm animal breeding, and an increase of the risk of animals dying off from overheating. The forecast grave effects of excessive CO_2 content in the atmosphere cause the world of research to look for solutions and to initiate intensive research programs aimed at ensuring an equilibrium in the soil-plant-atmosphere system.

TAKS FACING AGRICULTURE TODAY AND IN THE FUTURE

In view of the above, the tasks facing agriculture today and in the future include the implementation of proper economy with respect to the organic soil matter resources. This can be achieved through the application of correct agricultural techniques, and primarily proper crop structure and organic fertilization. The importance of organic matter has been rediscovered after the 1980's, when it was observed that intensive agriculture resulted in a drastic reduction of organic mater content in soils. Intensive agriculture causes an increase in organic matter oxygenation, especially in the surface soil horizons, and consequently carbon dioxide emission to the atmosphere.

The above observations, as well as the fact that light soils – acidy and with a low content of organic matter easily susceptible to oxygenation - predominate in Poland, show that it is important to search for solutions aimed at increasing the organic matter content. This is an extremely important economic problem whose solution is necessary to maintain the soil environment in a condition ensuring proper growth and development of plants. The task, nevertheless, is very difficult, as successful results may only be achieved when the soils provide a possibility of binding their humus substance in complex humus-mineral compounds which slow down their rate of decomposition. There are many ways of increasing the humus content in light soils, and extensive research in that direction has already been done. This included attempts at improving the humus content through proper selection of crops, so as to supply a lot of post-harvest residue, through proper soil cultivation and manure fertilization, but also through the application of loam, clay, fertilization with peats or liquid sewage sediments. The tasks facing contemporary agriculture include the search for new successful and realistic solutions of the problem.

REFERENCES

1. Janssen B.H. 1984. A simple model for calculating decomposition and accumulation of „young" organic matter. Plant and soil 76, 297-304.

2. Jenkinson D.S., Rayner J.H. 1977. The turnover of soil organic matter in some of the Rothamsted classic experiments. Soil Sci 123, 298-305.
3. Luo Y., Reynolds J. 1999. Validity of extrapolating field CO2 experiments to predict carbon sequestration in natural ecosystems – Ecology , 80, 1568-1583.
4. Noij G.A.M., 1986. Simple model for calculation of nitrogen or phosphorus mineralization from Yang soil organic matter. DRAFF. AGN, 108.
5. Russel I.S. 1980. Simulation of nitrogen behaviour of soil- plant systems. Wegeingen, 222-232.
6. Singh J.S., Gupta S. R. 1977. Plant decomposition and soil respiration in terrestrial ecosystems – Bot. Rev. 43, 449-527.
7. Veen J.A., Paul E.A. 1981. Organic carbon dynamics in grassland soils. A Background information and computer simulation. Can. J. Soil Sci, 61, 185-201.

ELECTRIC MEASUREMENT OF MOISTURE OF SELECTED AGRICULTURAL MATERIALS
DIELECTRIC MEASUREMENT OF SOIL MOISTURE BY TDR METHOD

Malicki M A., Skierucha W.

STATUS OF WATER AS SIGNIFICANT ISSUE OF AGROPHYSICS

Increasing demands of water management result in the continuous development of its tools. One of the most important, beside the simulation models of water balance (Walczak and Sławiński, 2000), is monitoring of water status in porous materials defined as a space-temporal recording of the water properties that stimulate the phenomena and processes observed in the soil-plant-atmosphere system.

Concerning agrophysics, water status in porous materials is the issue of first priority, because each phenomenon or process examined in its scope depends on water status.

Monitoring of water status is accomplished using digital systems. The digital data acquisition systems react only on electric signals and the applied sensors must convert the measured value into the proportional electric signal.

Water status of soil as a porous material should be expressed by minimum five variables: amount of water in the soil (i.e. soil moisture), soil potential, salinity, oxygenation and temperature (Malicki, 1999).

The most difficult are the electric measurement of soil water potential and soil water content (soil moisture), therefore they are the subject of permanent research. It is assumed here, that the method successfully verified for soils will be also applicable for other porous agricultural materials because their structure is not so complex as soil.

The study discusses, on the example of soil, selected electric measurement methods applied for the monitoring of porous materials to determine the agrophysical variables. These methods have been elaborated and developed in IAPAS.

SELECTIVITY OF THE METHOD

The key feature of the applied method is the selectivity of the measurement, i.e. the lack of sensitivity of the conversion function (calibration) on the influence from the factors other than the measured one. Proper selectivity liberates the user from frequent, specific for each soil, *in situ* calibration measurements.

The solution to the problem of electric measurement of the physical quantity in selective way is to find such an electric property of the medium conditioning it, that is specific to the considered medium. For example, the specific property of molecular oxygen in electrolyte (“soil water”) is small activation energy of electrode reaction of its reduction. It can be concluded that electric measurement of oxygenation may be based on the amperometric measurement of the current of electrode reaction of oxygen molecules reduction (Malicki, Bieganowski, 1999).

Concerning the problem of electric soil moisture measurement, the medium conditioning moisture is water and its specific property is the polar structure of water molecules (a water molecule has a permanent dipole moment of 1.87 D). Polarity of water molecules is the reason that dielectric permittivity (dielectric constant) of water is much higher than permittivity of soil solid phase (the relative dielectric constant of water in the electric field of frequency below 10 GHz and 18ºC temperature is 81, while the relative dielectric constant of solid phase is 4÷5 at the same conditions). The dielectric constant of soil strongly depends on its water content, therefore it may be concluded that electric measurement of soil moisture should be based on the measurement of its dielectric constant.

Similarly, concerning the issue of electric measurement of soil salinity, the media conditioning salinity are salts present in soils and the specific property is their ionic form. The ability to transport electric charge by the ions in "soil water" allows the soil to conduct electric current. Therefore the electric measurement of soil salinity should be based on the measurement of its electric conductivity.

ELECTRIC MEASUREMENT OF SOIL MOISTURE

When the considered porous material is a moist dielectric (isolator), the measurement of its moisture is not a problem because it is enough to measure electric capacitance of the capacitor filled with the considered material and then recalculate the received value into moisture on the base of the conversion function (calibration).

In the case of materials conducting electric current, such as moist soil, the selective electric measurement of moisture on the base of dielectric permittivity is complicated because soil has features of dielectric and conductor simultaneously. The soil dielectric constant, ε, is a complex value (Hasted, 1973):

$$\varepsilon = \varepsilon' - j\left(\varepsilon'' + \frac{\sigma}{\omega\varepsilon_0}\right) \tag{1}$$

where:

$$\mathrm{Im}(\varepsilon) = \left(\varepsilon'' + \frac{\sigma}{\omega\varepsilon_0}\right) \tag{2}$$

is imaginary part of the relative complex dielectric permittivity of the soil, ε' – real part of the relative complex dielectric permittivity of the soil, ε'' – negligible contribution from the soil dielectric loss connected with dielectric polarization (mutual friction of permanent and induced dipoles), ρ- dry bulk density of soil [gcm^{-3}]), σ - electric conductivity of electrolyte [Sm^{-1}], ω - electric pulsation of external field stimulating the sensor, equal to $2\pi f$ [s^{-1}], f – frequency of electric field [Hz], ε_0 – dielectric permittivity of vacuum [Fm^{-1}] j – operator equal to $\sqrt{-1}$.

Practically the real part, ε', of the complex dielectric constant depends solely on its moisture, θ, and soil dry bulk density, ρ. The imaginary part depends on electric conductivity of the soil, σ, as well as the frequency of electric field, f. The bigger the value of the imaginary part (practically the bigger the value of soil electric conductivity), the more visible are conductive features of the soil.

From (2) it comes that the value of the soil complex permittivity depends also, besides its moisture, on the electric conductivity (that changes with moisture and salinity), as well as the frequency of electric field, f, applied to the sensor. It was found (Malicki and Skierucha, 2001), that the imaginary part of ε is negligible above the sufficiently high frequency of the electric field, $f = f_{prog}$:

$$\lg f_{prog} = 8.87 + 1.06 \lg \sigma \tag{3}$$

Equation (3) helps to evaluate the minimal frequency of alternative electric voltage polarizing the sensor, f_{prog}, that should be applied for the defined soil electric conductivity (salinity), to minimize nonselective feature of dielectric measurement of examined material moisture.

If the applied frequency increases, the polarizing current (dependent on dielectic polarization) dominates the conductive current (not dependent of frequency, dependent on electric conductivity). Therefore the electric field applied to the sensor recognizes the soil as an insulator and the measurement becomes selective.

Considering that the electric conductivity of soils reaches values of 1 Sm^{-1}, the electric method of moisture measurement should apply the electric field of frequency not lower than 1 GHz. However the wave length in the frequency range 1 ÷ 10 GHz is 30 ÷ 3 cm, and is comparable with the size of the sensor electrodes. In such conditions the sensor generates standing waves of significant amplitude, that mask its own response. This measurement method is known as microwave interferometry. At every point of the measurement setup there are several discontinuities of impedances and the voltage standing wave ratio (VSWR) summarizes the interference effect, therefore interferometry cannot distinguish the individual effects of different impedance discontinuities of the generator-sensor system. This disadvantage does not exist in time domain reflectometry (TDR).

TIME DOMAIN REFLECTOMETRY APPLICATION IN ELECTRIC MOISTURE MEASUREMENT

Time domain reflectometry (TDR) known also as cable radar method consists in actuating the tested transmission line by the voltage pulse and registering the time instants of the reflections from the impedance discontinuities encountered along this line (i.e. the line failures).

The electric voltage pulse is the result of interferences of infinite number of sine waves having different frequencies. Its edge is composed of sine waves of the highest frequencies in the wave bandwidth. Arbitrary setting the right limit of the bandwidth, f_{max}, the estimated rise time of the pulse edge, t_r, is (Strickland):

$$t_r = 0.35 f_{\max}^{-1} \tag{4}$$

For example: to accomplish the condition $f_{max} > f_{prog}$ = 1.75 GHz the required rise time, t_r, of the pulse should be not longer than 200 ps.

THE PRINCIPLE OF ELECTRIC MEASUREMENT OF MOISTURE

It has been found that the dielectric constant, ε, of examined soils and other porous materials depends on volumetric water content, θ, and density, ρ (Malicki et al., 1996):

$$\sqrt{\varepsilon} = 0.819 + 0.168\rho + 0.159\rho^2 + \theta(7.17 + 1.18\rho) \tag{5}$$

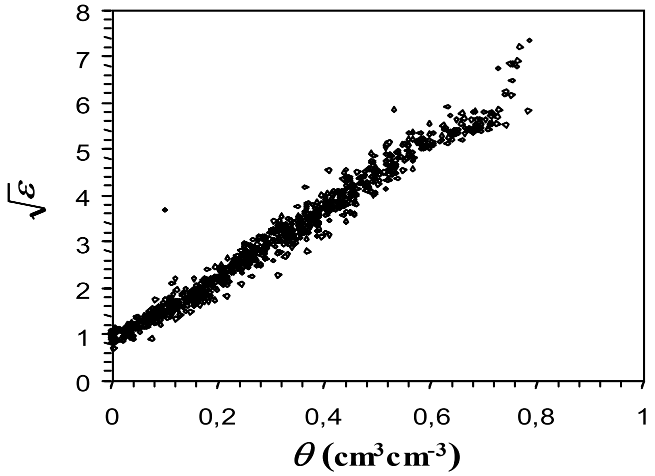


Fig. 1. *Relation between dielectric constant and moisture for 61 different porous materials of densities from 0.086 ÷ 1.77 g cm^{-3} (Malicki et al., 1996). The examined samples included mineral and organic soils, sawdust and wood shavings, wood, artificial soil substrates and others.*

Converting (5) leads to a new formula for determination of moisture from dielectric permittivity and density:

$$\theta = \frac{\sqrt{\varepsilon} - 0.819 - 0.168\rho - 0.159\rho^2}{7.17 + 1.18\rho} \tag{6}$$

The dielectric constant, ε, is calculated from the measurement of the propagation velocity, v, of electromagnetic pulse in the examined medium, for example in soil according to:

$$v = \frac{c}{\sqrt{\mu\varepsilon}} \tag{7}$$

where c is the velocity of propagation of light in vacuum. Assuming that for majority of considered materials the magnetic permittivity, $\mu=1$ and transforming (6) we can find the formula for the electromagnetic wave refractive index, $\sqrt{\varepsilon}$:

$$\sqrt{\varepsilon} = \frac{c}{v} = \frac{c}{2L}\,t \tag{8}$$

where c is the velocity of light in vacuum, L – the length of the sensor rods (Fig. 2), t is the time necessary for the pulse to travel the double length of the sensor rods $2L$.

THE PRINCIPLE OF THE MEASUREMENT OF ELECTROMAGNETIC WAVE PROPAGATION VELOCITY BY REFLECTOMETRIC METHOD

The principle of measurement of electromagnetic wave propagation velocity in soil (or other porous materials) is presented in Fig. 2. A section of transmission line, called the sensor, is constructed from two parallel, non-isolated metal rods. One ending of the sensor is connected by other transmission line (for example coaxial line), called the feeder, with an electric voltage pulse generator (Fig. 2a). The voltage step traveling along the feeder reaches at instant t_1 the beginning of the sensor and propagates further in the soil to reach the sensor ending at the instant t_2.

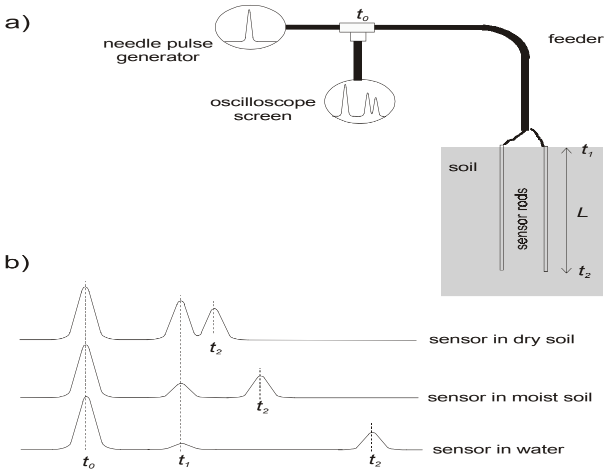


Fig. 2. *Principle of the reflectometric measurement of soil moisture. a) basic components of the system, b) the pulse and its reflections as seen on the screen of the oscilloscope.*

There is a discontinuity of impedance (feeder impedance differs from the sensor impedance) at the feeder/sensor connection, and a part of energy of the pulse is reflected at the instant t_1 and returns to the generator. The remainder continues to propagate further (in the soil) to reach the end of the sensor at the instant t_2 and reflects again towards the generator because of the impedance rise at the end of the sensor.

Fig. 2b shows the picture of the pulse and its reflections as is recorded on the screen of an oscilloscope connected to the feeder. The initial pulse reaches the T-adapter at the instant t_0, propagates further and is subjected to described reflections at the instants t_1 and t_2. The higher the soil moisture, the higher is the dielectric constant, ε, and the smaller propagation velocity, v, of the pulse in the soil, and the longer the time interval t_2-t_1. The measurement of $t=t_2-t_1$ between the reflections from the beginning and the end of the sensor and knowing the sensor length, L, allows to calculate, according to (5) the value of $\sqrt{\varepsilon}$ and then, according to (6), the corresponding volumetric water content, θ.

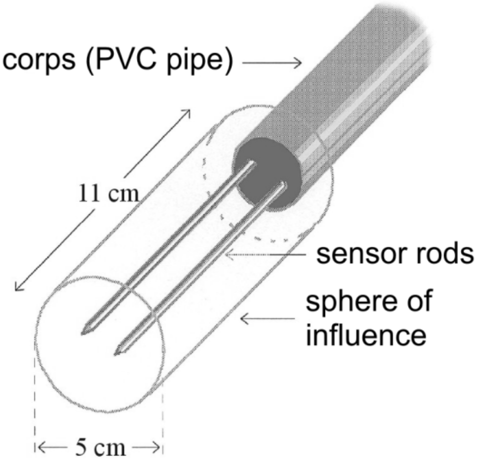


Fig. 3. *Sphere of influence of the TDR sensor*

Sphere of influence of the sensor is a cylinder circumscribed on the sensor rods, with the height equal to 1.1×L and the diameter about three times the distance between the rods.

Fig. 4 shows comparison of the soil moisture measurement results carried out by reflectometric method, θ_{TDR}, with the ones by thermograwimetric method, θ_{grav}, for 61 different mineral and organic soils of densities in the range $0.086 < \rho < 1.78$ g cm^{-3} (Malicki et al., 1996).

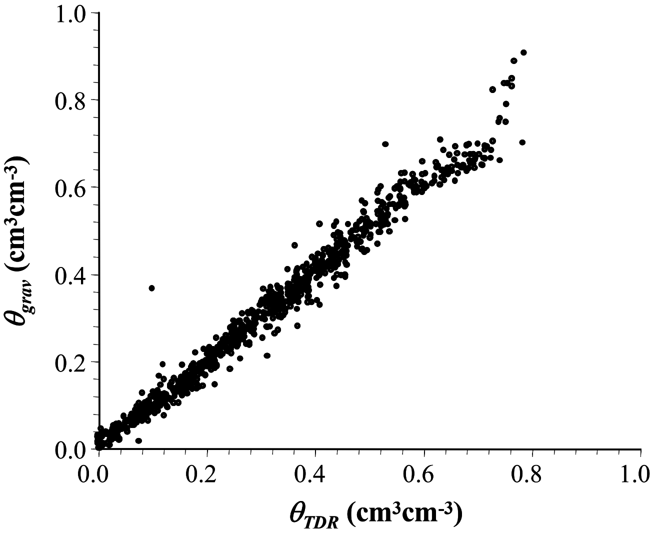


Fig. 4. *Comparison of soil moisture data obtained using TDR, θ_{TDR}, with data obtained using the oven-drying method, θ_{grav}, for samples having bulk densities $0.086 < \rho < 1.78$ g cm^{-3} (gcm^{-3}).*
$\theta_{TDR} = 0.0001 + 1.00\,\theta_{grav}$, $R^2 = 0.9801$, SD = 0.028 (SD is standard deviation).

Small scatter of data proves the TDR method of soil moisture measurement to be satisfactory. It should be noted that this method has been also proved in applications to grain and wood (Malicki and Kotliński, 1998a, 1998b).

TDR METERS FOR SOIL WATER CONTENT DEVELOPED IN THE INSTITUTE OF AGROPHYSICS POLISH ACADEMY OF SCIENCES IN LUBLIN

Following below are shown some TDR meters for soil water content elaborated and developed in the Institute of Agrophysics PAS in Lublin. Short comments can be found in the figure captions.

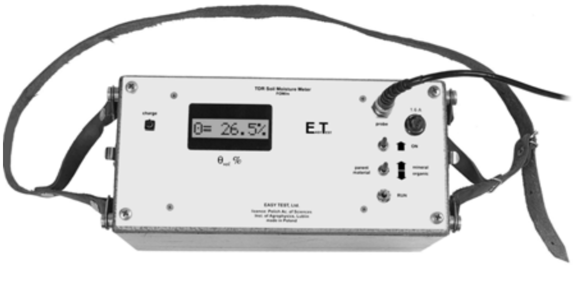


Fig. 5. *FOM/m, Field Operated Meter for determination of soil moisture.*

FOM/m (Fig. 5) is a portable, battery operated, microprocessor controlled device designed for *in situ* field measurements of soil moisture by means of TDR (Time-Domain Reflectometry) technology. It is designated for periodic measurements at random and/or fixed locations where water content distribution is to be determined by readings taken at various levels of the soil profile. It utilizes the FP/m-type probes. FOM/m is equipped with a 15 mm high 3.5 digit LCD to display moisture and provides a Mineral/Organic option switch for soils originated from mineral or organic parent material, thus no user calibration is needed to read the soil moisture.

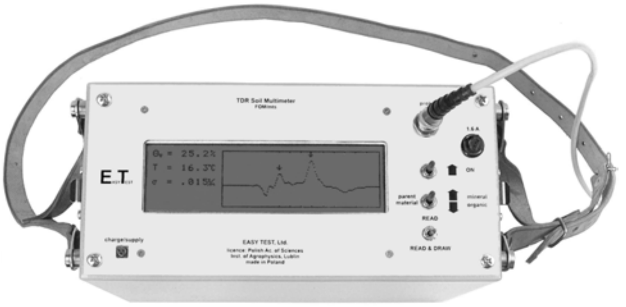


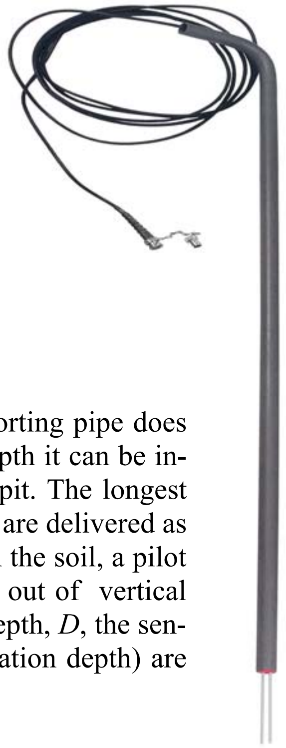
Fig. 6. *FOM/mts, Field Operated Meter for determination of moisture, temperature and salinity of soils.*

FOM/mts (Fig. 6) is a TDR (Time-Domain Reflectometry) based, portable, battery operated, microprocessor controlled device designed for in situ field measurements of soil moisture, temperature and salinity (bulk electric conductivity) from the same probe. It is designated for periodic measurements at random and/or fixed locations where moisture, salinity and temperature distribution is to be determined by readings taken at various levels of the soil profile. It utilizes the FP/mts-type probe. FOM/mts is equipped with a 256 by 64 dot matrix graphic LCD to display data and TDR trace simultaneously. The TDR trace is a voltage-versus-time record of the voltage pulse round-trip along the probe. It is helpful to check the probe status during (break, short) and after its installation (excessive attenuation of the pulse). FOM/mts provides a Mineral/Organic option switch for soils originated from mineral or organic parent material, thus no user calibration is needed to read the soil moisture directly. Also FOM/mts-RS equipped with the RS-232C serial port is offered. This makes it possible to operate the meter under control of any IBM compatible PC.

FP (Fig. 7) is a Time-Domain Reflectometry (TDR) probe for momentary or semiper-manent installation. Thin-wall PVC body of the probe provides ultimate low heat conductivity, thus allowing to avoid the parasite "thermal bridge" effects on distribution of soil moisture in the probe’s sensor vicinity. Through a preaugered pilot hole it can reach any depth without destroying either the soil structure or disturbing the heat and mass transport in the soil. For semipermanent installation the probe can be inserted horizontally through a sidewall of a soil pit or slantwise, from the soil surface. The probe installed once may be left intact in the soil for as long as necessary, then drawn out at the end of the experiment.

FP/m is a probe for *in situ* field measurement of the soil moisture whereas FP/mts is its version for simultaneous measurement of moisture, temperature and salinity conductivity) of the soil from the same sampling volume

Fig. 7. *FP/m, FP/mts, the Field Probe for moisture, temperature and salinity of soil*



Both probes are suitable for periodic measurements at random and/or fixed locations, where instantaneous profiles of water content, temperature and salinity are to be determined by readings taken at various levels of the soil profile. Each of them may also be applied as a mobile probe (FP/m/m or FP/mts/m) for momentary measurements in surface layer of the soil, by walking over the field and inserting the probe in the soil surface layer at

The shortest available probe is 15 cm long. Its supporting pipe does not have any bending. To place the probe at 5 - 15 cm depth it can be inserted horizontally through a side wall of a shallow soil pit. The longest possible probe is 400 cm long (probes longer than 150 cm are delivered as a kit to be assembled by the user). In order to install FP in the soil, a pilot hole has to be preaugered from the soil surface, deviated out of vertical of an appropriate angle, a. The probe length, L, and the depth, D, the sensor rods are meant to reach in the soil profile (the installation depth) are related as follows:

$$L = D/\cos(\alpha) - 5 + a$$

where L, D and a in cm and α is the out of vertical deviation angle. The length, L, is the distance between the base of the sensor rods and the bending point of the plastic support pipe and a is length of the part of the probe body sticking out the soil surface. Different combinations of L, α and a allow to reach the intended depth, D. Suggested magnitude for α is 30º (Fig. 8).

An example minimum set of probes consists of 7 probes for different depths of installation:

3 probes of L = 15 cm for D = 5 - 15 cm, 1 probe of L = 50 cm for D = 30 cm,
1 probe of L = 84 cm for D = 60 cm , 1 probe of L = 154 cm for D = 120 cm,
1 probe of L = 188 cm for D = 150 cm.

The shortest probes (L= 15 cm) can be placed horizontally. The remaining probes are calculated for α = 30º and a = 20 cm.

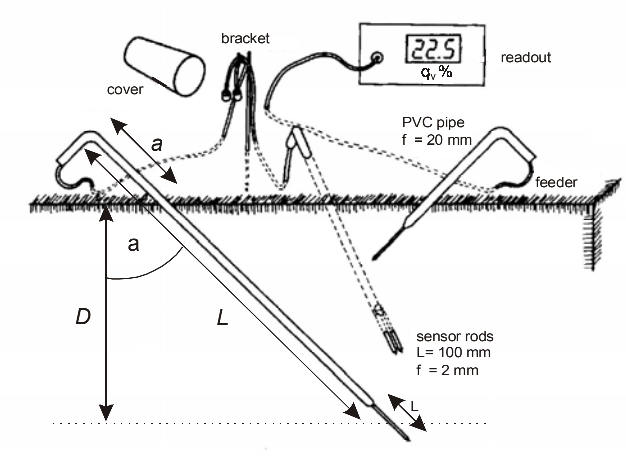


Fig. 8. *The principle of installation of the FP-type probes. In order to minimize disturbances in the soil structure the probes are inserted into the soil via pilot holes, circularly distributed over the soil surface. The holes run slantwise and converge along a chosen vertical line. The cables are buried below the soil surface to protect them against the UV sun radiation as well as against rodents.*

LOM (Fig. 9) is a TDR (Time-Domain Reflectometry) technology based, computer aided instrument, designed to record mass and heat transport data. It is suitable for controlling long-term laboratory experiments on soil columns which require monitoring of water, heat and salt transport. This is achieved by means of periodic recording of instantaneous profiles of moisture, matric potential (capillary water pressure, "suction force"), temperature and electric conductivity in chosen time intervals. To record moisture, θ, a factory installed conversion equation $\theta(\varepsilon)$ for mineral soils is implemented.

