MODERN PHYSICAL AND PHYSICOCHEMICAL METHODS AND THEIR APPLICATIONS IN AGROECOLOGICAL RESEARCH

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PREFACE

Recent view on our environment places soil and plant as the most important parts of our living space. The soil is not longer treated only as a building place (ground) or a background for yield production (field) but as a multifunctional object necessary for our survival and covering many of our needs, from practical to aesthetical ones. Not longer soil and plant are treated separately, but unified into an interactive soil-plant-atmosphere system. Maintaining proper functioning of this system is our primary duty. Therefore much attention has been paid to protection of the environment, waste land restoration, proper land use and not invasive industry. As a result a new policy has emerged during the past two decades, called sustainable development. It rests on the principle that 'we have to meet the needs of the present without compromising the ability of future generations to meet their own needs'.

Agriculture had to meet the needs of sustainability, as well. To provide harmonized use of our environment and its protection against degradation together with fulfilling food requirements and quality. To do this, advanced interdisciplinary studies are needed that should be oriented both on practical and on theoretical sides of the problem. Better understanding of complex interactions within and among all elements of agricultural activity is of primary importance for good future practices. Modern chemistry and physics provide specific tools that are helpful in understanding these interactions.

However, a direct “transfer” of pure physics and chemistry methods into agrophysical research of a soil-plant-atmosphere system is frequently very difficult or impossible due to time (e.g. plant-soil interactions, microbial activity, weather conditions) and spatial (high inhomogeneity of soil and plant materials) variability of the studied objects. Therefore validation of methods and standardization of measuring procedures is of primary importance.

This issue shows some examples of applications of modern methods of physics and physical chemistry in studies of agricultural materials and systems that have been presented during an international conference “Agroecological Interrelations of Physicochemical and Physical Parameters of Soils and Plants. Methods and Applications”, hold in Sofia, Bulgaria on 21st of September 2004 in the frame of the scientific activity and with financial support of:

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We address with pleasure our great appreciation to the Bulgarian Academy of Sciences for its constructive and fostering role in the cooperation between Polish and Bulgarian researchers.

SCIENTIFIC COMMITTEE

ANALYSIS OF A TECHNOGENICALLY DEGRADED SOIL USING A RAPID METHOD FOR CLAY FRACTION SEPARATION

Atanassova I., Benkova M., Raichev T., Jozefaciuk G.

ABSTRACT

The paper focuses on the physico-chemical and mineralogical properties of a soil polluted with Cu in the area of (MDK) Pirdop Copper smelter. The study soil (845 mg.kg^{-1} Cu) has been chosen from the area of Zlatitsa in the vicinity of the Pirdop Copper smelter. The intensity of the degradation processes taking place in the soils surrounding the plant accompanied by intensive acidification and pollution with heavy metals, particularly Cu, was a prerequisite for this study and the choice of that soil for analysis. The particular purpose of this study along with other studies carried out with this soil is to carry out physico-chemical and mineralogical analysis of the soil and clay fraction by making use of a rapid method for clay fraction separation combining the processes of electrodialysis and ultrafiltration. The simultaneous application of both methods renders colloid separation easier through: (1) disaggregating the particles and their settlement on the membranes – electrodialysis and (2) accelerating their movement in electric field thus avoiding simultaneous acidification. XRD-analysis showed the presence of equal mineral phases in the colloid fraction, the coarse residue fraction and the whole soil in decreasing order of abundance:
Illite (55.4 %) > chlorite (25.8 %) > kaolinite (13.9 %) > quartz (4.9 %).
The first two minerals are both of primary and secondary origin of soils, while kaolinite and quartz are products of weathering and podzolization processes which had taken place in that soil. The mineralogical composition in combination with the other physico-chemical properties is an indication of the advancement of the physical and chemical degradation which had taken place with the soil analyzed.

INTRODUCTION

Metallurgical activity in the vicinity of the Pirdop Copper smelter causes serious environmental problems due to gas (SO_2) and emissions of fine particulates of dust. These emissions contaminate surrounding soil and threaten agricultural production. Similar problems have been encountered also in the area of copper industry region of Legnica and Glogow, Poland, (Karczewska, A., 1995), where strong accumulation of heavy metals, especially Cu, occurred in an area covering more than 100 km^2.

It has been found (Dimitrov and Markov, 2000) that the soil types in the area surrounding the Pirdop Copper plant are alluvial-delluvial meadow, delluvial meadow and leached (podzolized) cinnamonic forest soils. These authors have not estimated statistically significant changes in the soil parameters such as pH, % humus, clay and silt contents of the soils from the land area of Zlatitsa situated at 0.5

– 4 km distance from the aerosol source of emissions. In general, this area is also being occupied by brown forest soils.

The study soil has been chosen from the region of Zlatitsa (school yard). The intensity of the degradation processes taking place in the soils surrounding the Pirdop plant, accompanied by intensive acidification and pollution with heavy metals, particularly Cu, was a prerequisite for this study and the choice of that soil for analysis.

The particular purpose of this study along with other studies carried out with this soil (some ameliorative measures), is to carry out physico-chemical and mineralogical analysis of the soil and clay fraction by making use of a rapid method for clay fraction separation, combining the processes of electrodialysis and ultrafiltration (T. Raichev and D. Donov, 1983).

MATERIALS AND METHODS

The method for clay fraction separation in brief, (T. Raichev and D. Donov, 1983) combines the methods of ultrafiltration and electrodialysis. It has been proved that the separate use of both methods is inappropriate due to the following reasons: (1) destruction of the clay minerals at higher current densities accompanied with acidification of the suspension; (2) settlement of the clay particles on the membranes is impeded because of movement retardation in the electric field;

(3) separate use of ultrafiltration requires a preliminary dispersing of the soil and is used for isolating soil colloids from suspension, separated from sedimentation of coarser soil particles.

The simultaneous application of both methods renders colloid separation easier through: (1) disaggregating the particles and their settlement on the membranes – electrodialysis and (2) accelerating their movement in electric field thus avoiding simultaneous acidification.

It has been also shown (T. Raichev and D. Donov, 1983) that clay fraction composition determined according to the sedimentation method of Gorbunov and the electro-ultrafiltration method was identical with slight differences in the quantitative analysis.

The soil samples have been taken from 0 – 20 cm layer of a degraded soil in the vicinity of the Cu smelter. The clay fraction has been separated by the above-mentioned method. The device for clay fraction separation is presented in Fig.1. X-ray diffraction analysis was carried out on diffractometer DRON-1, 30 Kv voltage, 9mA current and monochromatic Cu-Kα light, rotation velocity 2deg/min.

RESULTS AND DISCUSSION

The total contents of the heavy metals and the cation-exchange properties are presented in Tables 1 and 2. According to Ganev (1990) at a mineralogical level, the soil belongs to the family of illite-kaolinitic soils, i.e. % base saturation (V) < % CEC $_{SA}$ (68%), exch. $H_{8.2}$ > CEC_A, exch. AI > 0, pH < 6.0. The advanced soil acidification has occupied the strongly acidic cation exchanger leading to destruction of 2:1 minerals' octahedral layer and formation of 1:1 minerals such as kaolin.

Table 1. Total heavy metal contents of the studied soil with values of pH and organic carbon.

pH	%C	Cu	Zn	Fe	Mn	Pb	Cd	Co	Ni	Cr
H_2O		mg . kg^{-1}								
4.0	0.8	845	87	33300	650	66.5	<1	18.5	28.0	87.0

Table 2. Cation exchange properties of the studied soil.

CEC	CEC $_{SA}$	CEC $_{WA}$	Exch. $H_{8.2}$	Exch. Al	Exch.Ca	Exch. Mg	V
cmol. kg^{-1}							%
22.8	15.5	7.3	11.2	3.7	9.5	2.2	51

X-ray diffraction analysis was carried out with the whole soil, with the clay fraction being separated on the anode and the coarser fraction settled at the bottom of the glass jar. The results from the X-ray diffraction analysis (d_{001} spacings) are presented below and indicate the presence of equal mineral phases in whole soil, clay and coarser fraction.

Clay fraction:
With chemical pretreatment (H_2O_2, citrate-bicarbonate-dithionite), air dry
d (Å): ($MgCl_2$ saturation): 14.26; 10.04; 7.12; 5.01; 4.73; 4.46; 4.27; 3.53; 3.35; 3.20.
d (Å): (KCI saturation): 14.24; 10.03; 7.07; 4.99; 4.72; 4.48; 4.27; 3.53; 3.35; 3.19.
d (Å): ($MgCl_2$, glycerin): 14.24; 9.92; 7.06; 5.00; 4.71; 4.45; 4.26; 3.53; 3.33; 3.19
d (Å): ($MgCl_2$, 550º C): 13.9; 9.9; 7.02 (very low intensity); 4.98; 4.48; 4.25; 3.49; 3.33; 3.2
Without chemical pretreatment, air dry:
d (Å): 14.24; 9.94; 7.07; 4.98; 4.71; 4.45; 4.25; 3.53; 3.33; 3.19
d (Å): (glycerin): 14.22; 10.04; 7.13; 5.01; 4.71; 4.45; 4.26; 3.53; 3.34; 3.21
d (Å): (550º C): 14.19; 10.13; 7.14 (very low intensity); 5.03; 4.49; 4.28; 3.53; 3.35; 3.24
Whole soil:
d (Å): 14.04, 9.92, 7.07, 4.98, 4.71, 4.46, 4.25, 3.53, 3.34; 3.19
Coarse residue:
d (Å): 14.22; 10.01; 7.06; 4.98; 4.71; 4.46; 4.25; 3.53; 3.33; 3.19

The clay fraction was analyzed without treatment and with the conventional chemical pretreatment, i.e. air-dry samples saturated with Mg, K, glycerin and heated at 550º C. Similar diffractions were seen at both types of X-ray spectra. No impurities of crystal forms of sesquioxides were seen and peaks were with sharp intensities in both chemically treated and untreated samples, which indicates low and insignificant presence of amorphous materials.

According to the diffraction pattern, it could be concluded that the three most abundant minerals were illite, chlorite and kaolinite. It should be stated, that distinguishing between kaolinite, chlorite and highly-charged quickly rehydrating vermiculite when present simultaneously in the sample, is a difficult task, because of peak overlapping. The diffraction analysis was carried out with KCI saturation to exclude the hypothesis of the presence of highly-charged vermiculite. No reduction of d_{002} spacing (with K^+ saturation) was encountered and no d_{002} increase with glycerin saturation was found.

From the X-ray analysis it could be seen, that identical minerals are present in whole soils, clay fraction and coarser fractions. The soil genesis has not lead to the formation of other specific minerals with expanding lattices such as montmorillonite, rather to disintegration of larger well-crystallized minerals into smaller ones. The reason must be due to the semi-arid climatic conditions of this area, combined with the technogenic deterioration of the soil, caused mainly by the acidification (Dimitrov and Markov, 2000).

The high presence of chlorite is rare in the Bulgarian soils (0-5 %). According to their formation pattern, chlorites can be both of primary and secondary origin. That has been proved in this study by the fact that chlorites were found in the three samples: clay, coarser fraction and whole soil, so these minerals in the clay fraction might have been inherited from the primary well crystallized chlorites or be due to transformation of micas (biotite). Illite in the clay fraction originates from primary micas and feldspars. The fact that kaolinite was found both in the clay and coarser fractions, is an indication of the advancement of the podzolization processes.

The semiqualitative analysis of the clay fraction composition revealed the following minerals in decreasing order of abundance:

Illite 55.4 % > chlorite (25.8 %) > kaolinite (13.9 %) > quartz (4.9 %)

CONCLUSION

This study with a technogenically deteriorated soil from the vicinity of the Pirdop Cu-smelter, indicated unfavorable physico-chemical and mineralogical characteristics. This could lead to an easy susceptibility of the upper and subsoil horizons to further pollution with heavy metals, due to comparatively low CEC, and especially % CEC (strongly acidic exchanger), low organic C and minerals such as illite, chlorite and kaolinite, possessing low cation sorption capacity.

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PROBLEM OF A QUALITY OF AGROPHYSICAL RESEARCH

Bieganowski A.

Agrophysics is rather new interdisciplinary branch of science, that was originated from agronomy in late fifties of 20th century. The etymology of the word "*agrophysics*" indicates the subject of the investigation (soils, plants, plant and animal materials) as well as the scientific methods, specific for physics and all the natural and technical sciences (precise defining of the studied values, measurement, monitoring, analysis, interpretation and modelling).

Despite the definition of agrophysics still undergoes changes and is being improved in many discussions, one considers the agrophysics as an interdisciplinary science that applies physical methods for research of properties of agricultural materials and products, sustainable plant and animal production, modern food processing technology, especially concentrating on the quality of substrates and food products, as well as for studying processes in the soil-plant-atmosphere, and plant-machine-crop systems (Haman and Konstankiewicz 2002; Bieganowski et al. 2003).

As this holds for other natural sciences, the activity of agrophysicists can be divided into two general groups. The first is connected with the development of new and the adaptation of the existing methods for agrophysical purposes. The second group is connected with application of these methods. The present article is addressed to researchers working in both the above groups. Its aim is to begin a discussion on the quality of agrophysical research.

SPECIFICITY OF AGROPHYSICAL RESEARCH

Prior to the discussion on the specific character of agrophysical tests this seems worth to define the term "test" itself. According to the ISO/IEC guide this is a technical activity to estimate, according to a defined procedure, of one or more properties or abilities of a given object (product, material, equipment, organism, phenomenon, process or service) [ISO/IEC Guide 25]. In a slightly narrower sense, the test is concerned as a measurement, defined as a set of operations to estimate of a value of a given quantity [VIM]. In the present article both definitions are used concurrently.

Agrophysical methods have their own specific character, that is not always met in the other branches of science. As one of the important aspect of this specific character one can regard the enormous diversity of the studied objects. Examples are two of them, being classified by the agrophysics as granular-porous media: soil clay fraction of micrometer dimensions where microscale transport, diffusion and adsorption processes are studied [Malicki 1990] and a grain silo of hundreds tons capacity for which much effort is directed on its macroscale properties as a way of filling and emptying to minimize lost of quantity and quality of the stored material [Molenda et al. 1998].

The second, even more important aspect of the specific character of agrophysical research, is a space and time variability of the studied objects. Agrophysics studies properties of the objects themselves, as well as the processes taking place within and among the objects. Main groups of objects under the interest of agrophysics are presented in Fig. 1. Majority of these objects can be treated as living organisms or their residues. So the space and time variety of agrophysical objects may be very high and dynamic.

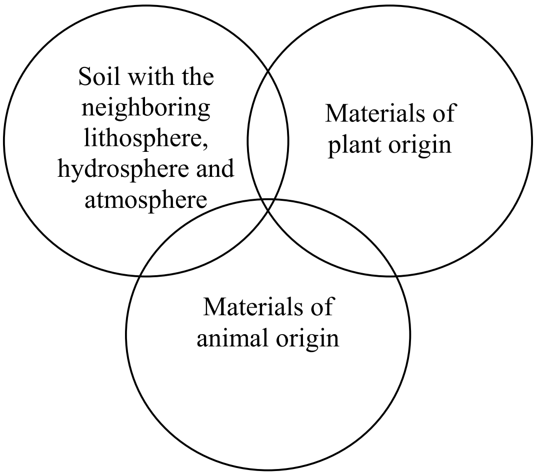

Fig. 1. *Objects of agrophysical studies.*

QUALITY OF THE MEASUREMENTS

To characterize the quality of the measurements one should define a client i.e. the recipient of the results. Three main groups of the clients of the agrophysical studies can be listed as follows:

- government – in case of research realized in the frame of the statutory activity of agrophysics-related institutions and/or for state-financed projects
- other institutions (because of not buying the results, according to the regulations these are better defined as consumers) by studying the literature and conference presentations
- industry – both by studying the literature and conference presentations and by financing research projects

As a rule, the same results are received by various clients.

The quality of all research results (including agrophysical) lies on three „pillars”: validation of measuring methods, estimation of the result uncertainty and traceability – Fig. 2. This is worth noting that all the above elements are closely interrelated e.g. traceability of the measurements (although may be considered separately) is an important component of the method validation.

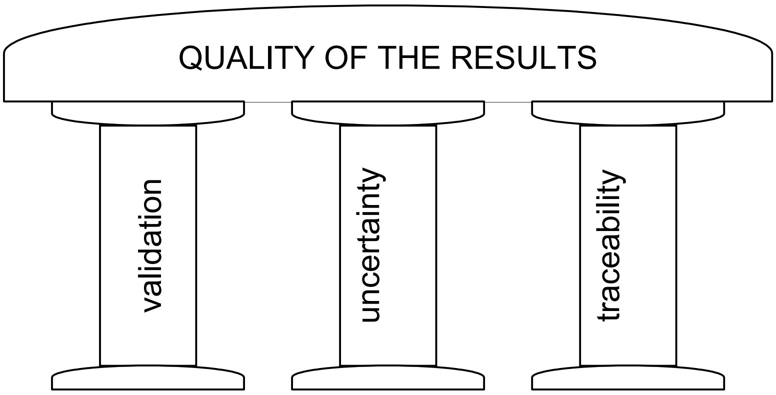

Fig. 2. *Elements necessary for the quality of the results [Bulska 2004]*

Particular elements forming the quality of the agrophysical measurements will be described briefly in the forthcoming parts of the article. As mentioned before, the purpose of the work is not to entirely describe the related problems, but to form a background for their further discussion in the community of agrophysicists and related researchers. As so far, similar discussions were successfully performed among physicists and chemists (the success is understood as a problem wide-spreading in a community thus giving rise to evaluation of standards in a given branch of science). It seems that such discussion should be performed nowadays by other natural science disciplines dealing with living objects i.e. biology, biochemistry, microbiology (including environmental microbiology) and agrophysics, as well.

VALIDATION OF AGROPHYSICAL METHODS

The validation defined by ISO/IEC 17025: 2000 standard is a confirmation by examination and the provision of objective evidence that the particular requirements for a specific intended use are fulfilled. In other words the validation should answer a question whether a given research purpose may be achieved by the selected research method and whether this method is properly used.

The literature shows a big effort of researchers to fulfill the above metrological postulates. It is seen also in the requested particular scheme of published research articles, wherein the „Materials and Methods" section presses the authors to comment the validation problems. However one may observe also that persons realizing research do not understand (and not rarely) the essence of the studies thus interpreting erroneously the results obtained. This is particularly important in agrophysical research where the studied objects (Fig. 1.) usually impose interpretational limitations and restrictions that does not exist in the analogical methods used by "pure" physics or chemistry. As an illustration of the above statement one may consider the electrochemical estimation of the potential stream of oxygen in soil, where outside of a certain range, the results can not be interpreted at all.

This seems that the most important problem of the agrophysical methods validation is to answer the questions what is the purpose of the studies and what the results will be used for. The unambiguous answer can facilitate or even make possible approaching the problem of the measuring methods validation.

Validation of agrophysical methods (similarly to the other ones) may be realized by one or a combination of the following manners [ISO 17025]:

- calibration using reference standards or reference materials (see the part on traceability)
- comparison with the results obtained with other methods (if possible)
- interlaboratory comparisons (practically lacking in agrophysical research)
- systematic assessment of the factors influencing the results
- assessment of results uncertainty based on scientific understanding of the background of a method and research practice

UNCERTAINTY OF AGROPHYSICAL RESEARCH DUE TO SPECIFICITY OF THE STUDIED OBJECTS

Measurement uncertainty is estimated as a parameter, connected with the result of the measurement, characterizing the dispersion of values that may be attributed to the measured quantity [VIM] in a justified way.

Taking into account high and dynamic space and time variability of the studied objects, the intrinsic feature of agrophysical measurements is rather high uncertainty of the results, as compared to "pure" physics or chemistry. However this can not be stated that any method of low uncertainty is better than any method of high uncertainty.

So, factors affecting the uncertainty of agrophysical research can be divided into two groups:

- objective – resulting from the object specificity
- subjective – resulting from a decision and a practice of a researcher

Important in the first group is realizing the problem and estimation of the uncertainty. For example, assuming a representative character of soil samples, the uncertainty of moisture measurements on a single field may be rather high and practically independent on the person performing the studies that is due to the inhomogeneity of the moisture distribution.

To a certain extent, there exists a possibility to minimize the objective effects on the results uncertainty. Obviously, enlarging the representative character of the sample via e.g. increasing a number of measurements leads to the uncertainty decrease. However, this has to be rationally compromised with economical aspects.

The primary criterion for this compromise is usually a purpose of the studies i.e. answer on a question on the results utility (see the part on validation).

The second "subjective" group of uncertainty reasons regards a decision (or its lack) and a rationality of the tests (or its lack) undertaken by a researcher. In the above mentioned example on moisture tests the representative character of the samples was assumed. This assumption is, however, difficult to be proved, particularly from a technical side. Soil is a complex and dynamic natural formation in which decay and synthesis of organic and mineral substances occur consecutively and are accompanied by dislocation and transport processes [Zawadzki 1999]. Even this single definition, addressing soil as living and dynamic system, certifies the problem of variability. This problem may be solved using statistical methods, allowing for estimation of a sample number and a way of sampling necessary for minimizing (but not eliminating) the uncertainty. Unfortunately this approach is rare in practice, and most frequently arbitrary decisions on sample quantity and way of sampling are taken out. Despite such decisions are based on the researchers practice, these are based on any calculations thus being more intuitive.

The practice shows that many researchers do not percept this problem. The others, understanding the problem, are frequently not able to solve it due to lack in procedural knowledge, lack of sufficient information on the studied object, or to technical impossibilities, either.

In the experimental practice three replicates are used as a standard. Why this number and not the other? Even having some certification of this three, other questions arise, which need to be answered in an aspect of the results quality:

- was one sample taken and divided into 3 parts in a lab
- were 3 samples taken separately but from one place (neighboring sampling points) – this is related to the uncertainty level
- were 3 samples taken from different sampling points

The above questions do not satisfy the whole problem for not bringing up important aspects of the history of the tested object prior to sampling. For example, different results of soil microbial activity are observed after a rainfall and after a dry period. Important to note is that information on soil moisture in a moment of sampling is not sufficient for the above experiment. Most of environmental microbiology papers does not contain information necessary for realistic interpretation of data.

As a summary of the present part of the discussion this should be stated that an estimation of an uncertainty budget for commonly used agrophysical measurements is a new challenge for agrophysical metrology.

TRACEABILITY OF AGROPHYSICAL MEASUREMENTS

A definition of measurement traceability is given in an International Dictionary of Basic and General Terms of Metrology [VIM], according to which the measurement traceability (adequacy with standards) is a property of a measurement result allowing for its connection with a defined measurement standard, usually with state or international measuring units, through an uninterrupted and continuous chain of comparisons, each having its own uncertainty.

An important element of the above definition is the defined measurement standard that are e.g. accepted standards or certified reference materials. As far as in "pure" physics and chemistry such standards are common, in the area of agrophysics practically any discussion on standards has been undertaken until now.

The next important element is the uninterrupted and continuous chain of comparisons that assumes an existence of measuring standards. Even only a question whether in given agrophysical measurement a standard exists is an essential field of discussion. One can expect, that at least for a part of agrophysical research such standards cannot be found. This constitutes an initial point for the solution of the problem. Lacking the answer on the placed question makes the results of different laboratories incomparable.

SUMMARY

It seems, that a great need for starting the discussion on the quality of agrophysical research exists in the community of agrophysicists. A market forces undertaking such the discussion also, wherein the tests are contracted to accredited laboratories, and the accreditation, according to EN ISO/IEC 17025:2001 standard is not possible without solving the quality problems.

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PRESENCE OF BUILDING MATERIALS AND THEIR POTENTIAL INFLUENCE ON SOIL PROPERTIES

Bowanko G.

INTRODUCTION

As a result of human activity, area of anthropogenic soils, including urban soils, expands every year [5, 7]. In urban soils complete destruction of natural soil profile is a common phenomenon. Buildings or roads cover the significant portion of urban areas, which makes proper circulation of air and water impossible [2]. Engineering works leave different kinds of building materials in the soil, which corrode under atmospheric and soil environment factors, leading to long-term changes in soil properties, particularly in soil structure thus affecting gases, water and nutrients retention and transport [4, 6].

One of the most popular building material which is used on the building places is a reinforced concrete, called solid electrolyte [3]. The pores and capillaries in the concrete are full of different solutions. The concentration and kind of solutions govern the speed and level of destruction. Corrosion of concrete proceeds faster in industrial regions, which are more polluted.

Another building material which was used in the research is brick. The properties of brick depend on composition of ceramic mass and course of technological process. Improper preparing of ceramic mass cause defects making a brick susceptible to all corrosion processes and of weak mechanical properties [4].

Similar properties as brick has mortar. Original calcium mortar has large absorbability and good capillary properties.

Water and temperature are major factors affecting destruction of all building materials. During capillary rise together with water some of salts are taken. These salts crystallize that made mechanical strength of building materials weaker [1]. Building materials which are leaved in soil after finishing building, corrode in the same way like in building constructions but markedly faster. The aim of the present work was to find how the addition of building materials into the soil affects its properties under the influence of cyclic changes of temperature.

MATERIALS AND METHODS

Selected building materials: wastes of brick, concrete, foam concrete, mortar and rubble (the latter was composed from equal quantities of each above material) were added to a loessial-soil in 1:1 w/w ratios, moistened with distilled water to 25% w/w and subjected to cyclic changes of temperature. One cycle consisted of one-week treatment at -20°C following by one-week treatment at 30°C. The material for investigations was taken after 6th, 12th and 18th week.

Basic properties of the investigated soil and the mixtures are presented in Table 1.

Table 1. Basic properties of the soil and its mixtures under investigation.

Probes		Granulometric composition (%, Φ in mm)			Specific surface area ($m^2 \cdot g^{-1}$)	pH	
		1-0,1	0,1-0,02	<0.02		H_2O	KCl
Soil	**(S)**	6	56	39		6,3	5,8
Brick	**(B)**	39	44	17	3,6	8,7	8,5
Cement	**(C)**	81	15	4	9,2	12,3	11,6
Foam Concrete	**(FC)**	86	3	11	34,6	9,5	9,4
Mortar	**(M)**	84	9	7	8,6	8,2	7,8
Rubble	**(R)**	67	21	12	3,4	10,6	10,2
S-B		22	46	33			
S-C		34	42	25			
S-FC		36	42	22			
S-M		40	37	24			
S-R		45	36	20			

Various physical, physicochemical and biological properties of the soil and the above mixtures were investigated using standard and well known methods, that be referred to in the next section of the paper.

RESULTS AND DISCUSSION

Changes of pH (in water) before and after cyclic changes of temperature are presented in Figure 1.

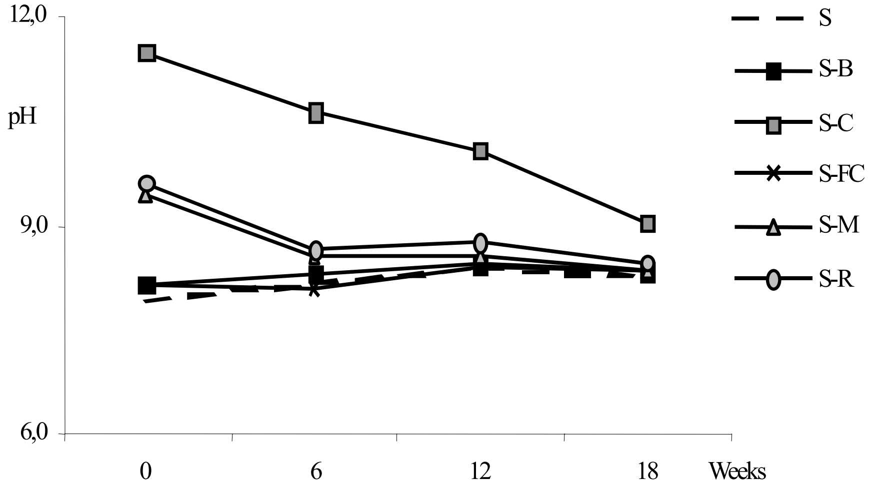
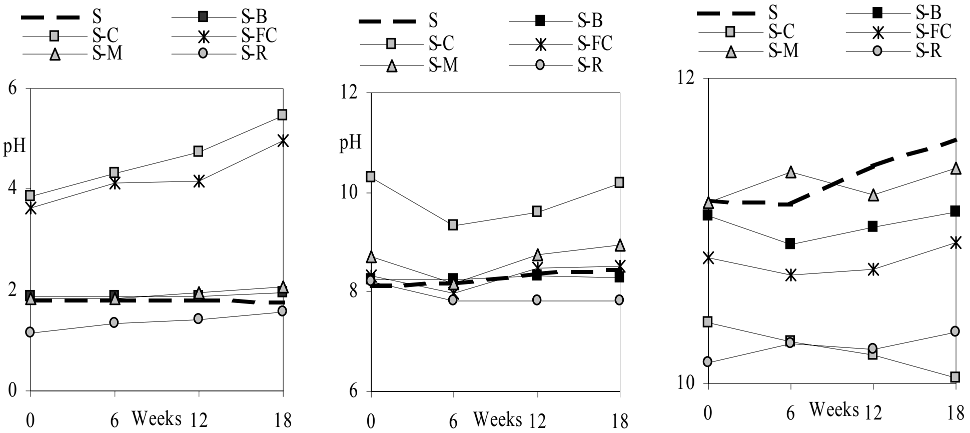


Fig.1. *changing of pH value of soil and its model mixtures under cyclic changes of temperature.*

Natural soil is neutral and after building material addition soil pH increases to 11,5 (mixtures soil with concrete) and to less than 10 for the other materials. In original soil and its mixtures with brick and foam concrete the effect of cyclic changes of temperature on pH was small, and after the cycles pH value was slightly higher then in initial probes. In other mixtures the initial pH value was smaller, however higher changes due to temperature cycles were noted.

Figure 2. shows pH values of soil and its mixtures with building materials after water, HCl and NaOH addition (1 mol dm^{-3}), as well as changes of the pH after cyclic changes of temperature. These value characterise buffer capacity of the studied systems.



In 1M HCl　　　In H_2O　　　In 1M NaOH

Fig.2. *Changes in buffer capacity of soil and its mixtures at the cyclic changes of temperature.*

Cyclic changes of temperature affected soil mixtures with concrete and mortar to the largest extent. In these mixtures, at first the pH decrease (6 weeks) and after this rises to the initial value.

pH value in 1M HCl shows buffer capacity of investigated material in acid environment. The smaller the difference between the pH before and after addition of HCl then the value of ANC (acid neutralization capacity) is higher. Even that the pH value (in H_2O) of soil mixture with foam concrete was small, the ANC of this mixture was higher then for the other mixtures and the natural soil.

pH value in 1M NaOH shows buffer capacity of investigate material in base environment, BNC (base neutralization capacity). The BNC values of soil mixture with concrete and foam concrete were smallest then for the other mixtures and soil.

Changes of BNC and ANC of soil and its mixtures with building materials after cyclic changes of temperature were small.

Figure 3 shows changes in organic carbon content in soil and the mixtures at cyclic changes of temperature.

At the cyclic changes of temperature the drop of organic carbon content in all probes was observed.

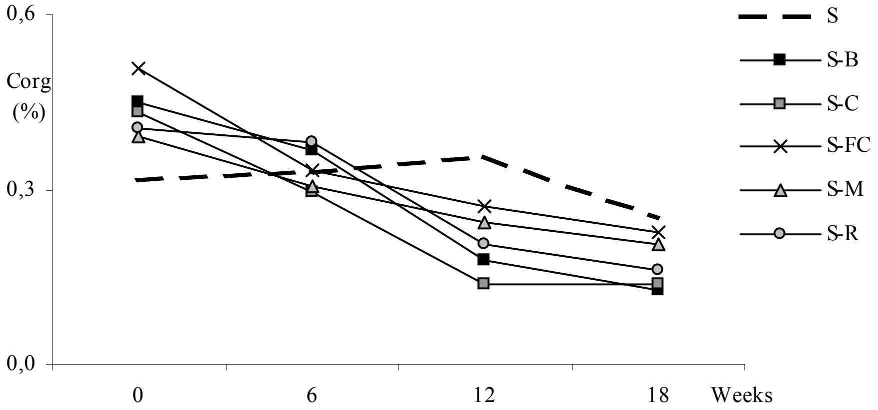


Fig.3. Changes of organic carbon content in soil and the mixtures at the cyclic changes of temperature.

Content of organic carbon correlate with dehydrogenase activity. Figure 4 shows changes in the dehydrogenase activity at cyclic changes of temperature.

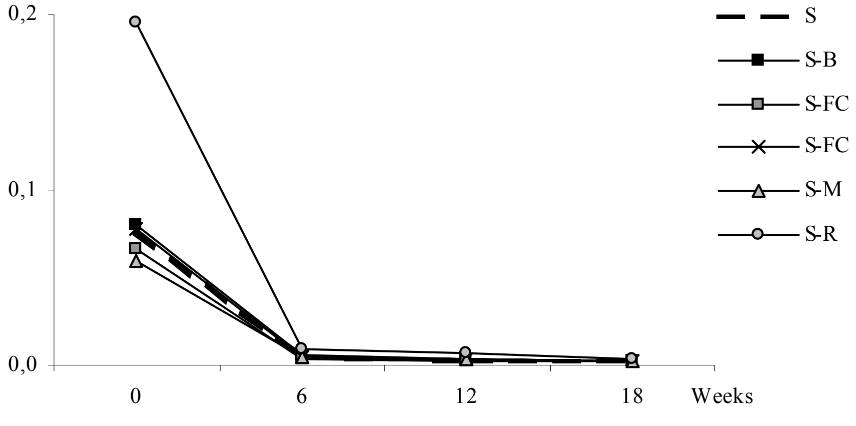
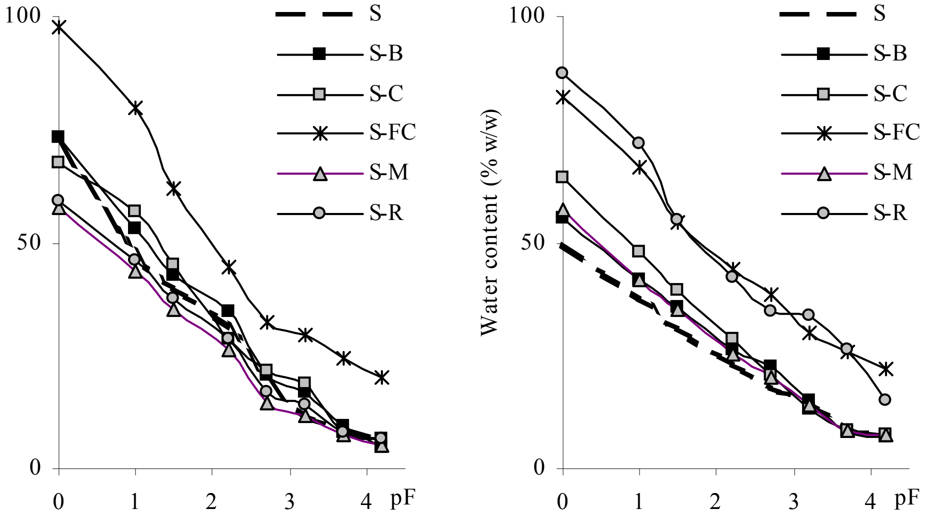


Fig.4. Changes of dehydrogenase activity in soil and the mixtures at the cyclic changes of temperature.

Cyclic changes of temperature caused strong decrease in dehydrogenase activity after the first cycle (6 weeks) of thermal treatment. In the next weeks this decrease was much smaller.

Water retention curves for the studied materials are presented in Figure 5.



Before thermal cycles After 18 weeks of thermal cycles

Fig.5. *Dependencies of moisture on water potential for the studied samples before and after cyclic changes of temperature.*

Soil mixture with foam concrete (S-FC) has significantly larger water retention capacity then the soil, just from the beginning of the experiment. The other mixtures have similar water retention capacity. After cyclic changes of temperature water retention in all samples increased slightly and very large in the soil mixture with rubble (S-R).

Addition of building materials into the soil change the specific surface area in all soil mixtures as compared to natural soil (Figure 6).

Natural soil has large specific surface area that decreases after all building materials except the foam concrete addition. The latter material increases the surface area twice. After 18 weeks of cyclic changes of temperature, values of specific surface in all samples was slightly larger then before thermal cycles.

Another characteristic value which qualify the structure of soil material is porosity. Figure 7, showing dependencies of pore volumes vs. pore radii, illustrates changes in porosity of soil after addition o building materials and after cyclic changes of temperature.

Addition a building materials into the natural soil changes its porosity. The mixtures containing foam concrete, much more porous material then natural soil, were affected to the largest extent, however high initial porosity of soil after addition of mortar decreases markedly after the temperature cycles. After cyclic changes of temperature porosity of soil and its mixtures was bigger then before.

The largest changes were observed in regions of largest and smallest pores, while the intermediate pore sizes were affected to the smallest extent.

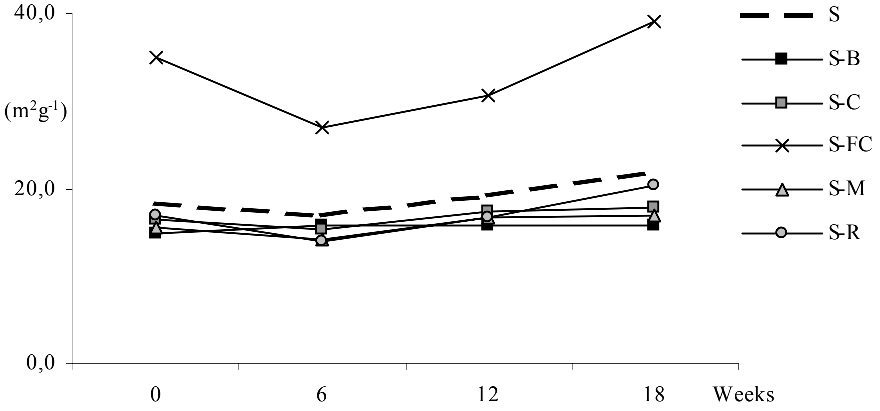
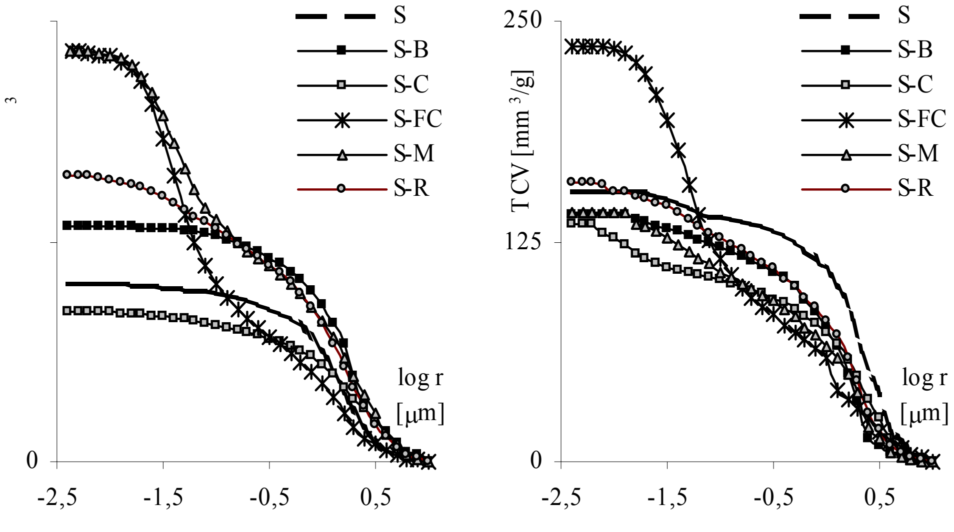


Fig.6. *Changes of specific surface area in soil and the mixtures at cyclic changes of temperature*



Before thermal cycles

After 18 weeks of thermal cycles

Fig.7. *Changes of porosity of soil and its mixtures before thermal cycles and after 18 weeks of thermal cycles*

CONCLUSIONS

1. All results confirm large influence of building materials on soil properties.
2. Addition of building materials increased soil pH value. After cyclic changes of temperature pH value decreased.
3. Addition of building materials increases soil buffer capacity.
4. Building materials increase soil porosity and specific surface area that increase further after cyclic changes of temperature.
5. Building materials and cyclic changes of temperature increase soil water retention.

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SOIL ADSORBENT OF ACID SOILS- PRINCIPLES OF COLLOID-CHEMICAL CENTER FORMATION AND INTERACTIONS

Dinev N., Benkova M., Raytchev T.

SUMMARY

On the basis of some special features in the structure of soil colloids and their behavior distribution of some specific adsorbent centers on the soil adsorbent has been presented that will serve as theoretical background in the choice of adequate technological solutions for more effective neutralization of toxic influence of heavy metal pollutants in acid soils.

Theoretical analysis on the specific features of the formed adsorbent centers on the totality of the soil colloids has shown that after a proper treatment soil processes can be activated leading to formation of “sandwich” charged structures between negatively charged colloids of the clay minerals and the humus compounds on the one hand and positively charged ions and hydroxide forms on the other hand.

References have been listed in which the results of the experimental checking of possibilities for overcoming some ameliorative problems with liming have been shown as well as the more effective neutralization of the heavy metal pollutant toxicity by:

Incorporate them in stable organic-mineral adsorbent structures

Improving the quality of the humus system and increasing the quantity of the stable binded calcium in the newly formatted organic-mineral structures

Creating a buffer system for decreasing of the negative effect of the overliming and stabilizing the optimal values of the soil reaction for a long period of time.

INTRODUCTION

The effectiveness of biogenic elements transmission through membranes by which the plant mineral nutrition has been accomplished is a reflection of the functional commitment between adsorbent competition and electro-chemical potentials of two colloid systems – the roots and the soil adsorbent. Besides the climatic conditions in food chains of the ecosystems serious problems have been originated the natural processes of degradation and anthropogenic activity. In this respect a risk factor is agricultural production especially when the applied technologies are not in conformity with the pedogenetic peculiarities of soils and their potential abilities to moderate the influence of every outside impact.

In recent years the studies on specificity of the colloid-chemical interactions in the soil adsorbent have been allowed to develop new ameliorative solutions of some problems connected with the system reaction to the changes in the environment (Raychev, 1996; Arsova, and Raychev, 2000; Arsova and Raychev, 2001; Raychev et al, 2002).

Insufficient information about the results of these studies is a reason theoretical basis concerning the bound among the specific features of the soil adsorbent structure and the colloid-chemical behavior in conditions of increased heavy metal presence to be discussed. Their effective detoxication has been determined both by their phisico-chemical condition and technological precision having in mind the necessity for balance between microelement qualities on the one hand and the pollutants on the other hand.

Traditionally applied methods for remediation of acid soils with similar problems are based on two basic principles:

- Stabilization combined with a chemical amelioration and usage of plants that are tolerant to high levels of the heavy metal pollution. The amelioration effectiveness is determined by the ability to strong bases to ensure an optimal neutralization of the acid ion-exchanger of the soil colloids.
- Phytoremediation by using of suitable plants and supporting their growth with respect to reduce the negative effects on environment. Two basic technologic approaches are most actual- phytostabilization and phytoextraction. While the stabilization is related to growth of plant species, detaining the situation of soil but with acceptable quality of plant production, the phytoextraction is oriented to selection of plant and application of treatment leading to increasing of transfer of heavy contaminants from soil to plant tissues. A number of chemical agents (citric acis, EDTA etc) are used to support passing of heavy metals in more bio-available forms.

Ameliorative problems with the traditionally applied acid soils liming polluted by heavy metals basely are connected with:

- the short-term effect because of a significant loss of lime materials as a conscience of mineralogical peculiarities of the soils.
- a risk of incomplete hydroxyl deposition or overliming as a result of the strong bases usage
- the ability for a contact ion exchange between the hydroxyl forms of the amphoteric elements and the plant roots

Having of mind the possibilities for overcoming the part of these problems the distribution of some specific adsorbent centers on the soil colloid and their behavior in totality are presented in this study. This could be used as a theoretical basis in using technological solutions for the more effective neutralization of the toxicity of the heavy metal pollutants.

Hence the effectiveness of the technological approach for the neutralization of soil acidity and their toxic effect depends on the way of their organization with clay minerals, humus compounds and amphoteric elements. This as a reason to analyze the formation of the soil adsorbent colloid-chemical nature as a function of:

- crystal-chemical and electro-chemical properties of the clay materials and the nature of chemical bonds in their unified layers;

- functional character of the humus organic compounds and their activity related to mineral and organic-mineral interactions with the other soil components;
- colloid-chemical behavior of the amphoteric elements and their role in creation of bonds among the clay minerals and the humus substances.

FORMATION OF THE SOIL ADSORBENT

The soil adsorbent is a combination of local colloid fragments that determine dominating ion equilibriums in the soil volume. The nature of their organization is a result of two basic processes:

- geochemical transformation due to weathering in the earth crust (dissolvation, hydratation, hydrolization, oxidation, ion exchange) are the main reason for colloid dispersion of the general products of soil formation – clay minerals and oxides and hydroxides of Si, Al, Fe, Ca, Mg, K, Na etc.
- biosphere influence on the erosion crust provokes the biochemical transformations of dead plant and animal remains into a specific soil organic matter – humus.

In podzolic soils the low level of the organic remains and the high humidity facilitate the soluble hydroxides and peptized highly dispersed Fe and Al oxides washing out. In this migration also take part those that have colloid protection by organic films. This is a consequence of their strong coagulating action on a humate sol including the lowest molecular components. Their trend to form complexes with humic acids allows them to obtain the same migration abilities as humic acids. It is accepted that the significant part of them along with hydroxide products of destruction of the soil adsorbent in A-horizons of podzolic soils has been moved out to alluvial B-horizons. The result is structure formation enriching with SiO_2 in the upper horizons.

Biochemical transformation includes a series of elementary, parallel, induct ional and successive reactions whose intermediate products are used for catalization (product catalysis) the next processes between the basic sources of humus substances and the humus substances themselves. Generally this connection can be represented as a unified process that reaches different rates of destruction and permanent synthesis beginning on the each stage of destruction. According to Duchaufour (1968, 1972) humification is a series of processes leading to formation of a colloid complex by biochemical transformation of plant remains and afterwards binding with mineral colloids. The different rate of a humus substances development determines both their activity related to mineral and organic-mineral interactions with the other soil components and their role as a structure formatting element of the soil not only on the macro level but in micro level of organization too. This is a reason that humus acids are widely accepted as genetic combination of different in composition, structure and properties highly molecular ox carbonic nitrogen organic compounds (Orlov, 1985; Duchaufour , 1968; 1972; Grishina, 1986).

Biological stage on which microorganisms play the main functional role is relatively short. It ends with formation of so called “young” humus that makes weak bonds with the mineral part of the humus. The second stage is related to seasonal climatic contrasts that determine its duration ends with formation of “mature” humus and it’s including in stable organic mineral complexes.

If it is assumed that the solid phase of degrading in soil organic substances are soil components that are not yet transformed and the obtained products after enzyme action are in semi-liquid condition it might be possible a presence of intermediate phase of the biological mix enzyme-substrate with a different rate of biochemical interrelations. In the absence of taking intermediate components out of the reduction system convenient conditions for parallel caring out reactions of a synthesis of specific humus compounds and their relevant destruction have been created. Domination of the mineralizing processes will exclude the whole carbon mass out of the system and this will give a decreasing view of the general cycle wave character.

This peculiar natural selection in which the unstable organic substances are decomposing in the soil and are taken in by microorganisms and the resistant compounds are stabilized on a higher level of organization is a premise for their combination in different stable fractions that reflect the genetic characteristics of humus systems. A close dependence between the oxidizing stability and their functional nature to originate is possible (Raychev, 1996).

The more vulnerable fraction related to transforming processes includes preliminary compounds with aliphatic structure of carbohydrate chains, long-chain peripheral radicals and the various functional groups enriched by –OH and –COOH. Connection of some metals in the form of complex salts with similar organic compounds has a transitional character (Schnitzer, 1991).This fraction because of it’s specific susceptibility in relation to the environment gives a dynamic character of the properties of the colloid soil formation. Stable fraction is formed mainly by compounds with prominent cyclic core (nucleus?) of the macromolecules as well as those components of the humus substances that are in progressive development. It is characterized with a high resistance to the transformation processes (Schnitzer, 1991). Nevertheless, changing the condition of it’s building separate fraction component can be stabilized and the others to be degraded to the more unstable products which allow their natural transformation from one totality to the other. Its inclination to form organic-mineral formations and a high range of oxidation prerequisite it’s role as a structure formation or and stabilizer of the colloid-chemical condition of the soil adsorbent.

Acid ionized functional groups of humus colloids determine their cation exchange properties. They are able to exchange hydrogen ions for basic in a wide pH range – from the strong acid area (pH=1-2) to the strong alkaline (pH=10-12). A significant part of them could be involved in solid binding with hydroxide forms of the amphoteric elements and to be excluded from the cation exchange. The main factors for creating the stable organic-metal bonds are carboxyl and phenol groups.

In the acid soils the intensive destruction of humic acids takes part in formation of the lower molecular fulvic acids. Their increased migrating ability in these conditions facilitates their washing to the deeper profiles and deteriorates the process of structure formation.

The formation of organic-mineral mycelia is a consequence of a combination of non-soluble highly dispersed particles with organic remains with the humus characters in the presence of free hydroxides of SiO_2, Al_2O_3, and Fe_2O_3. Potential determining nuclear ions (hydroxide, phosphate, silicate, carboxyl etc.) are connected in a sorption way on its surface. The compensating ions (exchanged cations) are distributed in immobile and mobile parts of its diffuse layer.

It could be assumed that the primary organic-mineral core of the soil adsorbent is formed in the process of humus formation from the decaying products of fermentative destruction of the condensed organic compounds (cellulose, lignin, proteins etc.) and partial connection of their active components with the mineral colloids. The parallel processes determine elasticity and a highly intensive activation of the organic fragments and enable formation of a stabile mononuclear layer on the mineral surface. There is a possibility for presence of a well developed core in it because of the early stage of these organic compounds formation that could be related to the group of non-hydrolyzed remain. In the presence of polyvalent cations new organic molecules can be adsorbed on this stabilized organic-mineral layer. After a time a surface of polymerizing units with prominent aromatic characters are formed.

THE SOIL ADSORBENT BEHAVIOR AS AN ACID

The process of soil pH decreasing two antagonistic cations play dominating role- H^+ and Ca^{2+}. The exchangeable equilibrium which is a function of organic-mineral colloid content and capacity depends on the specific soil and climatic conditions. The soil acidity has strongly relation to exchangeable Al. This amphoteric element in many cases affect plant growth (Coleman et al., 1960; Foy, 1974; Chouldjian, 1978; Ganev, 1990). The release of protons at process of hydratation of several amphoteric elements (like Al^{3+}, $[Al(OH)]^{2+}$ and $[Al(OH)_2]^+$) and capability to aggregate in hydrolitical- acid adsorption salts with strongly acidic ion of soil adsorbent predetermines acidic nature. The increasing of acidic actions follows the order

$$Fe^{+++}>Sn^{++}>Al^{+++}>Cu^{++}>Cr^{+++}>Zn^{++}>Co^{++}>Ni^{++}>Fe^{++}>Mn^{++}.$$

The behavior of aggregated hydrolitical- acid salt depends neither the presence or absence of electrolyte. The exchange of cations realized in soil is typical not only for the classical plant nutrition but for contact ion-exchange between root and soil adsorbent also.

Many authors accept that the border between toxic ion mobilization of amphoteric elements and their hydroxide immobilization is pH 6.0 (Ganev, 1990). This means that one pH value separate these two forms of presence in contrast of the individual excluding of each amphoteric element individually. During the neutralization of soil solution and increasing of pH the order of going out is (Ganev, 1990):

$$Fe(OH)_3 \rightarrow Al(OH)_3 \rightarrow Mn(OH)_3 \rightarrow Cu(OH)_2 \rightarrow Zn(OH)_2 \rightarrow Pb(OH)_2 \rightarrow Mn(OH)_2$$

The interest of investigation of acid soil increases with knowledge of processes carrying out in soil and affect on the bio-sphere and human health (Alloway et al., 1994; Alvarez et al., 1998; Castro and Logan, 1998; Foy et al. 1990; Ganev, 1990; Guralchuk, 1998; Jung et al.,1998; Kovacevic et al., 1998; Mocek and Owczarzak, 1993; Shamshuddin, 1998; Tari et al., 1998; Tsakelidou, 1995; Weber, 1993; Zonn, and Travleev, 1992).