Several LP type miniprobes of selected type (or of all types) can be inserted through the side wall of a soil column or a steel sampling cylinder, thus allowing for vertical scanning of instantaneous profiles of moisture, capillary pressure (matric potential, suction force), temperature and salinity (bulk electric conductivity).

This makes it possible to collect a set of corresponding data from transition of the soil solute (and temperature) front. From this, after processing, one can obtain a complete set of unsaturated water flow characteristics of the soil such as the water retention (PF) curve, the unsaturated water conductivity (k-function), the differential water capacity and the unsaturated water diffusivity as well as the solute transport data. Also the heat flow parameters (thermal conductivity, thermal diffusivity, specific heat) can be determined if a temperature gradient is applied and a heat flux meter is installed in the soil column. Probes are switched in two levels. For instance the LOM above is provided with a 3pole-4-throw first level multiplexer (FLM) to switch between 1 to 4 second level multiplexers (SLMs). To switch between the probes 3-pole-8-throw multiplexers can be applied as the SLMs, as shown in the picture. For such configuration up to 32 LP/ms, 32 LP/t and 32 LP/p probes can be switched. Other options are also possible. The TDR LP/ms probes for moisture and salinity use special microwave switches. Remaining probes (LP/p, LP/t) are switched using common solid state switches and/or reed relays.

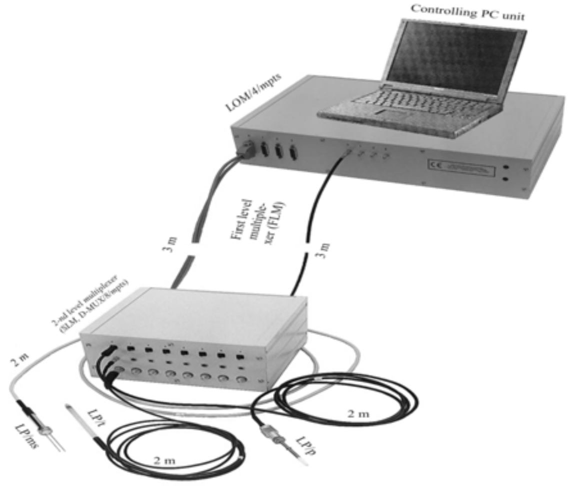


Fig. 9. *Example of structure of a LOM/4/mpts based stand for recording instantaneous profiles of soil moisture, capillary pressure of soil water, temperature and salinity (bulk electric conductivity) from soil column(s), with application of a single MUX/8/mpts.*

Fig. 10. *LP/ms, Laboratory miniProbes for soil moisture and salinity*

LP/ms (Fig. 10) is a laboratory miniprobe designed for monitoring changes in water and salt distribution in soil columns or in soil cores sampled with standard sampling equipment. Several LP/ms can be inserted through the side wall of a soil column or a steel sampling cylinder (Fig. 11), thus allowing for vertical scanning of the instantaneous moisture and electric conductivity profiles.

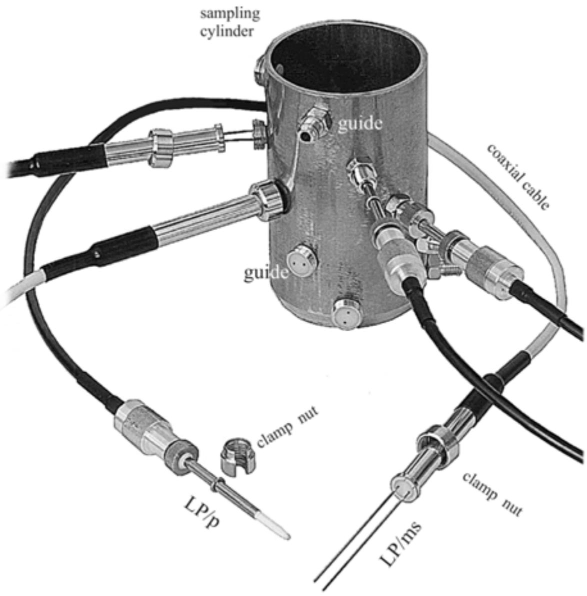


Fig. 11. *A set of LP/ms and LP/p LOM controlled miniprobes inserted through a 2.75 mm thick wall of a sampling steel cylinder, having height of 100 mm and 55 mm inner diameter. The wall of the cylinder is provided with tapped holes equally distributed along the cylinder height in order to monitor independent layers of the soil. The holes are aligned spirally to minimize mutual shadowing in the vertical.*

Such an array, when combined with similarly installed minitensiometers (LP/p), makes it possible to collect a set of corresponding water content and matrix potential gradient data from drying or wetting front transition. From this one can obtain a complete set of the soil unsaturated water flow characteristics, i.e.: water retention (PF-curve), water conductivity (k-function), differential water capacity and unsaturated water diffusivity.

D-LOG/mts (Fig. 12) is a TDR (Time-Domain Reflectometry) technology based, computer aided instrument, designed for periodic recording of instantaneous profiles of soil moisture, temperature and salinity (bulk electric conductivity) in chosen time intervals. It is suitable for long-term lysimeter-based investigations and also for field experiments, when monitoring of water, solute and heat transport is required.

D-LOG is equipped with a built-in local computer having an RS232C serial port. It serves for:

- controlling pulse circuitry action,
- recording voltage-versus-time traces,
- calculating pulse attenuation and velocity of propagation,
- calculating the soil dielectric constant, moisture and electric conductivity,
- communicating with a master PC via the RS232C serial port.

Fig. 12. An example of the D-LOG/10/mts-controlled stand incorporating six D-MUX/10/mts 2-nd level multiplexers. Maximum amount of the controlled FP/mts (or FP/m) probes is 60. For clarity only a single D-MUX was linked with the D-LOG and a single probe was connected to each D-MUX when taking the picture.

D-LOG uses probes type of FP/mts for moisture, temperature and bulk electric conductivity. Also FP/m probes can be applied if only moisture is of concern. To calculate moisture a factory-installed conversion equation can be used and/or a user-determined calibration function can be applied as well.

To switch between FP/mts or FP/m probes D-LOG is provided with an inherent 1-st level switch and optional amount of standing alone 2-nd level switches (D-MUX/n/...), as shown in figures. Each 2-nd level switch contains a moisture, temperature and salinity control circuitry and also a single-pole-n-throw microwave switch, where 2<n<16.

To protect against rainfall the D-LOG as well as D-MUXes are kept in metal, rain-proof exhausting boxes.

SUMMARY

1. Reflectometric method, TDR (Time Domain Reflectometry) has been verified in comparison to other electric (dielectric) methods of soil moisture measurement as the best one.
2. TDR is especially useful for measurements in salty soils because the frequencies of the sinusoidal components forming the pulse edge fall in the range of

0.5 ÷ 5 GHz, whereas for soil conductivity below 1 $\mathrm{Sm^{-1}}$ the parasite influence of conductivity current is negligible (the frequency dispersion of soil electric permittivity does not, practically, appear).

3. TDR is convenient in applications to parallel measurements of soil dielectric constant and electric conductivity from which the soil water content and salinity can be estimated. The readings of both variables refer to the same soil sample (the sphere of influence of TDR sensor is common for the both variables).
4. The TDR as applied to water monitoring systems should be developed in the direction of an independent, single-unit "intelligent sensor" to make the systems immune to global collapse in data collection (even if only few sensors break, the system will still work using the remaining sensors).

REFERENCES

1. Hasted, J.B.: Aqueous dielectrics. Chapman and Hall, London, 1973.
2. Malicki M. A.: Metodyczne zagadnienia monitoringu statusu wody w wybranych materiałach biologicznych, Acta Agrophysica, 19, 1999.
3. Malicki M. A., Bieganowski A.: Chronovoltammetric determination of oxygen flux density in the soil. International Agrophysics, Vol. 13 nr 3, 1999.
4. Malicki M. A., Kotliński J.: Dielectric determination of moisture of cereals grain using time domain reflectometry. International Agrophysics, Vol. 12, Nr. 3, 209-215, 1998.
5. Malicki M. A., Kotliński J.: Dielectric determination of moisture of wood using time domain reflectometry. International Agrophysics, Vol. 12, Nr. 3, 217-220, 1998.
6. Malicki M.A., Skierucha W.: Zagadnienie doboru częstotliwości pola elektrycznego w dielektrycznym pomiarze wilgotności gleb zasolonych. Acta Agrophysica. 53, 109-115. 2001.
7. Strickland J.A.: Time-Domain Reflectometry measurements. Tektronix Inc. Beaverton, Oregon 97005, 1970.
8. Walczak R., Sławiński C.: Badanie i modelowanie przenoszenia masy i energii w agrofizyce. Eksploatacja i Niezawodność. 4, 6-15, 2000.
9. Walczak R.T., Sławiński C.: Termodynamika procesów glebowych. Acta Agrophysica, 48, 133-139, 2001.

DISSOLVED SOIL ORGANIC MATTER AND ITS ESTIMATION

Matyka-Sarzyńska D.

HUMIFICATION

Soils contain large variety of organic materials that can be grouped into humic and non-humic substances. The process of humus formation is called humification. Until now the humification process has been a subject of much speculations and studies. In natural systems, biomass consisting of dead plant and animal residues is converted into soil organic matter (humus) by degradation reactions catalyzed by enzymes. A part of organic compounds is partially oxidized. So, humification can be defined as a conversion of degradation products by series of polymerization reactions into new types of polymeric species that are different from the precursor molecular species in the original biomass.

HUMUS

Humic substances can be divided into the following three main fractions: humic acids (HA), fulvic acids (FA) and humines. These three fractions differ mainly in molecular weight and functional groups content with FA having a lowest molecular weight, containing more oxygen but less carbon and nitrogen, and having a higher content of oxygen- containing functional groups per unit weight than the other two humic fractions.

FUNCTION OF ORGANIC MATTER IN SOIL

Organic matter contributes to plant growth through its effect on the physical, chemical,
and biological properties of the soil. It has:

- nutritional function in that it serves as a source of N, P for plant growth
- biological function in that it profoundly affects the activities of microflora and microfauna organisms
- physical and physico-chemical function in that it promotes good soil structure, thereby improving soil fertility, aeration, retention of moisture, buffering and exchange capacity of soils.

DISSOLVED ORGANIC MATTER

In nature some of organic matter substances (humus) are sorbed by soil solid particles and some are transported through unsaturated zone into the saturated zone, where they can remain dissolved in, and move with the groundwater. So, DOM is an important component of not only soil but also aquatic environments. The nature and the amount of DOM in soil solution can influence the quality of groundwater and surface waters. Furthermore, DOM is involved in a number of biogeochemical processes, including pH buffering, nutrient cycling, ionic balance, mineral weathering, metal leaching, pollutant toxicity, mobility and bioavailability.

FACTORS INFLUENCING THE RELEASE OF DOM

The availability of DOM and its mobility in the soil are the consequence of multiple sorption and desorption processes. The availability of organic matter and its mobility in the soil is a consequence of many factors, including properties of the soil, as well as changes in climate, especially **temperature** and rainfall patterns. Evidence for the importance of climatic factors comes from observations of seasonal variations in soil water, lakes, streams and rivers, in which summer and autumn maxima are found. These seasonal cycles have been positively correlated to soil temperature and groundwater flow rates. Particularly the **pH** is very important for adsorption of organic matter on soil particles and its release into soil solution. Changes in pH affect the electrostatic charge that induces repulsion-attraction of negatively charged surfaces of humic acids to other soil components. Significant increase in the amount of dissolved organic matter (DOM) is observed due to increase in pH of soil solution due to negative charge increase of organic particles and their electrostatic repulsion from solid phase to the solution, whereas the pH decrease may affect DOM in both directions. Evidence for the possibility of dissolution of a part of organic matter in acid condition (pH below 5) was found that, despite of the surface charge decrease, was most probably connected with acidic removal of organic matter cementing agents. It is reported that the first samples of humic matter were taken from surface water of natural acidic soils (peats). The **chemical composition of the soil** solution significantly influences the amount of organic matter released from soil, as well. These effects can be explained by interaction of inorganic electrolytes with soil organic matter leading to their sorption on metal oxides and clay minerals or precipitation (coagulation) of organic material itself.

DOM ESTIMATION BY SPECTROPHOTOMETRY IN UV/VIS

One of the easiest and most convenient methods to determine the concentration of DOM in soil solution as well as to perform its qualitative characteristic is spectrophotometry.

Basic Principles.

The method is based on possibility of the DOM to absorb light. A spectrophotometer is employed to measure the amount of light that an analyte (measuring medium) absorbs. The beam of light of an initial intensity I_0 is passing through the analyte and the lower intensity of light, I, reaches a detector (Fig.1). Both data are used to calculate the absorbance $A=\log(I_o/I)$. The absorbance and the concentration C of the analyte should follow Beer's Law, which predicts a linear relationship between the above values assuming all other experimental parameters do not vary.

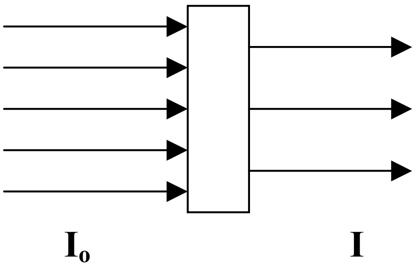


Fig.1. *Schematic view on light absorption in spectrophotometric measurements*

Absorbance Spectrum

The extent to which a sample absorbs light strongly depends upon the wavelength of the light. For this reason, spectrophotometry is performed using monochromatic light. To analyze a new sample, one has to determine its absorbance spectrum. This spectrum shows how the absorbance of light depends upon the wavelength of the light (Fig.2). The spectrum itself is a plot of absorbance vs. wavelength. Analytical measurements are made using this wavelength, λ_{max}, at which the absorbance is the largest. Generally, humic substances yield uncharacteristic spectra in the UV and VIS regions. Absorption spectra show neither maxima nor minima and the optical density usually decreases monotonically as the wavelength increases (Fig.3).

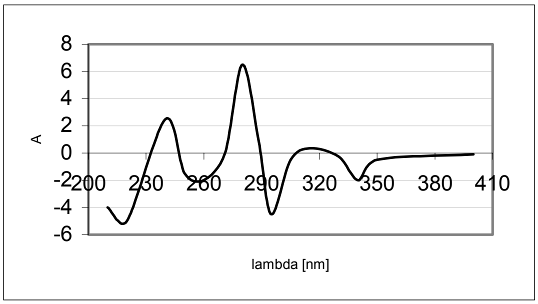


Fig.2. *Exemplary absorption spectrum with well defined absorption peaks.*

Despite the uncharacteristic shape of the spectrum, the composition of organic matter is frequently characterized by determining the ratio of absorbances at 465 (E4) and 665 (E6) nanometers. Because the absorbance at 465 nm is due to smaller molecules, and at 665 nm to larger molecules, the E4/E6 ratio is expected to be greater for larger molecular weight humic acids and smaller for smaller molecular weight fulvic acids. Based on Kononowa studies, the E4/E6 ratio is <5 for humic acid and 6-18,5 for fulvic acid. This ratio has been reported to be independent of concentrations of humic materials but to vary for humic materials extracted from different soil types.

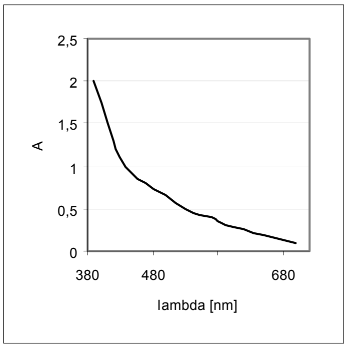


Fig.3. *Typical absorption spectrum of humic substances.*

ANALYSIS OF AN UNKNOWN SOLUTION

First of all the construction of a calibration curve is necessary. Then, the calibration curve is used to determine the analyte concentration in an unknown solution. In practice, series of standard solutions are prepared. A standard solution is a solution in which the analyte concentration is accurately known. The absorbances of the standard solutions are measured and used to prepare a calibration curve (Fig.4), which in this case is a plot of absorbance vs. concentration. The points on the calibration curve should yield a straight line. The slope and intercept of this line provide a relationship between absorbance and concentration:

A = slope + intercept

The unknown solution is then analyzed. Knowing the absorbance of the unknown solution, A_u, one uses the calibration curve to determine its concentration.

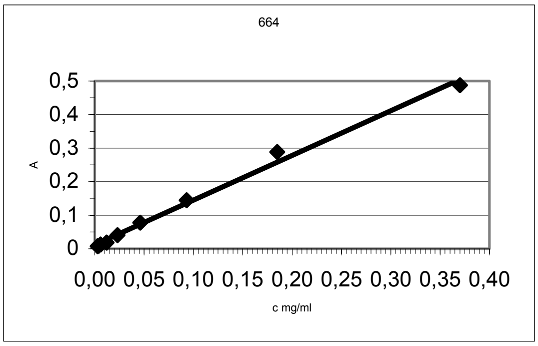


Fig. 4. *Exemplary calibration curve of humic acid.*

Experimental Procedure

Quantitative analysis procedure:

1. Designate the wavelength of the analysis – use the absorbance spectrum, if needed.
2. Measure absorbance of a blank probe - The blank is a solution that is identical to the sample solution but does not contain the analyzed substance. This measurement is necessary, because the pure medium scatter some of the light.
3. Measure standard samples.
4. Create calibration curve.
5. Measure unknown samples.

SPECTROPHOTOMETRY OF ORGANIC MATTER RELEASED FROM MUCKS

Effect of pH

Peatlands are large sources of dissolved organic matter. In Poland most of the peatlands have been drained and subjected to agricultural use. While water conditions change, soil mass decreases and gains more hydrophobic character, and soil sorption abilities become lower. The mechanism of the above changes is called mucking process. Due to peatland origin and various mineralization and oxidation processes, mucks are usually acidic. To renew their fertility, liming is usually applied that induces increase in pH and accompanying processes of DOM mobilization.

At present I report some model investigations on the effect of pH increase on the DOM release from mucks. These studies consisted a first step to investigate the effect of the advance of mucking process on the DOM release.

Materials

The study was conducted on muck samples (Terric Histosols) taken from upper layers of 14 differently transformed peat-muck profiles located in Polesie Lubelskie region and Biebrza river valley. Homoionic hydrogen forms of fresh mucks containing exactly 0,4 g of dry organic matter were treated by NaOH solutions at pH = 5, 6, 7, and 8 at 1:100 w/w solid to liquid ratio. Concentrations of the DOM in the 0.45 μm filtered extracts were determined spectrophotometrically at 470 nm using Jasco V-500 apparatus. A calibration curve was based on sodium humate solutions (Aldrich H1, 675-2).

Results

The amounts of DOM which was released in the process of alkalization are shown in Figure 5.

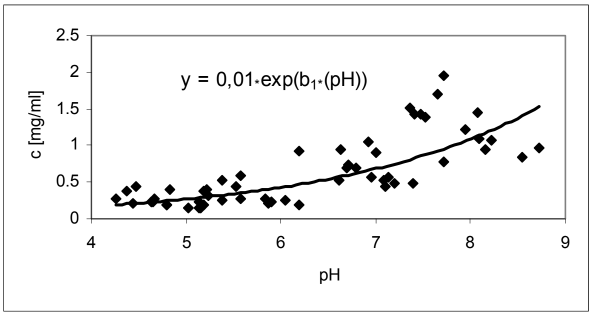


Fig. 5. *DOM release from mucks due to increase in pH.*

The dissolution of soil organic matter was significantly affected by pH. At low, initial pH values, the dissolved organic matter concentration was small. Generally the increase in pH resulted in the increase in dissolution of organic matter. The concentration of the DOM increased exponentially with the pH of the extraction. An equation $DOM(pH) = 0{,}01*\exp(b_1*pH)$ provided high correlation between the experimental data ($R^2>0.94$ in most cases). The b_1 index could be satisfactorily used to quantify the DOM release process from mucks in relation to the increase in soil pH.

REFERENCES

1. Brown S.B.: Ultraviolet and visible spectroscopy. P 1-15. In S.B. Brown (ed.) Introduction to spectroscopy for biochemists. Academic Press, New Yourk. 1980.
2. Ghosh K., Schnitzer M.: UV and Visible absorption spectroscopic investigations in relation to macromolecular characteristics in humic substances. J.Soil Sci. 30, 735-745, 1979.
3. Kononowa M.M.: Soil organic matter, Pergamon, Elmsford, N.Y., 1966
4. MacCarthy P., Rice J.A.: Spectroscopic methods (other than NMR) for determining functionality in humic substances. In G.R. Aiken et al. (ed.) Humic substances in soil, sediment and water. John Wiley and Sons, New York. 1985.
5. Schnitzer M., Khan S. U., Soil organic matter, Elsevier. Sci. Pub.Comp., N.Y., 1978.
6. Sposito G.: The Chemistry of Soils, N.Y., Oxford, Oxford University Press, 1989.
7. Stevenson J.: Humus Chemistry: Genesis, Composition and Reaction, J. Wiley and Sons, N.Y., 1982.
8. Wershaw R.: Membrane –Micelle model for humus in soils and its relation to humification. U.S. Geological Survey Water Supply, 2410, 1994.

ORGANO-MINERAL COMPLEXES IN SOILS AND THEIR INTERACTIONS WITH HEAVY METALS

Raytchev T., Benkova M.

INTRODUCTION

Colloidal nature of soil – plant root processes is governed by properties of surface adsorbents of soils and plants, being functions of physiological and genetic features of plant tissues and of soil characteristics, respectively.

Toxic content of heavy metals in soil leads to the disturbance of mineral plant nutrition and changes soil colloidal properties what induces serious problems in buffering features of ecosystems. Heavy metal detoxification methods should be based not only on the metal availabilities for plants, but upon a broader understanding of soil properties, including composition of multivalent cations and sensitivity of soil adsorbent against applied detoxification measures. Usually, liming is applied as a standard melioration method for heavy metals polluted soils, however potentially toxic amounts of the metals still remain in the soils as easily soluble precipitates. A new, method of increasing melioration effectiveness was elaborated basing on addition of organo-mineral limed composts that leads to strengthening of interactions between soil (and added) colloids and heavy metals (Arsova and Raichev, 2000; Arsova and Raychev, 2001; Raychev, 1996; Raychev et al., 1999; Raychev et al., 2002; Raichev et al., 2000; Raichev and Arsova, 1998 Raichev, 1997a,b; Raichev and Toncheva, 1997 Raychev et al., 2001; 2001a).

In the present paper, theoretical basis of the above approach is presented including a distribution of some basic colloidal adsorption centers of organo-mineral soil components, their changes due to organo-mineral additives, and heavy metal binding. Possible changes of soil microstructure during neutralization of soil electric charge are discussed.

BASIC HYPOTHESIS

The presented model concerns possible formation of organo-mineral compounds from negatively charged clay minerals, humus and positively charged ions or hydroxycomplexes of amphoteric elements into forms of “sandwich” colloidal structures. Such “mosaic” materials of various local structures determine ionic equilibria between the root system and soil sorption complex. These structures are hypothesized to be responsible for strong decrease of heavy metals toxicity due to addition of organo-mineral limed composts in comparison with standard liming.

ADSORPTION CENTERS ON SOIL COLLOIDS

Fate of polyvalent cations during melioration and a stability of the formed compounds are functions of soil components – clay minerals and humus.

Due to specific build-up of the crystal lattice and their colloidal nature, clays may exhibit complex adsorption behavior and structure forming properties (Berry et. al., 1987; Ganev, 1990; Cotton and Wilkinson, 1977a, 1977b; Fripiat et al., 1971; Grim, 1959; Lazarov, 2001; Orlov, 1985).

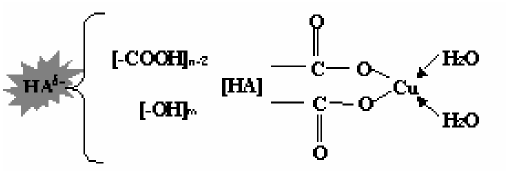
Large specific surface and high amount of active surface centers of all soils colloids promote sorption processes accompanied by changes in energetic status of the system. These processes depend on the density and locality of the active centers on soil components surfaces. The centers may be regularly situated on a surface (ordered geometrical structures) or irregularly (amorphous structures).

The specific role of humus compounds in soil adsorbtion complex depends on their genesis and evolution (Duchaufour, 1968, 1972). Their peculiar character is determined just from the beginning of a decay of plant or animal residues.

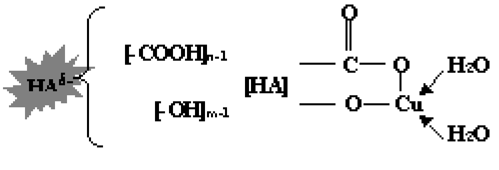
Formation of organomineral compounds is governed by activity of soil biochemical and enzymatic processes that produce a range of forms of decomposed organic material of various stereochemical character, elasticity and dimensions, finally interacting with mineral phases.

Polyvalent cations may be adsorbed on surfaces of stable organomineral complexes promoting subsequent adsorption of next organic layers, and so on, and in a time course these formations reorganize and polymerize to surfaces of more aromatic character.

The cation exchange properties of organic humus substances (**HA$^{\delta-}$**) origin from acidic surface functional groups (mainly carboxyls –COOH and phenolic hydroxyls -OH) and depend on the soil pH. With an increase in pH, the degree of dissociation of these groups increases. The increase in negative charge leads to conformational changes of organic macromolecules, from spherical or spiral forms to expanded strings (Arora et al., 1979; Schnitzer, 1991; Tarchitzky et al., 1993). High concentration of acidic groups promotes binding of polyvalent ions into chelate complexes:



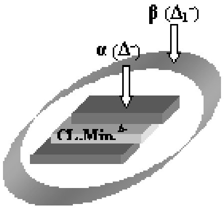
At high pH values, dissociated phenolic hydroxyls may participate in the above reactions (Orlov, 1985):



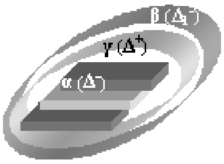
If the soil adsorbent can maintain high capacity, it can control equilibria of all ions in the soil, including hydroxyions (Ganev, 1990; Kokotov, et al., 1986; Orlov, 1985; Charlot, 1969). However, in acidic soils, only a part of soil adsorbent can be active (permanent charge on clay minerals and strongly acidic groups on organic matter) and this may be partly neutralized by positively charged sesquioxides or basal planes of clay minerals that leaves nonsorbed potentially active forms of heavy metals (Ganev, 1990; Boldyrev, 1983; Orlov, 1985; Charlot, 1969; Jozefaciuk et al., 1992).

During increase in pH the amount of exchange and ionic forms of heavy metals decreases and this of their hydroxylic forms increases. Colloid micelles can arise around polymeric hydroxyions having pH dependent surface charge. These hydroxyions have extremely high sorption ability due to high charge and mass of the micelles (Boldyrev, 1983; Ganev, 1990; Orlov, 1985; Charlot, 1969). Interactions of individual athoms or their groups leading to new structures formation may occur via athomic or ionic bonds.

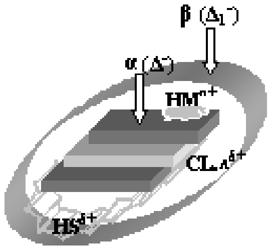
The basic source and carrier of the negatively charged centers in soils are basal planes (**CL.**$_{\mathbf{SA}}^{\boldsymbol{\delta-}}$) of clay minerals (**CL.Min.**$^{\boldsymbol{\Delta-}}$), that form an internal zone (**α**) with partial negative charge ($\boldsymbol{\Delta^- = \Sigma(\delta^- + \delta^+)}$, where $\boldsymbol{\delta^- >> \delta^+}$) and the acidic groups (**HA**$^{\boldsymbol{\delta-}}$) of soil humus substances that belong to the external zone (**β**) of the negative charge ($\boldsymbol{\Delta_1^-}$):



Except of hydrophobic and Van der Waals interactions, a partial positive charge on soil components may be involved in formation of the above structures. The source and carrier of the positive charge ($\boldsymbol{\Delta_1^+}$) are colloidal forms of polyvalent heavy metals (**HM**$^{\mathbf{n+}}$), edge surfaces of clay minerals (**CL.**$_{\mathbf{A}}^{\boldsymbol{\delta+}}$) and some fragments of humic substances (**HS**$^{\boldsymbol{\delta+}}$):



The compensation of the negative surface charge goes mainly by cation (**M**$^{\mathbf{n+}}$) adsorption, positively charged mineral colloids (**HM**$^{\mathbf{n+}}$) and fragments of humic substances (**HS**$^{\boldsymbol{\delta+}}$). Due to this, near the surface of the mineral center of the soil adsorbent a transition („bridge”) zone (γ) is formed that strengthen the overall interactions between humus and clay minerals:

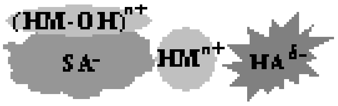


Such structure of the organomineral center (abbreviated further as **SA**$^-$), has its own external adsorption centers that may bind additional amounts of heavy metal micelles and next organic substances, and so on , and the system is stabilized in time in such way that polar (charged surfaces) remain inside and nonpolar (aromatic or aliphatic) groups are exposed. Most of heavy metals in acidic soils are in forms of hydroxyions (**HM-OH**)$^{n+}$, and a smaller part of free cations (**HM**$^{n+}$) is mainly bound to soil exchange positions. This is accepted that positively charged hydrosols form coagulation zones for particles of opposite sign of charge i.e negative parts of clays and humus. The above reactions may be illustrated as following:

At a presence of colloidal forms of heavy metal hydroxides (**HM-OH**)$^{n+}$, in acidic environments the following formation will dominate:

On negatively charged basal planes of clays (**CL.**$_{SA}$$^{\delta-}$) occurs adsorption of free metal cations (**HM**$^{n+}$):

This allows for an excess sorption of humic acids (**HA**$^{\delta-}$):



The diffuse double layer in such systems has now “triple zone“ configuration remaining this illustrated above, where the surface potential may change not only in the amount, but in sign, as well (Friedrichsberg, 1984; Kokotov et al., 1986).

SUMMARY

Distribution of negatively and positively charged specific adsorption centers in the colloidal soil components allows for structure formation and stabilization.

The soil structure may be further stabilized by different forms of polyvalent heavy metals via a range of adsorption, colloidal and ionic interactions.

The structure may have zonal character wherein the mineral center is surrounded by subsequent layers of organic substances bind together by various polyvalent cations forms.

REFERENCES

1. Arora, S., N. Coleman, 1979. The influence of electrolite concentration on flocculation of clay suspensions, Soil Sci., 127, 134-139.
2. Arsova, A., T. Raychev, 2000. Ameliorating copper polluted soil with carbonate deposit and coal powder. J. of Balkan Ecology, 3 (3): 85-89.
3. Arsova, A., T. Raychev, 2001. Effect of organo-mineral treatment on productivity of alfalfa grown on copper and zinc polluted soils. Sofia, Bulg. J. Plant Physiol., 27 (1-2): 25-35.
4. Berry, L.G., B. Mason, R. V. Dietrich, 1987. Mineralogy. Concepts, Descriptions, Determinations. Moskow. 592 pp. (Ru).
5. Boldyrev, A., 1983. Physical colloid chemistry. High school Ed., Moscow, 408pp. (Ru).
6. Charlot, G., 1969. Methods of analytical chemistry. Chemistry Ed., Moscow, 1206pp. (Ru).
7. Cotton, A.F., G. Wilkinson, 1977a. Advansed inorganic chemistry. Part I. Science and Art Ed., Sofia. 677 pp. (Bg).
8. Cotton, A.F., G. Wilkinson, 1977b. Advansed inorganic chemistry. Part II. Science and Art Ed., Sofia. 756 pp. (Bg).
9. Duchaufour, Ph., 1968. L'evolution des soils, Masson et Cie, Paris. (Fr).
10. Duchaufour, Ph., 1972. Processus de formation des soils, Academie de Nancy-metz. (Fr).
11. Friedrichsberg, D., 1984. Colloid chemistry. Chemistry Ed., Leningrad, 368 pp. (Ru).
12. Fripiat, J., J. Chaussidon, A. Jelli, 1971. Chimie-Physique des phenomenes de surface; Applications aux oxides et aux silicates, Masson et C^{ie}, Paris, pp.387. (Fr).
13. Ganev, S., 1990. Contemporary soil chemistry. Science and Art Ed., Sofia, 371 pp.(Bg).
14. Grim, R., 1959. Clay mineralogy. Moskow. 452 pp. (Ru).
15. Jozefaciuk, G., J. Stawinski, A. Arsova, A. Urumova, 1992. The influence of Al on negative soil charge. Zesz. Probl. Post. Nauk Roln., Warsaw, 398: 79-81.
16. Kokotov, J., P., Zolotarev, T. Elkin, 1986. Theoretical base of the ion – exchange. Chemistry Ed., Leningrad, 375pp. (Ru).
17. Lazarov, D., 2001. Inorganic Chemistry. Ed. "Kl. Ohridski". Sofia. 631 pp. (Bg).
18. Orlov, D., 1985. Soil chemistry. Univ. of Moscow Ed., Moscow, 376 pp. (Ru).
19. Raichev, T., 1997. Possibilities for increasing the efficiency of melioration in acid soil polluted with copper. Sofia, Bulg. J. Agric. Sci., 3: 563-571. (Bg).
20. Raichev, T., 1997b. Kinetics of the desorption of cations. II. Desorption of exchangeable calcium depending on humus quality in the soil. Sofia, Soil Sci., Agrochemistry and Ecology, 22 (4): 37-39. (Bg).

21. Raichev, T., A. Arsova, 1998. Regulation of soil adsorption properties in copper contaminated acid soils. Sofia, Bulg. J. Agric. Sci., 4: 25-30.
22. Raichev, T., A. Arsova, S. Popandova, G. Jozefaciuk, 2000. Effect of application of coal powder and lime on alfalfa growth on copper polluted acidic soil. Poland, International Agrophysics, v.14 (1): 121-126,.
23. Raichev, T., R. Toncheva, 1997. Kinetics of the desorption of cations. I. A mathematical model testing. Sofia, Soil Sci., Agrochemistry and Ecology, 22 (4): 34-36 (Bg).
24. Raychev, T., 1996. Influence of organo-mineral interactions on colloid-chemical state of the soil adsorbent. D. Sci. Thesis, "N. Poushkarov" Inst., Sofia, 161 pp. (Bg).
25. Raychev, T., 1997a. Colloid-chemical amelioration of soils, contaminated with copper and arsenic – Theoretical analysis. Sofia, Soil Sci., Agrochemistry and Ecology, 22 (5): 25-27. (Bg).
26. Raychev, T., A. Arsova, M. Benkova, 2002. Estimation of quantitative rates for organo-mineral liming heavy metal polluted acid soils. Sofia, Bulg. J. Agric. Sci., 8: 539-550.
27. Raychev, T., A. Arsova, S. Popandova, 1999. Meliorant for acid soils polluted with copper and method for its application. Sofia, Patent N 327 Y1 BG, 30.07.1999.
28. Raychev, T., A. Arsova, S. Popandova, G. Jozefaciuk, Z. Sokolowska, M. Hajnos, 2001. Mechanisms of Chelate Formation during Organo-mineral Melioration of Heavy Metals Polluted Acid Soils (I), Bulg. J. of Agr. Sci., 7:43-47, Sofia.
29. Raychev, T., A. Arsova, S. Popandova, G. Jozefaciuk, Z. Sokolowska, M. Hajnos, 2001a. Role of Chelating Processes in Formation of Buffer Systems under Organo-mineral Melioration of Cu and Zn Polluted Acid Soils (II), Bulg. J. of Agr. Sci., 7:167-174, Sofia.
30. Schnitzer M., 1991. Soil Organic matter-The next 75 years, Soil Sci., 151, 1: 41-59.
31. Tarchitzky J., Y. Chen, AS. Banin, 1993. Humic Substances and pH Effects on Sodium and Calcium - Montmorollonite. Flocculation and Dispersion ", Soil Science of America Journal, 57, 2: 367 - 372.
32. Zipper, C., S. Komarneni, D. Baker, 1988. Specific cadmium sorption in relation to the crystal chemistry of clay minerals. Soil Sci. Soc. Am. J., 52 (1), 49-53.

MECHANICAL PARAMETERS OF AGRO-BULK MATERIALS

Rusinek R., Stasiak M.

INTRODUCTION

Agriculture and the food industry are, next to chemical and pharmaceutical industries largest producers and users of granular materials. Two basic conditions have to be fulfilled by equipment for storage and processing of granular materials: predictable and safe operations and obtaining high quality of final products.

Granular materials are distinctly different than typical forms of matter: gases, liquids and solids. Sometimes the statement is made that granular materials should be treated as an additional state of matter. Three types of effects typical for granular materials make them different from the other forms of matter: static friction between particles, non-elastic collisions and approximately zero energy of thermal movements as compared to potential energy due to the gravity.

WALL FRICTION

Friction of grain against construction materials depends on numerous factors, which the most important are: type of material, moisture content of grain, normal pressure, sliding path, orientation of grain against direction of sliding, air temperature and relative humidity and grain genus and variety. Coefficients of friction of various grains differ sometimes distinctly. One of the reasons for this variability are differences in roughness and texture of grains surfaces. Grain moisture content is also considered as one of the main reasons for variability in grain coefficient of friction. Coefficient of friction of cereal grains increases with an increase in moisture content, particularly above 13% [3].

Frictional interaction between grain and the bin material may change the value of coefficient of friction. During prolonged sliding, cut in a wax-like substance from the grain seed coat accumulates on the smooth contact surface [4].

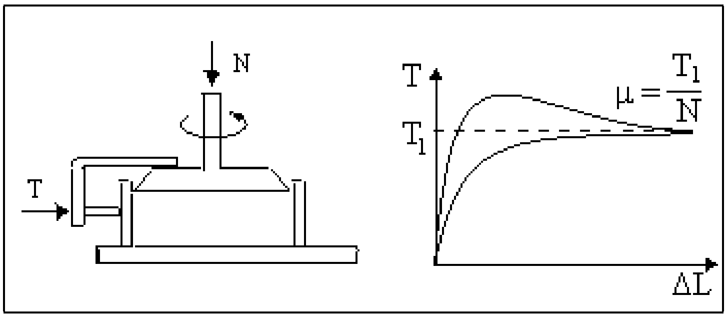


Fig. 1. Coefficient of wall friction for the determination of pressures is determined in the Jenike shear tester

INTERNAL FRICTION

The angle of internal friction depends on the properties of individual particles and on the geometrical structure of the bedding. In the case of cereal grains factors that influence physical properties of kernels are: moisture content, genus, variety, state of maturity and conditions of cultivation. Factors that effect density of packing and spatial structure of arrangement of grains are: bedding formation, moisture content, pressure and time of storage. Dry cereal grain is in general considered cohesion less, and should be considered free-flowing. Cohesion arises for high moisture contents and long storage time.

Angle of internal friction is based on the stress-strain relationship obtained from experiments as e.g. direct shear test. Investigations of granular materials have traditionally used a procedure proposed by Jenike [6] with his direct shear apparatus (Fig. 2.). The angle of internal friction φ and cohesion c is determine from the relationship:

$$\tau = \sigma_r \, tg\varphi + c.$$

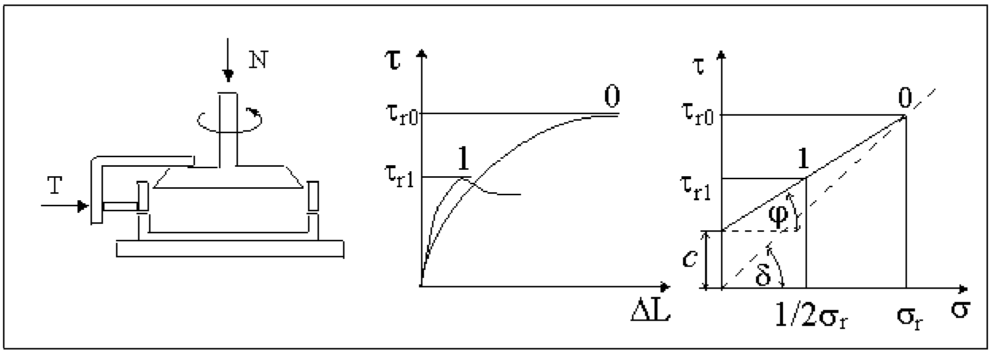


Fig. 2. The angles of internal friction and effective angle of internal friction and cohesion are determined in the Jenike shear tester

PRESSURE RATIO

The horizontal to vertical pressure ratio k is one of the three most important parameters required for the calculation of stresses that granular materials exert on the wall and floor of a silo, introduced by Janssen [5]. The author assumed the vertical pressure was uniform in a horizontal section of the silo and that ratio k was constant everywhere within the material.

Two states of stress are commonly associated with the pressure ratio in a deep silo: the active state for filling and storage and the passive state for discharge mode [8]. The pressure ratio k depends not only on stress state, but also on type of grain, moisture content, bedding structure of grain formed during the filling process, angle of internal friction [7] and coefficient of friction on the wall. Experimental determination of pressure distribution in a bulk of grain may be performed in a model silo or in practical conditions of silo operation. The most popular method of experimental determination of the lateral to vertical pressure ratio is the uniaxial compression test [2]. An experimental set for the uniaxial compression (Fig. 3) was built according to the general guideline of the Eurocode 1 [1] standard. The pressure ratio k_s appropriate for filling and storing is determine as:

$$k_s=1.1k_{so},$$

where

$$k_{so}=\Delta\sigma_x/\Delta\sigma_{zm}$$

at the reference vertical stress $\sigma_{zm}=100$ kPa, $\sigma_{zm}=(\sigma_z+\sigma_{zo})/2$.

The pressure ratio is calculate also from empirical formula relating pressure ratio k_φ to the angle of internal friction φ Eurocode 1:

$$k_\varphi=1.1(1-\sin\varphi).$$

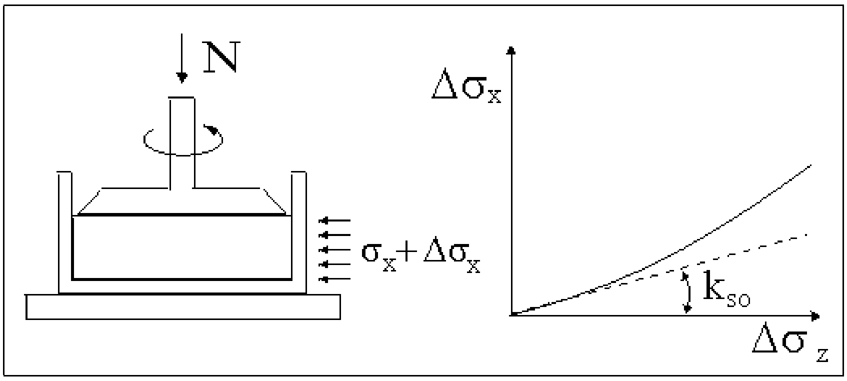


Fig. 3. The pressure ratio is determined in the uniaxial compression test. The tester measures the horizontal stress.

RESULTS

Values of coefficient of wall friction depend on wall's building material, levels of moisture content, surface properties of granular materials and normal stress (Tab. 1.). Coefficient of friction of cereal grains increases with an increase in moisture content. The highest values of coefficient of wall friction were found for concrete.

With the moisture content increase the friction force and the cohesion between grains increase. As a result smaller part of the vertical loading is transmitted into the lateral direction. Consequently, the lateral to vertical pressure ratio should decrease with an increase in moisture content. Tests performed for rape seeds, corn, oat and wheat grains confirm this relationship (Table 2). Nearly a linear decrease of the pressure ratio with an increase in moisture content was obtained for rape seeds and corn. Another course of changes were obtained for barley: the pressure ratio was almost constant in the range of moisture content up to 17.5% and then decreased. This indicates that probably also other factors could participate in the vertical to horizontal stress transmission.

Table 1. Values of coefficients of wall friction μ for different levels of the normal stress (20 - 60 kPa) for granular materials of moisture content of 10%

Granular material	Normal stress [kPa]	Coefficients of wall friction μ		
		Stainless steel	Galvanized steel	Concrete B 30
Barley variety Rudnik	20	0,176 ± 0,006	0,217 ± 0,014	0,487 ± 0,013
	30	0,163 ± 0,008	0,193 ± 0,009	0,468 ± 0,007
	40	0,157 ± 0,002	0,173 ± 0,010	0,451 ± 0,012
	50	0,160 ± 0,006	0,171 ± 0,003	0,444 ± 0,004
	60	0,150 ± 0,005	0,171 ± 0,007	0,426 ± 0,004
Wheat variety Begra	20	0,189 ± 0,003	0,174 ± 0,010	0,541 ± 0,014
	30	0,160 ± 0,002	0,183 ± 0,004	0,497 ± 0,020
	40	0,152 ± 0,004	0,170 ± 0,003	0,496 ± 0,007
	50	0,159 ± 0,006	0,169 ± 0,002	0,476 ± 0,010
	60	0,160 ± 0,004	0,165 ± 0,003	0,468 ± 0,005
Oat variety Borowiak	20	0,158 ± 0,004	0,195 ± 0,014	0,345 ± 0,005
	30	0,150 ± 0,001	0,200 ± 0,008	0,328 ± 0,001
	40	0,147 ± 0,004	0,180 ± 0,004	0,324 ± 0,002
	50	0,148 ± 0,003	0,180 ± 0,002	0,327 ± 0,001
	60	0,149 ± 0,004	0,176 ± 0,003	0,343 ± 0,009
Rye variety Amilo	20	0,205 ± 0,004	0,155 ± 0,005	0,349 ± 0,002
	30	0,195 ± 0,009	0,169 ± 0,001	0,354 ± 0,007
	40	0,219 ± 0,013	0,175 ± 0,014	0,349 ± 0,006
	50	0,214 ± 0,013	0,143 ± 0,001	0,337 ± 0,007
	60	0,218 ± 0,011	0,150 ± 0,003	0,337 ± 0,004

CONCLUSION

The friction force and the cohesion between seeds increase with increasing moisture content. As a result the pressure ratio decreases. The strongest decrease was obtained for rape seeds.

Values of coefficient of wall friction for stainless steel and galvanized steel were found lower than the values for concrete.

The coefficient of wall friction was found increasing with an increase in the moisture content of seeds.

Table 2. Measured (k_s) and calculated (k_φ) values of the pressure ratio of seeds and corresponding values the angle of internal friction φ for different values of the moisture content (mean ± st.dev).

Grain	Moisture content (w.b.) [%]	k_s	k_φ	φ [deg]
Barley	10	0.45 ± 0.02	0.59 ± 0.03	27.8 ± 0.4
	12.5	0.47 ± 0.03	0.56 ± 0.04	28.5 ± 0.5
	15	0.43 ± 0.02	0.50 ± 0.05	31.2 ± 0.3
	17.5	0.45 ± 0.03	0.54 ± 0.06	30.6 ± 1.0
	20	0.39 ± 0.03	0.51 ± 0.03	33.2 ± 0.5
Corn	10	0.48 ± 0.04	0.60 ± 0.01	26.7 ± 0.6
	12.5	0.40 ± 0.03	0.52 ± 0.02	31.7 ± 0.5
	15	0.36 ± 0.05	0.51 ± 0.03	32.0 ± 1.4
	17.5	0.34 ± 0.03	0.50 ± 0.02	33.4 ± 0.8
	20	0.30 ± 0.05	0.51 ± 0.06	33.6 ± 1.5
Oat	10	0.49 ± 0.03	0.67 ± 0.04	22.1 ± 1.1
	12.5	0.44 ± 0.04	0.68 ± 0.04	22.4 ± 0.9
	15	0.45 ± 0.03	0.64 ± 0.02	24.0 ± 0.5
	17.5	0.40 ± 0.03	0.66 ± 0.05	23.9 ± 1.0
	20	0.41 ± 0.06	0.63 ± 0.05	26.4 ± 1.7
Wheat	10	0.44 ± 0.02	0.62 ± 0.02	25.7 ± 0.3
	12.5	0.38 ± 0.01	0.61 ± 0.02	26.2 ± 0.4
	15	0.34 ± 0.02	0.60 ± 0.03	27.0 ± 0.5
	17.5	0.31 ± 0.02	0.50 ± 0.04	33.0 ± 1.0
	20	0.35 ± 0.01	0.46 ± 0.03	35.5 ± 0.5
Rape seeds	6	0.46 ± 0.02	0.64 ± 0.02	24.7 ± 0.5
	9	0.28 ± 0.04	0.54 ± 0.03	30.6 ± 0.4
	12	0.27 ± 0.02	0.52 ± 0.01	31.7 ± 0.7
	15	0.24 ± 0.02	0.47 ± 0.01	34.8 ± 0.7

REFERENCES

1. Eurocode 1. Actions on structures. Part 4. Actions in silos and tanks. DD ENV 1991-4: 2003.
2. J. Horabik, R. Rusinek: Pressure ratio of cereal grains determined in uniaxial compression test. International Agrophysics, 16(1), 23-28, 2002.
3. J. Horabik, M. Molenda, Grain pressure in a model silo as affected by moisture content increase, International Agrophysics, 14(4), (2000), 385-392.
4. J. Horabik, M. Molenda, R. Rusinek, M. Stasiak, Influence of selected parameters on friction of cereals grain, Acta Scientiarum Polonorum - Technica Agraria, 1(2), (2002), 81-87 (in Polish).
5. H. A. Janssen, 1895.Versuche über Getreidedruck in Silozellen. Verein Deutscher Ingenieure, Zetschrift (Düsseldorf), 39, 1045-1049.

6. A.W. Jenike, Storage and flow of solids, Bull. 123, Eng. Expt. Sta., Utah State Univ., (1964).
7. J. Łukaszuk, J. Horabik: Determination of the angle of internal friction of plant granular solids (in Polish). Acta Agrophysica, 64, 2002.
8. E.B. Moysey: Active and passive pressures in deep grain bin. Transactions of the ASAE, 77, 1409–1413, 1979.

SMART SENSORS IN THE MEASUREMENT OF SOIL PHYSICAL PARAMETERS

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

ABSTRACT

The study presents the project and partial implementation of a modern monitoring system for the measurement of soil physical parameters. It is provided with smart sensors equipped with signal conversion electronics, individual identification and communication means decreasing the complexity of the measurement system and also the measurement errors that can appear during analog signal transmission along the cables from the sensors to the measuring unit. The applied wireless communication system operates in the 433 MHz ISM (Industrial, Scientific, Medical) licence free frequency band for transmission of commands and data between a remote PC compatible computer (Master unit) and the smart sensors (Slave units) in the distance of several hundred meters. The presented partial implementation of the system measures the temperature at several locations in the soil profile in field conditions and communicates with the host PC computer in wireless way. The developed hardware and software is intended to be adapted to more complex monitoring systems working in compliance with IEEE 1451 smart transducer interface standard and covering large areas as an element of air-borne or satellite remote sensing and serve for ground reference measurements.