The first indication for negative effect of soil acidity could be seen in structural and functional harming of cell wall and membranes by insufficient Ca++ uptake and following gene- and protein expressed malformation. Resuming, the plant nutrition at acid soil is related to:

- Insufficiency of basic cations (Ca^{++}, K^{+}, Mg^{++})
- Insufficiency of nitrates, phosphates, molibdates;
- Predominating ammonium uptake

The presence of heavy metals strengthen the negative effects because of base charge of hydroxides forms and increasing anion adsorption of humatic, phosphates, sulfates and other ions, making its in available forms.

The full neutralization of strongly acidic anion of soil adsorbent with bases at pH 6 practically excludes ion expression of all amphoteric elements and of this reason many authors recommend calculation of ameliorative norm to be done by the content of exchangeable aluminium (Chouldjian, 1978; Ganev, 1990).

The application of lime materials leads to decrease of exchangeable Al and in increasing of the sorption capacity of soil adsorbent. This could be explained by neutralization of inter-packed Al-ions and their transfer to hydroxide forms. The new free exchangeable positions have been immediately occupied from other cations.

This philosophy is in the base of some traditional methods of liming of acid soils, as well as decreasing of toxic acidity and heavy metal effects on plant growth (Ganev, 1990; Ganev, and Arsova, 1980). By this way heavy metal mobility decreases due to precipitation of hydroxide forms at pH 6 (Ganev, 1990; Kokotov al.,1986; Orlov, 1985; Charlot, 1969; Boldyrev, 1983; Friedrichsberg, 1984).

In many cases lime norms are calculated having in mind acidity, included exchangeable H^{+} и Al^{3+}, which remove from soil samples is made by non-buffered neutral salt (Ganev, 1987; Ganev and Arsova, 1980).

The lime norm calculated according to hydrolytically acidity, includes excess of strong bases, do full neutralization of weak acidic ion- exchangeable with all negative effects on the plant growth also (Ganev, 1987; 1990).

Colloid- chemical nature of soil adsorbent presumes and other opportunities. Experiments showed that main role in creating of complexes between humic compounds and layers of alumo-silicates play polyvalent cations and positive charged oxide-hydroxide forms. The last ones have capacity to bind both the anions of humic acids and negatively charged groups on the surface of alumo-silicates. Thereby, parallel with the process of hydroxide precipitation of heavy metals during the liming several conditions for co-operative coagulation and bridge- connection between mineral and organo-mineral soil colloids are built up. The presence of ion forms of amphoteric elements in the range of pH 5.0- 6.0 supports the process of chelating which is in the concurrence of hydroxide precipitation. But, in both cases high-molecular organic-mineral colloid structures, included the toxic elements in the anion part of molecules are formed and as a result, the participation of these trace elements in the plant metabolism is fount it difficult (Ganev, 1990; Orlov, 1985; Raychev, 1996; Boldyrev, 1983; Charlot, 1969; Friedrichsberg, 1984; Jozefaciuk et al., 1992).

The stable role of soil clay at structure modeling of soil adsorbent supposes the importance of colloidal behavior of main parts involved in the process (Berry et. al.,1987; Ganev, 1990; Cotton and Wilkinson, 1977, 1977a; Fripiat et al., 1971; Grim, 1959; Lazarov, 2001; Orlov, 1985). They are secondary alumo-silicates ($SiO_2Al_2O_3.mH_2O$) and specific molar ratio $SiO_2:Al_2O_3 = 2 \div 5$.

Despite the fact that some of them are stable to very high temperatures, soil clay minerals are formed at native conditions during the several precipitation processes, diagenesis and weathering also.

The character of chemical and physico-chemical properties of formed surface reflexes on the buffer capacity of soil, its stability to acid- alkaline changes and behavior of typical forms of humic compounds and amphoteric elements. The last ones expresses high trend to hard coordination with O2- and OH- and make easier structures constructed of oxide-hydroxide types.

The acid soil conditions supports base change of amphoteric elements (Al, Fe, Mn, Cu, Zn) of their oxide-hydroxide structures and this process explain the specific colloidal reactions (Ganev, 1990; Boldyrev, 1983; Orlov, 1985; Charlot, 1969; Jozefaciuk et al., 1992).

The forming of colloidal mycelium starts with polymerization of hydroxyl ions and finishes with anion adsorption for compensation of positive charge in acid soil conditions.

The polymerized metal hydroxides express very high adsorption capacity because of the including a big part of bi-electrical layer around the micelle (Boldyrev, 1983; Ganev, 1990; Orlov, 1985; Charlot, 1969). The presence of organic acids, low pH, and phosphates increases the selectivity of the absorption. The possible explanation is the change of iso-electrical configuration of colloidal forms (Abd-Elfattah and Wada, 1981; Strivstava and Strivstava, 1990; Duquette and Hendershot, 1990).

It is known that the crystalline oxides and hydrated oxide gels of iron and aluminium sorb copper and zink at pH 4 and pH5 still their iso-electrical points lie and pH 8 and pH 9. The excess of organic compound decreases additionally the iso-electrical points (Kinniburgh et al., 1976; Benjamin and Leckie, 1981; Forbes et al., 1976; Shuman, 1977). Free oxides and organic compounds are used to thin layers films and block the access to usual ion- exchangeable positions on the clay minerals (Greenland, 1965).

The important rol on the effect plays the alumo-silicate content of the clay minerals (Cavallaro and McBride, 1984; Shuman, 1977; Sakurai et al., 1990).

Main roles in reactios of non-exchangeable adsorption of heavy metals on soil clay particles play the charge and places of broken of bounds in the ends of clay minerals. Therefore, the dominated model of adsorption for montmorillonite is probably cation exchange, and for illite and caolinite- organizing the polymeric hydroxil-ions, adsorbed on specific positions.

Positive charged zones are shown and on the basal surface as a result of destructive role of acid reaction and expression of colloidal forms if Al for partial neutralization of negatively charged centers.

ACTIVE CENTERS ON THE SURFACE OF SOIL ADSORBENT

Analysis of specific structure on main components of soil adsorbent give us reason to extract the following principles:

1. Type, number and interactive disposition of active centers on the surface limit the activity and specific properties of clay minerals. The clay minerals are complex adsorption colloidal systems consisted from limited number of atoms, bounded chemically. The neutralization of the negative charge and new positive charged zones support the bridge bounds with humic substances and this could have next specifics:
    - "point" character- by regular geometric distribution of the bounds with poly-valence cations or appears of hydrogen- bounds.
    - "zone" character- as a result of electrostatical connections among opposite charged colloids.
2. The basal surface of clay minerals and acid groups of humic acids are the main source of negative charged centers.
3. The process of compensatory of negatively charged surfaces cold be done by:
    A. Adsorption of cations.
    B. Adsorption of positively charged colloidal formations.
    C. Adsorption of segments from humic substances.
    D. Polyvalent metals (mainly aluminium and iron at lack of heavy metal pollution) and lateral surfaces of clay minerals are the dominating source of positive charge. Between these positive centers and acidic groups of humic substances could be made direct bounds. Because in this "bridge" zone there are both positive and negative charged centers, the bound is very stable and its destroying is possibly only at long-time actions with acid or alkaline solution.

CONCLUSION

The mentioned above process showed that after suitable treatments in soil processes of “sandwich” charged colloidal structures could be activated. These bounds are between negatively charged colloids of clay minerals and humic substances on the one side, and positively charged ions- and hydroxide forms of heavy metals, on the other side. By this way, is probably:

- Precipitation of heavy metal hydroxides
- Catching the ions into “collector” of newly formed gels;
- Occluding
- Coordination in alumi-silicates
- Forming of stable complexes with soil organic compounds.

In acid conditions a part of heavy metals is as metal hydroxides, and other part is into exchangeable positions of soil adsorbent. As a result the charge of humic substances tends to zero and the role of electrical factor decreases. This effect is realized by amelioration of contaminated with heavy metals acid soils by orhanic-mineral mixture with lime addition, where the electrical charge of humus compounds is activated (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). One of the regulation is humus to be in last stages of humification because in the opposite case the humic compounds reasonable increase solubility at alkalization.

Ameliorative affectivity increases (Raychev, 1996; Raychev et al, 1999; Boldyrev, 1983; Charlot, 1969; Friedrichsberg, 1984; Ganev, 1990; Jozefaciuk et al., 1992; Orlov, 1985) also when:

- The quality of humus system increases and the quantity of Ca in new organic-mineral complexes increases (Raychev, 1996; Raychev, 1997b; Raichev and Toncheva, 1997);
- The buffer system is stable and long time effective (Raychev et al 2001; 2001a).

The perspectives for similar scientific approach are it to be used in case of combined contamination.

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ORGANIC CARBON STOCKS IN BULGARIAN SOILS GROUPED ACCORDING TO THE REVISED LEGEND OF THE FAO-UNESCO SOIL MAP OF THE WORLD

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ABSTRACT

Knowledge on carbon stocks is desirable for both environmental protection and agricultural production. This paper reports estimates of the organic carbon stocks of the soils in Bulgaria based on available data of organic carbon and bulk density measurements along the profile depths of different soils grouped according to the revised legend of the soil map of the world (FAO-UNESCO, 1990). Fourteen soil groups, (Chernozems, Phaeozems, Luvisols, Vertisols, Fluvisols, Litosols, Cambisols, Solonchak, Solonetz, Acrisols, Gleysols, Histosols, Planosols and Rendzinas) occur in the territory of Bulgaria. Average organic carbon density ranges from 2.7 kg m^{-2} to 13.3 kg m^{-2} for the surface soil, from 4.8 kg m^{-2} to 22.3 kg m^{-2} for the layer 0-50 cm, and from 6.8 kg m^{-2} to 33.0 kg m^{-2} for the entire soil. The total national organic carbon stock is estimated at 1.3 Gt.

INTRODUCTION

Soils play an important role in the earth's carbon cycle because they contain most of the earth's carbon pool. This is important not only to the global carbon balance, but also to the present and future potential of the soil to produce sufficient food and fiber to feed and clothe the world and to meet the demand for wood for fuel, building, and other domestic uses. Human conversion of natural ecosystems to agricultural use has a strong effect on the fate of this stored carbon. Agricultural soils show large changes in carbon concentrations, carbon stock, and associated properties as bulk density and soil structure (Schleisinger, 1986).

Kobak (1988) estimated the global reservoir of terrestrial stored carbon at 5075 Pg yr^{-1}, while Greenland (1995) reported estimates of soil carbon from to 700 to 3000 10^9 t. Globally the upper meter of mineral soils contains 1300-1600 Gt carbon (Eswaran et al., 1993; Neill Ch. et al., 1997), twice the carbon stored in terrestrial biomass (Deevy, 1979; Post et all., 1982; Schleisinger, 1986). Zdruli et al. (1997) estimated the organic carbon stocks for the Albanian territory of 28.6 km^2 at 253 Mt.

Several papers on the carbon reserve in soils have been published in 1990-ies (Bohn, 1976; 1982; Kimble et al., 1990; Tarnocai and Ballarr, 1994; Zhong et al., 1997; Reich et al., 1997; Zdruli et al., 1997; Kern et al., 1997; Tarnocai, 1997; Lioubimtseva, 1997; Kolchugina et al., 1995; Eswaran et al., 1993). Some of these papers concluded that additional data were needed to improve the world scale estimates of carbon reserves.

The organic carbon reserve and energy reserve have also been estimated in Bulgaria (Gerasimov et al., 1960, Boyadgiev et al., 1994; Raichev and Filcheva, 1989; Simeonova et al., 2001). Knowledge on carbon stocks is desirable both for environmental protection and for agricultural production. Filcheva et al. (2002) estimated the organic carbon stocks of Bulgarian soils grouped according to Soil Taxonomy. This paper reports estimates of the organic carbon stocks of the Bulgarian soils, based on available data of organic carbon and bulk density measurements along the profile depths of different soils grouped according the revised legend to the soil map of the world (FAO-UNESCO, 1990).

CONCEPTS

The soil cover of Bulgaria is very complicated and often inadequate to modern climate conditions. Fourteen soil groups (FAO, Table 1) can be distinguished on the country's territory of 11.1 10^6 ha (Rousseva, 2004), while agricultural land covers 6.85 10^6 ha, woodland covers 3,85 10^6 ha, and urban area covers 0.4 10^6 ha. Cultivated land covers 4.6 10^6 ha, 83.1 % of which is occupied by cropland, 10.5 % by grassland, and 13.7 % by pastures.

Table 1. Soil cover of Bulgaria according to the FAO soil classification.

Soil group	Area, million ha	Number of samples
Chernozems	0,841	6
Phaeozems	1,435	11
Luvisols	2,229	75
Vertisols	0,644	38
Planosols	0,336	48
Fluvisols	0,731	68
Gleysols & Histosols	0,062	7
Solonchak & Solonetz	0,021	2
Litosols	2,417	6
Cambisols	2,035	8
Acrisols	0,027	2
Rendzinas	0,268	0
Total	11,044	271

Soil organic carbon stocks were estimated for the layers 0-25, 0-50, and 0-100 cm, considering the area occupied by each soil type and the respective average soil organic carbon density, which was calculated from measured values of soil organic carbon and soil bulk density. Soil organic carbon was determined by modified Turin's method (Kononova, 1966) (dichromate digestion at 125° C, 45 min., in presence of Ag_2SO_4 and $(NH_4)_2$ SO_4 $FeSO_4$ $6H_2O$ titration). Soil bulk density was determined by soil cores of volume 200 cm^3 at field capacity (Revut and Rode, 1969).

Relevant information was organized in a database including data for both virgin and cultivated soils, where measurements of soil organic carbon and soil bulk density were available along the soil profile depths.

ESTIMATES OF THE ORGANIC CARBON RESERVES

Tables 2, 3, and 4 show the average carbon density and total organic carbon calculated for each of the nine soil orders. These data demonstrate that the greatest carbon density occurs in Gleysols & Histosols for both layers 0-25 and 0-50 cm. Gleysols & Histosols are characterized by greatest carbon density of the whole soil (0-100 cm) as well. The average carbon densities of the remaining soils are much lower. Litosols show lowest average carbon densities for all studied depths.

Table 2. Organic carbon stocks in the layer 0-25 cm.

Soil group	Organic carbon density		Total organic carbon, Mt
	Average, kg m^{-2}	Standard deviation	
Chernozems	5,5	1,5	46,5
Phaeozems	5,3	2,0	75,9
Luvisols	3,9	1,2	87,4
Vertisols	5,1	2,0	32,9
Planosols	3,4	2,1	11,3
Fluvisols	3,6	1,9	26,2
Gleysols & Histosols	13,3	3,6	8,2
Solonchak & Solonetz	3,0	0,7	0,6
Litosols	2,7	1,1	64,4
Cambisols	10,9	5,7	221,8
Acrisols	3,7	0,0	1,0
Total			576,3

Average organic carbon density ranges from 3.1 kg m^{-2}(Litosols) to 18.6 kg m^{-2} (Gleysols & Histosols) for the surface soil, from 4.6 kg m^{-2} (Litosols) to 23.7 kg m^{-2} (Gleysols & Histosols) for the layer 0-50 cm, and from 6.7 kg m^{-2} (Litosols) to 33.0 kg m^{-2} (Gleysols & Histosols) for the entire soil. The average organic carbon density of the most widely distributed soils, Luvisols, Phaeozems, and Cambisols are 6.6, 8.8, and 15.0 kg m^{-2} for the layer 0-50 cm.

Presented values of the standard deviations of average organic carbon densities show significant variation among the soil profiles. The reason for this variability should be attributed to the numerous combinations of climatic conditions, native vegetation (about 10% of the soil profiles included in this study represent virgin soils), crops grown, soil characteristics and land use, and management. Comparing virgin and arable lands, Boyadgiev et al. (1994) estimated organic carbon reserves coefficients of decrease for the arable land ranging from 1.1 to 2.3 depending on the quality and the quantity of soil organic matter.

Table 3. Organic carbon stocks in the layer 0-50 cm.

Soil group	Organic carbon density		
	Average, kg m^{-2}	Standard deviation	Total organic carbon, Mt
Chernozems	10,0	3,3	83,7
Phaeozems	8,8	2,9	126,2
Luvisols	6,6	2,1	147,3
Vertisols	8,8	3,6	56,4
Planosols	5,4	2,8	18,0
Fluvisols	6,0	3,1	44,2
Gleysols & Histosols	22,3	8,8	13,8
Solonchak & Solonetz	4,9	0,4	1,0
Litosols	4,8	1,7	116,8
Cambisols	15,0	7,1	305,2
Acrisols	4,8	0,4	1,3
Total			913,9

Table 4. Organic carbon stocks in the layer 0-100 cm.

Soil group	Organic carbon density		
	Average, kg m^{-2}	Standard deviation	Total organic carbon, Mt
Chernozems	14,4	4,2	120,7
Phaeozems	12,7	3,9	182,3
Luvisols	10,6	3,5	235,4
Vertisols	14,4	7,3	92,7
Planosols	8,0	3,4	26,8
Fluvisols	9,5	5,3	69,4
Gleysols & Histosols	33,0	21,5	20,4
Solonchak & Solonetz	7,6	0,1	1,6
Litosols	7,3	2,5	175,2
Cambisols	17,4	7,8	353,7
Acrisols	6,8	0,3	1,8
Total			1280,1

The total organic carbon stock of the soils in Bulgaria is estimated at 1.3 Gt, which is about 1/1000 of the world reserve estimate of 1576 Gt (Eswaran et al., 1993). Percentage distribution of organic carbon stocks among soil orders for the studied soil layers is presented in Figure 1. Cambisols, which occupy about 18.4 % of the territory, contribute about 27.6 % of the total national carbon stocks. Chernozems, Phaeozems, Luvisols and Vertisols, which cover respectively 7.6, 13.0, 20.2 and 5.8 % of the territory, contribute about 9.4, 14.2, 18.4 and 7.2 % of the national carbon stocks.

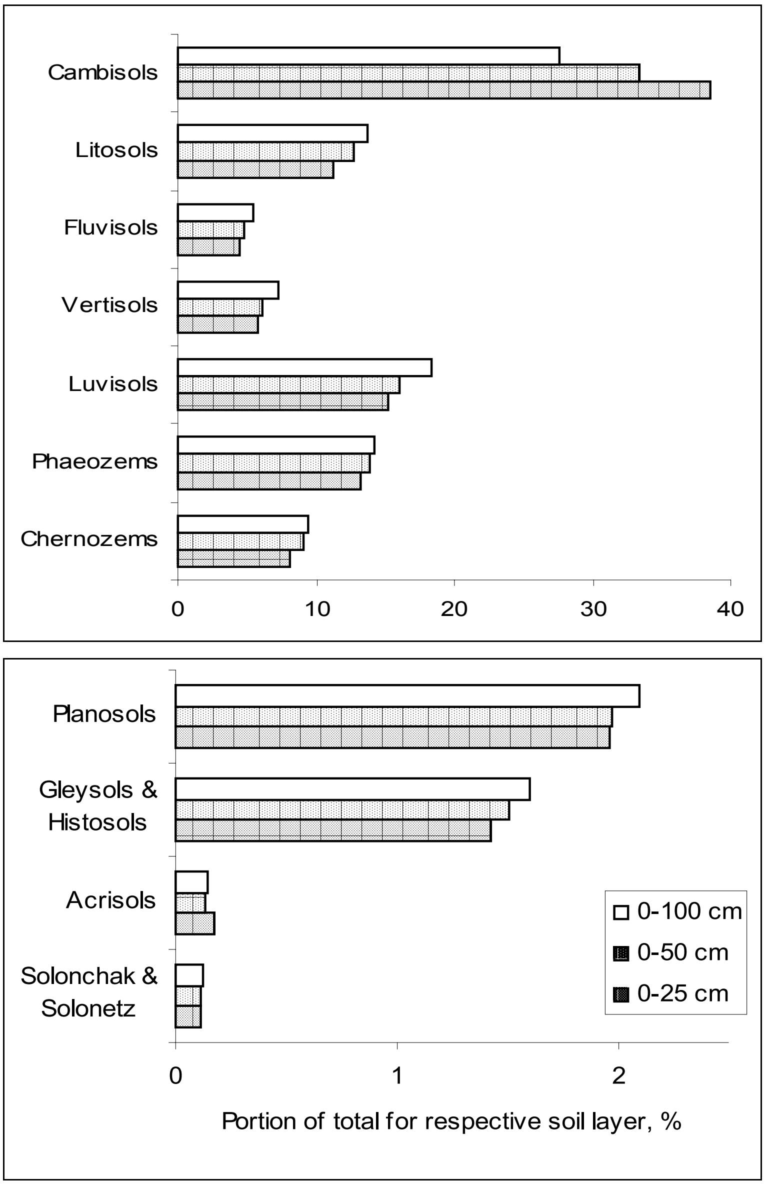

Fig. 1. *Percentage distribution of organic carbon stocks among soil orders for the studied soil layers.*

The other soils do not contribute greatly to the carbon stock. Gleysols &Histosols occupy about 0.6% of the total area but contribute 1,6 % of the national carbon stock.

CONCLUSIONS

Fourteen soil groups, (Chernozems, Phaeozems, Luvisols, Vertisols, Fluvisols, Litosols, Cambisols, Solonchak, Solonetz, Acrisols, Gleysols, Histosols, Planosols and Rendzinas) occur in the territory of Bulgaria. Average organic carbon density of the entire soil profile ranges from 7.3 to 33.0 kg m^{-2}. Cambisols, Phaeozems, Chernozems, Luvisols, Vertisols and Litosols contain about 90 % of the total national organic carbon stock, which is estimated at 1.3 Gt.

Even though Bulgaria is a small country, the soil organic carbon stock of different soils varies considerably. The high variability in a small part of the world points to the need for more detailed national assessments to obtain a more reliable estimate of soil organic carbon stocks.

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FREE Fe, Al, AND Mn COMPOUNDS AND THEIR INFLUENCE ON SOIL PROPERTIES

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DISTRIBUTIONS OF EXTRACTABLE COMPOUNDS OF Fe, Al AND Mn ALONG DEPTH OF SOILS

Free compounds of elements are results of weathering and soil - forming processes (Zonn, 1982). Their distributions along depth (depth functions) illustrate the intensity and duration of these processes, i.e. the amounts of the released compounds and their changes during soil development. As these processes are more advanced as the free compound content is higher. Different forms of the free compounds are extractable by different reagents. Because of the differences in their chemical properties of these compounds the depth functions reflect the various predominating processes in different extent.

Oxalate extractable forms, determined by the method of Tamm (1934) of iron and aluminium free compounds are poorly ordered or “amorphous”, mainly results of the modern processes of weathering. Dithionite extractable form of iron, determined by Mehra - Jakson method (1960) is the total content of the free iron forms and it was a sum of the poorly ordered and crystalline ones. Pyrophosphate extractable forms (method of Bascomb, 1968) are organic matter bound compounds and their depth functions illustrate organic matter accumulation and migration. Since the free forms are a part of the released compounds from primary minerals, unincluded in the clay minerals lattices, their content reflect the intensity of clay formation. Therefore, the distributions of these forms along depth are influenced by paleo and modern processes have occurred during the soil development: weathering, complex formation with organic matter, migration, clay formation, crystallisation with time.

The aims of the studies were: 1) the distributions of the extractable forms of Fe, Al, and Mn along depth of main Bulgarian soils differed in soil development stages; 2) to find the depth functions that are strongly affected by given soil processes so to be used as their chemical indicators.

Objects of the studies were soils from different regions, developed under different conditions of climate, parent materials, altitude: Total content of Fe, Al, and Mn was determined by acid dissolving (HF + $HClO_4$) of soil samples (size < 1 mm). Dithionite, oxalate, and pyrophosphate extractable forms of their compounds were determined by the method of Mehra - Jackson, Tamm (by Arinoushkina, 1970) and Bascomb, respectively (designated “d”, “o”, and “p”). The concentrations of these elements in the solutions obtained were determined by AAS method. A part of results is given in Tab. 1.