It is shown that the currently available technical means enable to apply smart sensors and wireless communication in the environmental monitoring in the economically justified way. The small increase of the system price by providing the measuring smart sensors, already equipped some element of control or computation, with radio communication assures the decrease of measurement errors and makes the collection of environmental data convenient for the system operator.

INTRODUCTION

A sensor is the portion of a measurement system that responds directly to the physical variable being measured (Figliola, 1999) such as thermal energy, electromagnetic energy, acoustic energy, pressure, magnetism, or motion by producing quantitative, usually electrical signals. Sensors are input devices of the measurement system while actuators are output devices translating electrical signals into usually mechanical actions. Transducers are defined as devices that convert one type of energy to another, for example temperature to an electrical signal. A sensible distinction is to use 'sensor' for the sensing element itself and 'transducer' for the sensing element plus any associated circuitry. All transducers would thus contain a sensor and most (though not all) sensors would also be transducers.

Smart transducers must incorporate some element of control, computation or decision-making. They enhance functionality, performance or cost of the measurement system.

Sensors and actuators are everywhere: at home appliances, in the office, in factories etc., and they are intended to increase the control of human environment, increase production efficiency and enhance our security. Because of the inherent intelligence smart sensors implementation would give many advantages as compared to standard sensors, e.g.:

- self-test and self-calibration,
- increased accuracy of the measurement by minimizing analogue signal wire transmission,
- remote programmability, digital communication, networked wireless and WEB based remote monitoring and control,
- implementation of Plug-and-Play features.

Smart sensors and smart sensor interfaces

The driving forces that develop smart sensor technology are mainly: aerospace, automotive and military industries, industrial control and automation, building automation, security and also environmental monitoring.

Currently there are two ways for the development of smart sensing technologies (Wiczer, 2001). The first one represents basic physical and (bio) chemical research in sensor's conversion phenomena: thermoelectric, photoelectric, photomagnetic, electromagnetic, thermooptic, etc. in the context of integrating the sensing element with microelectronic-based "smart" capabilities. The problems facing researchers in this field concern selectivity, materials compatibility and integration of different technologies. The example of technology and material incompatibility is a thermocouple operating at temperatures 300 °C to 500 °C enhanced by "smart" microelectronic element. The most microelectronics circuits do not work at temperatures above 150 °C and the materials used to manufacture thermocouples are generally not compatible with high purity conditions of silicon based microelectronics fabrication process. Other example is the Micro-Electro-Mechanical System (MEMS) that integrate mechanical elements, sensors, actuators, and electronics on a common silicon substrate through micro-fabrication technology. The successful applications of MEMS sensors are: pressure transducers integrated with analogue signal processing circuits and digital interfacing circuits, accelerometers available in the form of integrated circuits. Apart from technical obstacles there are also economical reasons that hamper the wide implementation of integrated smart sensors, i.e. users and producers implementation costs as well as the lack of widely accepted standards.

Use of smart interfaces is another way for implementing smart sensor technologies. Smart interfaces allow moving technology specific sensor elements from microelectronics of analogue signal conditioning, conversion, digital signal processing and communication to enhance existing sensors with intelligence by means of smart interfaces (Wiczer, 2001). This solution enables to use existing sensors the users are accustomed to, and do not force the sensor producers to sometimes expensive research in solving technology and material incompatibilities. A set of standards under development, aimed to simplify sensors connectivity is coordinated by National Institute of Standards and Technology (NIST) and is adopted by Institute of Electrical and Electronics Engineers (IEEE) under the name IEEE 1451 (Lee, 2003).

The purpose of IEEE 1451 standards (http://ieee1451.nist.gov) is to define a set of common interfaces for connecting transducers to microprocessor-based systems, instruments and field networks in a network-independent fashion. The IEEE 1451 standard include five complete sub-standards. The IEEE 1451.1 and 1451.2 have been published and accepted by the IEEE. The sub-standards IEEE P1451.3, IEEE P1451.4 and IEEE P1451.5 are in progress, which is denoted by the letter "P". The IEEE 1451.1 defines the way the transducers are connected by a Network-Capable Application Processor (NCAP) to networks such as Ethernet. This standard supports all of the interface module communication with transducers used by the rest of the IEEE 1451 family. IEEE 1451.2 standard defines point-to-point digital communication between a Smart Transducer Interface Module (STIM) and the NCAP (Fig. 1) by means of a Transducer Independent Interface (TII). The STIM contains a Transducer Electronic Data Sheet (TEDS) with information (the manufacturer data, and the optional calibration and correction data) in standardized format about every transducer connected. TEDS is always attached to the transducer and its content is electronically transferred to NCAP or a host computer connected to the arbitrary network, thus the human errors associated with manually entering sensor parameters are avoided and Plug-and-Play features can be implemented.

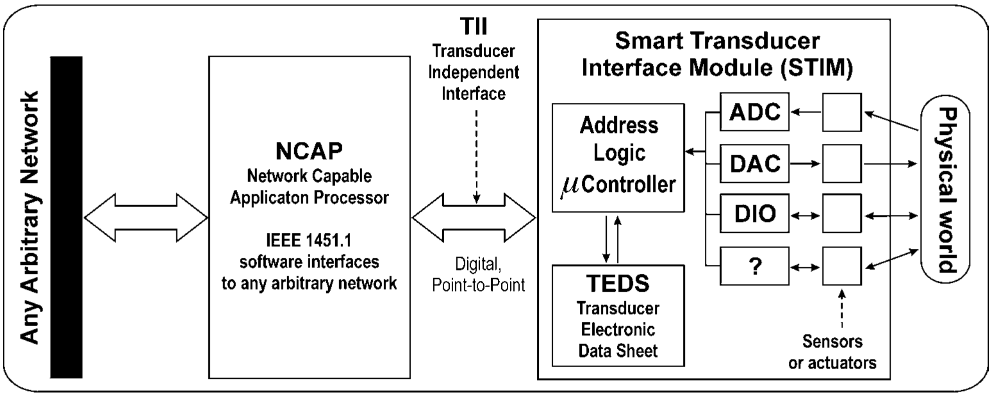


Fig. 1. *IEEE 1451.2 standard of digital point-to-point system interface, ADC-Analogue to Digital Converter, DAC-Digital to Analogue Converter, DIO-Digital Input/Output*

The IEEE P1451.3 standard is designed for distributed multidrop smart sensor systems, where a large amount of sensors need to be read in a synchronized manner. In some cases it is not possible to locate the TEDS with the transducers, as it is accomplished in the IEEE 1451.2 standard, for instance due to harsh environment. The physical representation of the proposed IEEE P1451.3 standard is presented in Fig. 2. A single transmission line is intended to supply power to the transducers and to provide the communication between the bus controller located in NCAP and the Transducer Bus Interface Modules (TBIM). A transducer bus is expected to have one bus controller and many TBIMs, and a TBIM may contain one or more different transducers.

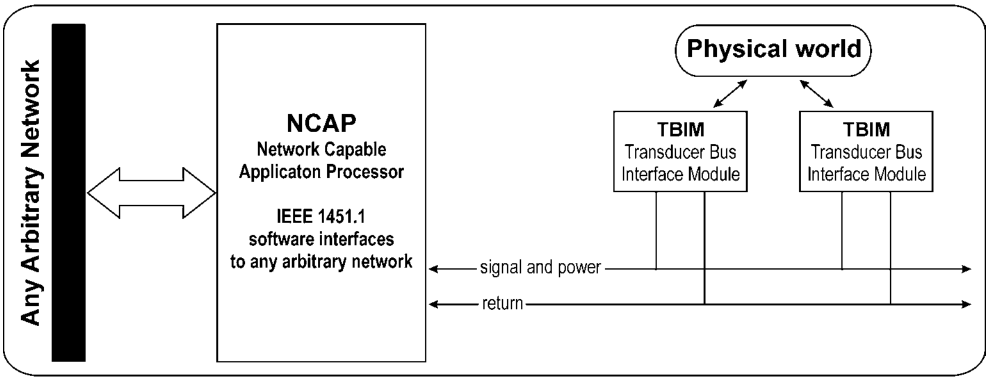


Fig. 2. *IEEE P1451.3 proposed standard of the digital multidrop system interface*

The proposed standards IEEE P1451.4 and IEEE P1451.5 are intended for: mixed-mode (analog and digital) communication and wireless communication protocols, respectively.

Measurement systems in Agrophysics

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.

Soil physical parameters change continuously for climatic reasons and human activity. 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 (Fig.3).

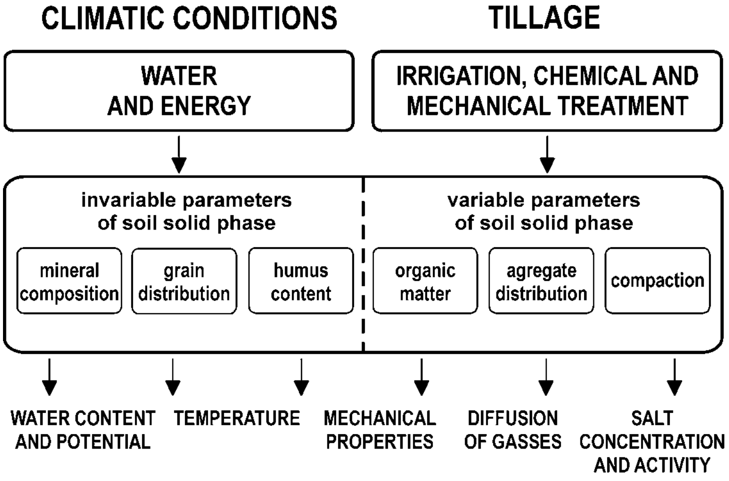


Fig. 3. *Factors influencing invariable and variable parameters and physical quantitative indicators of soil solid phase*

The selected field sensors used to determine the basic soil solid phase by means of direct or indirect indicators 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. A very promising method for soil moisture determination is based on Time Domain Reflectometry – TDR (Topp et al., 1980; Malicki and Skierucha, 1989; Malicki et al., 1996; Malicki and Walczak, 1999; Skierucha and Malicki, 2002). Its methodology and measurement equipment including TDR soil moisture sensor has been developed in the Institute of Agrophysics Polish Academy of Sciences (IAPAS) since 1985. Also the concentration of selected ions in the soil giving the information about its fertility and/or intoxication seems to be of major concern. Research on the application of ion selective electrodes in three-phase medium has recently become the research subject of IAPAS.

MATERIAL AND METHODS

The measurement system under development in IAPAS is intended to work in compliance with IEEE 1451.3 standard of digital multidrop system interface (Fig. 2). Also it will accomplish some elements of wireless communication (IEEE 1451.5). The schematic description of this system is presented in Fig. 4.

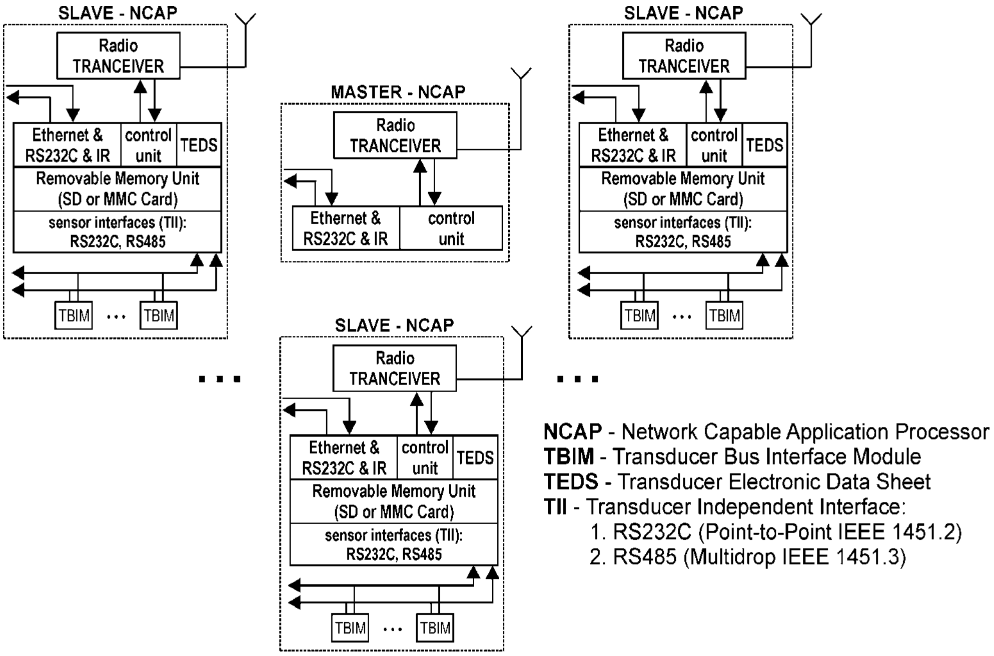


Fig. 4. *System under development in IAPAS for the measurement of agrophysical properties, working in compliance with the IEEE 1451 standard*

The main element of the system is the NCAP for communication with the Ethernet network from one side and the transducers from the other side. NCAP may work as a MASTER or SLAVE unit, both based on the same electronics, but the MASTER unit serves only as an interface between multiple SLAVEs and the Ethernet network, without the ability to manage transducers (sensors or actuators). The transducers are connected to the SLAVES by means of a digital multidrop system interface constructed on the hardware base of a serial RS485 interface, serving as a small and cheap TBIM that fits easily into a transducer. For the purpose of compatibility with old versions of sensors and instruments developed in IAPAS there is also RS232C asynchronous serial interface for digital point-to-point communication, like in the IEEE 1451.2 standard. In the case of multiple SLAVEs they communicate with the MASTER unit by means of wireless communication using 433 MHz ISM (Industrial, Medical and Scientific) licence free frequency band. Each SLAVE has a large amount of non-volatile memory, for the storage of data collected from transducers, in the form a popular and not expensive removable Secutity Digital (SD) or Multi-Media Card (MMC). The information about the connected transducers is stored in TEDS being a part of the microprocessor unit.

The main technical features of the soil physical parameters monitoring system with wireless communication link are as follows:

- radio communication in the license-free ISM (Industrial, Scientific and Medical) frequency bands 433 MHz,
- the hardware and software of the communication system is designed with the following major criteria:
    - minimize the transmission errors,
    - maximize the radio link range,
    - minimize the current consumption (SLAVEs are battery operated),
- each SLAVE device has facilities to connect it directly to the Ethernet network, as a Plug-and-Play device, with unique identification parameters (TEDS),
- sensors, smart sensors-transducers, measuring devices from various vendors (i.e. TDR units, tensiometers, temperature sensors, etc.) are connected to the SLAVEs by the sensor interfaces,
- SLAVEs are equipped with memory cards (Secure Digital or MultiMedia Cards) to store collected data (memory capacity is up to 128 MB).

Basic functional features of the wireless communication system:

- MASTER device works as a converter of radio data 433 MHz (other frequencies in ISM bands: 868 MHz and 2.4 GHz are planned for implementation) to Ethernet data accessible from any personal computer (PC) connected to Internet. It mediates between PC computer and SLAVE devices in data and commands transfer.
- The SLAVE device executes commands from a text script file stored in a memory card. After execution the last command in the script file, the sequence starts from the first command.
- The commands in the script file allow the SLAVE to:
    - change the parameters of the serial interfaces,
    - send commands and receive data by the sensor interfaces,
    - create an output file in the memory card and store data from the sensors in it,
    - change the format of data output file (insert time or data, number of the script executions, name of the script file executed currently),
    - initiate the sleep mode of the SLAVE (with minimized power consumption) for a fixed time (in seconds).
- Configuration and control of SLAVE device is performed by radio communication (default), Ethernet or serial interface RS232C and it enables to:
    - read the state of the SLAVE device (local real time clock, battery voltage, temperature, free memory card area, number of the script executions, the name of the current script),

    - read whole or partial files from the memory card,
    - write a new script file to the memory card,
    - stop the script execution and start it again,
    - give an unique identification number of the SLAVE.
- The application software is an Internet browser (e.g. Internet Explorer or Netscape) running on any PC computer connected to Internet accomplishes the control of the measurement system. The individual IP number and password guard the access to the selected SLAVE.

RESULTS AND DISCUSSION

The presented system of wireless communication was tested by connecting seven temperature sensors to the SLAVE unit, one of which measured the ambient temperature, the others were placed in the soil at the depths: 5, 10, 15, 20, 30 and 40 cm below the ground level. The SLAVE unit was placed in metal enclosure, protecting the electronics from rain, in a field plot at the distance about 70 m from the building with the PC computer controlling the MASTER unit. Detailed description of the experiment and the wireless communication protocol is presented in Wilczek et al., 2003.

The experimental setup worked several days measuring and transmitting the temperature data by the radio link. The quality of the link is presented in Fig. 5. Totally there were 2772 radio connections with 97% performed in the first attempt. Only 3% connections were repeated; 11 1-time, 74 2-times and 1-time the attempt of radio connection had to be repeated 3 times to succeed.

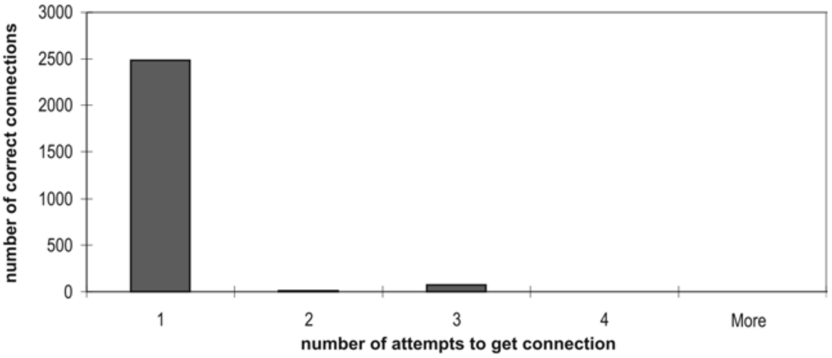


Fig. 5. *A histogram presenting the frequency of successful data transfer between MASTER and SLAVE devices*

The developed transmission protocol allows 10-times repetitions of sending the data or command frame. If the connection is not established the PC computer registers this event and records it in a text file, and then the system continues the operation. It was experimentally checked that the SLAVE unit worked well enough at distance about 500 m from the MASTER unit, provided that there was no obstacle (trees, buildings, etc.) between them. In other words the devices have to see one another.

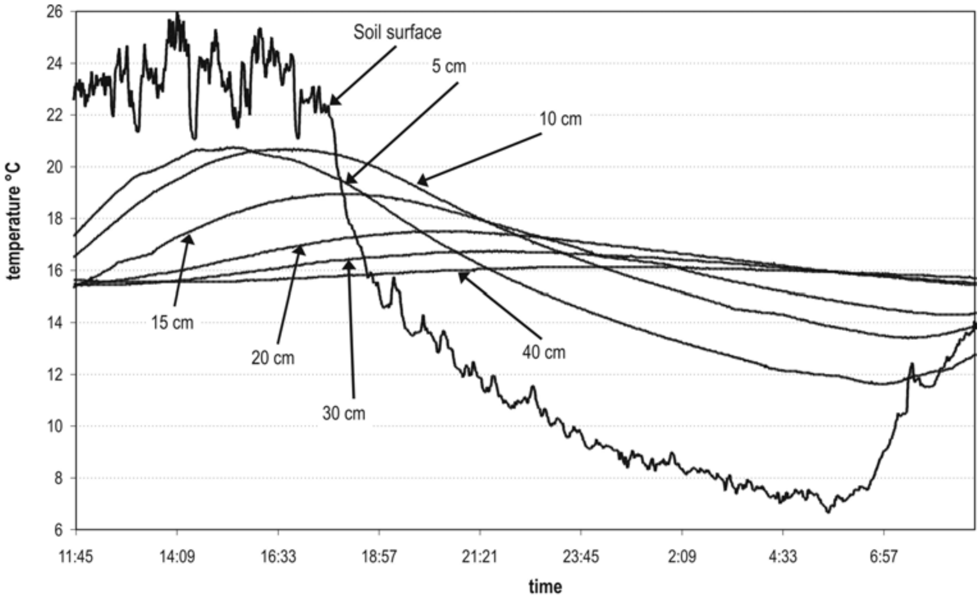


Fig. 6. *Example readout of temperature sensors located on different depths of soil profile*

The readouts from the temperature sensors placed on various depths in the soil profile are presented in Fig. 6. As expected, the sensor that measured the ambient temperature had the shortest response time to the temperature change. The deeper the sensor was located, the slowest reaction on the temperature change was observed. Additionally, the reaction of the sensors to temperature changes was shifted in time because of the limited speed of temperature change in the soil profile (Walczak, 1987).

The main motivation for the measurement system (Fig. 4.) design and implementation was the need to modernize the existing monitoring system of soil physical parameters: moisture measured by Time Domain Reflectometry method (Topp et.al., 1980; Malicki et al., 1996), water potential, salinity, and temperature. Such a system has been manufactured in IAPAS (http://www.easytest.lublin.pl) and used in many research centres in the world for soil physical properties analysis. It enables to verify the models of mass and energy transport in the soil in field conditions. Also, it may be applied for analysis of other porous media: building materials, food products, etc. as well as their storage and transportation. Particularly important parameter for monitoring is water content directly influencing the physical and chemical processes in these media.

New technical developments concerning the implementation of smart sensors and data transfer enhance the functionality of the measurement system. The applied ISM frequency band of 433 MHz in many cases does not provide the required speed for data transfer, which is limited to 9600 kbit/sec. However at the design stage the electronic components for wireless data transmission assuring the assumed criteria existed only for this frequency band. Being aware of new telecommunication developments this part of the system can be the most easily modified to fulfil the lowest power consumption and highest speed data transfer. The measurement system will be enhanced by other existing and popular sensors that are applied in soil physics and chemistry as well as environmental protection (psychrometric sensors, porous blocks, wind gauges, solar gauges, redox potential, oxygen diffusion rate sensors and pH sensors, ion selective electrodes, etc.). These sensors with additional electronics as an element of control and computation are intended to form Plug-and-Play smart sensors working according to IEEE 1451 standard.

CONCLUSIONS

The presented monitoring system for the measurement of soil physical parameters is intended to be equipped with smart sensors and wireless communication in the ISM (Industrial, Scientific, Medical) frequency band 433 MHz.

Partial implementation of the system in the form of two-point communication for the temperature measurement in a soil profile proves that the availability of advanced technology enables to enhance the existing measurement systems and sometimes only the sensors with functional and not expensive radio communication the distance of several hundred metres.

The developed hardware and software can be adapted to more complex monitoring systems working in compliance with IEEE 1451 standard and covering larger areas including air-borne or satellite remote sensing and serve as a source for ground reference measurements.

ACKNOWLEDGMENTS

This study was supported by the Polish State Committee for Scientific Research, Research Project 2 P04G 032 26.

LIST OF SYMBOLS AND ABBREVIATIONS

IAPAS	Institute of Agrophysics of Polish Academy of Sciences in Lublin, Poland
IEEE 1451	Set of smart sensor network standard under development by the Institute of Electric and Electronic Engineers
ISM band	Industrial, Scientific and Medical licence free frequency band
MEMS	Micro-Electro-Mechanical System
MMC	Multi-Media memory card

NCAP	Network-Capable Application Processor
NIST	National Institute of Standards and Technology
ODR	Oxygen Diffusion Rate
SD	Security Digital memory card
STIM	Smart Transducer Interface Module
TBIM	Transducer Bus Interface Module
TDR	Time Domain Reflectometry
TEDS	Transducer Electronic Data Sheet
TII	Transducer Independent Interface

REFERENCES

1. Figliola, R.S. (1999): Operational Modes of Instrumentation. In Webster J.G.: The Measurement Instrumentation and Sensors Handbook, Boca Raton, FL, CRC Press/IEEE Press.
2. Lee, K.B. (2003): The smart transducer interface standard (IEEE P1451). NIST Workshop on Data Exchange Standards at the Construction Site. NIST. Gaithersburg.
3. Malicki, M.A, Plagge R., Roth C.H. (1996). Reduction of soil matrix effect on TDR dielectric moisture determination by accounting for bulk density or porosity. European Journal of Soil Science, Vol. 47, No. 3, 357-366.
4. Malicki M.A., Skierucha W.M. (1989). A manually controlled TDR soil moisture meter operating with 300 ps rise-time needle pulse. Irrigation Science. 10:153-163.
5. Malicki M.A., Walczak R.T. (1999). Evaluating soil salinity status from bulk electrical conductivity and permittivity. European Journal of Soil Science, 50, 505-514.
6. Skierucha W., Malicki M.A. (2002). Dielectric mixing models: validation in mineral soils. Poster Presentation. 17th World Congress of Soil Science. Bangkok. Thailand.
7. Walczak R. (1987). Basic problems of mass and energy transfer in the soil-plant-atmosphere system. Zeszyty Probl. Post. Nauk Roln., vol. 346:12-22.
8. Wiczer, J. (2001) Connectivity: smart sensors or smart interfaces. ISA 2001 Emerging Technologies Conference, Huston, TX, Sept. 10-13.
9. Wilczek A., Mazurek W., Skierucha M. (2003). Application of wireless communication in automatic monitoring of temperature in soil profile. Acta Agrophysica 93:123-133.
10. Topp G.C., Davis J.L., Annan A.P. (1980). Electromagnetic determination of soil water content: measurements in coaxial transmission lines. Water Resources Research. 16:574-582.

ASORPTION AND SURFACE AREA OF AGRICULTURAL MATERIALS

Sokołowska Z.

Two factors, surface area and porosity are recognised to play complementary parts in adsorption phenomena for a vast range of solids. To understand the way, in which measurements of the adsorption of gases or vapours can be used to obtain information about surface area and porosity, it is necessary to deal briefly the concept of the adsorption isotherm.

ADSORPTION OF GASES OR VAPOURS ON SOLIDS

The term *adsorption* appears to have been introduced by Kayser in 1881 to connote the condensation of gases on free surfaces, in contradistinction to gaseous *absorption* where the gas molecules penetrate into the mass of the absorbing solid. The term *sorption* proposed by McBain in 1909, embraces both types of phenomena, adsorption and absorption. When a solid is exposed in a closed space to a gas or vapour at some definite pressure, the solid begins to adsorb the gas or vapour. The amount of gas adsorbed can be then calculated from the fall in pressure (by application of the gas law if the volumes of vessel and of the solid are known), or it can be determined directly as the increase in weight of the solid. The adsorption is a consequence of the field force at the surface of the solid (*the adsorbent*), which attracts the molecules of the gas or vapour (*the adsorbate*). The forces of attraction emanating from a solid may be of two main kinds, physical and chemical, and they give rise to physical adsorption and chemisorption, respectively. The physical adsorption is also called as van der Waals adsorption. In the present paper we are concerned with physical adsorption.

MEASUREMENT OF THE ADSORPTION OF A GAS OR A VAPOUR

Static method

The adsorption-desorption isotherms of a gas or a vapour are measured by *gravimetric method* as following: The solid is contacted with gas or vapour during a time necessary for equilibration. The time is dependent on the relative gas or vapour pressure and on the nature of solid. The amount of adsorbed gas or vapour is computed as the difference between the weight of the sample with gas (after adsorption) and the weight of initial sample of solid (before adsorption).

Dynamic method

The method described above is static method. There is also a dynamic method of measuring of adsorption. It is used almost exclusively for determining the adsorption of gas mixtures, but can be employed just as well for pure gases also. The gas is filtered through a bed of adsorbent. The gas pressure ahead of the filter is kept constant. At the beginning of the filtration the gas pressure behind the filter is very small, practically the whole amount of gas reaching the bed is adsorb in it. This pressure gradually increases and finally becomes equal to that ahead of the bed, and the adsorbent becomes saturated with gas at the selected pressure.

THE ADSORPTION ISOTHERM OF A GAS OR A VAPOUR

At the boundaries between solids and gases an accumulation of the particles occurs. The amount adsorbed per gram of a solid depends on the equilibrium pressure p, the temperature T, and also on the nature of the gas and the solid: $N=f\,(p, T, \text{gas, solid})$. This function at a constant T is called the *adsorption isotherm* if p increases, and *desorption isotherm* - if p decreases. For a given gas adsorbed on a given solid, maintained at a fixed temperature, this equation simplifies to: $N=f\,(p)_{\mathrm{T,\ gas,\ solid}}$, and if the gas is below its critical temperature the alternative isotherm equation is: $N=f\,(p/p_0)_{\mathrm{T,\ gas,\ solid}}$, where p_0 is the saturated vapour pressure of the gas. The adsorption, N, may be measured in any suitable units i.e. grams or milligrams, moles or millimoles, and cm^3 (N.T.P.).

The adsorption isotherm is the most popular expression of adsorption data. A complete adsorption isotherm covers the whole range of equilibrium pressures from very low pressures to the neighbourhood of the saturation pressure. Complete adsorption isotherms are common pointing by plotting along the abscissa the relative vapour pressure p/p_0. The isotherm naturally start at the origin of the coordinates and they end is at a nearly of the saturated vapour. No simple interpretation can be given to the main part of the curve. It is often supposed that at the higher relative pressures (at which adsorption hysteresis occurs) the adsorbed substance is capillary condensed, while at the lower p/p_0 the surface of adsorbent is covered with a thin layer of gas molecules. The beginning part of the isotherm is used to obtain the surface area, and the end part to evaluate the pore structure in a solid body. The volume of liquid which is adsorbed at nearly saturated vapour by 1 gram of adsorbent is called the pore volume of the adsorbent.

Types of adsorption isotherms

In the literature of the subject there are recorded tens of thousands of adsorption isotherms, measured on a wide variety of solids. The majority of those isotherms, which result from the physical adsorption, may for convenience be grouped into five classes. This classification commonly referred as the Brunauer, Emmett and Teller (BET) classification. These types are shown in Figure 1.

To the estimation of the surface area a kind of the soils mainly adsorption isotherm type II to be considered.

Theory and equation of the adsorption isotherm

In many instances an algebraic expression of the adsorption isotherm is more convenient than its graphic presentation. A few equations have been found to reproduce a large number of experimental isotherms.

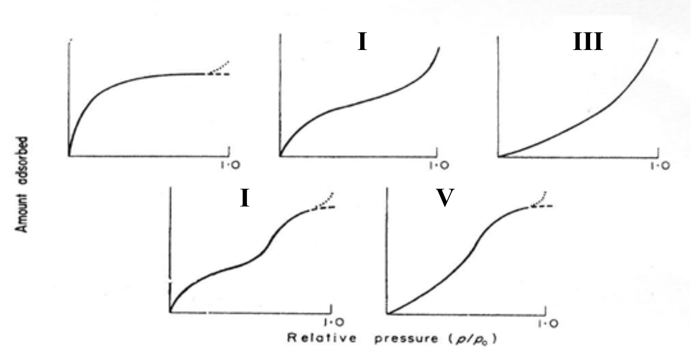


Fig. 1. *The types of adsorption isotherm in BET classification*

The older one, commonly know as Freundlich isotherm: $N = kp^{1/n}$, where N is the amount of adsorbed of gas, *p* is the pressure, *k* and 1/*n* are constants. Many gases and vapours have 1/*n* values between 0,3 and 0,5.

The other equation is knows as Langmuir isotherm: $N = (N_m kp)/(1 + kp)$, where *k* is the constant. Langmuir regarded the surface of the solid as array of adsorption sites, each site being capable of adsorbing one molecule, and all sites were characterised by the same adsorption energy, and the attractive interactions between adsorbed molecules could be ignored. The Langmuir equation described localised monolayer adsorption on the homogeneous surface of adsorbent.

Brunauer, Emmett and Teller approach the problem of adsorption kinetically. In 1938, they explicitly extended the Langmuir evaporation-condensation mechanism to second and higher molecular layers. The state of affairs when equilibrium is reached at any given pressure may be represented formally as varying numbers of molecules being condensed on any one site. The BET model assumes that the surface is energetic uniform i.e. that all adsorption sites are exactly equivalent. The model neglects horizontal interactions between the molecules within the adsorption layer, and takes into account only the vertical interactions, and postulate that the heat of adsorption in the higher layers is equal to the latent heat of condensation. The BET equation described localised multilayer adsorption on the homogeneous surface of adsorbent:

$$N = \frac{N_m x C_{BET}}{(1 - x)\left[1 + (C_{BET} - 1)x\right]}$$

where $x = p/p_0$ relative pressure of water vapour, *N* amount of adsorbed water vapour, and C_{BET} constant.

Fig. 2. *The BET model for adsorption*

The range of validity of BET equation does not always extend to relative pressure as high as 0.30 or 0.5. Many additional equations for the polymolecular adsorption isotherm have been published in the literature, for example the Dubinin-Radushkevich (DR), the Huttig, the Frenkel-Hasley-Hill (FHH) or the Aranovich equation

SURFACE AREA OF SOLID

Kind of the surface area

Solid phase of a soil is a mixture of different inorganic constituents as nonporous materials of different size and shape, porous materials with microcapilares or pores and phyllosilicates with the interlayer structure, as well as organic species, mainly organic matter.

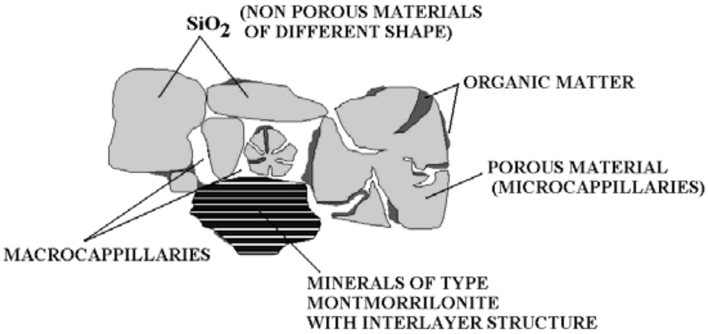


Fig. 3. *Scheme of solid phase of the soil (geometric scheme)*

Different kind of the surface area may be found in soils. The *geometric* surface area is calculated, knowing shapes and dimensions of representative soil particles. *The internal surface area* is the surface inter walls of the microcapillares (the term "internal surface" is usually restricted in its application to those cavities, which have an opening to exterior of the grains). T*he external surface are*a is defined as the sum of geometric and internal surface area. T*he interlayer surface area* - the surface of interlayer walls of minerals type as montmorillonite. T*he total surface area* is the sum of the external, internal and the surface area of organic matter.

The specific surface area of a soil sample is combined surface area of all the particles in the sample as determined by some experimental technique and expressed per unit mass of the sample. As its definition implies, term *specific surface area* is an operational concept.

The numerical value found for a given soil depends which experimental method has been used. There are two principal reasons for this very important characteristic. First, the properties of the solid surfaces in soil can often be altered during preparation of the sample for a surface measurement. Secondly, if a surface reaction is involved in the measurement of the specific surface area, the data obtained reflect only the characteristics of the surface functional groups that participate in the reaction, and provides only information about the solid surfaces that were reactive under the condition of the measurement.

Methods of measure of surface area

The principal physical methods for measuring specific surface areas of soils are electron microscopy and X-ray diffraction.

The most of methods are based on measurement of adsorption of polar and nonpolar gases or vaporous. The adsorbable compounds used to determine specific surface area are chosen on the basis of their molecular properties. Nitrogen is commonly used as the adsorbate because it interacts weakly with a broad array of surface functional groups and therefore permits for the determination of exposed area of soil. The limitation on the use of this adsorbate is stereochemical. Relatively large radius of N_2 molecule prevents it from interacting with the surface functional groups occluded in very small void spaces. Polar adsorbates are water vapour, ethylene glycol or ethylene glycol monoethyl. Typical non polar adsorbates are nitrogen, argon, krypton.

In the present paper we shall consider the application of the physical adsorption of gases for the estimation of the specific surface area of soils. The starting point is the adsorption isotherm, and the problem reduces to determination of the specific surface area, or the *monolayer capacity* of the adsorbent from the isotherm by mathematical analysis. The monolayer capacity is defined as the quantity of an adsorbate which can be accommodated in a completely filled, single layer of molecules on the surface of the solid. The surface area, S, is directly proportional to the monolayer capacity N_m, and the relationship between these two quantities is given by the equation: $S = S = N_m \times \omega$, where ω is the area occupied per molecule of the adsorbate in a completely filled monalayer. To find the value of N_m from an isotherm it is necessary to interpret the isotherm in a quantitative manner. A number of different theories have been proposed for the interpretation of adsorption data. The best known and probably the most frequently used theory, is that proposed by Brunauer, Emmett and Teller (BET). It leads to the equation called *the BET equation*, which has proved remarkably successful in the calculation of specific surface from the isotherms of the type II.

Calculation the specific surface area from adsorption data

The surface area of soil samples was evaluated from adsorption-desorption isotherms in the BET range of relative water vapour pressure, using the Brunauer-Emmett-Teller (BET) method. The first step in the application of the BET method is to obtain the monolayer capacity (N_m) from the BET plot in the range of relative pressures $0<p/p_0>0{,}35$:

$$\frac{x}{N(1-x)}=\frac{1}{C_{BET}N_m}+\frac{(C_{BET}-1)}{C_{BET}N_m}x$$

Where are $x = p/p_0$ relative pressure of water vapour, N amount of adsorbed water vapour, and C_{BET} constant.

According to this, when $x/N\ (1-x)$ is plotted against p/p_0 a straight line should result with slope $s=(C_{BET}-1)/N_m\ C_{BET}$ and intercept $i = 1/\ N_m\ C_{BET}$. Solution of the two simultaneous equations gives N_m and C_{BET} - $N_m=1/(s+i)$ and $C_{BET}=(s/i)+1$.

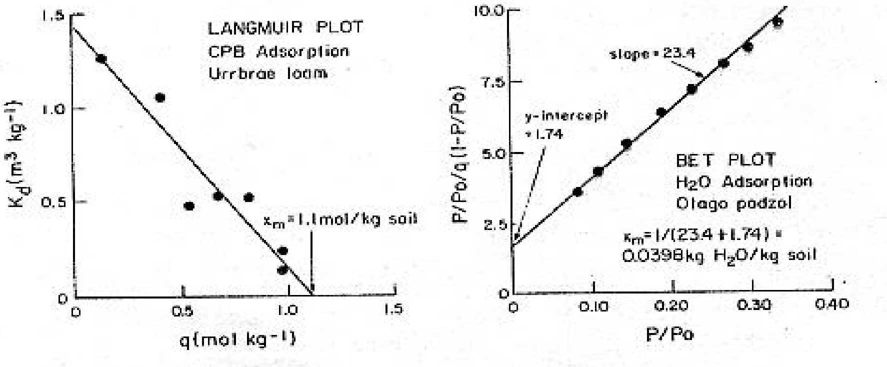


***Fig. 4**. The calculate of the value N_m (monolayer capacity) from Langmuir and BET plot*

The second step is to calculate the surface area from the dependence:

$$S=N_m\times M^{-1}\times L\times\omega,$$

where L is the Avogadro number (6.02×10^{23} molecules per mole), M is the molecular weight of water (gram per mole) and ω is the molecule cross-sectional area (10.8×10^{-20} m^2 for water molecule). If N_m is expressed in grams of adsorbate (water) per gram of solid the specific surface area S (m^2g^{-1}) is estimated from the monolayer capacity as

$$S=3612\times N_m.$$

In order to use of any of these formulae, it is necessary to know the value of the molecule cross-sectional area, ω. Emmett and Brunauer proposed that ω be calculated from the density ρ of the adsorbate in the ordinary liquid or solid form. This leads to the formula:

$$\omega = f(M/\rho N)^{2/3} \times 10^{16}$$

Here M is the molecular weight of adsorbate, N is Avogadro's constant, f is a packing factor and ρ is the mass density of the bulk liquid. With the hexagonal close packing at the density of bulk liquid phase the value of f is 1.091 and if ρ is expressed in kilograms per cubic meter ω is expressed in square nanometers. For nitrogen as adsorbate at -195^0 the value ω=0.162 nm^2 (16.2 Å^2). The adsorption of water vapour is complicated in that it is highly specific and it appears that the application oh the BET equation to water isotherms, in many cases, has no real validity. Early work indicated that the value of the molecule cross-sectional area is 10.6 Å^2 (0106 nm^2). The work of Harkins and Jura showed that it was necessary to adjust 14.8 Å^2.

TECHNIQUES OF MEASURE OF SURFACE AREA ACCORDING TO POLISH STANDARD PN-Z-19010-1 FOR MEASURING THE SURFACE AREA OF SOIL

Before the adsorption measurement the soil samples were dried in a vacuum chamber with the concentrated sulphuric acid until the weight of samples reached constant values. The soil sample of the weight equal approximately to 3g was put into the glass vessel and was placed over sulphuric acid solution. The sample was equilibrated with water vapour during two days. The amount of adsorbed water vapour was computed as the difference between the weight of the sample with water and the dry sample (dried in an oven at 105°C). The relative water pressures were obtained from the density of sulphuric acid solutions. Fife levels of relative pressure were selected in range of 0.034 to 0.352. The adsorption measurements were replicated three times keeping the temperature constant, T=20°C ± 0.5. The variation in replicated data did not exceed ±5% at the lowest vapour pressure and ±1% at the highest vapour pressure.

Calculation the specific surface area from adsorption data as above.

REFERENCES

1. Dechnik I., Stawiński J., 1973. Surface area in physicochemical and physical investigations of soil properties. Problemy Agrofizyki 6. (in polish)

2. Gregg S.J., Sing K.S., 1978. Adsorption, Surface Area and Porosity. Academic Press, London and New York.
3. Ościk J., 1982. Adsorption. PWS Ellis Horwood Ltd. Publish. Chichester.
4. Sing K.S.W., 1982. Reporting physisorption data for gas/solid systems (with the special reference to the determination of surface area and porosity). Pure&Appl. Chem., 54, 2201-2218.
5. Sposito G., 1984. The Surface Chemistry of Soils. Oxford Univ. Press. N.Y., Clarendon Press. Oxford.
6. Stawiński J., Gliński J., Ostrowski J., Stępniewska Z., Sokołowska Z., Bowanko G., Józefaciuk G., Księżopolska A., Matyka-Sarzyńska D., 2000. Spatial characterisation specific surface area of the arable soils in Poland. Acta Agrophysica 33. (in Polish)
7. Polish Standard PN-Z-19010-1, 1999. Soil Quality: Determination of the soil surface area – adsorption of water vapour method. (in Polish)

PARAMETERS OF ELASTICITY OF GRAIN BEDDING DETERMINED WITH OEDOMETRIC AND ACOUSTIC METHODS

Stasiak M, Rusinek R.

INTRODUCTION

Numerous food and agricultural materials are stored and processed in a particulate form. Cereal grains and rapeseed are also important raw materials for food industry. Properties of the material serve as parameters for engineers designing storage systems or processing plants.

Mechanical properties of grain bedding depend on properties of individual grains, friction between particles, interparticle contact geometry and load history. Recently demand of industrial practice resulted in revision of several silo design codes, which included standardization of methods for determination of mechanical properties of granular materials. European Standard Eurocode 1 (1996) and Polish Standard (Dyduch *et al.* 2000) recommends to determine properties under load condition which are similar to the operation loads. Some properties are determined using shear test (Jenike tester or triaxial compression test) other using uniaxial compression test.

The aim of experiments was to evaluate and comprise values of mechanical constants characterising elastic deformation (modulus of elasticity E and Poisson's ratio) determined with two methods adopted from geotechnique.

UNIAXIAL METHOD (OEDOMETRIC)

This method was proposed by Sawicki [1998] who distinguished two phases of the unloading in uniaxial compression experiment. The first phase is characterized by a purely elastic deformation and can be used for determination of elastic constants (the modulus of elasticity E and Poisson's ratio ν). Uniaxial compression test is presented in figure 1 [Horabik and Molenda, 2000].

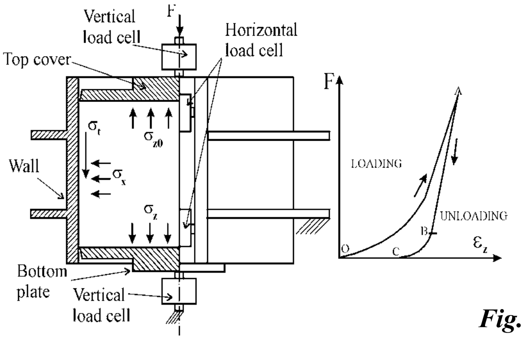


Fig.1. *Uniaxial compression test*

The granular material is poured into the test chamber, without vibration or other compacting action. The sample is 80 mm high and 21 cm in diameter. The bedding is load to the reference vertical stress σ_{z0} of 100 kPa using universal testing machine. Then the top cover of the apparatus moving down with a constant speed of 0.35 mm/min, while the displacement is measure with inductive sensor having accuracy of 0.01 mm. Next unloading take place with the same speed of deformation until to the 0 kPa of stress level is reached.

Two phases of the unloading can be observed (see Fig. 1). The first phase is characterized by a purely elastic deformation and is used for determination of elastic constants, the modulus of elasticity E and Poisson's ratio ν. The second stage of unloading is characterized by both elastic and plastic deformations. It is assumed that the material reversible response is governed by Hook's law:

$$\varepsilon^e{}_x = \frac{1}{E}\left[(1-\nu)\sigma_x - \nu\sigma_{z0}\right] , \tag{1}$$

$$\varepsilon^e{}_z = \frac{1}{E}\left[\sigma_{z0} - 2\nu\sigma_x\right]. \tag{2}$$

During the first phase of unloading (path AB) sample shows linear reaction which is characteristic for elastic deformation. Assuming that $\varepsilon_x = \varepsilon_x^e = \varepsilon_x^p = 0$ from (Eq. 1) $\frac{\sigma_x}{\sigma_{z0}} = \frac{\nu}{1-\nu}$ is obtained and applying assumption that $\varepsilon_z = \varepsilon_z^e$ to (Eq. 2) ε_z may be expressed as below:

$$\varepsilon_z = \frac{\sigma_{z0}}{E}\left(1 - \frac{2\nu^2}{1-\nu}\right). \tag{3}$$

Elastic constants can be determined using experimental results from linear phase of unloading. The ratio of horizontal stress σ_x to vertical stress σ_{z0} is constant (elastic state of stress) and a slope A of a straight line, $A = \sigma_x/\sigma_{z0} = \nu/(1-\nu)$, is estimated using linear regression procedure applied to experimental values of stresses. Then, with A estimated, values of Poisson's ratio ν can be calculated as:

$$\nu = \frac{A}{1+A}. \tag{6}$$

ACOUSTIC METHOD

Linear elastic theory allows to calculate elastic parameters on the basis of measured both shear and longitiual wave velocities [Lipinski, 2000]. Parameters obtained on the basis of equation of theory of elasticity refer to small strain of the order of 10^{-5} and therefore shear modulus G which is most required parameter in engineering application, is often termed initial modulus G_o or stiffness modulus G_{max}. Initial modulus can be calculated if only shear wave velocity V_s and mass density ρ is known as: $G_{max}=\rho V_s^2$ [Timoshenko at al., 1970]. And then modulus of elasticity of the material can be calculated [Jastrzębski at al., 1985].

With this method values of E is determined based on measurement of shear wave velocity. Experiments is performed under different hydrostatic pressure in triaxial chamber fitted with piezoelements in top and bottom covers of the apparatus that allowed for generating and recording of acoustic shear waves (Fig. 2).

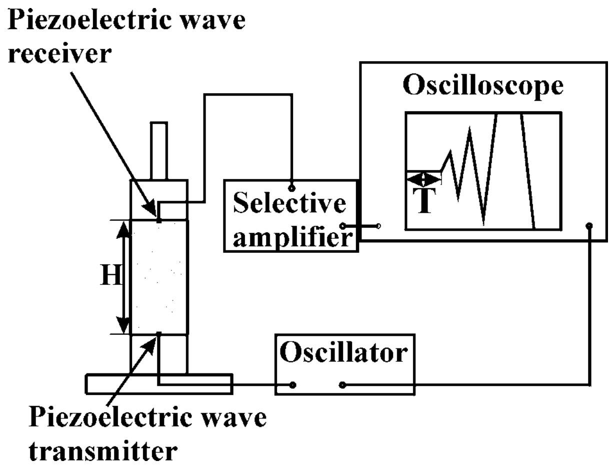


Fig. 2. *Hydrostatic chamber constructed to determine shear wave velocity*

The properties is determine under load condition similar to those encountered for bins in practical operation regime. The material is poured into the test chamber, without vibration or other compacting action. Maximum normal pressure applied in uniaxial compression test (of 100 kPa) corresponded to pressure produced by approximately 14 m high column of grain. Measurements of shear wave velocity in grain bedding is conducted under hydrostatic pressure ranging from 10 to 90 kPa. The sample is 150 mm high and 70 mm in diameter.

RESULTS

Uniaxial compression test

Figure 3 shows relationships of vertical stress σ_{z0} and total vertical strain ε_z for loading - unloading cycles for rapeseed of four levels of moisture content. First part of the loading curve reflects consolidation of the sample with translation and rotation movements of particles, but without their deformations. Second, steeper part of the curve shows an increase in the plastic and elastic stresses in the sample associated with deformation of particles. During this phase of loading deformation takes place mainly in contact areas between grains. Variation of moisture content resulted in large differences between experimental stress – strain relationships, which were reflected in values of model parameters.

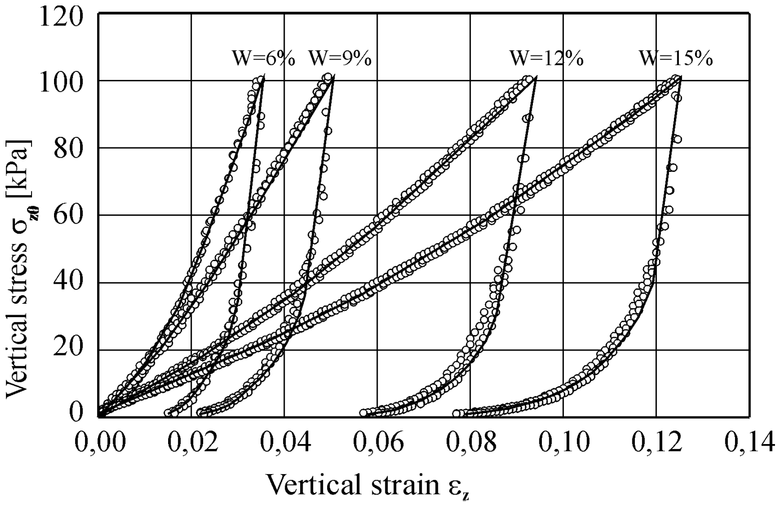


Fig.3. *Experimental data and fitted $\sigma_{z0}(\varepsilon_z)$ relationships for rapeseed of four levels of moisture content*

Results of estimation of elastic constants are presented in Table 1.