Table 1. Content of extractable forms of free Fe, Al and Mn (as a % of total content of the elements)

Horizon and Depth cm	pH H_2O	Fe_d	Fe_o	Fe_c	Fe_p	Al_d	Al_o	Al_p	Mn_o	Mn_p
Profile 1, Typic Chernozem (Calcic Chernozem), from Rasovo village, Pleven region, developed on loess parent materials										
Ap_1 0 - 18	7.7	24.44	4.80	19.64	10.22	2.42	3.16	12.03	55.99	9.00
Ap_2 18 - 40	7.8	21.20	5.16	16.04	9.56	1.63	2.24	10.68	44.90	
Bak 40 - 68	7.9	27.14	3.71	23.43	12.29	1.96	1.20	11.48	33.52	
Bk_1 68 - 118	8.0	23.94	3.17	20.77	13.98	1.59	2.16	12.98	35.02	
$Bk_2$118 - 148	8.1	25.52	6.16	19.36	22.53	2.57	3.15	38.55	49.68	
Bck148- 200	8.1	25.29	3.98	21.31	14.05	1.61	1.40	12.82	38.85	
Profile 3, Grey brown forest (Chromic Luvisol), from Slaviani village, Pleven regon, developed on old loamy quaternary parent materials										
Ap_1 0 - 12	5.5	-	19.06	-	7.20	4.84	4.28	8.22	66.12	13.52
Ap_2 12 - 22	5.1	29.52	13.13	16.38	4.74	2.65	2.10	4.05	59.45	6.34
AB 22 - 32	5.4	40.35	15.50	24.85	5.36	3.81	3.06	5.57	68.01	7.42
Bt_1 32 - 62	5.5	35.77	13.17	22.69	4.22	3.47	3.64	4.47	60.98	8.50
Bt_2 62 - 90	5.9	35.40	10.36	25.04	2.93	2.67	2.91	3.48	70.01	3.50
Bck 90 - 115	7.8	39.16	4.77	34.34	0.99	1.92	1.82	1.55	46.75	1.54
Profile 4, Pseudopodzolic forest gleic, from Oreshaka village, Pleven region, developed on alluvium of quaternary clay parent materials										
Ap_1 0 - 16	4.6	21.21	22.59	0.00	6.09	4.22	3.62	8.33	94.55	6.60
Ap_2 16 - 29	4.6	23.01	20.77	2.24	5.09	2.83	2.65	5.30	83.42	4.58
EB_1 29 - 37	4.6	23.48	19.96	3.52	8.41	5.29	3.48	20.31	69.11	3.03
EB_2 37 - 48	4.6	25.61	9.98	15.63	12.05	4.63	2.09	24.39	39.89	6.10
Bt_1 48 - 62	4.8	32.73	8.42	24.31	11.83	3.35	1.45	14.37	31.29	0.00
Bt_2 62 - 98	4.9	32.53	8.88	23.65	10.15	3.44	1.76	13.70	46.61	0.00
Bt_3 98 -136	5.1	38.46	12.33	26.13	6.08	2.90	1.35	6.12	50.05	0.00
BC 136-170	5.6	39.10	9.51	29.59	2.54	3.05	1.30	2.54	48.87	0.00
Profile 5, Calcic Cinnamonic forest (Calcic Luvisol), from Karnobat region, developed on limestone parent materials										
Ap 0 - 15	6.0	30.98	9.45	21.53	3.62	2.11	2.29	3.86	63.85	12.80
AB 15 - 24	5.4	25.80	8.17	17.63	6.45	3.62	3.03	7.33	64.42	10.08
Bt_1 24 - 41	4.9	24.72	7.87	16.85	6.45	3.36	3.17	9.24	55.98	10.00
Bt_2 41 - 56	6.8	22.34	6.03	16.31	2.4	2.19	2.11	2.84	54.32	7.04
BC 56 - 75	7.7	21.57	2.81	18.76	0.56	1.45	1.45	0.99	32.75	4.32
Profile 6, Cinnamonic pseudopodzolic forest (Eutric Planosol), from Primorsko village, Burgas region, developed on quaternary delluvial deposits										
Ap 0 - 20	-	32.77	10.56	22.21	3.05	3.06	2.50	1.67	51.21	13.02
AB 20 - 30	-	27.80	7.47	20.33	2.10	3.60	2.53	1.46	41.54	7.52
Bt_1 30 - 41	5.2	23.48	7.88	15.60	14.31	3.65	2.96	14.31	20.72	7.90
Bt_2 41 - 82	5.1	23.92	6.91	17.01	12.52	3.75	2.97	12.52	56.10	16.72
BC 82 -115	7.8	23.21	3.86	19.35	2.62	2.25	1.73	2.60	59.45	11.90

Table 1. Continued.

Horizon and Depth cm	pH H_2O	Fe_d	Fe_o	Fe_c	Fe_p	Al_d	Al_o	Al_p	Mn_o	Mn_p
Profile 10, Leached Smolnitza (Eutric Vertisol), from Aldomirovtzi village, Slivnitza region, developed on local colluvium from quaternary clay materials										
Ap 0 - 18	6.8	26.45	8.86	17.59	1.83	2.30	2.52	1.53	100.0	4.80
Ab 18 - 39	6.8	32.91	13.10	19.81	2.82	3.27	3.48	2.44	100.0	11.92
Bt_1 39 - 65	6.6	29.31	11.30	18.00	1.63	2.38	3.00	1.37	100.0	3.53
Bt_2 65 - 92	6.7	28.24	7.70	20.54	1.51	2.51	2.51	1.03	78.09	4.24
BC 92 - 123	7.5	21.65	3.24	18.41	0.44	0.69	1.85	0.23	-	-
Bck 123-140	7.8	18.26	3.30	14.96	0.31	0.80	3.09	0.25	63.77	6.02
Profile 11(2), Brown forest (Chromic Cambisol), from South - Eastern Rhodope mountain, at altitude 1100 m, developed on rhyolite parent materials										
Ah 0 - 5	4.9	55.18	14.81	40.37	2.75	1.95	1.56	0.52	33.05	3.23
Ab 5 - 20	5.7	56.79	12.88	43.91	0.42	2.23	1.35	0.72	53.85	5.38
B 20 -40	6.3	53.06	13.69	39.38	0.24	1.81	1.73	1.30	44.84	3.23
BC 40 - 60	7.1	65.39	19.60	45.79	0.46	2.24	1.61	0.54	23.64	2.58
Profile 12(18), Brown forest (Distric Cambisol), from South - West Pirin mountain, at altitude 1450 m, developed on granit*										
Ah A 0 - 5	5.3	17.60	42.83	-	2.11	1.87	1.02	0.58	97.03	7.32
A 5 - 12	5.3	18.34	52.19	-	2.22	2.57	1.12	0.73	98.17	11.82
Bh 12 - 25	5.0	22.84	44.51	-	3.62	3.87	2.09	1.45	94.00	7.30
BC 25 - 40	5.1	8.75	2.18	-	0.72	-	-	0.30	-	6.34
CR 40 - 60	5.5	8.24	52.57	-	0.27	0.92	0.52	0.12	82.45	4.92
Profile 13(5), Brown forest (Humic Cambisol), from Vitosha mountain, at altitude 1580 m, developed on andesite **										
A 0 - 16	5.4	24.00	10.10	13.90	7.10	8.64	8.92	7.21	36.76	18.59
AB 16 - 30	5.4	25.47	10.53	14.94	6.04	8.82	17.51	7.38	33.37	15.89
B 30 - 75	5.6	17.43	10.01	7.42	5.56	8.85	4.67	7.04	26.65	9.58
C 75 - 90	-	16.66	6.34	10.32	4.80	6.34	15.81	5.57	22.92	7.79
Profile 14(6), Dark coloured mountain forest (Humic Cambisol), from Vitosha mountain, at altitude 1800 m, developed on syenite**										
Ah 0 - 32	-	23.10	13.27	9.83	10.94	25.13	33.60	25.08	40.58	33.82
A 32 - 56	5.0	17.49	9.03	8.46	8.93	25.08	13.88	27.28	18.82	12.74
AB 56- 80	5.1	15.79	8.45	7.34	6.44	20.06	20.21	14.14	17.86	8.19
C 80 - 90	5.1	3.43	0.99	2.44	0.44	6.42	8.88	3.83	2.68	1.79

* Fe_d was determined after 3 - fold extraction, ** - after 5 - fold extraction. In brackets - according to FAO Legend. Soils are descried and classified: Profiles 1 - 10 - by T. Boyadjiev, Profile 11 (2) - by T. Shishkov, Profile 12(18) - by M. Teoharov, Profiles 13(5) and 14(6) - Fifth National Conference on Soil Science, 1994. Confidence intervals at P 0.95 of the content of Fe_d, Fe_o, Fe_p, Al_d, Al_o, Al_p, Mn_o, Mn_p are: 0.07, 0.06, 0.06, 0.08, 0.06, 0.06%, 61 mg/kg, 61 mg/kg.

The content of the extractable forms is expressed as a % of the total content of elements (relative content), illustrating the parent material transformation. The depth functions of the relative content are more preferable to be studied since the influence of the spatial changes in the content is partly avoided.

Al^{3+}, Fe^{3+}, and Mn^{2+} are competitive to be included in the clay mineral lattices. According to the increasing metallic (or the decreasing amphoteric) character these elements are ranged: Al < Fe < Mn, . The activity of the inclusion of the Al released is highest, followed by that of Fe and Mn. This corresponds to the increase in the atomic radius amphoteric character of these elements. Therefore, the relative content of the free compounds increases in the range: Mn > Fe > Al. The influence of the various soil processes on the distribution of the extractable compounds along depth would be differently expressed.

Since Mn is more easily reducible than Fe (Lindsay, 1979) and the relative content of its extractable forms is highest, the Mn depth functions are indicative mainly to the migration and gley processes. Mn is a bio - genic element and in most Bulgarian soils the dithionite and oxalate extractable compounds (Mn_d and Mn_o) are accumulated in the surface horizons, as well as the total manganese content (Mn_t). Exceptions are the Chromic Luvisols and Terra rossa soils from South Bulgaria formed from calcareous parent materials under well oxidised climate conditions where a Mn - bearing mineral (pyrolusite) is the most stable and the content of Mn_d, Mn_o, and Mn_t increases with depth (Jokova and Boyadjiev, 1993; Jokova, 1994). The organic matter bound compounds of Mn are accumulated in the surface horizons of all soils. Their complexes are more stable compared with Fe and Al ones and they migrate along the profiles more intensively.

In the periodically surface waterlogged soils (Planosols) in the zone between Bt and upper horizon the reduction of Mn has occurred and the obtained Mn^{2+} compounds are more soluble and they have moved to the lower and mainly to the upper part of the profile. Minimum's of the depth functions of Mn_t, Mn_d, and Mn_o observed in the soil solum shows the zone of gley processes (Profiles 4 and 6). As they are more expressed, as these processes are more intensive (Jokova, 1994). With soil development the maximums in the depth functions corresponding to the surface horizons and the minimum's corresponding to the gley horizons are better expressed. According to Khan et al (1996) the depth distribution of secondary Fe and Mn in Mollisol catena contributes to a better understanding of aquic and nonaquic conditions than the colorimetric Fe^{2+} tests and refinement of the definitions (as defined in Soil Survey Staf).

It was found that in some rich in Mn brown forest soils (Cambisols) the ratios between humic and fulvic acids (C_H/C_F) were higher than 1. In the most soils of this soil unit C_H/C_F is not higher than 0.9. (Koinov et al, 1980). Bartlett (1990) concluded that the presence of Mn favoured the formation of mull type horizon of a Spodosol, i.e. this hypothesis involved the role of Mn in the formation of humic polymers by oxidative polymerisation. According to Shindo and Higashi (1989) the abiotic synthesis of humic substances from phenolic compounds by Mn oxides takes place more rapidly in upland well drained fields than in submerged poorly drained fields. Taking into account these conclusions, it was supposed that Mn contributes to the increase in the ratio between humic and reductive fulvic acids (C_H/C_F) due to its higher oxidative power (Jokova, 1994). Achkov et al (1991) found that in soils from Garwal Hymalaya, Uttar Pradesh, at altitude 3950 - 4200 m, the organic matter mineralization and humification had occurred with relatively high activity , that had resulted in mull humus (C/N being 9.8 - 10.2). It could be ascribe to the high content of Mn (980 mg/kg at the surface).

Because of the highest activity of Al inclusion in the clay mineral lattices, the processes of formation, transport, and accumulation of the clay fractions are better described by the depth functions of its extractable forms. The content of Al_d and Al_o compounds is nearly close. They are accumulated in the richest in clay fractions horizons. These depth functions are indicative to the lessivage process. The maximums of their depth functions correspond to B or Bt horizons of well developed ones (McKeague and Day 1966; Jokova and Iolevsky, 1988). In a weakly developed soil the maximum of this content corresponds to the A horizon. The appearance of one more maximum at the lower part of the profiles shows the onset of the B horizon formation in the latter soil. Two maximums of Al_o are observed in soils with advanced stages of soil development: in the textural differentiated pseudopodzolic forest gleyed - at A or A_2 horizons and at Bt horizons (Profile 4), due to waterlogging and more active weathering; in soils developed on calcareous parent materials or on other firm parent materials - at the surface and at the lowest parts of the profiles (Profiles 10, 13(5)). In the acid soils the presence of Al^{3+} has led to the following. In most of them the content of Al_d is higher than that of Al_o , a result of the isomorphous replacement of aluminium for iron in Fe - bearing minerals (Profiles 4; 11(2); 12 (18); 14 (6)). It is a strong indication of its origin in a crystalline matrix (Norrish and Taylor, 1961; Georgieva and Jokova, 1986 and 1990). In a Podzol soil from Komi (Russia) the content of organic matter bound form Al_p is much higher than that of amorphous Al_o (Boyadjiev et al, 1990), because of the very high Al^{3+} content, dissolving in the pyrophosphate solution (pH 10).

Since Fe is in the middle of the range of the relative content of the extractable compounds and its depth functions are less indicative for the reduction, migration and clay formation processes than these of Mn and Al ones, respectively. The poorly ordered forms Fe_o gradually crystallise with tome. The content of the crystalline form Fe_c (as well as the ratio Fe_o/Fe_d) depends on the pedoclimmate conditions and soil development stages. Coarser well crystallised oxides (magnetite, hematite) are not completely soluble in the dithionite - citrate - bicarbonate solution (DCB), but they are attacked by the oxalate one (Vodyanitskii, 2001, 2002) So, the depth functions of Fe_d , Fe_o and Fe_p are more indicative for the moisture and temperature regimes than Mn and Al ones, as well as for comparison of the processes stages in soils formed from the similar parent materials at nearly close relief conditions. Therefore, studies on the extractable forms of Fe are required in the following soils: developed on rich in Fe parent materials, with advanced development stages, from the regions under well oxidised conditions (in soils from regions influenced by Mediterranean climate) (Boyadjiev, 1986; Jokova et al., 1995; Jokova and Boyadjiev, 1998; Jokova and Teoharov, 1999; Jokova et al., 1999).

In Pseudopodzolic soils from North Bulgaria the dithionite and oxalate extractable iron forms (Fe_d, Fe_o) are accumulated in the upper parts of the profiles and in the Cinnamonic pseudopodzolic forest from South Bulgaria - in the Bt horizons (richest in clay content) along the profiles (Hadjiyanakiev, Jokova and Boyadjiev, 1993). In all Pseudopodzolic forest soils the ratios between total content of iron and clay content drastically decrease at the Bt horizons, since a part of the released iron compounds have migrated out of the profiles.

The released iron compounds from primary mineral lattices have gradually crystallised. It is favoured by higher temperature, lower moisture and low organic matter content. The depth functions of iron extractable compounds by the ratio between amorphous (Fe_o) and crystalline (Fe_c) forms is result of the pedoclimate conditions.

A big part of Bulgarian soils are developed under mesoudic climate conditions (Boyadjiev, 1996). In these soils Fe_o predominates. In most Leached cinnamonic forest soils (Chromic Luvisols, colour < 7.5YR) from South Bulgaria developed under thermoxeric and mesoxeric climate conditions, more than 80% of the free compounds Fe_d are crystalline. In the latter soils the ratio Fe_d/clay is higher and it is related to the red soil colour (Jokova and Teoharov, 1998). Terra rossa soil from Malko Ternovo with colour < 5YR, developed on the less permeable parent materials (marble) distinguishes by high content of clay (size < 0.001 mm) and fine clay fraction (size < 0.0001 mm), as well as high amounts of hematite and goethite in them. It is a result of the advanced soil development stages under thermoxeric climate conditions. The colour (< 5YR) of the Leached cinnamonic forest soil (Chromic Luvisol) from Ivailovgrad with less advanced development stages is inherited from rich in Fe parent materials (Jokova and Boyadjiev, 1998). In Brown forest soils (Chromic Cambisols) from Rhodope mountain (Profile 11(2)) the content of Fe_d and Fe_o is higher in the ryolite derived ones (colour < 5YR) than that in gneiss derived (colour 7.5 YR - 10 YR). It is due to the differences in the weathering stages of the parent materials, influence of the higher degree of fracturing and permeability of ryolite than that of gneiss (Shishkov and Jokova, 1997). Studies on the free Fe by Mossbauer spectrometry show that Bulgarian Cinnamonic soils (leached and podzolic) are older than the other main soils, since in these soils Fe^{2+} was absent in Fe - bearing minerals, i. e. iron of the silicate and nonsilicate forms exists as Fe^{3+} (Georgieva, 1989).

The following features of Pseudopodzolic soils in relation to the free compounds distributions along depth are observed. The ratios between the total content of Fe and clay content drastically decrease at the Bt horizons, since a part of the released iron compounds have migrated out of the profiles. There is one more maximum at Bt horizon of the depth functions of Fe_p, Al_p, and Mn_p, that shows active migration of the organic matter substances downward (Profiles 4 and 6). .

The increase in pH during the gley processes is due mainly to the amounts of the reduced Fe, but their parts of the total iron is much lower than the respective part of Mn. It was concluded that a part of the reduced Fe was reincluded in the clay mineral lattices after oxidation (Georgieva et al., 1994) According to Kanivets (1987) the main reactants of the reduction reactions are the free (nonsilicate) compounds. After oxidation of the reduced compounds Fe - Mn concretions have formed and their amounts are higher in soils with more advanced soil development. These concretions are much richer in Co, Pb, Cu, Zn, Ni, P than the respective soils due to the binding role of Mn (Jokova and Dilkova, 1997)

In some Brown forest soils (Distric Cambisols) the content of the dithionite, oxalate and especially pyrophosphate extractable compounds of Fe, Al, and Mn increases with the increase of the altitude due to the higher rates of weathering. It is result of the increase of moisture and the content of organic matter and aggressive fulvic acids. The content of pyrophosphate extractable forms increases in the range: $Al_p < Fe_p < Mn_p$ .with the decrease in the amphoteric character of these elements and increase in the complex stability (Georgieva and Jokova, 1986; 1990, Jokova and Georgirva, 1989, Jokova et al, 1995). Fe_p content is higher than the content of inorganic form (Fe_o - Fe_p) and it is the main form of the transport of Fe, whereas Al migrates mainly as the inorganic form (Al_o - Al_p) (Jokova and Petkov, 1994). In the Brown forest soils richest in the extractable compounds the differences pH_{H2O} - pH_{KCl} are decreased showing the decrease in the negative charge of soils (Jokova and Georgieva, 1991, Jokova et al, 1995). There are Bulgarian soils investigated for the determination of pH values (ZPC), at which the positive and negative variable charges are balanced.

Fe_d depth function is not indicative of processes that have occurred during profile development of some Brown forest soils (Distric Cambisols) at altitude above 1000 m or in some peat soils (Histosols). In these soils the nonsilicate iron form is not completely dissolved after 3- fold extraction and the content of Fe_d is lower than that of Fe_o . After 5 - fold extraction of the soil samples (Profiles 13(5) and 14(6)) the coatings of the free compounds are nearly dissolved (confirmed by Mossbouer spectrometry) and Fe_d content increases (Georgieva and Jokova 1986; 1990; Jokova and Georgieva, 1993, Jokova et al, 1996). It is due to the presence of the stable Fe - bearing minerals magnetite unaffected by the dithionite solution. The high content of organic matter and fulvic acids with high reductive power have favoured the formation of magnetite or they have reacted with $Na_2S_2O_4$ (dithionite). Jokova et al. (1996) also found that in Brown forest soils (Distric Cambisols) from Pirin mountain that $Fe_o > Fe_d$ at nearly such altitude (Profile 12(18)). According to Lindsay (1979) the poorly ordered Fe_o compounds can be transformed to magnetite, which is the stable form of Fe at reduction conditions, corresponding to the sum $pe + pH < 11.53$ (where $pe = Eh/59.2$).

The distributions of the free extractable forms support the conclusions about the role of inorganic complexes of Si, Al and Fe in their transport along the soil profiles (Ganev, 1973; Farmer et al. 1980, 1984) In the Bt horizons of the well developed soils from South Bulgaria the molecular ratios between the content of the oxalate extractable compounds Si_o/Al_o are 1.6 - 2.5. They are close to this ratio between the total content of these elements of kaolinite (2). Probably in these horizons there are complexes between amorphous compounds of Si and Al, which are first stage o the interaction between the negative charged colloidal SiO_2 and positive charged Al_2O_3 (Jokova et al, 1998)

It is observed that in the calcerious soils (Profile 1) the content of the extractable forms of Fe_d, Al_o, and Mn_o, i.e. the rates of release of their compounds from the primary mineral lattices, are close to the content in the neutral and acid ones It is due to the amphoteric character of these elements. The presence of $CaCO_3$ contributes to neutral or slightly alkaline soil solution and to binding with the oxides and hydroxides of these elements. Their accumulation zone along the profiles depends on the depth of leachingr and it is observed at the calcareous horizons. These conclusions contradict to some extent current theories about the role of carbonates in protecting the minerals (1997).

The arable layers of most cultivated soils are richer in Fe_d than the surface horizons of the respective virgin soils, due to the increase of Fe, i.e. tillage increases the more available to plants iron compounds. In most cultivated soils the content of Mn extractable forms increases in the arable layers and decreases more strongly in the gley horizons than the respective horizons of the virgin soils. The influence of tillage on the extractable compound depth functions is due to the higher permeability of the arable layers. The depth functions of Fe and Mn forms are more affected by tillage than these of Al (Jokova and Dilkova, 1997).

There are a lot of studies on the distributions of the free Fe, Al, and Mn along depth of the main Bulgarian soil units. The depth functions of their extractable forms are well known (Hadjiyanakiev, 1989; Jokova and Iolevski, 1988; Georgieva and Jokova, 1986; Jokova and Andonov, 1989; Jokova and Boyadjiev, 1993, 1998; Jokova et al., 1995; Jokova et al., 1999; etc.). The changes in the depth functions of some soil units are observed in soils developed on nonuniform parent materials. It was concluded that they could be used as criteria for establishment of parent materials discontinuity. The depth functions of Fe_d, Al_o and Mn_o are the most indicative (Jokova and Teoharov, 1998). The total content of these elements is less useful because the big part of the silicate compounds does not participate in soil processes. There are changes in the distributions of the free forms of Fe, Al and Mn in soils, affected by sulphuric acid used for uranium production (Jokova and Raichev, 2001).

Therefore, the distributions of the studied forms of Fe, Al and Mn free compounds are influenced by paleo and modern processes of weathering, complex formation, clay formation and illuviation, migration upward and downward the profiles, leaching and accumulation. They are useful as diagnostic criteria for these processes. It is required the extraction time of the compared soil samples to be the same, since the amounts extracted increase as the extraction time increases (Niskanen, 1989).

INFLUENCE OF EXTRACTABLE COMPOUNDS OF Fe AND Al ON SOME SOIL PROPERTIES

The released free compounds of the elements from the primary mineral lattices are mainly constituents of the clay soil fraction. A part of them have precipitated as hydroxides or oxides (like coatings) on the soil particles. Since free forms of the amphoteric elements are positively charged in the soil pH range they influence the adsorption properties of soils through blocking the surface negative charges on the clay particles and associated with that soil aggregate stability.

1. Influence of extractable forms on cation exchange capacity (CEC)

Studies on the influence of extractable compounds of Fe and Al on CEC are required, since it is related to the soil melioration and amendment of plant nutrition. Sakurai et al (1990) found that fresh precipitated Fe and Al hydroxides on the partakes of montmorillonite, kaolinite and strongly weathered soil decreased their CEC and increased the pH at which the positive and negative charges are equivalent. Jozefaciuk et al. (1992) found a decrease in the clay negative charges of acid soils, due to the adsorption of Al polycations at pH rang 4 - 6, as well as to the bonding of this element with organic matter at wide range of pH.

The relation between the amounts of the free iron and aluminium compounds and CEC values of some Bulgarian soils was examined (Jokova, 1999). Objects of the studies were the following soils, classified according to Bulgarian classification and FAO Legend: 2 profiles of Leached smolnitza (Eutric Vertisols) and 1 profile of Leached cinnamonic forest (Calcic Luvisol). The content of dithionite extractable free compounds Fe_d and Al_d was determined by the method of Mehra - Jackson (Table 2). Cation exchange capacity $T_{8.2}$ of soil samples was determined by the method of Ganev and Arsova (1980) before and after the separation of Fe_d and Al_d, as well as T_{CA} and T_A, corresponding to the permanent and variable negative charges, respectively.

The results showed, that after Fe_d and Al_d separation $T_{8.2}$ and T_{CA} were drastically increased and T_A - decreased (Table 3). Therefore, Fe_d and Al_d influence adsorption properties of soils through blocking of the negative charges. This increase was better expressed (33 - 81%) in the richest in montmorillonite and free compounds soil - Profile 360 of Leached smolnitza, followed by Profile 10 of Leached smolnitza (34 - 58%) and Profile 5 of Leached cinnamonic soil (15 - 32%). The range of the decreasing changes in T_{CA} corresponds to the range of decreasing content of the dithionite extractable compounds (expressed as a % of soil mass). The amounts of the dithionite extractable form of Al are lower, because it is much more included in the clay minerals lattices than Fe. and Al from the interlayer spaces is almost not attacked by the dithionite reagent of Mehra - Jackson method. In the soils richer in montmorillonite (Profile 360) the changes are higher.

Table 2. Content of silt and clay fractions (%) and dithionite extractable Fe and Al

Horizon and Depth cm	< 0.01mm	< 0.002mm	Fe_d^* %S	Fe_d^* % TC	Al_d^* %S	Al_d^* % TC
		Profile 5, Leached cinnamonic forest (Calcic Luvisol)				
A_0 0 - 15	46.2	35.3	1.54	30.98	0.23	2.11
AB 15 - 24	48.2	38.7	1.20	25.80	0.37	3.62
Bt_1 24 - 41	52.0	45.9	1.35	24.72	0.36	3.36
Bt_2 41 - 56	52.6	48.6	1.37	22.34	0.30	2.19
BCk 56 - 75	39.7	47.7	1.15	21.57	0.19	1.45
		Profile 10, Leached Smolnitza (Eutric Vertisol)				
Ap 0 - 18	67.5	53.2	1.73	26.45	0.39	2.30
AB 16 - 39	63.3	60.6	2.10	32.91	0.47	3.27
Bt_1 39 - 65	69.0	60.1	1.97	29.31	0.38	2.38
Bt_2 65 - 92	69.7	61.9	1.87	28.24	0.39	2.51
BC_1 92 - 123	61.1	51.7	1.47	21.65	0.12	0.69
		Profile 360, Leached Smolnitza (Eutric Vertisol)				
A'p 0 - 28	75.4	57.8	2.52	40.26	0.42	3.58
A" 35 - 45	74.7	58.9	2.66	42.49	0.45	2.98
A"' 58 - 68	70.0	54.0	2.46	39.61	0.46	3.12
ABk 80 - 90	66.5	49.2	2.68	46.21	0.33	2.82

Legend; d - determined by the method of Mehra - Jackson. * - expressed as R_2O_3. %S content in soil; %TC percentage of total content. Confidence intervals at P 0.95 of Fe_2O_{3t} , Al_2O_{3t}, Fe_d è Al_d are: 0.46 ; 1.45 %; 0.07 % è 0.08%. Profiles 5 and 10 are classified by T. Boyadjiev, profile 360 - by Strahil Mihailov.