Acoustic examination

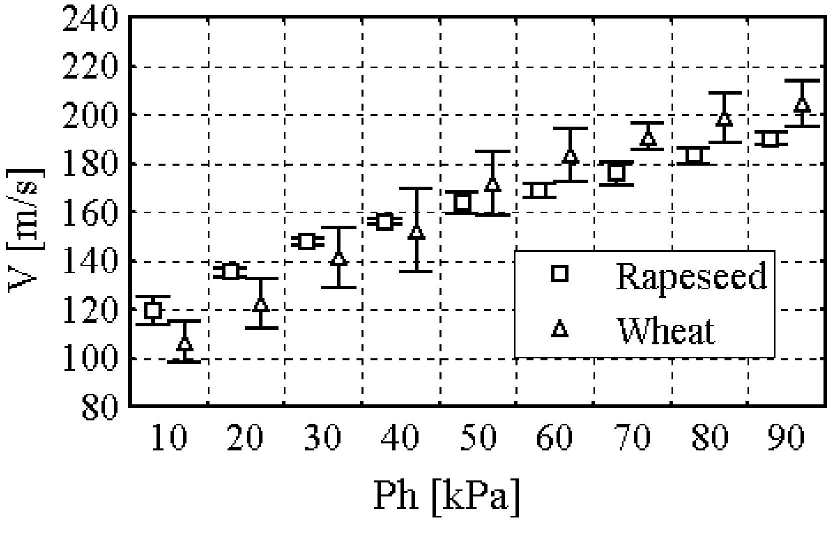


Fig. 4. Relationship between hydrostatic pressure and shear wave velocity determined for rapeseed and wheat

Table 1. Parameters of rapeseed and wheat determined in experiments

Grain	Moisture content [%]	Modulus of Elasticity E [MPa]	Poisson's ratio ν
Wheat	10	22,4 ± 4,6	0,22 ± 0,01
	12,5	22,2 ± 4,4	0,18 ± 0,02
	15	19,3 ± 2,5	0,20 ± 0,03
	17,5	17,2 ± 3,6	0,20 ± 0,01
	20	11,1 ± 1,1	0,19 ± 0,01
Rapeseed	6	9,0 ± 0,6	0,24 ± 0,03
	9	8,7 ± 0,8	0,17 ± 0,02
	12	7,1 ± 0,6	0,16 ± 0,01
	16	6,6 ± 0,9	0,10 ± 0,01

	$E=2\rho V_s^2(1+\nu)$	
Hydrostatic pressure [kPa]	*E* [MPa] evaluated for ν=0,2	*E* [MPa] evaluated for ν=0,4
	Rapeseed	
10	22,6 ± 1,9	26,4 ± 2,2
20	28,9 ± 0,9	33,8 ± 1,1
30	34,6 ± 0,6	40,4 ± 0,7
40	38,7 ± 0,5	45,1 ± 0,5
50	42,5 ± 1,3	49,6 ± 1,6
60	45,4 ± 1,6	53,0 ± 1,8
70	49,4 ± 1,8	57,6 ± 2,1
80	53,5 ± 0,7	62,4 ± 0,9
90	57,5 ± 1,0	67,1 ± 1,2
	Wheat	
10	20,2 ± 3,3	23,6 ± 3,8
20	26,8 ± 4,6	31,3 ± 5,4
30	35,8 ± 6,5	41,8 ± 7,5
40	41,8 ± 9,4	48,8 ± 11,0
50	52,9 ± 8,5	61,8 ± 9,9
60	60,6 ± 7,2	70,7 ± 8,4
70	65,6 ± 4,2	76,5 ± 5,0
80	71,1 ± 7,6	82,9 ± 8,9
90	75,4 ± 7,4	88,0 ± 8,6

Velocity for wheat was found in a range from 106 m/s at 10 kPa of hydrostatic pressure to 204 m/s at 90 kPa. In the case of rapeseed velocity ranged from 119 m/s to 190 m/s (Fig. 4). Values of modulus of elasticity for wheat (from 23,6 to 88,1 MPa) were found varying in a wider range then those for rapeseed (from 26,3 to 67,0 MPa) for hydrostatic pressure in a range from 10 to 90 kPa (table 1). This is probably a result of difference in a ranges of sample deformation which were very small (strain of 10^{-5}) in shear wave velocity estimation while in uniaxial compression tests the level of 12% of strain was applied.

CONCLUSIONS

1. Values of material constants determined in uniaxial compression test were found dependent on species and on moisture contents of the material.
2. Values of ***E*** decreased with an increase in moisture content.
3. Values of modulus of elasticity, determined in uniaxial compression test in a range from 6.6 MPa to 32.6 MPa, were close to those recommended by standards.
4. Values of Poisson's ratio (0.1÷0.24) were found lower than the value of 0.4 recommended by Polish Standard.
5. Shear wave velocity measured in hydrostatic chamber with acoustic method increased with an increase in hydrostatic pressure.
6. Values of modulus of elasticity E estimated based on measurement of shear wave velocity were found higher then those estimated with uniaxial compression test.

REFERENCES

1. Dyduch M., Kamiński M., Łapko A., Runkiewicz L., 2000. Amendment of Polish Standard PN-89/B-03262 „Concrete bins for storing granular materials and silags. Design rules", XI Conference „Reinforced and prestressed concrete containers for liquids and granular materials", 65-69, Świeradów Zdrój (in Polish).
2. Eurocode 1, 1996. Basis of design and actions on structures – Part 4: Actions in silos and tanks. European Committee for Standarization. Central Secretariat: rue de Stassart 36, B-1050 Brussels.
3. Horabik J., Molenda M., 2000. Device for determination of pressure ratio of granular materials. Patent Application No. P-340014, Bulletin of Patent Office No. 22(700), A1(21) 340017 (in Polish).
4. Jastrzębski P., Mutermilch J., Orłowski W., 1985. Strenght of materials. Warsaw (in Polish).
5. Lipiński M.J., 2000. Shear wave velocity for evaluation of state of cohesionless soils. Annals of Warsaw Agricultural University. Land Reclamation No29, 11-20.
6. PN-89/B-03262, 1989. Polish Standard. Concrete bins for storing granular materials and silage. Design rules (in Polish).
7. Sawicki A. and Świdziński W., 1998. Elastic Moduli of Particulate Materials. Powder Technology, vol. 96, 24-32.
8. Timoshenko S.P., Goodier J.N., 1970. Theory of elasticity. Tokyo.

SOIL REDOX RESISTANCE AND ITS ENVIRONMENTAL IMPORTANCE

Stępniewska Z., Gliński J., Stępniewski W.

The suitability of the environment for normal plant development is determined by the pool of oxygen stored in the soil (in the gas and liquid phase) and by the ability of its continuous supply from the atmosphere (through the soil or through the plant itself). After exhausting of the soil oxygen pool, and without further oxygen supply, plants start to suffer from oxygen stress, the root system perishes, and finally, the whole plant dies (Stępniewski and Gliński 1985, Bennicelli 2000).

The time of oxygen exhaustion in soil depends on the size of oxygen pool and the actual oxygen consumption rate. After the exhaustion of oxygen in soil the redox process sequence begins, starting with the reduction of nitrates, then manganese and iron oxides, and finally sulphides and methane (Gliński et al.1992).

The redox process in soil can be express by the redox potential (Eh) and by ability of the soil to stabilize Eh on the given level what describe of soil redox resistance to reduction (Gliński and Stępniewska 1986).

DEFINITION OF Eh

Redox potential (Eh) express tendency of an environment to receive or to supply electrons in solution. Electron transfer between donors and acceptors involves in any redox reaction changes in oxidation states of two components (Stumm and Morgan 1970).

In a water sample or in a soil solution the redox potential is determined by the amount of dissolved oxygen and it's use by organisms. In oxic environments a higher redox potential is observed because present of 0_2 likes to accept electrons. In environments reach in oxygen heterotrophic organisms capitalize on the use of O_2 as a powerful electron acceptor. Electrons are generated in the soil from the metabolism of reduced organic compounds that are oxidized to CO_2 (Reddy and Graetz D.A.19880.

Electron free energy scale for mole of electron can be expressed in ΔG (cal) or in E (V) or in pe (dimensionless). The energy gained in the transfer of 1 mole of electrons from oxidants to H_2, expressed in volts is the redox potential Eh. Redox potential measurement is done with the use of inert (platinum) and reference (saturated calomel or chloro silver) electrodes. Redox potential Eh is expressed as a voltage by Nernst equation:

$E_h = E$ oxidation-reduction $^o - (0.0592/n) * \log Q$

where $Q = [(C)^c\ (D)^d]/[(A)^a\ (B)^b]$ (a,b,c,d or products/reactants) n = number of electrons transferred in reaction and E^o = is the standard electrode potential at 25 C in which all substances are at 1.0M concentrations at pH = 7 in equilibrium

Standard Redox Potential (E^o): tendency of a reducing agent to donate electrons when Q=1.

Redox is often times expressed in terms of pe, which is derived from the equilibrium constant of the oxidation-reduction reaction (Tab.1.). For any reaction:

Oxidized species + e^- + H^+ <-> reduced species

And the equilibrium constant, K, is determined by:

Log K = log[reduced]-log[oxidized]-log[e^-]-log[H^+]

If we assume that the concentrations of oxidized and reduced species are equal then

pE + pH = log K

Because the sum of pE and pH is constant, if one goes up, the other must decline

When a given reaction occurs at lower pH, it will occur at higher redox potential, expressed as pE.

E_h can be converted to pe:

$$Pe = \frac{E_h}{(RT/F)2.3}$$

where R = universal gas constant (1.987 cal mole $^{-1}$ K^{-1}), F is Faraday's constant (23.06 kcal V^{-1} $mole^{-1}$), T is the temperature in Kelvin, and 2.3 is a constant.

The use of pe makes calculations simpler than to use Eh because every tenfolds change in the activity ratio causes a unit change in pe. But in making electrochemical measurements electromotive force (in volts) is being measured.

AFFECTS PH ON THE REDOX POTENTIAL IN THE ENVIRONMENT

Between pH and redox potential exist strong relationship. In natural waters or soil solutions which are in a highly dynamic state with regard to oxidation-reduction and rather far from equilibrium states. Most oxidation-reduction reactions in this conditions have a tendency to be much slower than acid-base reactions, particularly in the absence of biochemical catalysis (Sposito G.1989).

For example:

At pH 5, and equilibrium between Fe^{2+} and Fe^{3+} is established at a redox potential of about +400 mV:

•Fe^{2+} + 3 H_2O <-> $Fe(OH)_3$ + $3H^+$ + e^-•At higher pH, the equation will proceed to the right so Fe^{3+} will prevail in neutral and alkaline environments.

•At lower pH, such as the acid, anoxic waters of peat bogs, Fe^{2+} will prevail.The redox potential (Eh) for the reaction, which is going on in any water solution containing soluble oxygen (for example : $\underline{8\ mg/dm^{-3}\ O_2}$= $10^{-3.6}$ M= 32,000 mg/mol)$O_{2(Aq)}$ + $4H^+$ + $4e^-$ = $2H_2O$ Log Q = [$1/(O_2)(H^+)^4$] because H_20 is taken as unity. So:

$E_h = +1.27 - (0.0592/4) \log [1/(10^{-3.6})(10^{-28})]$

$E_h = +1.27 - (0.0592/4) \log 1/(10^{-31.6})$

E_h for different pH, at pH 5, 6, 7, 8 and 9 would be:

$Eh_5 = 0.921$ V, $Eh_6 = 0.862$ V, $Eh_7 = 0.802$ V, $Eh_8 = 0.743$ V.

Changes in temperature also influences E_h, but not to the same extent as pH. A rise in temp 1 C will decrease E_h by 0.0016 V.

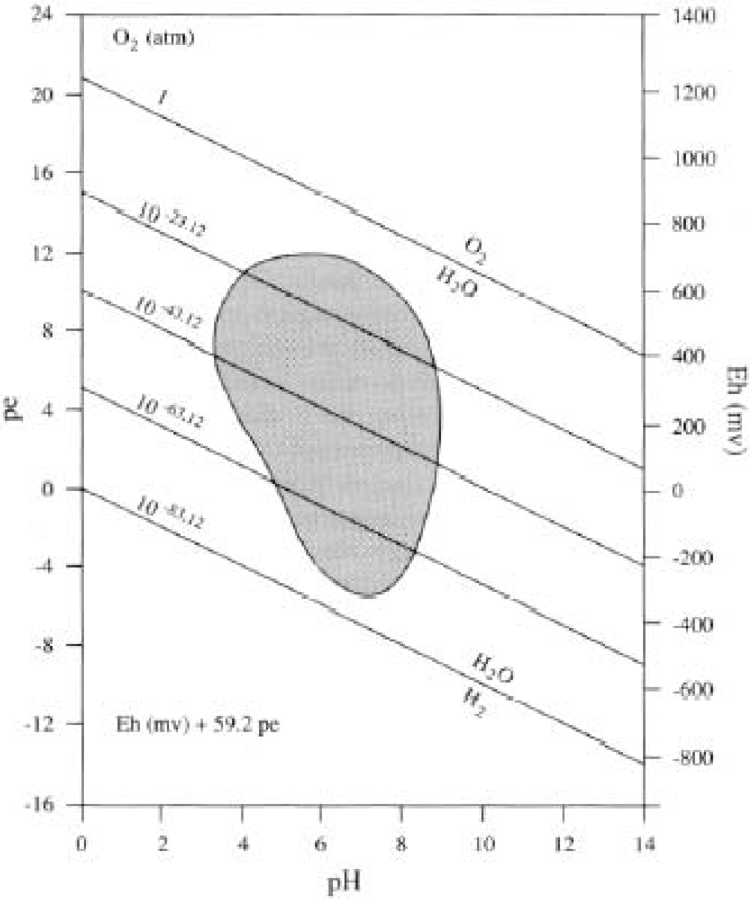


Fig.1. *The range of Eh that are found in natural environments.(after Schlesinger W.H.,1997).*

REDOX AND ELEMENTS TRANSFORMATION

Some elements can exist in a number of oxidation states in near-surface geologic environments, among of them are:the macroelements C, N, O, S ,Mn, Fe and trace elements or contaminants: As,Se,Cr,Hg,U,Mo,V,Cu,Ag,Pb (Fig. 2.).

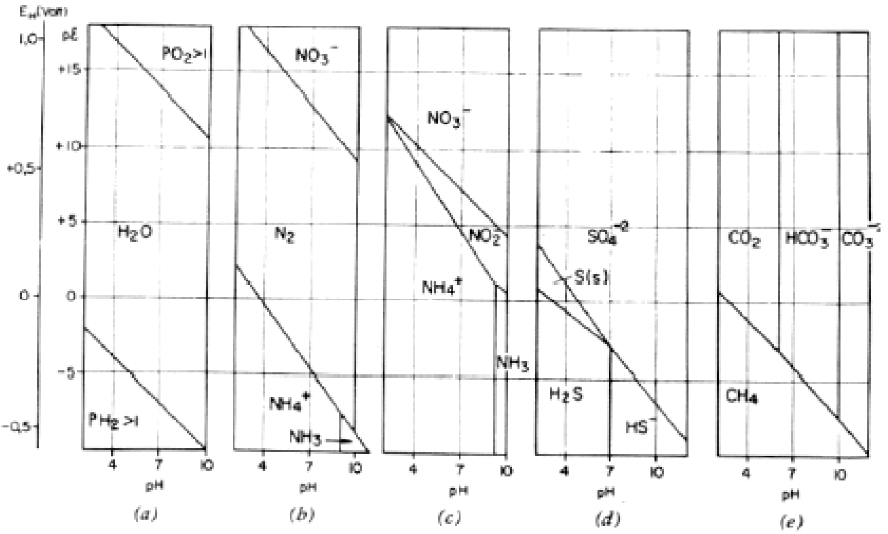


***Fig.2**. pe-pH diagrams for biologically important elements (at 25^0C). (a) The oxygen and hydrogen equilibrium with water. (b)and (c) The nitrogen oxidation states with regard to N_2. (d) Sulfur species stable for assumed conditions. (e) The thermodynamically possible existence of C compounds.(after Schlesinger W.H.,1997).*

ENVIRONMENT REDUCTIONS AND OXIDATION PROCESSES

Few oxic environments have redox potentials less than +600 mV.

–A well-oxygenated water Eh ~ 802 mV (0.802 V)
–A well oxygenated surface water Eh ~ 560 mV
–Anaerobic waters or soils Eh ~250 mV

Soils and sediments that resist changes in their redox potentials are said to be poised. Poise is to redox and buffer capacity is to pH (Fig.3).

As long as the environment is exposed to the atmosphere, O_2 will maintain a high redox potential and the environment is poised.

In the absence of O_2, a rapid decline in redox potential as various weakly oxidizing agents are reduced (nitrate, Mn^{4+}, Fe^{3+} and $SO4^{2}$-) .

Facultative anaerobe (can tolerate periods of aerobic conditions). After O2 is depleted by aerobic respiration, denitrification begins when the redox falls to +747 (at The driving force causing a decrease in the redox potential is the consumption of

oxygen by microbial respiration and the use of organic matter as a carbon source. All aerobic organisms must have O_2 to survive. Denitrifying bacteria use nitrate as an alternative electron acceptor during the oxidation of organic matter. Below a redox of +526 mV, nitrate is depleted and reduction of Mn^{4+} begins. Facultative anaerobe (can tolerate periods of aerobic conditions). Obligate anaerobes. At Eh < -47 mV reduction of Fe^{3+}.
Iron (Fe^{+2}) is used as the index of the transition from mildly oxidizing to strongly reducing conditions. • Seasonal fluctuations of water table or water level in surface water may expose a once flooded situation to the air and the position of the redox reactions will shift downward in the profile (Januszek K.1987).

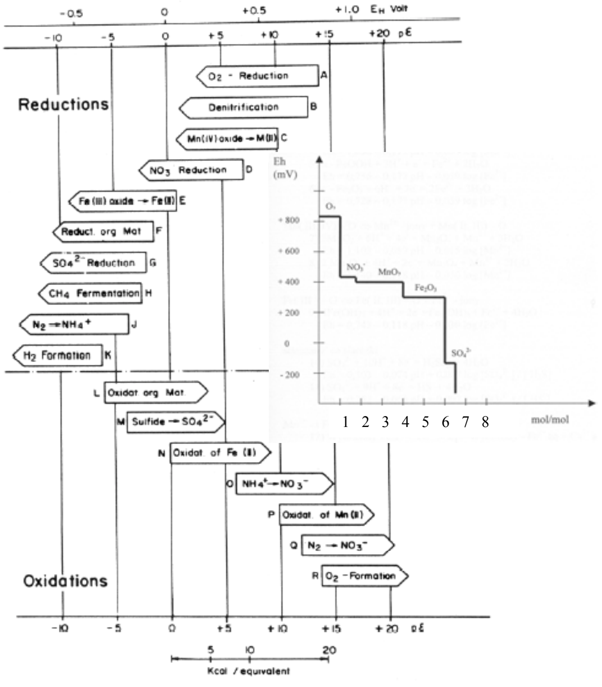


Fig.3. *Redox reactions which are occur during wetting and rewetting of soils (after Schlesinger1997).*

Products of previous reduction reactions become substrates for oxidizing bacteria.

Denitrification is enhanced when seasonal periods of aerobic conditions stimulate the mineralization and nitrification of organic nitrogen which makes nitrate more available for denitrifiers when the water level later rises. Generally, pH and Eh (pE) are considered the master geochemical variables controling the geochemical reactions of elements in geologic and aquatic environments (Schlesinger 1997).

REDOX CAPACITY – REDOX RESISTANCE

The redox capacity r (eq/L) at any Eh is defined as the quantity of strong reductant which must be added to reduce the Eh by 1 volt (Nightingale 1958).

- $r = dC/ d(Eh)$
- or as a time which is needed to decrease of redox potential (Eh) to given value:

to +400 mV corresponding to beginning of nitrate decomposition,to +300 mV corresponding to the beginning of manganese and iron reduction.

- Buffer capacity can help interpret important reactions that control pH of natural wasters (Van Breemen and Wielmaker 1974) and sediments (Hutcheon et al. 1993).The status of progress in the redox process is expressed by the redox potential, Soil redox properties are especially important in the effective use of fertilizers and the environmental impact of agriculture in expected climatic change, which intensify the redox process and, among other things, mobilize the accumulated toxic substances (CTB – Chemical Time Bomb) (Fig 4 and 5).

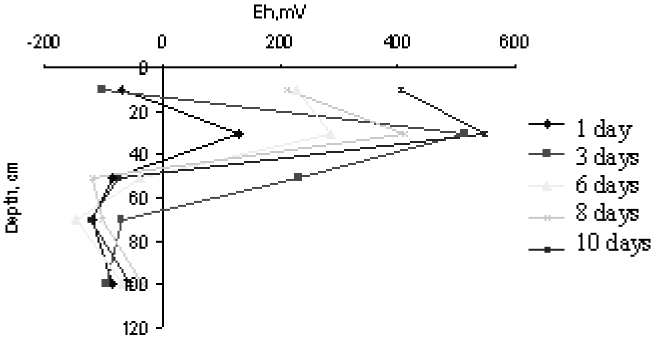


Fig.4. *Eh at different soil depth after irrigation of meadow soil with waste water*

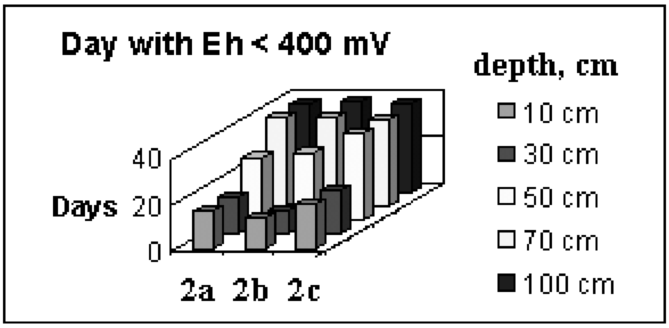


Fig.5 *Sum of days with Eh<400 mV after irrigation of meadow soil with waste water*

RELEASE OF PHOSPHORUS

When conversion of agricultural lands to wetlands took place in anoxic conditions of water saturated soil increase of P concentration in soil solution is observed. Fluctuations of water table in wetland can decrease of soil redox potential and influence on reactive P in soil. In this transformation temperature and microbial activity play important role (Fig.6-8). The effect of Eh on P solubility was reported by Patrick (1964) who demonstrated the reduction of insoluble ferric phosphate was directly related to reduction. In noncalcareous soils release of P is connected with reduction of –Fe(III)- or Mn(IV). and took place between 300 mV (pH5) to 100 mV (pH 7).

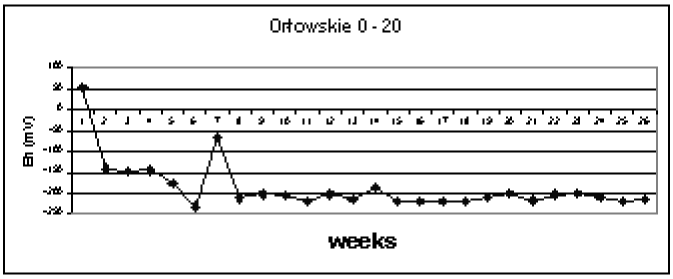


Fig.6. *Redox potential after irrigation of Orłowskie peatland (Poleski National Park).*

In soil environment this behaviour of P is express by positive feedback: because:

- anaerobic bacteria store less P
- more dissolved P results in more production
- more production sustains/enhances anoxic conditionsegative feedbacks: operate via oxygen and carbon dioxide in the atmosphere and their effect on weathering, hence riverine P fluxes operate via nitrogen cycle: denitrification/nitrogen fixation.

In calcareous system apatite equlibrium may be responsible for controlling P solubility. In this case solubility of Ca-bound phosphates such as apatite, tricalcium phosphate, octacalcium phosphate and brushite or monetite is controlled rather by pH than Eh.

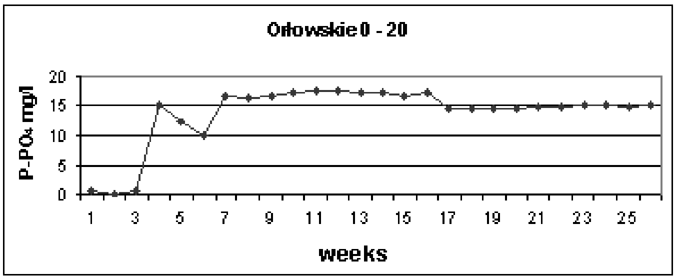


Fig.7. *Concentration of P-PO$_4$ changes after irrigation of Orłowskie peatland.*

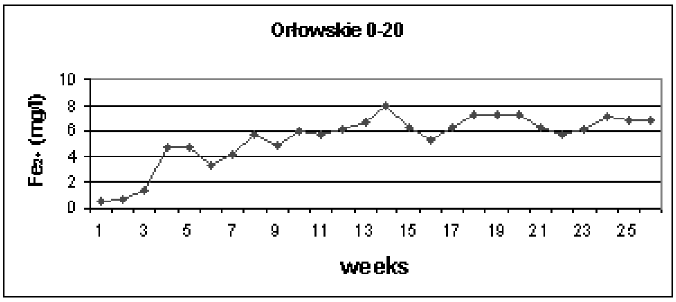


Fig.8.*Concentration of Fe^{+2} after irrigation of Orłowskie peatland (Poleski National Park).*

EH AND PESTICIDES STABILITY

Behaviour and transport of introduced pesticides in a soil profile is connected with their solubility, availability to microbes and climatic conditions i.e. water content and temperature. It was shown that a period of oxygen inhibition could be survived by the responsible soil microorganisms and can be accelerate when oxygen become again. The effect of redox potential appears to be an important screening parameter to assess their environmental risks (Vink J.P.M.1997) .