According to Jozefaciuk (1992) this influence is strongest in acid brown and podzolic soils. Oades (1984) concluded that Al hydroxide blocked stronger the negative charges on the surface of the clay minerals than Fe hydroxide. The first exists as polycation containing 15 - 30 atoms in planar configuration, which covers higher surface of the particles and interlayer space of the mineral lattices, the second exists as sphere and it increases positive charges. Sakurai et al. (1990) confirmed that Al hydroxide decreases the interlayer spaces of montmorillonite and Fe hydroxide caused the variable negative charges.

We may conclude the following. The results are related to the better expressed metallic character of Fe than that of Al. Fe is bonded more actively with the negative permanent charges (that are stronger than variable ones), whereas Al - more actively with the negative variable charges depending on pH (mainly differently charged radicals of organic matter substances). The dithionite extractable form of Al is a part of the free Al, which is on the surface of soil particles. Uehara (1995) concluded that with age soils loose negative charges and the bound with them cations (of Ca, Mg, K, Na) and gain positive charges and bound with them anions. Tese conclusions to some extent contradict these of Sakurai et al.(1990) and Oades (1984).

Table 3. Cation exchange capacity before and after separation by the method of Mehra - Jackson of the free Fe and Al

Horizon and depth cm	$T_{8.2}$		T_{CA}		T_A	
	before	after	before	after	before	after
Profile 5, Leached Cinnamonic forest (Calcic Luvisol)						
À$_0$ 0 - 15	30.40	35.95	23.72	34.78	6.68	1.17
AB 15 - 24	32.10	47.47	25.53	46.73	6.57	0.74
Bt$_1$ 24 - 41	30.93	36.50	26.42	35.86	4.48	0.64
Bt$_2$ 41 - 56	39.52	48.03	38.02	47.28	1.48	0.21
Profile 10, Leached Smolnitza (Eutric Vertisol)						
Ap 0 - 18	51.32	69.01	44.50	69.01	6.78	0.00
AB 16 - 39	49.40	78.25	42.52	78.25	6.88	0.00
Bt$_1$ 39 - 65	50.50	70.32	43.50	70.32	7.00	0.00
Bt$_2$ 65 - 92	51.32	78.25	42.60	78.25	8.67	0.00
BC$_1$ 92 - 123	50.60	-	-	-	-	-
Profile 360, Leached Smolnitza (Eutric Vertisol)						
À'p 0 - 28	58.72	78.25	49.67	78.25	9.04	0.00
A" 35 - 45	57.42	104.34	49.45	104.34	7.97	0.00
A"' 58 - 68	55.84	108.90	49.78	108.90	6.06	0.00
ABk 80 - 90	53.05	-	-	-	-	-

Legend; $T_{8.2}$ - cation exchange capacity, T_{CA} and T_{CA} - strong and week acid exchange capacity.
All data in meq/100g of soil mass .

Relationships between the increase in T_{CA} and the content of Fe $_d$ and Al$_d$ are polynomial type equations with high correlation coefficients. They suggest that at high amounts of the free forms of the elements there is a competition between the positively charges constituents in bonding with the negative charges, that causes the deprotonation.and relative increase in the latter.

With soil development the amounts of the constituents bearing variable charge pH - dependent (mainly Fe and Al hydroxides and oxides) increase and becomes higher than that of the pH independent colloids (the results of isomorphic substitution). Main characteristics of the variable - charge soils are: zero point of charge (ZPC) - pH at which the net variable charge is zero; the surface charge (σ_p) at ZPC, where H^+ and OH^- are balanced. The values of these characteristics were determined in rich in free Fe, Al and Mn strongly weathered soils from South Bulgaria and upland soils, where the variable charges dominate over the permanent ones. These studies are important since the variable charges depending on pH can be modified (by adding of meliorating agents) and CEC would be partly changed.

2. Influence of extractable forms on the soil aggregate stability

The surface charges on the clay particles are related to the soil aggregate stability, It is important characteristics of arable layers, since it is associated with soil porosity and aeration and plant available water capacity, as well as to soil erosion

There are a lot of studies on the soil aggregate stability. The experiments of Humblin and Greenland (1977), Tisdall and Oades (1982), Giovanini and Sequi (1976) showed the role of the oxalate extractable iron in the binding of the mineral particles with the organic matter and contributed to the aggregate stability.

The structure of the arable layers of most Bulgarian soils is poor (Dilkova et al., 1995). Studies on the influence of the extractable forms of Fe and Al on the soil aggregate stability were carried by Dilkova et al (1998a, c; 2000). The objects of the studies were the. arable layers of the following soils: Leached smolnitza, Glinest chernozem, Grey - brown forest, Pseudopodzolic forest and Cinnamonic pseudopodzolic forest (according to FAO Legend: Vertisol, Veric Chernozem, Haplic Luvisol, Distric and Eutric Planosols). The results were compared with these of the respective layers of the virgin soils of the same soil units. The following characteristics were determined: soil particle distribution (Katchinski, 1958); organic matter content (OM) (Tjurin, 1965); soil aggregate stability (Vershinin and Revut, 1952), expressed by the ratio (MWDR) of the mean weight diameters of the aggregates after and before wet sieving, oxalate extractable iron (Feo) and aluminium (Alo) by the method of Tamm. The correlation analysis and regression models were used .

Dilkova et al, (1998) obtained a good relationship between water stability of water aggregates and the ratio organic matter content/oxalate extractable aluminium (Al_o) in some virgin soils:

$MWDR = a_o + a_l(OM/Alo)$.

For A horizons (n = 24) the equation is: MWDR = 0.04 + 0.04(OM/Alo), $R^2 = 0.75$; for A + B horizons (n = 54) the equation is: MWDR = 0.14 + 0.03(OM/Alo), $R^2 = 0.74$. On the base of this equation aggregate stability values MWDR were classified according to the values of OM/Al_o (Table 4).

The influence of the oxalate extractable iron (Fe_o) and content of organic matter and clay on the aggregate stability was estimated more completely (Dilkova et al., 2000). The prediction of MWDR is obtained by the regression model with the ratio OM/Fe_o. clay, with high coefficient of determination and involves the data from arable and virgin layers:

$MWDR = -.2.88x^2 + 2.69x - 0.0001$, (where $x = OM/Fe_o$. clay), $R^2 = 0.61$.

Table 4. Classification of aggregate stability according to the ratio organic matter content (OM)/oxalate extractable aluminium (Al_o)

OM/Al_o	MWDR	assessment of stability
<3	<0.25	poor
3 - 10	0.25 - 0.50	middle
>10	>0.50	good

The classification of the aggregate stability depending on the values of MWDR is given in Table 5.

Table 5. Classification of aggregate stability according to MWDR and OM/Fe_o. clay

MWDR	assessment of stability	OM/Fe_o. clay	
		mean	minim. - maxim.
<0.25	poor	0.11	0.05 - 0.30
0.25 - 0.50	good	0.21	0.09 - 0.58
< 0.50	very good	0.36	0.21 - 0.58

The relationships between MWDR and OM or OM/clay were obtained by .Dilkova et al (2000). They are with lower correlation coefficients (R^2 0.07 and R^2 0.44, respectively) and confirm the role of the extractable compounds in the soil aggregate stability.

CONCLUSIONS

The distributions of the studied extractable forms of Fe, Al and Mn free compounds are useful as criteria for different soil processes. The distributions of Mn extractable forms better illustrate the intensity and duration of the gley and complex formation processes; of Al - the clay formation and illuviation; of Fe - the crystallisation and associated with it pedoclimate conditions and soil development stages. The migration substances upward is better indicated by the distribution of Mn extractable forms, followed by Fe ones, and migration downward - by the oxalate extractable form of Al. In the Brown forest soils (Distric Cambisols) at altitude above 1000 m, peat soils (Histosols), dark coloured forest (Humic Cambisols) the 3 - fold extraction of Fe by the dithionite solution is not complete and studies on pyrophosphate extractable forms of Fe are preferable, as well as the studies on the free forms of Al and Mn. The changes in the depth functions of a given soil unit indicate the parent materials discontinuity or they are results of anthropogenic influence. The higher content of Mn in upland aerated soils contributes to the increase in the ratio between humic and fulvic acids, due to its higher oxidative power.

The dithionite extractable iron (Fed) is more effective in the blocking of the permanent negative charges, dithionite extractable aluminium (Al_d) - in the blocking of the variable ones . These differences are due to the differences in the metallic (or amphoteric) character of these elements.

This seems that the balance between the negative and positive charges is required so the aggregate stability to be good or very good. It is depended on the ratio beaten the amounts of the constituents bearing these charges (negative - OM, clay fraction; positive - oxides and hydroxides of Fe, Al, Mn).

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SURFACE CHARGE CHARACTERISTICS OF SOME BULGARIAN SOILS

Jokova M.

INTRODUCTION

Free compounds of amphoteric elements are results of weathering and soil - forming processes. In the strongly weathered soils the content of the extractable forms of the free manganese, aluminium and iron hydroxides and oxides is high and it is even nearly close to that of the silicate forms.The free compounds generate pH dependent (variable) charge on the clay particle surface, whereas the isomorphous substitutions in clay minerals have resulted in pH - independent (permanent) charge. With soil development the variable charge is getting more increased and predominates over the permanent.

According to Van Raij and Peech (1972) soils from the temperate regions are characterized by permanent surface charge on colloid surface, whereas soils from the humid tropics - by variable surface charge and constant surface potential, determined by H and OH. The surface charge density of the soil colloids is the sum of permanent charge (with constant magnitude and generally negative sign), and variable charge (with negative or zero or positive sign and magnitude depending on the charge and concentration of potential determining ions. The pH value, at which the net surface charge is zero point of charge (ZPC). Cation exchange capacity (CEC) is due to the two types charges, which may occur on a single particle (Uehara and Gillman, 1980). Parker et al. (1979) concluded that the isoelectric point IEP) was pH, at which the net charge is zero and specific adsorption is absent, (but excluding H and OH^-), whereas. ZPC is pH, at which the specific adsorption (Ca^{2+}, $SO4_{2}^{-}$) is present. The error in the determination of this value increases with the increase in the permanent charge and exchangeable ions.

In Bulgaria there are soils, rich in the free forms of Al, Mn and especially of Fe. Studies on the surface charge of the clay particles in such soils are required, since they contribute to the more complete electrochemical characteristics and cation exchange capacity. They contribute to the use of more appropriate methods of analyses and more accurate prediction of the soil response to the surrounding changes. Important surface characteristics of the strongly weathered soils are: ZPC (pH at which equal amounts of H^+ and OH^- are adsorbed) and σ_p (the value of permanent chaRge at ZPC).

ZPC is a chemical parameter which characterizes the adsorption ability of the soil constitueents. ZPC of quarz and organic matter is 2 - 3, Fe and Al oxides - 8 (Uehara, 1995); precipitated Al and Fe oxides - 4.1 - 6.3 and 3.5 - 5.6, respectively (Jozefaciuk et al., 1992). Laverdier and Weaver (1977) found that these values for the crystallized Fe and Al were 8 - 9, for organic matter - 4.15 -4.90. At ZPC < pH the net charge is negative, at ZPC > pH this charge is positive. At pH of most soils quarz, organic matter are negatively charged, Fe and Al compounds - positively. Fe and Al oxides contribute to the increase of ZPC towards higher pH, the organic matter and clay minerals - towards lower pH. The net charge is negative or positive if the differences $\Delta pH = pH_{KCl} - pH_{H2O}$ are negative or positive (Van Raij and Peeech, 1972; Dolui and Dey, 1990).

The purpose of this paper is the determination of surface charge characteristics of Bulgarian soils with appreciable amounts of the free Fe and Al compounds.

MATERIALS AND METHODS

Objects of the studies were soils of the main soil units from the plain, hilly and mountainous theritories of Bulgaria: Leached cinnamonic, Grey - brown forest, Pseudopodzolic (cinnamonic, light - grey - brown, yellow) forest soils; Leached and calcareous chernozems, Leached smolnitza, Brown forest, Dark coloured mountain - forest, Mountain - meadow soils. Content of the dithionite and oxalate extractable forms of the free Fe and Al compounds (designated: Fe_d, Al_d, Fe_o, Al_o) was determined by the methods of Mehra - Jackson and Tamm (by Arinoushkina, 1972), respectively. Total content of these elements was determined by acid dissolving ($HF + HClO_4$) of soil samples. The concentrations in the obtained solutions were determined by atomic absorption AAS method. The degree of the primary mineral transformations is illustrated by the content of the extractable forms, expressed as a % of the total content of the respective element.

ZPC and σ_p were determined with Salt method (ST) and Salt method combined with potentiometric titration method (STPT), according to Sakurai at al (1988). ST method is based on the following. Suspension of a negative variable charge soil after addition of neutral electrolyte (NaCl) becomes more acid due to deprotonation of hydroxyl groups and the released protons lower pH, whereas the addition of such electrolyte to a suspension of positive variable charge soil leads to the increase in pH, due to the adsorption of protons from the solution on the surface radicals. There is a pH value indifferent to the electrolyte concentration since the net variable charge is zero, designated as pH_0. With STPT method after calculating of adsorption of PDI was determined ZPC and the value of remaining permanent charge σ_p at ZPC - the amount of H^+ or OH^-, adsorbed and balanced on the components bearing variable charge.

The values of the surface charge characteristics were not established in all studied soils. The results showed that the values of ZPC and σ_p were estimated in some soils from South Bulgaria and in the mountainous soils at the altitude higher than 1000m They are with advanced stages of weathering and soil forming processes, which are results of the influence of Mediterranean climate (Boyadjiev, 1986). The released free elements (mainly Fe and Al) have been gradually aged and crystallised or included in the clay mineral lattices. The intensity of their migration out of the profile is low, i.e. they have remained in the soil solum, contributing to the development of the variable charge.

SURFACE CHARGE CHARACTERISTICS OF SOME CINNAMONIC FOREST SOILS

The cinnamonic forest soils compared with the other soil units are older, poor in organic matter content, higher pedogenic age, i. e. with higher degrees of the primary minerals transformation (Koinov et al., 1980). In the silicate and nonsilicate parts of these soils mainly Fe (III) is present, (Fe II) is not observed (Georgieva, 1989).

The cinnamonic forest soils are textural differentiated, distinguished by high content of free compounds In most of them the content of the crystalline form of Fe is high and even dominates, resulting in red colour (< 5YR). It is related to the more advanced stages of weathering and soil forming processes, higher temperature and low moisture regimes, as well as to rich in iron parent materials (Jokova and Boyadjiev, 1998)

The surface charge characteristics were established for the following soils: i) from South Bulgaria -Red leached cinnamonic forest (Profile 18 and Profile 113), developed on marble and mica - gneiss parent materials, under mesoustic and thermoxeric pedoclimate conditions, respectively; Leached cinnamonic forest soil (Profile 15) - on quaternary deposits, from Karnobat region (Tchoukarka village), Cinnamonic pseudopodzolic forest (Profile 16) - on quaternary delluvial deposits, from Burgas region (Primorsko village); Strongly leached to slightly podzolized cinnamonic forest (Profile 113a) - on loamy deposits from South Bulgarian granite, from Plovdiv region (Otetz Kirilovo village). The results were compared with the soil from North Bulgaria - Grey - brown forest (Profile 13), developed on old loamy quaternary deposits, under mesoudic pedoclimate conditions. These soils were classified according to FAO Legend by Boyadjiev et al, 1989; Jokova and Boyadjiev, 1998: Profiles 13, 18, 113, 113a - Chromic Luvisols; Profile 15 - Calcic Luvisol; Profile 16 - Eutric Planosol. The values of: pH, the content of clay fraction (< 0.001 mm) illustrating the soil evolution stages, the content of the studied extractable forms, ZPC and σ_p are shown on Table 1 and 2.

The results show that the values of pH_0 and ZPC, determined by ST and STPT methods are close. Profile 18 (Table 1) is rich in clay fraction content and in the free forms Al_o and Fe_d, including the amorphous Fe_o and especially the crystalline part Fe_c (Fe_d - Fe_o). In Profile 113 the contents of clay fraction and extractable forms are lowest, but it is developed on rich in Fe parent materials (the total Fe content in both soils solum is similar). The results show the much more advanced stages of evolution, i. e. of the primary mineral transformation in the first soil. The predominance of pH - dependent charge components over the pH independent charge components is due: to: high pedogenic age of the soils (which confirms the conclusions of Doloui and Dey (1990) and Sakurai et al (1989); ii).rich in Fe parent materials, which contributes to the positive values of the permanent charge σ_p at ZPC (Profile 113) by substitution of hydroxy-Al and -Fe for K^+ in micas structures. The sign of σ_p is related to the mineralogical composition of clay fraction.

Table 1. Content of clay* fraction and extractable forms of free Fe and Al (as a % of total) and ZPC and σ_p

Horizon and depth, cm	Clay %	Fe_d %	Fe_o %	Fe_c %	Al_o %	pH_0 a	ZPC b	σ_p meq/ 100g
Profile 18, Red Cinnamonic forest soils (Terra rossa), Chromic Luvisol								
BA 6 - 13	40.4	50.65	6.91	43.74	3.28	3.45	3.40	2.40b
Bt_1 13 - 23	49.4	47.10	7.39	39.71	2.43	4.75	4.95	0.45b
Bt_2 23 - 53	67.9	38.86	4.33	34.53	2.45	-	-	-
Profile 113, Red Cinnamonic forest soils (Terra rossa), Chromic Luvisol.								
A 0 - 20	10.0	19.00	3.00	16.00	1.00	7.15	7.20	-0.30b
Bt_1 20 - 40	17.8	24.00	4.00	20.00	1.00	-	-	-
Bt_2 40 - 65	15.6	28.55	3.05	25.50	1.00	-	-	-
CD 65 - 85	5.1	11.05	1.00	10.05	0.88	-	-	-
Profile 13, Grey - brown forest soil, Chromic Luvisol								
Ap_1 0 - 12	33.6	-	19.06	-	4.28	-	-	-
Ap_2 12 - 22	33.0	29.55	13.13	16.38	2.10	-	-	-
AB 22 - 32	36.2	40.35	15.50	24.85	3.06	-	-	-
Bt_1 32 - 62	44.3	35.77	13.17	22.65	3.64	-	-	-
Bt_2 62 - 90	38.8	35.40	10.36	25.04	2.91	-	-	-
BC 90 - 135	32.7	39.16	4.77	34.34	1.81		-	

* < 0.001 mm; d, o - dithionite and oxalate extractable; c - crystalline; a, b - determined by ST and STPT method. Soils were studied by T. Boyadjiev.

The soil from North Bulgaria (Profile 13) is rich in the amorphous form Fe_o due to the higher moisture and lower temperature regimes. The clay content is higher than of the Profile 113, but probably a part of it is inherited from the parent materials and is not a result of advanced soil development. The determination of ZPC and σ_p of this soil was not possible.

The results (Table 2) show that in Profile 15 and 16 the contents of the dithionite extractable form Fe_d, poorly ordered ("amorphous") oxalate extractable form Fe_o and of crystalline part Fe_c are close. The distribution of Fe_d and Fe_o along depth of Strongly leached to slightly podzolized cinnamonic forest soil (Profile 113a) corresponds to the high textural differentiation. The maximum of the oxalate extractable form Al_o is observed at the illuvial horizon. In the latter soil the content of Al_d is higher than that of Al_o , which is a result of isomorphous substitution of Al for Fe.(Jokova, 1999). In the latter soil the content of Fe_d is highest, (including Fe_o and Fe_c) and it is close to the silicate form content, i. e. the degree of the transformation of the primary minerals is highest

In Profile 15 there are high amounts of the positively charged constituents, which lead to low values of the net charge at the upper part and to the positive σ_p at Bt horizon. It is a result of calcite and isomorphous substitution of Ca^{2+}.for K^+. The positive σ_p at the surface of Profile 16 is a result of the liming.

Table 2. Content of clay* fraction and extractable forms of free Fe and Al (as a % of total) and ZPC and σ_p

Horizon and depth, cm	Clay %	Fe_d %	Fe_o %	Fe_c %	Al_o %	pH_0 a	ZPC b	σ_p meq/ 100g
Profile 15, Leached cinnamonic forest, Calcic Luvisol								
A 0 - 15	29.4	30.98	9.45	21.53	2.29	6.90	6.95	-0.65
AB 15 - 24	32.9	25.80	8.17	17.63	3.03	6.80	6.80	-0.35
Bt_1 24 - 41	38.8	24.72	7.87	16.85	3.17	3.85	3.80	-4.00
Bt_2 41 - 56	39.3	22.34	6.03	16.31	2.11	7.25	7.25	+0.65
BÑk 56 - 75	28.9	21.57	2.81	18.76	2.81	-	-	-
Profile 113a, Strongly leached to slightly podzolized forest, Chromic Luvisol								
AE 0 - 11	32.3	50.56	19.31	31.25	1.01	-	-	-
A 11 - 25	39.3	50.55	17.36	33.19	1.55	3.35	3.30	-4.00
AB 25 - 37	60.4	52.38	17.58	34.80	1.85	4.95	4.90	-1.50
Bt_1 37 - 55	52.8	42.07	20.00	22.07	2.28	-	-	-
Bt_2 55 - 93	39.2	58.67	6.63	52.04	1.30	-	-	-
Profile 16, Cinnamonic pseudopodzolic forest, Eutric Planosol								
A 0 - 20	22.2	32.77	10.56	22.21	2.50	$7.60^{\#}$	$7.65^{\#}$	$+2.35^{\#}$
AB 20 - 30	29.9	27.80	7.47	20.33	2.53	$7.50^{\#}$	$7.50^{\#}$	$-0.15^{\#}$
Bt_1 30 - 41	43.4	23.48	7.88	15.60	2.96	-	-	-
Bt_2 41 - 82	38.7	23.92	6.91	17.01	2.97	-	-	-
BC_1 82 - 115	10.4	23.21	3.86	19.35	1.73	-	-	-

* < 0.001mm; d, o - dithionite and oxalate extractable; c - crystalline; a, b - classified by ST and STPT method; # - determined after liming. Profiles 15 and 16 were studied by T. Boyadjiev, and 113a - by I. Kolchakov

The data of the clay minerals show the following. Profile 18 differs from the other soils in the clay mineral composition. The predominating mineral in all horizons is kaolinite, followed (in the range of decreasing amounts) by hematite, goethite, montmorillonite. In Profile 15 montmorillonite and kaolinite dominate, followed by illite, vermiculite and calcite (in the lower part of the profile; in Profile 13, 16 and 113 montmorillonite dominates; in Profile 113a at the elluvial part-. kaolinite and illite dominate over montmorillonite, and in the illuvial part montmorillonite dominate (Koinov et al., 1998). The enrichment by kaolinite confirms the more advanced stages of soil development, related to. ZPC, which is a diagnostic criterion of the pedogenic age of soils (Doloui and Dey, 1990).

In the surface horizon of Profile 113a the amounts of the soil constituents, bearing permanent charges is low because of the strong leaching, destruction of alumosilicate minerals, migration of the products of weathering. In the horizons where kaolinite and illite dominate the variable charge is higher than the permanent, in the horizons where the amounts of montmorillonite are highest, the permanent charge dominate over the variable because of the high specific surface of this mineral.

The values of ZPC and σ_p were determined for the upper and middle parts of the studied soils, which is a result of the predominating of the variable (pH - dependent) surface charges over the pH - independent ones. It is due to the advanced soil development stages and high amounts of the free compounds of the amphoteric elements. Liming of soils and enrichment with Fe of parent materials also cause such prevalence of the variable charge. The sign of σ_p is related to the mineralogical composition of clay fraction In the soils from North Bulgaria, rich in the free forms, these values were not found, since although the high content of the free compounds the permanent charges are dominate due to the high amounts of montmorillonite with high specific surface. These differences are due to the differences in soil age.

SURFACE CHARGE CHARACTERISTICS OF MOUNTAINOUS SOILS

a. Brown forest soils from Balkan mountains

There are a lot of studies on the free forms of Fe, Al and Mn along depth of brown forest soils at altitude of 400 - 600 m.(transitional to brown); 600 - 1000 m; 1000 - 1500 m and 1500 - 1800 m. Georgieva and Jokova (1986, 1990) and Jokova and Georgieva (1989, 1989) found that with the increasing altitude the content of the extractable forms in Brown forest soils (Distric Cambisols) from West Balkan mountains are increased because of the increase in the weatheing intensity. At the highest altitude this content is close to that in the silicate parts of soils. These conclusions are supported by the studies on the soils from Pirin, Rhodope, Rila mountains (Petkov at al (1989; Jokova and al, 1991; Jokova and al, 1996; Shishkov and Jokova, 1999). Jokova and Petkov (1994) concluded that complexes between oxalate extractable Fe, Al and Si are forms of the transport of these elements. Therefore, studies on the surface charge characteristics of these soils are required (Sakurai et al., 1989).

The values of the studied characteristics were established in soils from West Balkan mountains at altitude higher than 1000 m. The values of ZPC and $\sigma_{\delta.}$ are given in Table 3.

The results show that intensive weathering processes have occurred, which have resulted in high content of the extractable forms of the free compounds, i. e. in high degree of the transformation of the primary minerals. Compared with soils possessing B horizons in the studied soils the content of the dithionite extractable form Fe_d and of Al_d, as well as of the oxalate extractable Fe_o and Al_o is higher and their distribution along depth is similar: Fe_d is accumulated at the surface horizons, Al_o - at the horizon with highest clay content along depth: A, (AB) or B, depending on the development stages (Georgieva and Jokova, 1986, 1990; Jokova and Georgieva, 1989, 1991; Jokova, 1999). The content of the crystalline iron form Fe_c is also high, inherited from the primary minerals and stable under pedoclimate and oxidative - reduction conditions.

Table 3. Content of extractable forms of Fe, Al and Mn (expressed as a % of total) and ZPC and σ_p

Profile horizon	Fe_d%	Fe_o%	Fe_c%	Al_d%	Al_o%	pH_0	ZPC	σ_p meq/ 100g
73 A	23.92	10.71	13.21	4.17	4.17	-	-	-
AB	22.06	12.03	10.03	4.94	4.85	3.50	3.50	-9/4
B	20.18	16.32	3.86	2.58	4.82	-	-	-
74 À	41.15	11.00	30.15	2.55	2.12	3.80	3.90	-1.75
B_1	28.92	16.87	12.05	1.85	2.15	3.80	3.85	-1.75
BC	26.02	3.34	22.68	1.58	1.05	3.80	4.00	-1.00
75 Ŕ	16.53	6.10	10.43	13.29	5.24	3.75	3.85	-3.90
AB	13.41	5.83	7.58	3.24	2.64	3.35	3.60	-2.35
76 A	35.18	5.76	29.42	3.49	2.05	3.25	3.15	-7.25
B	34.96	10.26	24.70	3.11	3.32	3.20	3.15	-6.9
BC	19.23	5.59	13.64	1.50	3.26	2.85	2.80	-9.4
77 A	-	12.62	-	2.51	2.51	3.75	3.85	-1.7
AB	25.24	9.22	14.02	0.97	0.78	-	-	-
B	20.96	4.37	16.59	0.39	0.35	2.60	2.90	-8.5
24 A	28.72	12.46	16.26	2.96	2.88	4.75	4.90	-0.75
B_1	22.89	11.75	11.14	1.16	3.77	3.95	3.90	-1.80
B_2	15.46	8.59	6.87	3.03	2.49	3.90	3.90	-1.5
CD	44.49	2.79	41.70	1.24	1.24	3.70	3.70	-2.35
48 A	35.41	9.58	25.83	10.78	6.70	3.55	3.55	-1.70
B	32.51	10.98	21.53	11.95	8.83	4.00	4.10	-0.60
C	35.93	3.25	32.68	10.49	4.63	4.50	4.10	-1.10

d, o - dithionite and oxalate extractabl, c - crystalline; a, b - determined by ST and STPT method**.** Soils were classified by V. Donov.

Profile 76 is rich in the free compounds (due to its situation at the denudation and accumulation of the transported compounds), 48 and 24 (developed on granodiorite parent material, less resistant to the weathering) as a difference from the other profiles. In Profiles 75 and 48 Al_d is higher than Al_o, which is observed in Brown forest soils with isomorphous substitution of Al for Fe (Jokova and Georgieva, 1989; 1991, Jokova, 1999). On the base of the differences between pH_{H2O} and pH_{KCl} was approximately estimated that the negative charge is nearly decreased

2.5 times in brown forest soil at altitude of 1500 - 1800 m in comparison with these at altitude of 6000 - 1000 m of West Balkan mountains (Jokova and Georgieva, 1991).

At most horizons ZPC was determined with exception of A and B of Profile 73, as well as AB of Profile 77. At the latter horizons the permanent charge dominates over the variable, i. e the enrichment with the free compounds is less expressed than that with clay fraction. The situation of Profile 73 suggests the influence of colluvial processes, and Profile 77 is at the automorphous position. The ratio between the permanent and variable charge is influenced by the migration intensity. Profile 76 is influenced by the accumulation processes and σ_p is highest. In the soils from the temperate regions where the difference between the amounts of permanent and variable charge is small the error in the determination of ZPC (and σ_p).is increased.

The results show high contents of the extractable forms (results of intensive weathering and migration processes), which have caused the predominance of variable charges over pH -independent ones. ZPC and σ_p values were found in the most horizons of all studied profiles.

b. Soils from West and East Rhodope, Rila and Pirin mountains

The surface charge characteristics were determined for the following soils: Brown forest - Profile 21, developed on gneiss, from Batac part of West Rhodope mountains, at altitude 1200 m.; Profile 15, on trahirhiolite, from East Rhodope mountains (Panitchkovo village), at 1000 m.; Dark ranker - Profile 24, on granite, South West Pirin, at 1900 m.; Dark coloured mountain - forest- - Profiles 41, 51, 31; Mountain - meadow - Profile 5, on granodiorite, from South Rila mountain, at 1750; 1990; 2084 and 2550 m., respectively. According to FAO Legend these soils are classified: Dystric Cambisols, Umbric Leptosol, Humic Cambisols, Orthic Umbrosol (Ninov, 1998).

The results (Table 4) show high degree of primate minerals transformation. The content of the dithionite extractable (Fe_d, Al_d) and oxalate extractable (Fe_o, Al_o) forms is higher than that in the soils with B horizons from the plane areas. The predominance of the permanent charge over the variable is acossiated with the ratio between the constituents, bearing these charges. The high content of the free compounds and the low content of the clay fraction have caused the relative increase in the variable charge, i. e. the presence of ZPC of the studied soils. Since pH_{H2O} is lower than ZPC, the permanent charge (σ_p) is negative. They are lowest in Profile 31 (Dark - coloured mountain - forest), formed at the highest altitude and in Bhf horizon of Profile 5 (Mountain - meadow), and the highest values are observed in Profiles 21 and 15 (Brown forest soils). According to Van Raij and Peech (1972) the very low ZPC (and high values of σ_p) are results of the influence of the permanent charge in soils from the temperate regions.

In the studies soils (situated at altitude of 1200 - 2550 m). ZPC and σ_p values are results of intensive weathering processes, which have caused the prevalence of the variable charges over the pH - independent. The values of the pH - independent (permanent) charges $\boldsymbol{\sigma_p}$ are negative.

Table 4. Content of extractable forms of Fe and Al (% of total) and ZPC and σ_p

Profile, horizon and depth, cm	Fe_d %	Fe_o %	Fe_c %	Al_d %	Al_o %	pH_0 a	ZPC b	σ_p meq/100g
21 A 0 - 8	15.31	8.03	7.28	2.01	0.74			
A_1 20 -50	23.72	16.92	6.80	0.93	2.23	3.60	3.55	-7.90
A_2 50-100	16.11	9.60	6.51	1.30	1.10	3.20	3.25	--9.40
15 A_{11} 0 - 5	39.38	15.00	24.38	5.33	3.43	5.60	5.65	-7.00
AB 22 - 35	45.39	17.11	28.28	6.50	4.90	3.50	3.55	-3.10
24 Ah 0 - 17	77.27	50.00	27.27	7.62	8.40	4.15	4.0	-3.50
Af 17 - 40	70.79	37.12	33.67	8.65	5.99			
41 A_1v 0 - 9	46.50	26.75	19.75	15.98	15.03			
A_{11} 9 - 22	44.41	24.02	20.39	17.11	14.09	3.80	3.75	-7.15
A_{12} 22 - 42	35.99	19.78	16.21	-	1	4.00	4.05	-3.65
AB 42 - 52	27.95	16.15	11.80	16.49	31.20	4.30	4.05	-3.65
BC 52 - 72	17.08	4.65	12.43	8.58	15.34	3.47	3.40	-8.75
51 A_1v 0 - 9	37.63	24.73	12.90	7.58	15.11			
A_{12}f 29 - 44	23.16	13.05	10.11	14.59	9.64			
BC 44 - 64	8.50	2.40	6.10	6.42	9.83	3.80	3.80	-4.70
31 A_1v 0 - 12	36.02	23.14	12.88	9.56	11.26			
A_{11} 12 - 32	34.25	20.86	13.39	15.34	14.23	4.00	4.00	-1.75
A_{12} 32 - 55	22.30	15.63	6.67	14.82	12.85	4.19	4.15	-1.75
C 55 - 75	12.09	2.59	9.50	7.12	8.74	4.15	4.25	-1.65
5 A_1 0 - 3	25.14	13.68	11.46	5.70	4.31	3.60	3.30	-6.65
A_{11} 3 - 18	29.00	21.27	7.73	11.72	-	3.75	3.75	-3.75
Ahf 18 - 35	22.72	23.33	-	14.34	13.88	4.0	4.0	-1.75

d, o - dithionite and oxalate extractable, c - crystalline; a, b - determined by ST and STPT method. Profile 21 was classified by L. Tritchkov; 24 - by M. Teoharov; 15, 41, 51, 31 and 5 - by- A. Koulikov, N. Atchkov, N. Petkov, I. Iliev, S. Nedialkov.

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SURFACE PROPERTIES OF SOIL AND PLANT MATERIALS MEASUREMENTS, THEORIES AND APPLICATIONS

Józefaciuk G., Raytchev T.

Theoretical and methodical aspects of characterizing specific surface area of soil and plant materials and its energetic and geometric features using adsorption – desorption isotherms are discussed. Some examples of applications of surface characteristics in soil and plant studies are shown.

INTRODUCTION

Number of environmentally important processes occur on surface of solid phase of soil and plant roots. Due to extremely complex composition and structure of such solids, their surfaces are highly non-uniform. Among many methods developed to study such surfaces an analysis of gas (vapor) adsorption-desorption isotherm is probably the easiest and most convenient one (Gregg and Sing 1967). From adsorption-desorption data one can estimate an overall amount of the surface i.e. the surface area (specific surface) of the solid as well as its energetic and geometric properties.

The idea of the estimation of the surface area is to find a number of adsorbate molecules that cover the adsorbing surface as a monolayer, and to multiply this number by the area occupied by a single molecule.

Surface energetic heterogeneity is estimated assuming that different surface sites bind adsorbate molecules with different forces (energies) thus influencing adsorption pathways. Because the free energy is constant throughout the system in equilibrium, the energy of gas/vapor at a given pressure is associated with adsorption energy on a given site. The number of these sites is estimated from the amount adsorbed. An adsorption energy distribution function is constructed showing fractions of sites of distinct adsorption energies, from which one derives an average adsorption energy providing global energetic character of the surface.

From geometric point of view surface heterogeneity can be characterized by a surface fractal dimension and micropore features. The fractal dimension is a measure of the surface roughness. If a surface is fractal, higher fractal dimension characterizes a rougher one. Basic property of fractal objects is that they are geometrically similar to their parts. Surface fractal dimension can be estimated from dependencies of adsorption vs. adsorption potential, plotted in logarithmic coordinates. Micropore characteristics are evaluated from desorption isotherms assuming that the desorption is equivalent to evaporation of adsorbate from the micropores.

ADSORPTION-DESORPTION ISOTHERM

The adsorption isotherm is a function relating the amount of adsorbed gas (vapor) to its equilibrium pressure during the pressure increase at a constant temperature. The desorption isotherm is the same function measured during the pressure decrease. Two adsorbates: water vapor and nitrogen are most frequently used. While measurements of the isotherms for nitrogen at liquid nitrogen temperature require advanced instrumental techniques, the water vapor isotherms can be measured at a room temperature using a simple vacuum chamber method. The samples are placed as rather thin layers (few mm) in weighing vessels and closed in the vacuum chamber. The relative water vapor pressure, p/p_0, in the chamber is controlled by sulfuric acid solutions of stepwise decreasing concentrations (adsorption) and/or of stepwise increasing concentrations (desorption). The amount of adsorbed water at a given p/p_0, a(kg/kg), is measured by weighing after at least 48h of equilibration. The dry mass of the samples is estimated after completing the measurements, after 24h oven drying at 378K.

The above drying procedure usually removes physically adsorbed water (Cases et al. 1997). This does not necessarily mean that the samples are dehydrated fully. For example drying of a montmorillonite at temperatures between 100 to 500 °C results in a removal of water molecules linked to the exchangeable cations. An amount of this kind of water can account of c.a. 3% of the final mass. At higher temperatures the further lost of c.a. 5% of the final mass represents dehydroxylation of the structure (Cases et al. 1997). However, more severe dehydration of the samples, because of the removal of water molecules bound with higher energies, should be avoided, as this can lead to the results not describable by the model of physical adsorption, applied for adsorption-desorption data description.

Large differences in adsorption isotherms of nitrogen and water vapor on the same material occur usually. These may arise from differences in water and nitrogen molecules polarities: water is adsorbed on polar surfaces while nitrogen on nonpolar ones. The molecular sieving effect is believed to differentiate the entrance of various size gas molecules into narrow spaces (Volzone *et al.*, 1999) leading to differences in adsorption measured with various size adsorbates. The kinetic effects may diminish the adsorption of nitrogen to a great extent when entrances to larger spaces are of nitrogen molecule dimensions. To easily pass such narrow entrance, the thermal energy of the molecule should be similar to the energy barrier of the adsorption field among the entrance walls. At liquid nitrogen temperature the thermal energy is low and therefore the adsorption equilibrium may not be reached within a standard time of the measurement. Many restrictions hold also for interpretation of adsorption of water vapor, among which is different hydration of different surface cations, strong lateral interaction of polar water particles in adsorbed layer and/or dependence of adsorption on surface charge density. Also, the nitrogen adsorption method requires prior evacuation and heating of the sample, which thins water films and brings the structural elements (grains, particles, tissues) of the studied sample closer. The quasi-contact of these elements can extend over a significant portion of the surface that becomes inaccessible for nonpolar (nitrogen) molecules. If the sample contains expansible or swelling material it can collapse on evacuation, giving the same effect. Comprehensive discussion on the above problems is presented by Gregg and Sing (1967).

SURFACE AREA

Vapor adsorption on natural surfaces is usually polymolecular. A simple and thermodynamically correct equation to describe polymolecular adsorption was proposed by Aranovich (1992). In linear form this equation reads:

$$x/[\, a(1-x)^{1/2}] = 1/(a_m C) + x/a_m, \tag{1}$$

where $x = p/p_0$, a_m (kg/kg) is the statistical monolayer capacity and $C = \exp((E_a - E_c)/RT$ is the constant related to the adsorption energy, E_a (J), and condensation energy of water, E_c (J). In contrast to the standard Brunauer-Emmett-Teller (BET) model (Brunauer *et al.*, 1938), the Aranovich isotherm allows for the presence of vacancies in the adsorbed layer and fits the experimental polymolecular adsorption data over a broader range of relative pressures (c.a. $0.05 < p/p_0 < 0.8$) than the BET does (c.a. $0.05 < p/p_0 < 0.35$). Having calculated a_m values from the slopes ($1/a_m$) of Eq (1), the surface areas of the studied samples, S, can be calculated:

$$S = L\omega\, a_m M^{-1}, \tag{2}$$

where L [mol^{-1}] is Avogadro number, M [kg] is molecular mass of the adsorbate and ω is the area occupied by a single molecule of the adsorbate (sitting area). The ω value for water is $1.08 \cdot 10^{-19}$ m^2 and for nitrogen as $1.62 \cdot 10^{-19}$ m^2 (Gregg and Sing, 1967). In these cases, where the adsorption data plotted within the linear coordinates of the Aranovich isotherm (Eq. 1.) gave no satisfactory linear fit, one can estimate the monolayer capacity, using the formula:

$$a_m = \max\{a(1-x)^{1/2}\}. \tag{3}$$

The monolayer capacities calculated using Eqns 1 and 3 are usually very close to each other.

ADSORPTION ENERGY AND ITS DISTRIBUTION

Among various models used to find adsorption energy distribution function f(E), (Jaroniec and Brauer, 1986; Polubesova et al, 1997) probably the simplest one is to model a complex surface as a combination of energetically homogeneous patches having distinct energies. According to the theory of adsorption on heterogeneous surfaces (Jaroniec *et al.*, 1975; Jaroniec and Brauer, 1986; Rudzinski *et al.*, 1982) the total adsorption at a given pressure p can be expressed as a sum of local adsorptions a_i on a given sites of energy $E_i = (E_{a,i} - E_c)$, where $E_{a,i}$ is adsorption energy of i-th site:

$$a(p) = \sum_{i=1}^{n} a_i(p, E_i), \tag{4}$$

Thus the total adsorption isotherm, $\Theta_\tau(p)$, can be written as a sum of adsorptions on each sites, $\Theta_i(p,E_i)$, weighted by their fractions, $f(E_i)$:

$$\Theta_\tau(p) = a(p)/a_m = \sum_{i=1}^{n} a_i(p,E_i)/a_{m,i}(a_{m,i}/a_m) = \sum_{i=1}^{n} \Theta_i(p,E_i)f(E_i), \quad (5)$$

where $a_{m,i}$ is the monolayer capacity of sites kind i and values of $f(E_i)$ fulfill normalization condition:

$$\sum_{i=1}^{n} f(E_i) = 1. \quad (6)$$

If the local adsorption isotherm in Eq. 4 is expressed by the Aranovich equation, one has:

$$\Theta_\tau(p) = (1\text{-}x)^{-1/2} \sum_{i=1}^{n} C_i x/(1\text{-}C_i x)f(E_i), \quad (7)$$

where C_i is the value of the constant C of sites kind i.

Solving of Eq. 7 in respect to $f(E_i)$ is an ill-conditioned problem. Small variations in experimental data can cause large variations in estimation of site fractions. The least sensitive on experimental error, reasonable accurate and most convenient way to overcome this problem is to apply a condensation approximation CA (Cerofolini, 1974; Harris, 1968; 1969). This method is based on the replacement of the true local isotherm by a step-function. Every pressure value becomes associated with the corresponding value of the adsorption energy which provides the adsorption equal to one-half of the adsorption at infinite energy. Following this definition, the final formula for calculation of site fractions is:

$$f(E_i) = [(1\text{-}x_{i+1})^{1/2}\,\Theta_\tau(E_{i+1}) - (1\text{-}x_i)^{1/2}\,\Theta_\tau(E_i)]/(E_{i+1} - E_i). \quad (8)$$

The maximum energy value in the condensation approximation should relate to the minimum value of the p/p_0 applied. However, this value can be considered only as a first estimate of the maximum energy because of the lack of experimental data at lower relative pressures. Therefore the maximum energy is set at some arbitrary level (higher than this corresponding to the minimum experimental pressure) in the belief that if there were no sites with higher adsorption energies than the corresponding values of $f(E_i)$ will be close or equal to zero.

Having $f(E_i)$ values, average adsorption energies were calculated from Eq. 9From $f(E_i)$ values, the average water vapor adsorption energy, E_{av}, can be calculated as:

$$E_{av} = \sum_{i=1}^{n} E_i f(E_i). \quad (9)$$

More details on the above calculations can be found in Jozefaciuk (1996).

MICROPORE CHARACTEISTICS

From desorption isotherms, characteristics of pores ranging from about 1 to a few tens of nanometers can evaluated. These pores are usually referred to as "micropores". The micropore radius r can be related to the desorption pressure p by the Kelvin equation for the hemispherical meniscus with zero water/solid contact angle (Oscik, 1979):

$$r = 2M\,\sigma\cos\alpha/\rho\underline{R}T\ln(p_o/p), \tag{10}$$

where M is molecular mass of water, σ is water surface tension, α is a water-solid contact angle (assumed here to be zero), ρ is density of water, $\underline{R}$ is the universal gas constant and T is the temperature of the measurements.

The volume of the condensed water in the pores at a given pressure, $v(p/p_o)$ [m^3], can be treated as a sum of pore volumes, $v_i(r_i)$, of the radii $r_i \le r(p/p_o)$,

$$v(p/p_o) = \sum_{i=1}^{n} v_i(r_i). \tag{11}$$

Dividing the above equation by the total pore volume, v_t, the scaled desorption isotherm, $\Xi(p/p_o) = \Xi(r(p/p_o))$, can be treated as a sum of fractions of particular pores, $f(r_i)$:

$$\Xi(p/p_o) = v(p/p_o)/v_t = \sum_{i=1}^{n} v_i(r_i)/v_t = \sum_{i=1}^{n} f(r_i) = 1 \tag{12}$$

Assuming that the condensation in micropores occurs above $p/p_0=0.35$ (below this value surface adsorption processes dominate), the total micropore volume, is taken as the volume of adsorbed water at the maximum p/p_0 value minus the volume of adsorbed water at $p/p_0=0.35$.

The pore fraction in a given range of pore sizes can be calculated as:

$$f(r_{i,av}) = [\Xi(r_{i+1}) - \Xi(r_i)], \tag{13}$$

where $r_{i,av}$ denotes the arithmetic mean of r_{i+1} and r_i. Knowing the latter values one easily constructs a pore size distribution function i.e. pore fraction vs. pore radius dependence.

The average pore radii, r_{av}, in the measuring range can be calculated as:

$$r_{av} = \sum_{i=1}^{n} r_i\, f(r_i) \tag{14}$$

FRACTAL DIMENSION

Evaluation of the surface fractal dimension, D, can be performed employing a single adsorption isotherm. The adsorption data, a, are fitted to the equation (Neimark, 1990):

$$\ln(a) = -(1/m)\ln(-\ln(p/p_0)) + C, \tag{15}$$

where C is a constant and the parameter $1/m$ is related to the surface fractal dimension of the sample. The determination of the D value requires knowledge of the adsorption regime. The magnitude of the parameter 1/m distinguishes two possible adsorption regimes:

- the van der Waals regime for $1/m<1/3$, yielding the surface fractal dimension $D=3(1-1/m)$;
- or the capillary condensation regime for $1/m>1/3$, yielding $D=3-1/m$.

ADSORPTION STUDIES OF SURFACES OF SOILS AND PLANTS

Energetic and geometric properties of soil surface become increasingly used for description and modeling of soil physical, chemical and biological processes as well as for quantitative analysis of soil physical, typological and genetic properties. Surface physicochemical models provide a framework within which several multidisciplinary studies of soil and plant can be conducted and complex relation between different soil and plant processes can be understood (Pachepsky et al., 2000; Sokolowska, 1989). In the following part of the paper let me select, from huge amount of literature reports, a few of these performed more recently in our Centre.

Hajnos et al. (2003) and Sokolowska et al. (1995) used water vapor isotherm to study genetic differences of raw humic, epihumic and endohumic horizons of acidic sandy forest soils rich in organic matter and of typical Bulgarian soils of various origin, respectively. In organic forest soils the surface areas were proportional to organic matter content and the CEC of the soil, however adsorption energy was govern by the degree of humification of organic matter. Similar observations were performed by Hoffmann et al. (1999) for sandy organic soils in a column experiment. Toth and Jozefaciuk (2002) used water vapor adsorption studies to diagnose profile genetic features of a solonetzic toposequence: Mollic Solonetz, Salic Solonetz and Haplic Solonetz. Among the profiles studied, upper, eluvial A horizons differed to the greatest extent and the lowest C horizons appeared to be most similar. Surface characteristics were mostly governed by organic matter and clay content. Organic matter and clay fraction increased soil surface area. The surface area increased also with amount of exchangeable bases and the CEC of the soils. Our long-term studies of surface area of soils revealed its usability in diagnosis of soil quality, as this is correlated with clay and organic matter content, cation exchange capacity, water holding capacity and other factors governing soil fertility. Therefore, for practical applications, we constructed maps of water vapor and nitrogen surface areas of Polish arable soils (Stawinski et al. 2000).

Our adsorption-related research were also directed to use water vapor and nitrogen adsorption isotherms to study surface properties of different soils and plant roots and their changes under degradation processes.

Sokolowska et al. (1993) used adsorption of water vapor to investigate the influence of organic matter, iron and aluminum on surface area and energetic heterogeneity of soil clays. The removal of organic material increased the surface area most probably due to opening of surface pores glued by organic matter. The removal of other components decreased the surface area. Changes in surface energetic heterogeneity were different for clays coming from various soils. The addition of humic acid (HA) to kaolin and quartz (surface coverage) masked the adsorption properties of the minerals at low HA doses (Sokolowska et al., 1996). Raychev et al. (2003) revealed that the organic matter removal from soil clay fraction makes the clay surfaces smoother. Soil OM seems to have rougher surface than clay minerals. Jozefaciuk et al. (1996) showed that the leaching of DOC from a sandy soil makes it more hydrophobic. Pachepsky et al. (1995) studied surface parameters of selected soils under laboratory degradation (organic matter removal, silica accumulation, cyclic wetting-drying) showing that surface parameters may be used for degradation diagnosis.

Jozefaciuk et al. (1993) showed that the acid treatment of soils lead to non-uniform changes in the surface properties of the water dispersible clay (WDC) which may be explained not only by destruction of the minerals present in clay fraction but also by the appearance of new minerals in WDC. Jozefaciuk and Bowanko (2002) studied behavior of bentonite, biotite, illite, kaolin, vermiculite and zeolite under 0.1, 1.0 and 5.0 mole dm^{-}3 acid and alkali treatments on surface areas and adsorption energies of selected minerals. With a few exceptions, surface areas of the minerals computed from both water and nitrogen adsorption isotherms increased with acid and alkali treatments. With increasing reagents concentration the nitrogen surface area increased faster than the water surface area. Well defined trends were noted neither in changes of average water or nitrogen adsorption energies nor in relative amounts of adsorption sites indicating that the effects of acid and alkali attack are controlled by the individual character of the minerals. Similar studies but at lower acid and base concentrations (0.001 to 1 mol dm^{-3}) were performed by Jozefaciuk et al. (2000) for six Polish and three Korean soils of different origin and mineral composition. The surface area and average adsorption energy decreased in general in both treatments. The treatments induced the decrease in amount of high and medium energy centers, however the fraction of low energy centers increased. The behavior of surface properties differed from the above at treatments at highest reagent concentrations, especially for Korean soils, rich in clay fraction and iron oxides. The fractal dimension decreased after acid treatment showing a smoothing of the soil porous surface. Alkaline treatment affected the fractal dimension to a lower extent, however its slight rise was noted in most cases.

Jozefaciuk et al. (2001) studied effects of different soil cultivation practices (no tillage, ploughing, disking and the two last treatments combined with loosening) on surface properties of a brown forest soil. Surface were markedly lower in mechanically tilled soil. Surface fractal dimension had changed very slightly, indicating that general geometrical structure of the fine pore system remained unaltered despite pore size-shift. Decrease of water vapor adsorption energy accompanied mechanical tillage treatments. Sokolowska et al. (1999) found markedly higher surface areas in soils under organic farming than under conventional cultivation.

Jozefaciuk et al. (2001, 2003) studied effect of cyclodextrins, polysaccharides increasingly used in soil decontamination from organic hydrophobic compounds, on soil and clay minerals physicochemical properties using water vapor adsorption-desorption technique. As compared to clay minerals, pure randomly methylated β-cyclodextrin (RAMEB) had very large surface area. Energy of interaction with water vapor and fractal dimensions of RAMEB were lower than those of the minerals. When increasing amounts of RAMEB were added to the minerals, the surface area and micropore volume decreased and adsorption energy increased. As deduced from the fractal dimensions increase, the pore structure of the minerals became more complex with RAMEB addition. RAMEB increased water adsorption and surface area in sandy soils and decreased in clayey soils. An increase in adsorption energy of water in RAMEB treated soils indicated that desorption of nonpolar pollutants can be enhanced. Behavior of the soils after RAMEB treatment depended on their clay content and the dose of cyclodextrin. In clay-rich soils strong interactions of cyclodextrins with the soil solid phase governed the resulting soil properties. In clay-poor soils the cyclodextrin excess (not interacted with clays) played a dominant role.

Concluding, surface adsorption parameters are highly sensitive indicators of various processes occurring in soils: organic matter accumulation, leaching and oxidation, soil acidification, alkalization, silica accumulation, wetting-drying cycles and many others.