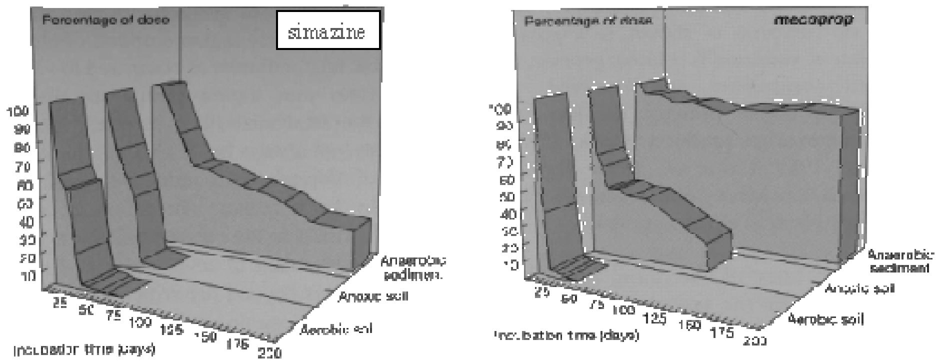


Fig. 9*. Stability of simazine and mecoprop in oxic soil (Eh=+330mV), low oxic soil (Eh=+180 mV) and anaerobic lake sediment (Eh=-120mV (after Vink 1997).*

REFERENCES

1. Bennicelli R. P., 2000 Effect of soil aeration on plant biomass production, Pol. J. Soil Sci., v. XXXIII/2, 5 – 11.
2. Gliński J., Stępniewska Z.1986.Wskaźnik odporności gleb na redukcję, ZPPNR, z. 315, 81 – 92.

3. Gliński J., Stępniewska Z., Stępniewski W., Ostrowski J. 1992. Znaczenie warunków tlenowych gleb w programach melioracyjnych, Probl. Agrof., 67, 62 – 73.
4. Januszek K. 1987. Potencjał oksydacyjno – redukcyjny wybranych gleb leśnych Polski południowej w świetle badań polowych i laboratoryjnych. Roczn. Gleb., XXXVIII, 3, 13 – 20.
5. Patrick W.H.Jr.1964.Extractable iron and phosphorus in a submerged soil at a controlled redox potential. 8th Int. Cong. of Soil Science, Bucharest, Romania, IV, 66, 605-609.
6. Reddy K. R., Graetz D. A., 1988. Carbon and nitrogen dynamics in wetland soil, The Ecology and Management of Wetlands, vol. 1, D. D. Hook (eds), Clemenson University, 307 – 318.
7. Schlesinger W. H. 1997. Biogeochemistry. An analysis of global change, Academic Press, San Diego, pp. 231 – 238.
8. Sposito G.1989. The chemistry of soils. Oxford University Press.106-122.
9. Stępniewska Z. 1986. Zmiany potencjału redoks, odczynu oraz zredukowanych form manganu i żelaza w glebach o zróżnicowanym natlenieniu i wilgotności, ZPPNR, z. 315, 242 – 269.
10. Stępniewski W., Gliński J. 1985. Reakcja roślin na stan aeracji roślin, Probl. Agrof., 45.
11. StummW., Morgan J.J 1970. Aquatic Chemistry., WILEY INTERSCIENCE, 33-382.
12. Vink J.P.M. 1997 Pesticide biotransformation and fate in heterogeneous environments. Van Zee tot Land 63. ISBN 90-5485-710-2., 77-93.

REACTION OF PLANTS ON ALUMINUM STRESS

Szatanik-Kloc A.

A reason of plant yield decrease in acidic soils is not low soil pH but accompanied secondary effects: high aluminum and manganese ions concentration, deficit of basic Ca, Mg and K cations, decrease in P and Mo uptake, and generally lower acidic soils fertility due to leaching of nutrient elements. Particularly severe toxic effect on plants is caused by aluminum. Low Al concentrations may cause total degradation of plants, as this is illustrated for winter wheat plants in Fig. 1. The Al toxicity in soils is responsible for around 40% of the crop yield lost worldwide.

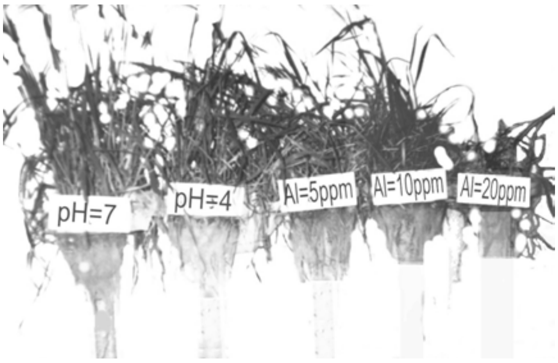


Fig. 1. *Reaction of wheat on Al in nutrient solution at pH=4*

Below pH = 4 the Al toxicity is due mainly to mononuclear Al ions $Al(OH)^{++}$ and $Al(OH)_2^{+}$. Polynuclear forms of aluminum ions may be much more toxic than the mononuclear ones. For example, the toxicity of $AlO_4Al_{12}(OH)_{20}(H_2O)^{+7}$ ion, called Al_{13} is 10 times higher than mononuclear ions. The Al_{13} forms usually in the boundary between zones of solutions of different pH's, at pH 4,4±0,4. Therefore, maximum Al toxicity occurs at pH around 4.5. Aluminum species occurring at higher pH values are believed to be nontoxic. Complexes of aluminum with silica, fluorides, phosphates, sulfates are nontoxic, as well.

Positively charged aluminum ions compete with other ions (Ca^{++} and Mg^{++}) for exchange positions in plant roots. Therefore an increase in Al species concentration leads to nutrient deficiency. Very important factor of Al toxicity is, obviously, its concentration. Above 60 $\mu M\ dm^{-3}$, even in low pH range, Al occurs in polymeric forms and to preserve their low level, 0,1 μM of Al in solution is required.

In the course of the evolution and as a result of plant breeding works, the plants exhibited several mechanisms of minimizing Al toxicity. Apoplastic and symplastic mechanisms are distinguished. Within the first group are: formation of a high pH bareer in the root zone, immobilization of Al ions in the rizosfere, on root surface and in intercellular spaces, as well as Al binding by pectin in the cell wall.

The symplastic mechanisms are Al chelating in cytosol, compartmentation in vacuoles, production of Al binding proteins, evolution of and/or increase in activity of specific enzymatic systems. Chelating of Al on surfaces of root tips is due to a secretion of polysaccharides and uronic acids. Tolerant plants evolve more citric, abscinic, phosphoric or maleic acids, binding the aluminum. Tolerant plants have smaller root cation exchange capacity, which causes smaller uptake of cations than anions that simultaneously leads to increase of pH in the root zone.

Phytotoxicity of Al ions on plants is the effect of various cellular processes, of different mechanisms and intensities for different plants. Therefore the plants differ in aluminum tolerance. For cereal plants the most sensitive is barley, then wheat, triticale, oat and the most resistant rye. Within plants of a given family, different varieties may exhibit different tolerance, as well. Al tolerance of rye, determined as Al concentration at which first plants start to suffer, is between 20 ppm, to around 70 ppm.

Symptoms of Al toxicity in upper parts of the plants are of secondary character. They are mainly connected with the deficit of water and nutrients, mainly calcium and phosphorus. Deficit of Ca is a reason of shoot apex necrosis, lost and curling of leaves. Yellowing of leaves, necrosis of leaf inceptions, stem purple coloring are symptoms of P deficit. As a result, aluminum causes hindering or breaking of plant shooting, deformation of spikes and grains leading to a decrease in plant yield.

Phytotoxic influence of aluminum on plant roots is of primary character. Early stage of aluminum toxicity is a fast process, connected with sorption of Al ions on root surface and its entering and accumulation in the apoplast. The next steps are slower and Al sorption is lower due mainly to a decrease of Al concentration in soil solution. Also, the Al-induced biochemical processes lead to decrease of metabolic energy of root cells that leads to retardation of leaving processes and the Al sorption, as well. Aluminum entering to the cells interior requests crossing of plasma membranes, which usually become more permeable due to Al reaction with phospholipids and formation of hydrophilic channels allowing for Al entering to the symplast. Aluminum ions may also disrupt transport of other ions by formation of ATP-Al complexes. Most of aluminum is accumulate in cell walls, mitochondria, nuclei and ribosomes and reacts with DNA and RNA affecting processes of replication and protein synthesis.

An early and dramatic symptom of Al phytotoxicity is inhibition of root growth. With extended exposure the roots thicken, become stubby, darker in color, and breakable. The necrosis of the root apex leads to formation and growth of secondary and ternary roots, which undergo the necrosis, as well, which may be seen in Fig. 2.

***Fig. 2.** Normal (left) and Al stressed (right) roots. The arrow shows boundary of side roots zone.*

Destruction of merysthematic and elongation zone tissues are primary anatomical changes. At first the destruction of epidermic cells occurs and in internal layers caves and slits are formed, which extends towards the primary cortex, that may be observed in Fig.3.

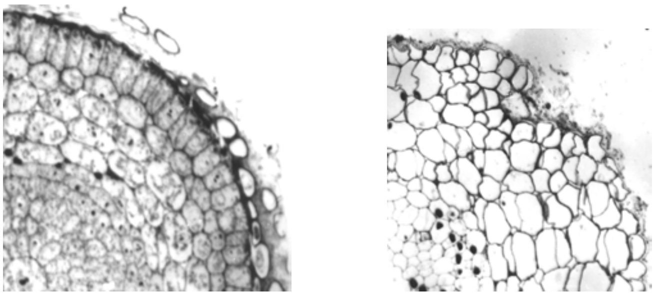
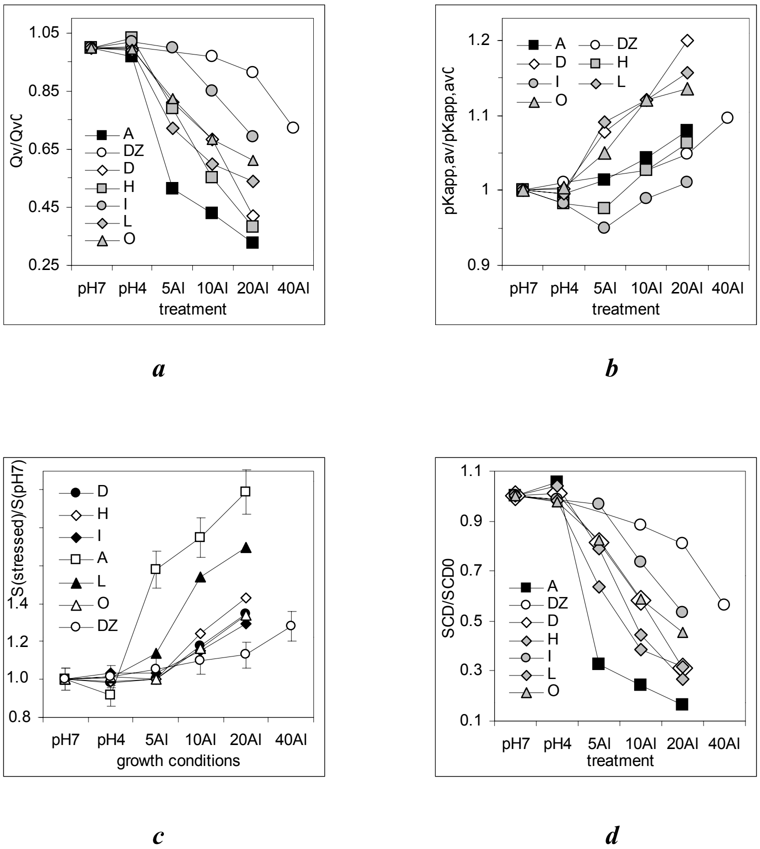


***Fig. 3.** Cross sections of normal (left) and Al injured roots (right).*

Changes in root tissue under aluminum stress and accompanied strong bonding of aluminum by cell components lead to marked changes in root physicochemical properties.

With the increase of the concentration of the aluminum treatment, the variable surface charge of the roots decreases (Fig. 4a), and a strength of surface acidic groups decreases (Fig. 4b). The latter may be deduced from the decrease in average surface dissociation constant of the root surface and is connected with an increase of the relative number of weakly acidic surface sites and a simultaneous decrease in surface groups of medium and strong acidity. The surface area markedly increases after the Al stress (Fig. 4c) that can be attributed to the physical damage of the root tissue: increase of the amounts of cracks and increase of the intercellular spaces. However, during the Al stress the density of variable surface charge of the roots decreases markedly (Fig. 4d) that may lead to significant depression of the relative amount of multivalent aluminum ions present at the root cation exchange sites.



a *b*

c *d*

Fig. 4. *Relative changes in variable surface charge (a), average surface dissociation constant (b), surface area (c) and density of variable surface charge (d). On the y-axis the ratio of a value of a given parameter estimated for the stressed roots to its value for the control roots is shown. The letters in the legends denote various species of cereal plants: A-barley, DZ-rye, D-triticale and H, I, L and O –different wheat varieties.*

APPLICATION OF THERMOGRAPHY IN AGROPHYSICS

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

INTRODUCTION

The specificity of agrophysical studies, connected with high differentiation of the investigated objects, e.g. soil-plant-atmosphere system or various plant materials, requires the use of modern measuring methods to determine the investigated features and physical quantities. A method that fulfils all these requirements is thermography.

Thermographic devices measure the thermal radiation emitted by investigated objects and transmitted through the "atmospheric windows" in two ranges of electromagnetic spectrum": 3,5-5 μm and 8-13 μm. They enable to visualise the distribution of radiation temperature on the emitting surface. Thermal images obtained from high levels (airborne, satellite) are used to create maps of thermal differentiation of large areas. It eliminates the necessity of performing huge number of point measurements to obtain temperature distribution by the way of interpolation. The only needed data come from the measurements in several chosen reference points which are necessary for qualitative analysis of the thermal images.

Radiation temperature in the form of thermographic images is used for investigations of numerous phenomena in agricultural sciences. It is required as one of the parameters for detection and evaluation of plant water stress and for determination of actual evapotranspiration of large arable areas. Plants attacked by diseases show different temperature than healthy ones. Thermal images help to localise shallow ground waters. Recently, the investigations have been performed to apply thermography for determination of physiological and physical status of agricultural materials, controlling of transpiration in the pre-harvest stage, measurement of stomata conductance, detection of plant diseases and in the studies of individual living cells.

EVALUATION OF PLANT WATER STRESS AND ACTUAL EVAPOTRANSPIRATION

The aim of the investigation performed in the Institute of Agrophysics, Polish Academy of Sciences, 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:

$$L \cdot E + H + R_n + G = 0 \qquad (1)$$

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:

$$H = \rho \cdot c_p \frac{T_c - T_a}{r_{ah}} \tag{2}$$

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 ($L=2,45 \cdot 10^6$ $J \cdot kg^{-1}$); 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; r_{ah} - the diffusion resistance for transport of heat [$s \cdot m^{-1}$]; ρ- 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 (Hs and Hc) and latent (Les and Lec) 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 (Ec) follow the best, evapotranspiration calculated according to the 63-Penman (63Pn) and Kimberly-Penman (KPen) 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.

SEEDS GERMINATION

In the Institute of Agrophysics Polish Academy of Sciences investigations have been initiated on the possibility of application of thermography for the determination of the quality of plant materials. These preliminary investigations showed that within seeds, the hydration forces of particular tissues are not the same. The highest force is characteristic for healthy germs. The use of the telephoto lens of 7° made it possible to observe and analyse the image of a surface of a part of the germ. The spatial resolution of the system enabled to separate individual pixels of the seed cover surface of the size 0.4 mm. It was concluded that during the process of swelling, when the imbibition forces decrease, further water absorption of seeds is supported by osmotic and metabolic forces. In natural conditions water absorption through the seeds is influenced by different factors as in the laboratory. In laboratory conditions, the intensity of swelling depends considerably on the way the seeds are placed on the wet bed. Unfavourable respiration conditions, e.g. caused by complete immersion of seeds in water can limit the swelling process. Some seed varieties do not sprout at all when immersed in water. The radiation temperature of these seeds does not differ significantly from the surrounding temperature.

DETECTION OF PLANT AREAS ATTACKED BY DISEASES AND INSECTS

The interpretation of airborne and satellite thermal images in connection with other remote sensing data coming from other ranges of electromagnetic spectrum, enables to gain information about the localisation of different crops, fragments of canopies attacked by diseases and genotypes.

In ENSA Research Station in Rennes, France, the measurements were performed of radiation temperature of wheat canopy in the field with homogenous soil conditions. It occurred that some fragments of this field showed increased temperature values in the morning hours when the aerial imaging was taken. The ground studies in these sites of the field revealed that the rooting system of plants was damaged by nematodes what lead to decrease of water uptake from the soil and decrease of transpiration intensity.

The recent studies showed that plants attacked by fungous diseases have temperature lower, than surrounding healthy plants due to the change of metabolic processes in their tissues caused by fungous layer, coating and damaging plant surface.

Thermography found its application in quantitative determination of the surface of canopy influenced by weeds. It was observed that although a part of a field with dense weed contribution, seems not to have significant tonal differentiation in visible image, it can be clearly distinguished in thermal image because of the average temperature higher by 2°C than the rest of the field.

STUDIES OF TEMPERATURE CONDITIONS IN GREENHOUSES IN THE ASPECT OF THEIR PROPER EXPLOITATION

Thermographic method enables dynamic registration of radiation temperature distribution of different surfaces. It is useful in the studies of thermal conditions during the plant production in greenhouses.

Thermal conditions in various parts of cultivated sites have considerable impact on plant growth and particular plant species characterise with different temperature requirements. Thermographic measurements of the whole cultivated surface of indoor cultures make it possible to get to know temperature conditions and respectively to schedule and appoint the most convenient sites for particular cultures. In case of incomplete cover, a casual thermographic inspection of the thermal condition on the surface of the bed is desirable. Thermography is also very helpful when checking the heat isolation of the greenhouse.

SUMMARY

The use of the method of thermal imaging enables to determine the heat and water conditions of different cultures. It also enables to determine the approaching or persisting plant water stress and, with high accuracy, the actual evapotranspiration from arable areas. The analysis of temperature map of a crop surfaces helps to select precisely the ranges of negative changes which are not observed by eyes, e.g. plant diseases in the early stage, root system damages etc. Thermography is a good tool for controlling of the thermal conditions in hot-bed cultures and is more and more often used for plant materials quality determination.

REFERENCES

1. P. Baranowski, W. Mazurek, R.T. Walczak, The investigation
2. of actual evapotranspiration with the use of thermography, Quantitative Infrared Thermography QIRT'98, Politechnika Łódzka, 7-10.09, (1998)
3. P. Baranowski, W. Mazurek, R.T. Walczak, The relation of actual to potential evapotranspiration as an indicator of plant water stress for meadow plant cover, Acta Agrophysica, 53, 17-28, (2001)

MODELLING OF MASS AND ENERGY TRANSPORT IN POROUS BODY

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

The problems connected with studying and modelling of mass and energy transport in porous body are presented for an example of the description of mass and energy transport in soil and modelling of the dynamics of water potential, water content and temperature.

The quantity describing the energetic state of water in soil and its availability for the plant rooting system is soil water potential, which in statistical thermodynamics is called the chemical potential:

$$\mu_i = \left(\frac{\partial G}{\partial n_i} \right)_{P,T,n_i \neq n_j} \tag{1}$$

where G is Gibbs thermodynamic potential.

The total potential of soil water is a total differential and is connected with the forces of interaction between solid, liquid and gaseous phases and existing external forces:

$$d\mu = \left(\frac{\partial \mu}{\partial P} \right)_{T,W,C} dP + \left(\frac{\partial \mu}{\partial T} \right)_{P,W,C} dT + \left(\frac{\partial \mu}{\partial W} \right)_{P,T,C} dW + \left(\frac{\partial \mu}{\partial C} \right)_{P,T,W} dC + g \cdot dz \tag{2}$$

where:
P- external pressure,
T - temperature,
W - soil water content,
C - salt concentration in the soil,
g - acceleration due to gravity,
z - co-ordinate.

For the description of physical processes taking place in the investigated systems the constitutive physical equations are used, expressing the laws of momentum, mass and energy conservation. The equations resulting from the conservation laws, describing a chosen phenomenon in this system, e.g. transport of water, salt and heat in the soil, soil deformation and stress as a result of reaction of wheels and working parts of machines and cultivation tools, need for their solution, the knowledge of kinetic coefficients characterising the investigated object. Furthermore, for the proper verification of the solution of the applied equation, the knowledge of the dynamics of a studied physical quantity is indispensable, e.g. the dynamics of soil water content, salinity, gases and temperature, agroclimatic parameters such as amount of rainfall, radiation, air humidity and temperature. Therefore it is necessary to monitor the parameters of the investigated systems.

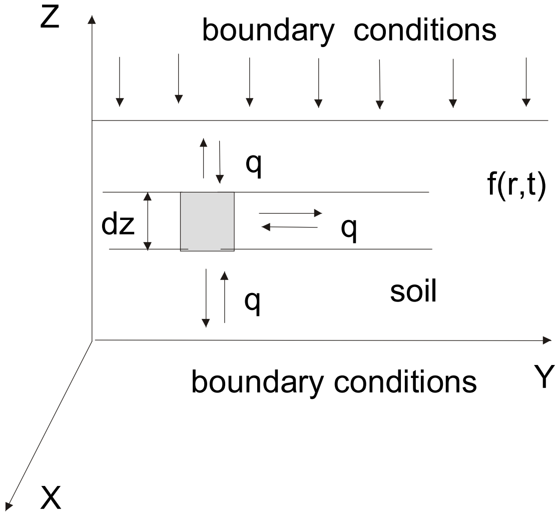


Fig. 1. *Mass flow in the soil profile*

The basic physical law is the law of mass conservation which says that the amount of a substance in the volume **V** changes only in the case when exists the resultant non-zero flux of this substance through the surface **S** limiting the volume **V**. This law is expressed by the equation of continuity, which for solenoidal field can be written as:

$$\left(\frac{\partial\theta}{\partial t}\right) + \nabla \cdot \vec{q} = 0 \tag{3}$$

and for the field with sources:

$$\left(\frac{\partial\theta}{\partial t}\right) + \nabla \cdot \vec{q} = f(\vec{r},t) \tag{4}$$

Comparing the equation of continuity for a field with sources with Darcy's equation of water flow in unsaturated zone:

$$\vec{q} = K(\theta) \cdot grad\Psi \tag{5}$$

the Richards equation is obtained (Fig. 1) in the form:

$$\frac{\partial\theta}{\partial t} = -\nabla \cdot K(\Theta) grad\Psi + f(\vec{r},t) \tag{6}$$

where:

q - water flux [cm/s],
K(Θ) - water conductivity coefficient in unsaturated zone [cm/s],
Θ - soil water content [m^3/m^3],
Ψ - soil water potential [hPa],
F(r,t) - source function (e.g. water uptake by the roots, watering-dewatering drainage systems).

Darcy equation is used in the case when the flux density is a linear function of potential gradient, i.e. when the inertial term in Navier-Stokes equation can be omitted. As a determinant of applicability of Darcy's equation the critical range Reynolds number values from 1 to 100 is used.

By solving Richards equation for given initial and boundary conditions it is possible to predict the dynamics of soil water content changes in the soil profile. For stability of solving the differential equation (e.g. Richards equation), the errors of its solution generated in successive time steps should be of decreasing amplitude.

The function f(r,t) is used for the description of negative and positive sources of water in the system. The negative water source in the soil profile is the plant rooting system and its intensity depends on the stage of phenological development of plants and on actual agroclimatic conditions, so it changes in time and space. The positive as well as negative source of water can be a drainage system, installed in the soil profile. The correct description of positive and negative water sources occurring in the soil profile is a very difficult task and it requires the co-operation of specialists from many disciplines of knowledge, especially plant physiologists.

The equation (6) describes the dynamics of water content in capillary-porous medium under isothermal conditions where the transport takes place under the influence of water potential gradient. In situation of non-isothermal conditions water moves also under the influence of temperature gradient. These two gradients cause that water can displace as vapour or liquid. In general, the equation of water flow in capillary-porous medium is as follows:

$$\frac{\partial\theta}{\partial t} = -\nabla\cdot((D_{\theta l} + D_{\theta v})\nabla\theta) - \nabla\cdot((D_{Tl} + D_{Tv})\nabla T) - \nabla K \tag{7}$$

In analogical way it is possible to present the equation of heat flow:

$$c_v \frac{\partial T}{\partial t} = \nabla\cdot(\lambda\nabla T) - L\nabla\cdot(D_{\theta v}\nabla\theta) \tag{8}$$

and the equation of salt flow:

$$\frac{\partial C}{\partial t} = \nabla\cdot(D\nabla C) - \nabla\cdot(v\cdot C) \tag{9}$$

where:

c_v - the heat capacity [J/m^3·^{0}C];
T - the temperature [^{0}C];
t - the time [s];
λ - the thermal conductivity [W/m·^{0}C];
L - the latent heat of vaporisation of water [J/m^3];
Θ - the volumetric soil water content [m^3/m^3];
$D_{\Theta v}$ - the water vapour diffusion coefficient in isothermal condition [m^2/s];
$D_{\Theta l}$ - the liquid diffusion coefficient in isothermal condition [m^2/s];
D_{Tv} - the water vapour diffusion coefficient in non isothermal conditions [m^2/s];
D_{Tl} – the liquid diffusion coefficient in non isothermal condition [m^2/s];
C - the salt concentration [m^3/m^3];
D - the coefficient of diffusion and hydrodynamic dispersion [m^2/s];

The equations of the dynamics of water content, temperature and salt concentration (5), (6), (7) are connected by the gradients of particular physical quantities. Applying the laws of thermodynamics these equations can be generalised by the expression:

$$J_i = \sum_{k=1}^{n} L_{ik} X_k \tag{10}$$

in which stationary thermodynamic fluxes J_i are homogeneous, linear functions of thermodynamic forces X_k. The coefficients L_{ik}, which in general depend on temperature, water content and salt concentration etc., are called the kinetic coefficients.