The adsorption studies are useful in characterizing not only soils but other agricultural materials, as well. Jamroz et al. (1999) used water vapor adsorption to characterize reversibility of moisture sorption on potato starch extrudates used in food industry. Szatanik-Kloc and Jozefaciuk (1997) revealed that surface areas of plant roots measured using water vapor adsorption isotherms are close to the “real“ root surfaces estimated using microscopic photographs as a sum of geometric areas of roots + root hairs. Such surface areas amounts to a few hundred meters per one gram of the roots, contrary to a few square centimeters estimated from other commonly used indirect methods than the adsorption isotherm. More recently Szatanik-Kloc et al. 2001 and Jozefaciuk and Szatanik-Kloc (2001) used water vapor adsorption isotherms to study the effect of pH and Al on surface area and surface heterogeneity of roots of cereal plants of different Al tolerance: barley, triticale, wheat and rye. The pH did not induce any measurable effect whereas Al toxicity induced an increase in root surface area, and a slight decrease in average water vapor adsorption energy. The above studies indicated that the adsorption characteristics may be indicators of the toxic influence of Al ions on plants.

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INSTRUMENTAL EVALUATION OF SOIL MOISTURE, TEMPERATURE AND SALINITY BASED ON SPACE DISTRIBUTED MEASUREMENTS

Kolev N. V.

INTRODUCTION

Europe environment is changing and some of these changes are mainly under the influence of human activities. Soil, as an element of the environment, is a complex dynamic system which comprises a matrix of organic and mineral constituents enclosing voids and pores which contain liquids and gases. The modern agriculture need quantitative information about the main soil properties of the open field for successful management of soil fertility and soil pollution protection. Many of the processes essential to soil and to nitration movement and plant growth, such as exchange of heat, moisture and movement of contaminants depend significantly on the soil properties and canopy foliage (Nielsen et al,1983; Perry et al,1988).

Number of authors (Warrick et al, 1986; Bazza et al., 1988; Vereceen et al, 1989; Popova et al, 1999) illustrate, by field data, the influence of canopy height and structure and leaf orientation on the soil surface moisture and temperature. It also depends on the soil profile. Kolev et al (1996), Castrignano (1998) and other authors show that the measurements have to carry out in the representative places on the field.

The present study attempts to show a way to organise express and continuous electronic measurements for evaluation of main soil properties on some fields of Bulgaria.

MATERIALS AND METHODS

The soil properties have different values in different zones of the agricultural field. No effective method for evaluating one or other property distribution is established, but there is an opportunity to use a pattern for an ordered set of closed isolines. In other words, it is possible to consider the unhomogeneous field as numerical homogeneous zones displaying these with tree-root structure (Fig.1), a concept first suggested by Uchitomi and Mine (1988). Within the soil properties, only the soil surface temperature T_S can be consider. The conclusions will be referred to soil moisture and others.

Subset regions H_i, with high soil temperature T_{si}^1, and subset regions L_i, with low temperature T_{si}^2, can be found in the whole region S_o of the field with background temperature T_s^o. Then:

$$H_i \in S_o \text{ and } L_i \in S_o \qquad (1)$$

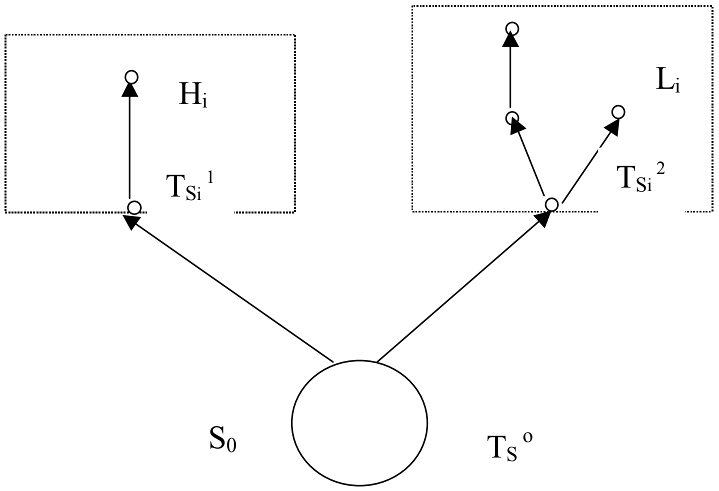

Fig.1. *Soil surface temperature picture of an inhomogeneous field with homogeneous zones H_i and L_i.*

Getting the patterns M_o of the region S_o, M_i^1 of the region H_i, M_i^2 of the region L_i, can be written:

$M_o = \{C_k(T_S) \mid T_S^2 < T_S < T_S^1, k = 1, 2, 3, ..., \}$ (2)

$M_i^2 = \{C_k(T_S) \mid T_S^2 < T_S < T_S^0, k = 1, 2, 3, ..., \}$ (3)

$M_i^1 = \{C_k(T_S) \mid T_S^0 < T_S < T_S^1, k = 1, 2, 3, ..., \}$ (4)

where $C_k(T_S)$ are the isotemperature closed lines at a temperature T_S, T_S^1 is the maximum of the temperature T_S, T_S^2 is the minimum temperature and T_S^0 is the background temperature at the S_0 region. M_i^1 is high temperature pattern set and M_i^2 is low temperature pattern set and

$M_i^1 \in M_0$ and $M_i^2 \in M_0$.
(5)

The values of the soil surface temperature T_S for high and low temperature regions (T_S^1 and T_S^2) and the whole set T_S^0 can be presented in tree-root structures as shown for T_S^1 and T_S^2 in Fig.1.

Then can be written:

$T_S^0 = f(T_S^1, T_S^2)$ (6)

Canopy structure is another factor setting restrictions on the homogenity of the soil properties. The soil temperature and the soil moisture, for example, differ under the plants and between the rows of row-crop canopies, and depend on the fraction of soil surface exposed to direct sunlight. The area of this fraction can be calculated based on the relationship between the sunlight transpiration, leaf area index and leaf angle distribution. The concept of this relationship can be approximated by Beer's Law.

The soil surface temperature in the regions H_i is T_S^1 and in the regions L_i is T_S^2. Then:

$$(T_S^1, T_S^2) = \varphi(f) \qquad (7)$$

$$f = \exp(-k.LAI) \qquad (8)$$

where f is the fraction of soil surface in direct sunlight, k is an absorption coefficient and LAI is the leaf area index. The coefficient k is a function of the canopy leaf angle distribution, random of the leaves and the sun zenith angle θ. For a given sun angle, k represents the fraction of leaf area projected onto the soil surface. The latitude of Bulgaria is 42°N, and the solar zenith angle, θ, changes from 30° to 70° during the active agricultural season.

For canopies where the foliage is horizontally homogeneous, the absorption coefficient is (Perry et al, 1985):

$$k = \int_0^{\pi/2} \frac{g(\alpha).\cos\delta}{\cos\theta}.d\alpha \quad , \qquad (9)$$

where α is the angle between the leaf normal and the vertical, δ is the angle between the normal to the leaf surface and the incoming ray of sunlight, and g(α) is the density function of leaf normals with the vertical.
Combining eq.8 and eq.9, the fraction of soil surface in direct sunlight becomes:

$$f = \exp(-LAI\int_0^{\pi/2} \frac{g(\alpha).\cos\delta}{\cos\theta}.d\alpha) \qquad (10)$$

Equation (10) defines the integral relationship between canopy structure and area of soil surface in direct sunlight. This equation is based on the assumptions of an uniform distribution of leaf azimuth angles and homogeneous positioning of the foliage in the horizontal.

To solve equations (7) and (10) for the unknowns g(α) and LAI, the fraction f, can be measured at various sun angles θ, and a system of integral equations be defined. The leaf angle distribution and leaf area index LAI can be estimated using methodology of direct measurement of canopy structure, described by Perry et al (1988).

There is a simple measurement approach to evaluate the fraction of soil surface in direct sunlight by a battery-powered device where a silicon diode is used as a sunlight sensor. The sensing cell is propelled through the canopy making traverses along the canopy. Three or four traverses of ten meters between rows at constant speed will take about 10 min and each scan will provide sunlit and shadow segments. As a result, the sunlit and shadow percentage of 1 m^2 area can be derived.

The distance between the plants is x_{opt} and the distance between the rows is y_{opt}. The simple representative area is

$P_S = 2\ x_{opt}\ .\ 2y_{opt}$
(11)

where x_{opt} and y_{opt} are different for the different crops and depend on the point of view of the agronomists.

The sensors and electronic devices used for measurements have been designed to operate long time in field conditions. Gypsum-type blocks PVGTV-3, made in "N.Poushkarov" Institute, were used for soil moisture and chemical polutant movement measurements. A sensor consisting of two-metal electrode system joined with temperature sensible microdiode, all in a ceramic body, has been designed to monitor the soil salinity in the field. An alternating current digital bridge was used with sensors of soil moisture, temperature and salinity, every type with own callibration. Temperature measurements of the soil surface were obtained by an infrared distant thermometer, Raynger II-AG type. A portable conductometer and pH-meter, Metrohm type, was used for evaluation of electrical conductivity and pH of the soil solution in the field. The soil and air temperature and the humidity were measured by "Grant" Squirrel meter/logger. The fractional sunlight and shadow areas were obtained by traversing measurements with a voltage-output sensor with wide spectrum sensible photodiode.

RESULTS AND DISCUSSION

Maize and cotton fields were selected where systematic electronic measurements of soil moisture, temperature, electrical conductivity $EC_{S,}$ and pH, were carried out during the period from May to September, 1999. Series of measurements were taken periodically in the beginning of every new phenophase during the vegetation of maize and cotton, and started after the sprout of the plants.

Soil moisture and temperature measurements were carried out in representative single areas of the fields at 9:00, 12:00 and 15:00 o'clock on the day. Soil salinity and pH measurements were made one time a day. The sites for the study were a pilot maize field of the Nikola Poushkarov Institute of Soil Science near the city of Plovdiv, and a pilot field of the Cotton and Durum Institute near the city of Chirpan, both unirrigated and located in South Bulgaria. There are showed measurement results only of some expeditions on the field near Chirpan. The soils (near Chirpan), are classified as tipic calsixererts and contain 6 - 7% clay, 2.5 - 3% humus and with 1.2 - 1.3 $g.cm^{-3}$ density. Field capacity of the soils is 0.33-0.35 (Kolev et al., 1995).

Five surface covers were defined with homogeneous soils with W_S^1, T_S^1, and five with W_S^2, T_S^2, at the two plot fields. Every of them had sunlight and shadow fractions obtained by calculations and measurements as described previously.

For example, cotton canopy had LAI near 0.3 on 28 May 1999 and LAI near 0.6 on 18 June 1999. The exact values of sunlight fraction f(θ) were calculated by integration of equation (10). These canopies contain lives oriented mostly at oblique angle of near 50^o. Perry et al. (1988) showed the shapes of the leaf angle distributions and $g(\alpha) = 0.42$ for cotton canopies. On 18 June 1999, the solar zenith angle θ was = 70^o and the angle was $\delta = 20^o$.

$$f(70°) = \exp(-0.6\int_0^{\pi/2} 0.42\frac{\cos 20°}{\cos 70°}d\alpha) = 0.32 \qquad (12)$$

The gypsum blocks were buried at 20, 40, 70 and 100 cm depth, the temperature sensors were installed at 5, 10, 20 and 40 cm depth and the salinity ceramic blocks-at 20 and 40 cm depth. The sensors were situated in the soil profile after drilling holes. The soil moisture was measured within ±1% accuracy and soil temperature was measured within ±0.1°C accuracy.

Results of every day measurements of soil moisture, temperature, salinity and pH were computed from equations (5) and (6), for obtaining W_S^0, T_S^0, EC_S^0 and pH^0

A series of soil moisture and temperature profiles is presented in Table 1 as a result of data obtained in expeditions from 28 May to 20 August 1999. The values of W_S^0 correspond to microclimatic conditions and they decrease systematically near the soil surface due to the intensive evapotranspiration. The cotton was in phases from 2 - 3 leaves on 28 May with LAI = 0.2 to the beginning of boxes let out on 20 August with LAI=2.

Table 1. Soil moisture and temperature on the expedition days of 1999 at the cotton field.

Date	28.05			18.06		
Depth, cm	Ws %	T_s °C		Ws %	T_s °C	
		9 h	12 h		9 h	12 h
Soil surface	0.12	36.2	40.0	10.0	36.6	27.0
3	-	28.0	33.6	-	27.6	26.8
5	0.18	24.5	30.6	0.16	25.6	26.6
10	0.30	20.4	25.0	0.27	23.8	24.8
20	0.32	17.4	19.0	0.31	24.0	24.4
40	0.33	17.0	18.5	0.33	24.5	24.6
70	0.33	-	-	0.33	-	-
Date	16.07			20.08		
Depth, cm	Ws %	T_s °C		Ws %	T_s °C	
		9 h	12 h		9 h	12 h
Soil surface	0.28	24.2	25.1	0.12	30.2	37.2
3	-	22.2	22.3	-	28.4	34.2
5	0.30	22.0	22.2	0.13	26.6	30.0
10	0.32	22.0	22.2	0.27	24.8	27.2
20	0.33	22.0	22.2	0.24	24.7	25.0
40	0.33	22.0	22.0	0.23	24.5	24.6
70	0.33	-	-	0.22	-	-

The measurement results of soil electrical conductivity (EC), pH of the soil solution (1:2.5) and soil salinity, obtained by the first and last expeditions on 28 May and 20 August 1999, are shown in Table 2. Table 3 includes the measurement results of the main energy balance elements characterizing the microclimate on the test region.

Table 2. Results of pH, soil electrical conductivity and salinity measurements in 1999.

Depth, cm	28.05			20.08			Field capacity
	pH	E.C_e mS/cm	salinity mS/cm	pH	E.C_e mS/cm	salinity mS/cm	
Soil surface	5.2	0.40	<2 mostly neglig.	5.7	0.24	<2 mostly neglig.	0.33 - 0.35
20	5.1	0.36		6.1	0.20		
40	5.7	0.20		6.5	0.18		

Table 3. Results of microclimate measurements on cotton field region on 28.05.1999.

Agrometeorological parameter	Unit	Type	Time of measurement	
			9h	12h
Solar radiation	$W.m^{-2}$	total reflected	740 120	840 160
Radiation balance	$W.m^{-2}$		620	680
Temperature of ground air	^oC		30.1	32.6
Moisture of ground air	%	relative	66	52
Wind velocity	$m.s^{-1}$		0.5	0.5
Cloudiness	%		10	20
Temperature on the cotton canopy surface	^oC		25.6	30.0
Temperature of bare soil	^oC	on surface	32.1	36.2

The soil moisture increases down of the soil profile. Results of earlier our measurements showed that the soil moisture in the row and between rows does not differ greatly in the root-inhabited soil layer whereas. It is less in the row than between rows up to 40 cm in depth, while, at depth of 70 cm, soil moisture in the row and between rows is already one and the same.

The electrical conductivity of the soil is depending on the soil content, the fertilizers and the weather conditions during the plant growing season. Data showed that the soil salinity is less than 2 mS/cm. The scale, recommended by the U.S. Salinity Laboratory for general use in appraising the effect of soluble salts on crops, showed that the soil salinity is negligible throughout the growing season since no fertilizers have been applied to the cotton unirrigated field. It expresses the relation of crop response to soil salinity showed in terms of the electrical conductivity of the saturation extract (in mS/cm).

The results of microclimatic measurements showed that the air temperature for a sunny day is less than the temperature of the sunny soil surface in sunlight places. The profiles of the soil temperature show the way it decreased with depth. The reduction rate depends on solar radiation, phases of cotton plant growing and soil moisture content.

The results of space distributed soil moisture and temperature measurements on the cotton field by infrared thermometer are shown in figures 2 and 3.

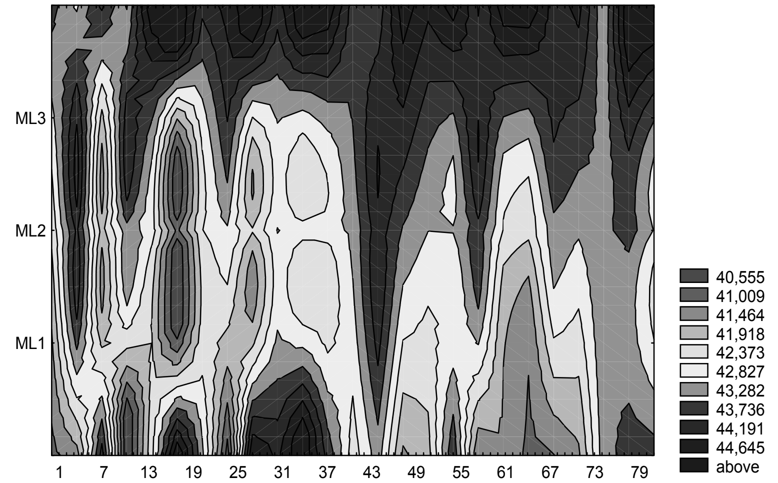

Fig. 2. *Soil surface thermal map at 11:00 h on 28.05.1999 based on results of 240 temperature measurement points.*

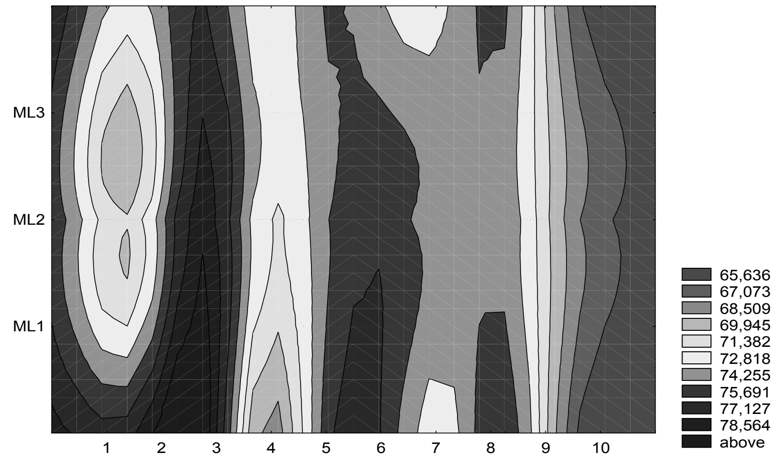

Fig. 3. *Soil surface moisture map of a cotton field at 11:00 h on 28.05.1999 based on 33 soil moisture measurement points.*

CONCLUSIONS

A way to manage electronic measurements for evaluation of soil properties at heterogeneous fields based on tree-root method and a single representative area has been presented. Gypsum blocks for soil moisture and temperature, and salinity sensors, interfaced to alternating current bridge made at “Nikola Poushkarov” Institute, proved to be useful in soil profile temperature and moisture measurements and in determination of the soil heat, water and solution fluxes following rain or irrigation and fertilization. These measurements in single representative areas, combined with space distributed soil surface measurements done by an infrared thermometer can be widely used to evaluate the main components of the heat and water budget of the heterogeneous agricultural field.

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MANAGEMENT OF SPACE DISTRIBUTED MEASUREMENTS ON THE BULGARIAN AGRICULTURAL FIELDS: ORGANIZATION, SYSTEMS AND RESULTS

Kolev N. V.

INTRODUCTION

The agricultural research and practice of the plant growing and the irrigation management in Bulgaria has to be changed radically to meet the requirements of the new economical and ecological situation caused by the restitution of the private ownership of the land and the free market orientation of the whole Bulgarian economy during the last few years. The irrigation could be done effectively only on the basis of a reliable agrometeorological information on the "soil - plants - atmosphere" continuum by measuring soil moisture, soil temperature, wind velocity, solar radiation and some other variables.

Having an instrumental evaluation of the main properties of the soil-plant-atmosphere system on the fields and calculated evapotranspiration is not difficult to organise an automated management of irrigation.

A number of authors describe different methods and instruments to estimate the evapotranspiration based on the measurement of energy balance components. Kalma and Jupp (1990) describe a field evaluation of the sensible heat flux, latent heat flux and the flux density of water vapour.

Brunel (1989), Vogt and Jaeger (1990), Pieri and Fuchs (1990) use the aerodynamic method and method of thermal infrared emission of natural surface to estimate latent heat flux and evapotranspiration.

Sanoyan (1982), Ashktorab et al(1989), Ham et al (1990), Pieri and Fuchs (1990) determine evapotranspiration by measuring the surface energy balance of the field using the Bowen ratio method and describe systems measuring meteorological elements and calculating the evapotranspiration. It is important that all measurements are carried out consecutively in time. When it is necessary to calculate temperature and water vapour differences the process of measurement should be fast. The major difficulty associated with the approach is that the instrumentation must detect small changes of the magnitude. In other hand, scientists, making their research in the agricultural field, have recognized variation of soil –plant systems properties from place to place. They have portrayed visually the variation and have devided field into small plots which are relatively homogeneous for property evaluation and survey (Kolev, 1991). Their measurements of some physical properties yield set of discrete values for particular "point" locations within sampling area. This procedure requires appreciation of the scale of change of the properties, the degree of correlation among soil-plant-atmosphere system properties, and of relations in the landscape. Moreover, the soil-plant-atmosphere system is a mixed class (Mishev, 1986, 1992) and has also had its disappointments, in cases of plots with uncorrelated properties of interest.

Many of the processes essential to soil and to plant growth, such as transpiration, evapotranspiration, exchange of heat and moisture, depend significantly on the soil surface, canopy foliage and microclimate.

Number of authors (Ludlow and Fisher, 1976; Bazza et al., 1988) illustrate, by field data, the influence of soil surface, canopy structure, leaf orientation, and height of canopy on the soil surface moisture and temperature. It also depends on the soil profile moisture and solar radiation. Drying of the soil can elevate soil surface temperature, causing an increase of moisture and temperature gradients in the soil profile.

For better interpretation of the results of discrete measurements, the regionalized variables transforms point discrete data to the soil –plant continuum (Nielsen et al, 1973; Webster, 1985; Kutilek and Nielsen, 1994). Now, because scientists increasingly require quantative evaluation of soil–plant properties for field of varying sizes and wish to measure and survey more economically, described over procedure have to be augmented by more rational geostatistical methods.

The purpose of the present study is to use agrophysical methods and micro-computer agrometeorological systems for evaluation of main properties of the soil - plant - atmosphere system in the field based on spatial distributed electronic measurements.

MEASUREMENT METHODS AND INSTRUMENTATION

Data from field measurements of the soil - plant - atmosphere system properties in the agricultural fields helps to calculate the soil evaporation, canopy transpiration, evapotranspiration E and sensible heat flux H. This operating mode requires reliable estimates of evapotranspiration. It concerns both continuous measurement of the basic variables on the field and supplying information for irrigation management on the base of the estimated conditions.

The evapotranspiration E is estimated based on energy balance method (Bowen ratio method) as:

$$E = \frac{1}{L} * \frac{(R_n - G) * \Delta e}{(\Delta e + 0.64 \Delta T)} \qquad [W * m^{-2}],$$

where: L=latent heat of vaporization, Rn=net solar radiation, G= soil heat flux, Δe and ΔT are humidity and temperature gradients.

The sensible heat flux is calculated from:

$$H = \frac{0.64 * \Delta T * (R_n - G)}{\Delta e + 0.64 * \Delta T} \qquad [W * m^{-2}].$$

STRUCTURE AND PERFORMANCE OF THE FIELD MEASUREMENT SYSTEMS

Agrometeorological parameters have been estimated using several american ARAX systems (Automatic Reporting Agricultural Weather System) (Sampey, 1986) and a Bulgarian AMIS - 01 (Agricultural Meteorological Information System) which is a similar one created by the authors team (Kolev et al.,1988). Both systems use satellite measurement stations (up to 16) mounted in representative places of crop growing areas. Fig.1 shows an ARAX satellite installation. The soil moisture and temperature sensors are placed at two depths in the crop root zone. The air temperature and humidity are measured at two levels over the canopy. In addition a rain gauge, wind velocity, wind direction, and solar radiation sensors are situated on the satellite top. The satellite can be set up to collect the data at time intervals of 3 min to 4 hours. Frequent measurements need more power and reasonable compromise should be achieved especially in winter. ARAX satellite units transmit the data collected to the base computer station in the High VHF Band (150-174 MHz). In perfectly flat terrain the maximum range for satisfactory reception is not more 22 km.

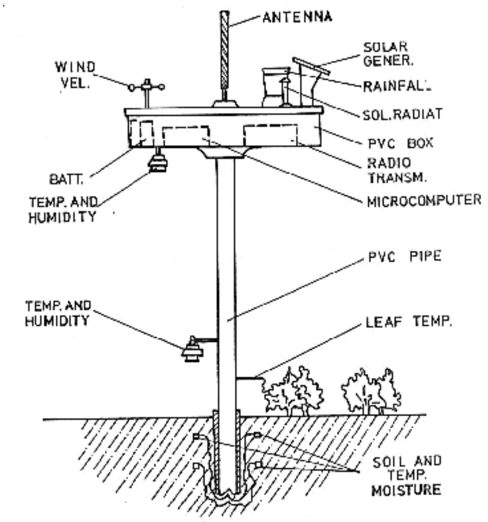

Fig. 1. *Structure of an satellite station of ARAX system*

Reports received by the base computer are filed in memory as current weather reports. Regardless of the report period on each hour, the current weather reports from every one of the satellites are averaged or totaled as hour reports. On the same way 24 hourly and monthly reports are filed.

The AMIS-01 system uses sensors basically designed in the Department of Agrophysics of the Nikola Poushkarov Soil Science Institute. The PVGTV-3 type gypsum blocks are used as soil moisture sensors. The soil temperature is estimated by measuring the resistance of a diode or transistor element, built in a gypsum block. Electric psychrometers with ventilated wet and dry thermometric sensors measure the air temperature and humidity at two levels over the canopy to determine the gradients of these variables. In addition to the net solar radiation, measured by standard pyranometers, the scattered light is estimated by a shaded pyranometer. Data is registered every 3 min or less and filed in the local computer memory. Up to 64 stations can be linked by a two-wire duplex computer network. The base computer operator can change the set-ups of every station at any time. Every day the operator reads each station agrometeorological file into the base computer memory.

The basic structure of a space distributed in different agrofarms or cooperatives ARAX system is shown in Fig.2.