The kinetic coefficients fulfil the following symmetry conditions:

$$L_{ik} = L_{ki} \tag{11}$$

The above condition is called Onsager's law.

The contribution of particular fluxes in water transport in capillary-porous bodies has a large impact on temperature and salt concentration because the vapour flux is accompanied by the energy flow of gas-liquid phase change (the heat of vaporisation) and the salts are transported with the liquid flux. The water flux in the form of vapour is very important under lower water content values.

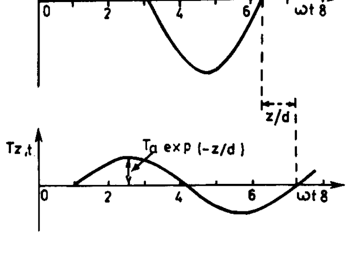


Fig. 2. *Cyclic change of temperature on the soil surface and at the depth z.*

Because of the complex character of the flow processes and forming, in natural conditions, the thermodynamic state of a system, the model investigations are used which rely on incorporating simplifications. They enable for the chosen aims of the investigation describing the change of system state with satisfactory accuracy. The example of such a process is forming of temperature field in the soil profile which variability in time and space depends on many phenomena taking place in the soil and on atmospheric conditions which are the boundary conditions of this system. In this case, the observed daily periodicity of temperature changes in the soil profile is obtained by solving the equation of heat flow under assumed periodical boundary condition on the soil surface as a function describing a wave with decreasing amplitude (Fig.2):

$$T_{z,t} = T_0 - c \cdot z + T_a \cdot e^{-\frac{z}{d}} \cdot \sin\left(\omega t - \frac{z}{d}\right) \tag{12}$$

which reflects the changes of temperature in the soil profile in time and space, where:
$T_{z,t}$ –the temperature on the depth z at time t [°C],
T_0 – the air temperature[°C],
d - the depth of soil profile [m],
T_a – the temperature on the soil surface [°C],
c – the coefficient of temperature change with depth[°C/m] ,
t – time [s],
z – co-ordinate [m].

This sinusoidal model fulfils the conditions of decreasing amplitude and phase shift of temperature with the depth.

A practical example of the use of thermodynamic description of a process in agrophysics is the description of water content distribution in heterogeneous soil profile composed of horizontal homogeneous layers, in which under natural conditions exist both biological macropores (biopores) and macropores created as result of physical process of soil swelling and shrinking (Fig. 3). High values of hydraulic conductivity of such system makes it impossible to apply one-dimensional Richards equation. The elaborated model of preferential flow in the soil profile, in which as solenoidal term in Richards equation, Green-Ampt approach was used for the description of horizontal water redistribution from macropore to soil matrix, made it possible to describe the forming of water conditions in such a complex system.

An example of realisation of typical for the physical investigations research process is an improvement of the model of preferential flow and its experimental verification (Fig. 4).

The research problem which was put forward referred to the possibility of modelling of water distribution in the soil profile in natural conditions. The initial hypothesis was set forth that this process can be described by one-dimensional Richards equation. This hypothesis was checked experimentally and considerable discrepancy between water content values measured and predicted by the model (dotted line) were stated (Fig. 4). The correction of hypothesis was performed by adding the submodel of preferential flow (Fig. 3).

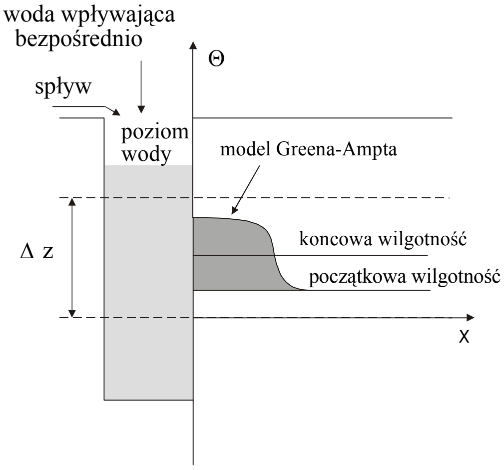


***Fig. 3**. A scheme presenting the way of modelling the phenomenon of preferential flow in the soil*

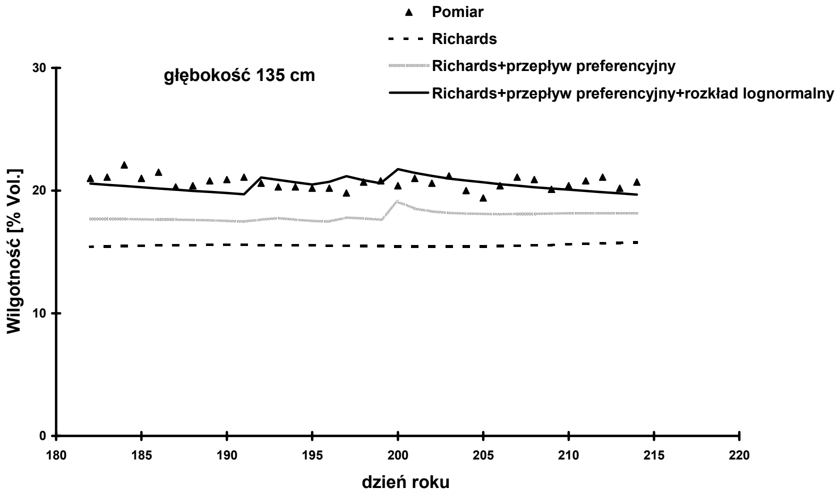


***Fig. 4.** Measured and calculated from the model values of water content (Grabów, 1993)*

Anew, the experimental verification of the considered hypothesis was done. The agreement between measured and calculated by the model values of water content increased (Fig. 4) (solid grey line), however the calculated by the model values of water content were always lower than measured values. The rainfall intensity, assumed in the model as constant 24 hours a day strayed from the real values of intensity occurring during the rainfalls and it did not exceed soil infiltration power.

It was the reason that runoff, as the necessary factor of occurring of preferential flow phenomenon could not appear. The performed analysis of rainfall enabled putting forward a hypothesis that distribution of rainfall intensity is characteristic for a given place and season and can be approximated by lognormal distribution. Thus, the hypothesis was corrected again by incorporating a submodel describing the distribution of rainfall intensity as lognormal distribution (Fig. 5).

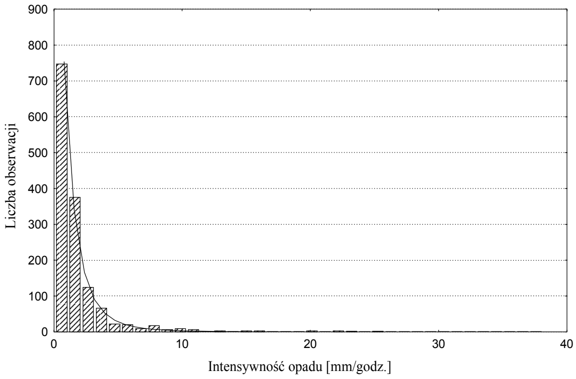


Fig. 5. *The way of modelling rainfall intensity using lognormal distribution.*

A satisfactory agreement was obtained between measured and predicted water content values (solid line) (Fig. 4).

Modelling of the physical processes occurring both in the soil-plant atmosphere system and in agricultural materials during harvesting, transport and technological processing, supplemented by the monitoring systems, enabling characterisation of the objects and the verification of the models, makes it possible to get to know the physical mechanisms taking place in the system, simulation of these processes and first of all predicting the state of a system under assumed boundary conditions and different modifications of a system.

Modelling makes it possible to predict the effects of human activity, what can save ecological system from its degradation which effects are not reperable.

Agrophysical investigations connected with modelling of physical processes in the soil-plant-atmosphere system supplemented by monitoring of the investigated systems are extremely important and should be dynamically developed because we can optimally use, protect and form environment only in the case when we have at our disposal the full possible information about physical parameters describing this environment and about their dynamics i.e. about trends of their change in time and space.

GREENHOUSE GASES EMISSION

Włodarczyk T., Kotowska U.

INTRODUCTION

Soils are important sources of number of greenhouse gases such as water vapour, CO_2, CH_4 and N_2O. 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.

N_2O production is affected by many physical and biochemical factors, such as nitrate concentration, redox potential, organic matter content, temperature, soil pH and soil moisture content.

NITROGEN IN SOIL

Nitrogen in soil occurs both in organic and inorganic form. **Organic nitrogen** is in reduced form, some of it as amide nitrogen, relatively easily available to decomposer organisms unless protected mechanically or chemically. Another part of soil organic nitrogen occurs as a constituent of large and often resistant molecules with nitrogen in heterocyclic aromatic rings.

Inorganic nitrogen is usually fully reduced, ammonium, or fully oxidised, nitrate. Intermediary oxidation stages also exist but do not accumulate in measurable amounts, except for nitrite under special circumstances. There are transfers not only between the various soil nitrogen pools, but also between the soil pools and gaseous phase, where nitrogen compounds at different oxidation levels also occur (NH_3, N_2, N_2O, NO).

MINERALIZATION OF NITROGEN (AMMONIFICATION)

The mineralization of N from decomposing materials with release of NH_4^+ by heterotrophic microbes is known as **ammonification.** Subsequently, a variety of processes affect the concentration NH_4^+ in the soil solution, including uptake by plants, immobilisation by microbes, and fixation in clay minerals.

Most of the mineralization reactions are the result of the activity of extracellular degradative enzymes, released by soil microbes.

NITRIFICATION

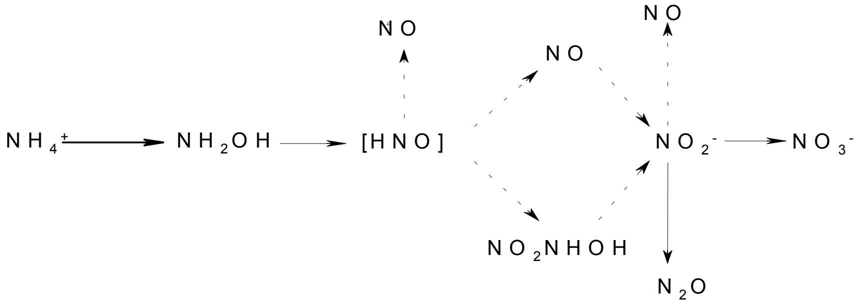
Nitrification is an aerobic process, performed both by autotrophs and heterotrophs in soils.

Autotrophic nitrification is defined as the biological oxidation of NH_4^+ to NO_2^- and NO_3^- in a two step reaction as presented in the following equations where *Nitrosomonas* performs the first energy yielding reaction:

$$NH_4^+ + 1.5\ O_2 \rightarrow NO_2^- + 2H^+ + H_2O + \text{energy}$$

and *Nitrobacter* the second energy yielding reaction:

$$NO_2^- + 0.5\ O_2 \rightarrow NO_3^- + \text{energy}$$



Although nitrification is understood to be an aerobic process there is strong evidence that it can also occur under anaerobic conditions. Nitrifying bacteria have been shown to produce NO and N_2O. Nitrate reduction is now thought to be the major process involved in those gaseous emissions, with NH_4^+ oxidation providing the electrons for this denitrification process. This process is thought to possibly conserve O_2 for ammonia mono-oxygenase, keep NO_2^- from reaching toxic levels, and maintain optimum redox levels

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 the dominant source of N_2O in "aerobic" soils.

ASSIMILATORY REDUCTION OF NITRATE

In the absence of NH_4^+ and organic-N and under conditions where only NO_3^- is available, bacteria, fungi, yeast and algae have first to reduce the NO_3^-. 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. The net reaction is shown in following equation:

$$\begin{tikzcd} NO_3^- \arrow[r] & NO_{2-} \arrow[r] & {[H_2N_2O_2]} \arrow[r] & {[NH_2OH]} \arrow[r] \arrow[d] & NH_3 \\ & & & N_2O & \end{tikzcd}$$

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.

DISSIMILATORY REDUCTION OF NITRATE

When the dissimilative reduction produces the gaseous dinitrogen or nitrous oxide compounds, the process is termed **denitrification**. However, since reduction, through the metabolic pathway of cytochromes, in some case results in the production of ammonia or nitrite, some authors prefer the more general name of **nitrate respiration** for the process.

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:

$$NO_3(+V)\xrightarrow{\text{nitrate reductase}}NO_2(+III)\xrightarrow{\text{nitrite reductas}}\overset{\overset{NO(+II)}{\vdots}}{[X]}\xrightarrow{\text{nitric oxide reductas}}N_2O(+I)\xrightarrow{\text{nitrous oxide reductase}}N_2(0)$$

Many microorganisms can use NO_3^- as their primary electron acceptor for obtaining energy from organic compounds when low O_2 availability restricts their metabolism:

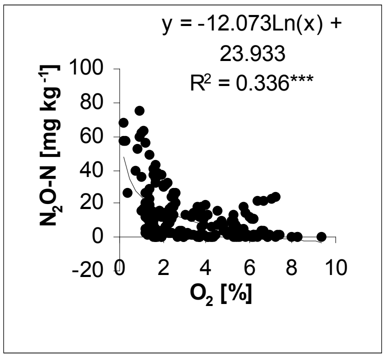
$$5(CH_2O) + 4NO_3^- + 4H^+ \rightarrow 5CO_2 + 7H_2O + 2N_2 + \text{energy}$$

Nitrification and denitrification are the main microbial processes producing N_2O and NO. Other biochemical oxidation or reduction reactions like N_2-fixation and dissimilatory nitrate reduction may yield some traces of N_2O and NO as well. Abiotic production may occur through chemodenitrification.

CONDITIONS INFLUENCING NITROUS OXIDE PRODUCTION IN SOILS

Oxygen: The oxygen status in soil, which is inversely, proportional to the amount of moisture held there, appears in many studies to be one of the key factors influencing nitrous oxide oxide production (Fig. 1).

Redox potential: Changes in soil redox potential are related to changes in oxygen levels. The occurrence of a variety of microbial processes is related to specific redox potential. Some of these are as follows: erobic carbon oxidation >0.2 V; denitrification 0.15 to 0.2 V; methanogenesis 0.2 to -0.1 V; sulfer reduction 0.2 to -0.1 V. The highest N_2O emission from Eutric Cambisol was observed at 200 mV (Fig. 2).



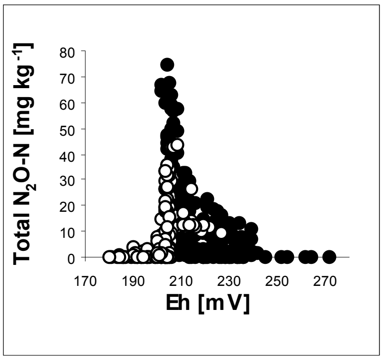
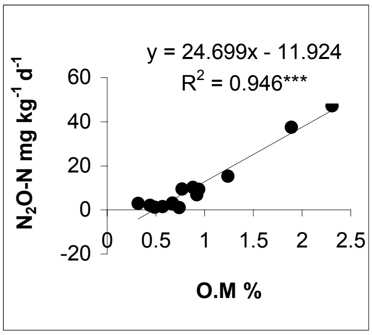


Fig. 1 *N_2O emission as a function of O_2 content for the day of maximum emission.*

Fig. 2 *N_2O emission as a function of Eh value (●emission ○absorption)*

Organic matter availability: Denitrification is a respiratory process, which requires an easily oxidisable organic substrate. The presence of readily metabolize organic matter and the availability of water soluble organic matter are closely correlated with the rate biological denitrification and hence the potential production of N_2O from soil. There is observed very high correlation between N_2O emission and organic matter content (Fig. 3).

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. 4).



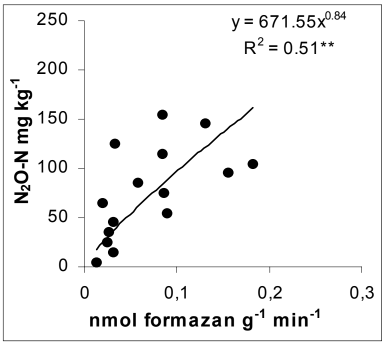


Fig.3 *N_2O emission as a function of organic matter content*

Fig.4 *N_2O emission as a function of dehydrogenase activity*

pH: Under conditions where NO_3^- concentrations do not limit potential denitrification, the overall rates of both denitrification and nitrification decline with decreasing pH from optima of about pH 7.5 (Fig. 5).

There is also the possibility of general susceptiblity of all the denitrifying enzymes to changes in pH, leading to modified production rates and the emission of N_2O from accumulated intermediates

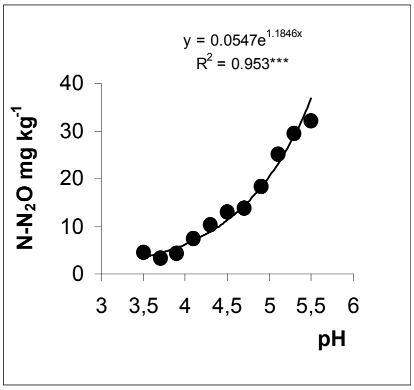


***Fig.5** Average of N_2O emission as a function of pH for the day of maximum emission.*

Nitrate concentrations: Total denitrification fluxes (N_2O plus N_2) are directly proportional to soil NO_3^- concentrations when 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.

I t is well established that an increase in soil or sediment NO_3^- concentration leads to an increase in the N_2O:N_2 ratio in the product gases. This is attributed to the inhibition of N_2O reductase by NO_3^- and, as noted earlier, this effect is further enhanced at low pH.

Soil texture: The soil texture and particle size distribution significantly affected the production of N_2O (Fig. 6). Nitrous oxide production from heavier-textured soils exceeds that from coarse-textured soils up to 6-times.

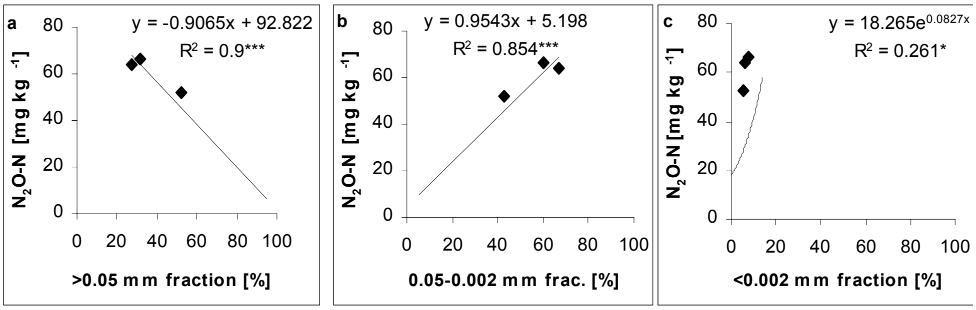


***Fig. 6** N_2O emission as a function of granulometric composition.*

REFERENCES

1. Bremner, J.M. and Blackmer, A.M. (1978) Nitrous oxide: emission from soils during nitrification of fertiliser nitrogen. Science 199:295-296.
2. Firestone, M.K. and Davidson, E.A. (1989) Microbiological basis of NO and N_2O production and consumption in soil. In Andrea, M.O. and Schimel, D.S. (eds) Exchange of the trace gases between terrestrial ecosystems and the atmosphere. pp. 7-22. Report for the Dahlem Workshop on Exchange of Gases between terrestrial Ecosystems and the Atmosphere, Berlin 1989. J. Wiley and Sons.
3. Granli, T. and Bøckman, O. (1994) Nitrous oxide from agriculture. Norw. Agric. Sci. Suppl. 12. p.128
4. Groffman, P.M. (1991) Ecology of Nitrification and denitrification in soil evaluated at scales relevant to atmospheric chemistry. In Rogers, J.E. and Whitman, W.B. (eds) Microbial production and consumption of greenhouse gases: methane, nitrogen oxides, and halomethanes. American Society for Microbiology, Washington D.C. 201-217
5. Horn R., Stępniewski W., Włodarczyk T., Walenzik G., Eckhard F.E.W. (1994) Denitrification rate and microbial distribution within homogenous model soil aggregates. Int. Agrophysics, 8, 65-74.
6. Mosier, A.R.; Parton, W.J.; Hutchinson, G.L. (1983) Modelling nitrous oxide evolution from cropped and native soils. In Hallberg, R. (ed) Environmental biogeochemistry. Ecol. Bull. (Stockholm) 35:229-241.
7. Payne, W.J. (1973) Reduction of nitrous oxides by micro- organisms. Bacateriological Rewievs 37: 409-452.
8. Skiba, U., Hargreaves, K.H., Fowler, D., and Smith, K.A. (1992) Fluxes of nitric and nitous oxide from agricultural soils in a cool temperate climate. Atmos. Environ. 26A; 2477-2488.
9. Schlesinger W.H. (1997) Biogeochemistry. An Analysis of Global Change. Academic Press. San Diego, London, Boston New York.
10. Tamm C.O. (1991) Nitrogen in Terrestrial Ecosystems. Ecological Studies, Vol.81. (Eds.) W.D.Billigs, F. Golley, O.L. Lange, J.S. Olson, H. Remmert. Springer-Verlag Berlin, Heidelberg, New York, London, Paris, 1991.

AUTHORS:

Baranowski Piotr	IA*, Department of Hydrotermophysics of Soil Environment and Agricultural Materials p.baranowski@demeter.ipan.lublin.pl
Benkowa Maya	Nikola Poushkarov Institute of Soil Science, Sofia, m_benkova@abv.bg
Bieganowski Andrzej	IA, Department of Hydrotermophysics of Soil Environment and Agricultural Materials biegan@demeter.ipan.lublin.pl
Bowanko Grzegorz	IA, Department of Physical Chemistry of Agricultural Materials gbowanko@demeter.ipan.lublin.pl
Brzezińska Małgorzata	IA, Department of Aeration and Gas Exchange in Soil Environment and Agricultural Materials m.brzezinska@demeter.ipan.lublin.pl
Fernandez Jose Enrique	Instituto de Recursos Naturales y Agrobiologia, Sevilla, Spain jefer@ irnase.csic.es
Hajnos Mieczysław	IA, Department of Physical Chemistry of Agricultural Materials mhajnos@demeter.ipan.lublin.pl
Horabik Józef	IA, Laboratory of Physics of Plant Granular Solids jhorabik@demeter.ipan.lublin.pl
Józefaciuk Grzegorz	IA, Department of Physical Chemistry of Agricultural Materials jozefaci@demeter.ipan.lublin.pl
Kotowska Urszula	IA, Department of Aeration and Gas Exchange in Soil Environment and Agricultural Materials ukot@ demeter.ipan.lublin.pl
Księżopolska Alicja	IA, Department of Physical Chemistry of Agricultural Materials aksiezo@demeter.ipan.lublin.pl
Lamorski Krzysztof	IA, Department of Hydrotermophysics of Soil Environment and Agricultural Materials lamorski@demeter.ipan.lublin.pl
Malicki Marek	IA, Department of Hydrotermophysics of Soil Environment and Agricultural Materials mmal@demeter.ipan.lublin.pl

Matyka-Sarzyńska Dorota	IA, Department of Physical Chemistry of Agricultural Materials dmatyka@demeter.ipan.lublin.pl
Mazurek Wojciech	IA, Department of Hydrotermophysics of Soil Environment and Agricultural Materials w.mazurek@demeter.ipan.lublin.pl
Molenda Marek	IA, Laboratory of Physics of Plant Granular Solids mmolenda@demeter.ipan.lublin.pl
Moreno Felix	Instituto de Recursos Naturales y Agrobiologia, Sevilla, Spain fmoreno@irnase.csic.es
Raytchev Toshko	N. Poushkarov Institute of Soil Science, Sofia, dr_raytchev@abv.bg
Rusinek Robert	IA, Department of Physical Bases of the Evaluation and Improvement Plant Materials r.rusinek@demeter.ipan.lublin.pl
Skierucha Wojciech	IA, Department of Hydrotermophysics of Soil Environment and Agricultural Materials skieruch@demeter.ipan.lublin.pl
Sławiński Cezary	IA, Department of Hydrotermophysics of Soil Environment and Agricultural Materials cslawin@demeter.ipan.lublin.pl
Sokołowska Zofia	IA, Department of Physical Chemistry of Agricultural Materials sokolows@demeter.ipan.lublin.pl
Stasiak Mateusz	IA, Department of Physical Bases of the Evaluation and Improvement Plant Materials m.stasiak@demeter.ipan.lublin.pl
Stępniewska Zofia	IA, Department of Aeration and Gas Exchange in Soils and Agricultural Materials stepniews@demeter.ipan.lublin.pl
Stępniewski Witold	Lublin University of Technology stepw@fenix.pol.lublin.pl
Szatanik-Kloc Alicja	IA, Department of Physical Chemistry of Agricultural Materials akloc@demeter.ipan.lublin.pl

Vanclooster Marnik	Universite Catholique de Louvain, Department of Environmental Sciences and Land Use Planning, Louvain, Belgium vanclooster@geru.ucl.ac.be
Walczak Ryszard	IA, Institute Director, Department of Hydrotermophysics of Soil Environment and Agricultural Materials rwalczak@demeter.ipan.lublin.pl
Wilczek Andrzej	IA, Department of Hydrotermophysics of Soil Environment and Agricultural Materials awilczek@demeter.ipan.lublin.pl
Witkowska-Walczak Barbara	IA, Department of Hydrotermophysics of Soil Environment and Agricultural Materials bwitwal@demeter.ipan.lublin.pl
Włodarczyk Teresa	IA, Department of Aeration and Gas Exchange in Soil Environment and Agricultural Materials teresa@ demeter.ipan.lublin.pl

* IA Institute of Agrophysics, Polish Academy of Sciences
ul. Doświadczalna 4, 20-290 Lublin Poland