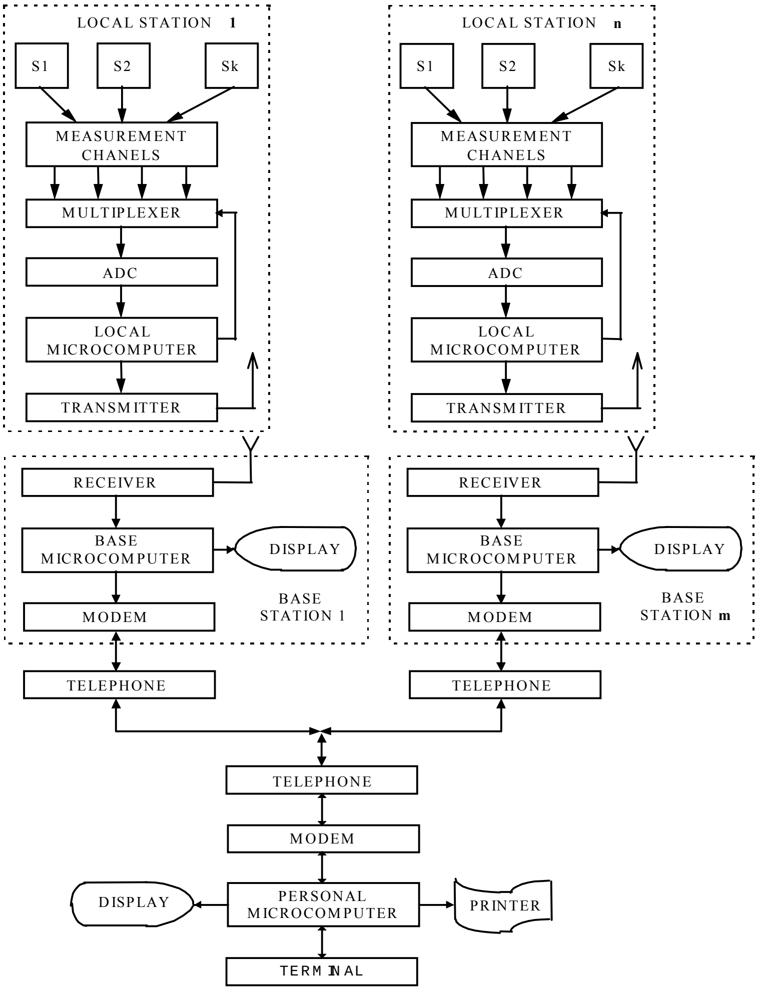

Fig. ***2.*** *Basic structure of ARAX*

RESULTS OF IN SITU MEASUREMENTS AND DISCUSSION

ARAX systems were installed within crop growing areas near towns of Razgrad, Plovdiv and Sofia in 1987 (Fig.3). Each consists of a base computer and 10, 6 and 8 satellite stations respectively. The agrometeorological parameters were measured at short intervals to estimate the errors due to rapid variations and their influence on the accuracy and reliability of the data gathered.

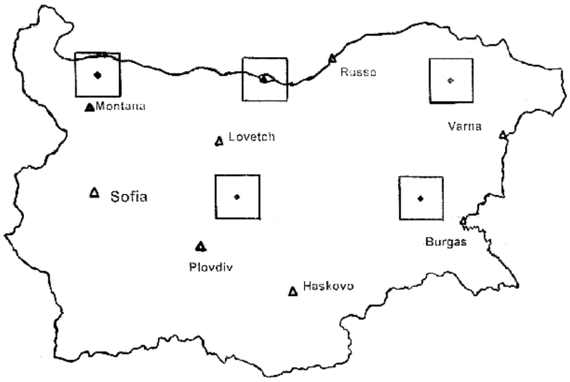

***Fig. 3.** Geographically distributed ARAX systems in Bulgaria*

Fig. 4 shows an allocation of other ARAX base system near the town of Loznitza (Razgrad district).

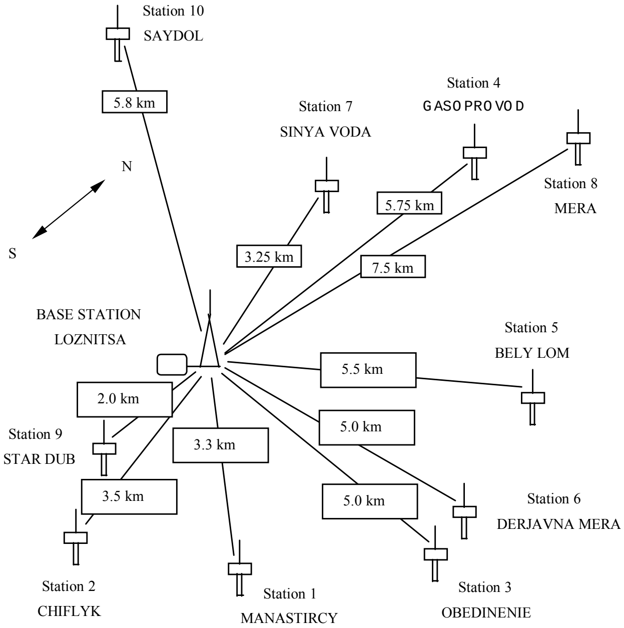

***Fig. 4.** Allocation of the ARAX system near Razgrad*

Agrometeorological parameters measured differ in their time constants. Variables as solar radiation or humidity may change in seconds while air temperature and wind speed vary in minutes, whereas it takes hours or days the soil moisture to change by 1%. Monthly records of some variables are shown in Fig. 5.

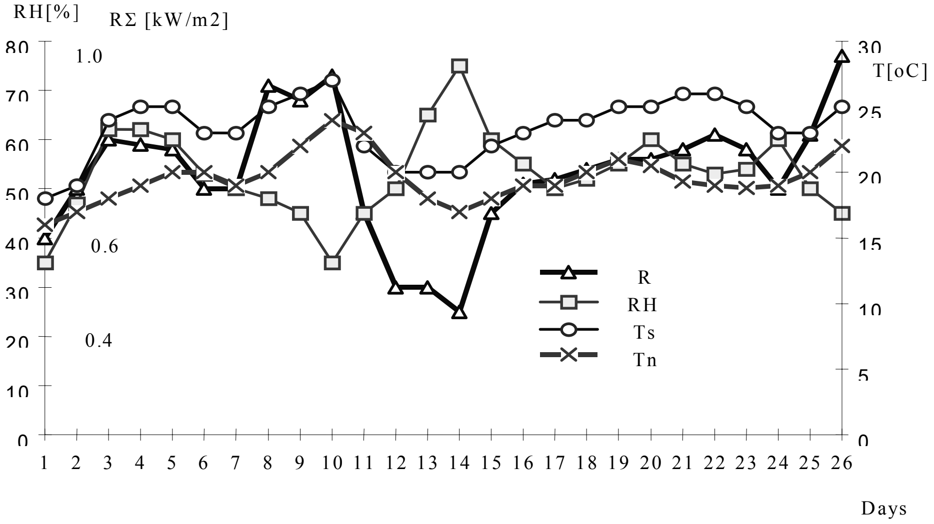

***Fig. 5**. Monthly record of some variables (solar radiation, R; air temperature, T ; humidity, e ;wind velocity, v) of one satellite ARAX station.*

Having the information collected by microcomputer meteorological systems agronomists can monitor the dynamics of the processes in the field and their influence on crop growth, plant diseases, insect activity, crop water stress, etc. Direct measurements of relative humidity and temperature differences in the field allow calculation of heat balance elements and evapotranspiration. The agrometeorological systems described are very sophisticated devices designed to operate automatically all year round. Nevertheless they need qualified maintenance and repair. According to the dust and soiling conditions of any particular area outer sensors and solar generator panel should be cleaned periodically.

Short report periods are not recommended in seasons of low temperatures and overcast because of shortage of charging current to the battery system.

The results of every 3 minutes measurement period were used for the calculation of the average hourly estimates of the energy balance components and the evapotranspiration.

Diurnal curves of evapotranspiration and other variables estimated using the Bowen ratio for DOY 162 are shown in Fig. 6.

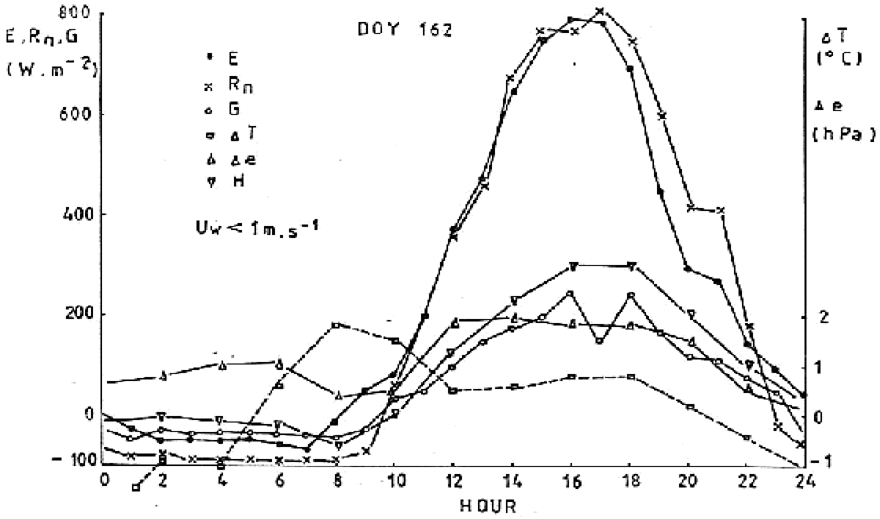

Fig. 6. *Diurnal curves of the evapotranspiration and other variables of the heat balance on the field.*

The figures show that E has values important for the irrigation practice between 9 a.m. and 6 p.m. The management of irrigation will be more successful if the water content in the field is better estimated knowing the evapotranspiration.

CONCLUSIONS

The structure of the microcomputer measurement systems submitted above suggests a direct and correct estimation of the evapotranspiration from the field, based on space distributed continuous measurements. The determination of the evapotranspiration by the energy balance method using the Bowen ratio allows to measure only some of the agrometeorological components. That is why the method and the measurement systems described are useful for the irrigation management in the agricultural practice.

The ever-changing fluctuations in environmental conditions need a relatively large instrumental effort. Measurements carried out by microcomputer systems and analysis of the data obtained showed that such systems could be useful both for the research and practice of agriculture. The possibility of creating a large microclimatic database of the field for long periods of time contributes to a careful study of the plant growth

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ROLE OF SOIL AND PLANT IN DETOXIFICATION OF ENVIRONMENT

Kotowska U.

Water plays particular role in ecosystem processes. This constitutes a basic and necessary element for living environment functioning and is a renewable natural resource. This specific role of water induces a need of its protection against pollution and rational and economical use.

Quality of Polish water resources is governed mainly by an input of insufficiently treated industrial and communal sewage as well as by surface runoff from agricultural fields. The sewage usually contains marked amounts of biogenic substances, mainly nitrogen and phosphorus compounds that may induce a range of negative effects, as: deoxygenation by nitrification, ammonia toxification or extended development of biomass (eutrophization). Therefore the amount of sewage input to waters should be regulated to minimize the above harmful effects.

The other possibility is sewage detoxification. Among the cheapest and a very effective method of sewage detoxification is their application for intensification of plant production that is achieved by improvement of soil water balance and fertilization. Natural methods of sewage utilization are performed in water, water-plant and in soil-plant systems. In the first system one uses accumulation reservoirs, sewage ponds, in the second hydrobotanical treatment plants, and in the third – irrigated fields mainly with meadow vegetation.

Soil is a very good filter protecting the groundwaters that is a result of sorption, ion-exchange neutralization, acid-base buffering, and decay processes. The protection capacity depends on soil thickness, permeability, organic matter, clay, silt and carbonate content. Therefore light soils are worse filters than heavy ones.

Plants are used for environment detoxification in a phytoremediation processes, which may occur via degradation, extraction and/or stabilization of pollutants (Cunningham et al., 1996).

ROLE OF PLANT IN ENVIRONMENT DETOXIFICATION

Phytoremediation is rather new, but rapidly developing branch of bioremediation (Boyajian and Devedjian, 1997). The plants may remove organic pollutants, heavy metals, radioactive substances or excess salts from soil, water and air. Despite its advantages, phytoremediation is still not sufficiently tested in field conditions so there still exists some risks in its application. This may occur that the toxified plants are consumed by local inhabitants or fauna, or that plants undergo genetic modification of unknown consequences (Wójcik, 2000).

Depending on the type of contaminant and the way of detoxification one may distinguish a few phytoremediation methods: phytodegradation, volatilization, phytostabilization, rhizofiltration or phytoextraction (Wójcik, 2000).

Phytodegradation – concerns toxic organic compounds, only. After entering a plant, the fate of a pollutant may be different (Cunningham et al., 1995; Boyajian and Sumner, 1997; Salt et al., 1998). It may be at first accumulated in plant tissues in original form and after some time is metabolized into nontoxic compound which may be next incorporated into cell structures or released out. In some cases the pollutant may be decomposed to CO_2 and H_2O. Many plant species are found to be useful in phytodegradation, among which the most effective are grasses and papillonaceous plants (Cunningham et al., 1996; Wiltse et al., 1998). Phytodegradation is used for wide range of pollutants: petroleum, aliphatic, polycyclic and aromatic hydrocarbons, herbicides, pesticides, chlorinated hydrocarbons, bleaches, insecticides, explosives, detergents or conservants (Cunningham et al., 1995, 1996; Cunningham and Ow, 1996; Boyajian and Carreira 1997; Salt et al., 1998).

Volatilization – is a process in which an inorganic pollutant taken by a plant from a soil is released to the atmosphere as a gaseous compound. As so far this method found an application for selenium pollution. However, some researchers consider that in this case the air pollution may be dangerous, as well.

Phytostabilization – is growing of highly tolerant plants on polluted environments thus protecting further entering of pollutants do waters and deeper soil layers by their uptake by plants. Despite phytostabilization protects the migration of pollutants, this is not very efficient way of detoxification, because the pollutants still rest in the environment. The removal of plants leaves the problem of the utilization of the toxic biomass and may change soil conditions leading to accelerated mobilization of pollutants. This method is considered to be very useful to prevent soil degradation and spreading of pollutants until more effective method can be applied.

Rhizofiltration – uses plant species which roots are able to absorption or precipitation of toxic substances (metals) from polluted solutions (Dushenkov et al., 1995, 1997). Ideal plant for rhizofiltration should have rapidly growing roots, high metal binding capacity and low possibility to transport the pollutants to the upper parts of the plant. Also large biomass and tolerance on toxicity and salinity are important. Rhizofiltration is used for cleaning surface and ground waters, communal, agricultural and industrial sludges, acidic mine waters or radionuclide solutions (Dushenkov et al., 1995).

Phytoextraction – uses plants of high biomass yield and high uptake of pollutants by upper parts for soil detoxification (Salt et al., 1995). Some algae, bacteria and fungi, also able for high accumulation of pollutants, may be applied only in liquid media (soil cleaning is useless because of difficulties in removal of toxified biomass). In proper soil-air-water-nutrient conditions the plants during vegetation period may uptake 350-700 kg N/ha, 150-300 kg P_2O_5/ha and a few kilograms of heavy metals as micronutrients (Siuta and Wasiak, 1995). Phytoextraction can also use plants of low pollutants accumulation, but of extremely high biomass yield (Chomczyńska, 1997). This ensures intensive overall uptake of mineral components, including heavy metals, and from the second side the concentration of the pollutants in the plant remains low and can not exceed the toxic level. Cereal plants are proposed for this purpose: wheat, rye, barley, oats, rape, buckwheat and maize.

SOIL-PLANT SEWAGE DETOXIFICATION

Communal sewage have usually much better composition of all nutrient substances than the other liquid wastes. For example, industrial sewage may contain much more nitrate and much less phosphate and potassium that these are useless for phytoremediation. For proper sewage cleaning, intensive and continuous plant growth is necessary. Not only the amount of particular nutrients is necessary, but also their appropriate ratios.

Many research concern removal of biogenic substances from sludges by using specific soil or plant root microflora (Obarska-Pempkowiak, 1991; Błażejewski, 1993; Kalisz, 1993; Wojciechowski, 1995; Białkowicz, 1995; Kotowski, 1998). Such approach has been used in around 40 treatment plants in Poland, whereas in US there has been over 150 of only reed-root plants, and many others (Reed and Brown, 1992; Kowalik and Obarska-Pempkowiak, 1997).

The root plants are becoming more frequently installed as near-farm objects. Wastewater cleaning in agricultural areas is recently regarded as an important problem connected with enlarging water deficit.

The Ministry of Environmental Protection and Natural and Forest Resources estimates that agricultural areas (65% of area of Poland) produce 1 billion m^3 of sewage yearly (GUS, 1996). This constitutes 25% of all registered sludges in Poland. Only 40 Mm^3 of sludges i.e. around 4% is subjected to treatment. And only 5% of farmers take care on homesludges cleaning (Sikorski and Wierzbicki; 1995).

Most frequently in small near-farm sewage cleaning plants, selected species of willow (Pettru and Kowalik 1997; Punshon and Dickinson 1997), poplar (Dix et al., 1997), reed, bulrush or other marshy or water plants (Dunbabin and Browmer, 1992; Kondzielski et al.,1996) are used. Willow and poplar are attractive as biofilters because of their fast growth, high transpiration coefficient as well as ability of accumulation and biodegradation of not only organic pollutants but also accumulation of heavy metals. These plants are not consumed by animals and their wood may be used as a cheap source of energy (heating). However both above plants can not be used on intensively watered peaty soils (Kotowski, 1998).

Turnover of nitrogen and phosphorus in root treatment plants is complex and includes both physicochemical and biological processes (Kadlec, 1987). Fixation of nitrogen, mineralization, denitrification and reduction of nitrates(V) to ammonium ion are very important processes in sewage cleaning by plant roots. Phosphate(V) ions (PO_4^{3-}) are removed from sewages by plant uptake and chemical reactions with Ca^{2+}, Mg^{2+}, Al^{3+}, Fe^{3+}.

Chemical and biological variability of sewage properties, spatial and seasonal differences in climatic conditions, geological and water landscape conditions, technical-economical possibilities or skill of potential users make that each sewage treatment project has to be approached individually.

Main elements of the soil-plant sewage treatment device to be rationally designed are (Siuta and Wasiak, 1995):

- sealed reservoir,

- sandy deposit of high permeability for air and water,
- drainage system for outflux of purified sludges,
- sewage dosing instalation,
- technical cropping, harvesting and composting equipment.

After mechanical-biological treatment the sludges may be repurified by plants growing on well permeable sandy soils for enriching groundwaters. In this case the dose of sludge has to be lower than in a well sealed and drained soil-plant treatment device. The above sewage treatment method may be rarely associated with agricultural (mainly fodder) production (Siuta and Wasiak , 1995), as far as usually the biomass contains excess of mineral compounds and nonprotein nitrogen forms. Common practice is to use biomass for compost production and as a green manure.

Soil-plant sewage treatment is possible only during a vegetation period. This causes that such methods can not replace typical sewage treatment plants for large urban areas. However these can fulfill all needs of summer-holidays objects and/or support the other sewage treatment measures (Siuta and Wasiak, 1995).

Soil-plant sewage treatment may be also realized in natural areas without sealing and drainage. For this purpose local landscape depressions, particularly flooded areas with rushy vegetations are most useful. Successive removal of the biomass is here the main factor of the sludge treatment.

SEMI-NATURAL SLUDGE TREATMENT TECHNIQUES

Recently semi-natural sludge treatment techniques are under increasing interest, because of using natural ecosystem ability to decay, mineralization, sorption and sedimentation of pollutants. Plants, soil and algae are the key factors governing the cleaning process (Chełmiński, 2002).

From far in the past sludges have been frequently used as fertilizers. Later on, using land as a biofilter was limited due to recognized danger of pathogens outflow to groundwaters. However more recently the rational irrigation of fields with sewage water become more popular again. One applies sludges on agricultural plots as fertilizers, and load them onto filtration fields for cleaning purposes only.

The sludges introduced onto a field percolate down the soil profile, wherein filtration, sorption and biological decomposition processes took place (Fig. 1).

Carrying off the excess of water is achieved through a drainage system placed on a depth of a few tens centimeters. Such techniques may be used also for cleaning of sewages of small individual farms (Fig. 2.).

Filtration fields consist from and embanked 0,3-0,5 ha plots, flooded with 5-10 cm sludge layer that is allowed to leave on the soil and finally dry of the sediment on the soil surface. The deposit is removed. Important is to allow the soil to aerate between subsequent floods that increases the effectiveness of sludge decomposition by aerobic bacteria.

Some sewage treatment plants use so called oxidation lagoons, which in smaller scales may be used in agricultural areas as algae-bacterial ponds with macrophytic vegetation (reed, sedge, knotgrass, duckweed), crustaceans and fishes.

Such ponds may be located near outlets of melioration ditches (Szymańska, 1983). The cleaning effectiveness of such ponds is around 90% of phosphorus and around 50% of nitrogen compounds.

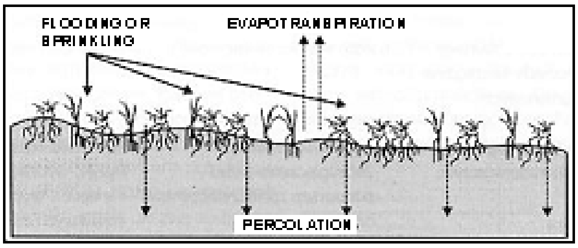

Fig. 1. *Sewage cleaning by flooding or sprinkling and slow infiltration (acc. to US EPA, Davisem and Cornwell, 1991).*

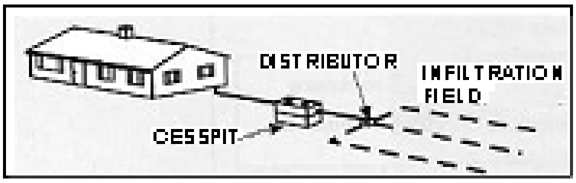

Fig. 2. *Small-scale sludge treatment (acc. to ReVelle and ReVelle, 1981).*

The other treatment method is to spill a sewage onto plant-covered slopes. While going down, the sludge undergoes sedimentation and the purified water migrates down the slope and enters the soil. In the lowest part of the slope around 50% of the purified sludge water is collected in the system of gutters (Fig. 3.).

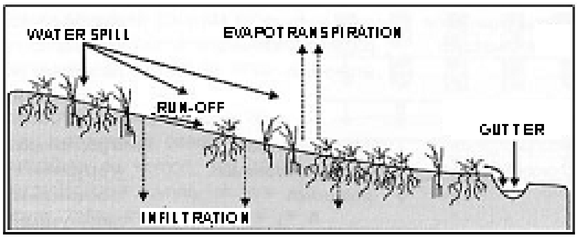

Fig. 3. *Sewage treatment by slope spilling (after US EPA, Davis and Cornwell, 1991)*

Sewage sludge deposition on swamp areas is one of the most effective treatment techniques. Similarly, as on the flooded fields, sedimentation and biological decay processes occur, however more intensively due to intensive vegetation.

Percolation of huge amounts of water through a soil is possible only at continuous supply of the atmosphere oxygen and nonlimited water outflow from the rizosphere. The oxygen deficiency may cause a range of harmful processes:

- limited plant growth
- disturbance of organic matter decomposition pathways
- changes of composition of soil water
- destruction of soil physical properties.

Many experimental works certify the importance of the above problem (Siuta and Wasiak, 1995).

Anthropogenic and environmental factors influencing oxygen deficiency should be well recognized prior to projecting and use of soil-plant sewage treatment measures. In the past 20 years the theories and techniques of sewage treatment have been rapidly developed thus an amount of treated sludge increases systematically.

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VALIDATION AND SENSITIVITY ANALYSIS OF HEAT TRANSPORT MODEL IN SOIL PROFILE

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INTRODUCTION

Mathematical-physical modelling is a very useful tool in agrophysical and environmental research. Mathematical models may be used with success in such areas of research there detailed experimental studies can't be carried. But modelling and experimentation are complementary methods enriching each other. Especially mathematical models need to be verified and validated in experiments. In general only successfully validated model may be used in further studies. In this paper we discuss some methods and tools used in process of model verification, on example model of heat transfer in soil medium with cylindrical object buried in it.

MODEL OF HEAT TRANSPORT

Model formulation. Let's consider model of heat transfer in soil medium. This model is based on Fourier equation, which treats soil as continuum medium, which can be fully described by partial differential equation. This equation is in the form of continuity equation as follow [1, 2]:

$$C_p \frac{\partial T}{\partial t} = \nabla(\lambda \nabla T) \tag{1}$$

where C_p is volumetric soil heat capacity [J/m3K], λ is a soil heat conductivity [W/mK], T is soil temperature. This equation is written in general form, independent on reference system. In our studies we describe axially symmetrical phenomena, so equation (1) we can rewrite in the cylindrical frame of reference, which rise following form of equation:

$$C_p \frac{\partial T}{\partial t} = \frac{1}{r}\frac{\partial}{\partial r}\left(r\lambda \frac{\partial}{\partial r} T \right) + \frac{\partial}{\partial z}\left(\lambda \frac{\partial}{\partial z} T \right) \tag{2}$$

where r is radial distance from axis of symmetry, z is a distance from soil surface. Such model formulation and use of cylindrical frame of reference allow us to describe heat flow phenomena in that cases where modeled object has axial symmetry. This may be for instance cylindrical object buried in soil (Fig. 1.).

Equation (2) describes changes in heat profile in soil medium, but solution of differential equation is dependent from boundary conditions. There is one especially important boundary of simulated area, that is soil surface. Processes occurring on the soil surface determine soil temperature profile. We need to evaluate heat flux flowing through soil boundary, which is Neumann boundary condition for top of simulated area. Soil surface heat balance equation has following form [1]:

$$R_n - H_S - LE - G = 0 \tag{3}$$

where R_n is net radiation, H_s is sensible air heat flux L is latent heat of vaporization, E is the rate of evaporation and G is soil heat flux which is used as boundary condition for heat transfer equation. R_n is a difference between R_g solar incoming radiation, R_l long-wave sky irradiance and long-wave soil surface emission. Following equation describes each of radiative heat transfer phenomena [1].

$$R_n = (1-al)R_g + R_l - \varepsilon\sigma(T_s + 273.16)^4 \tag{4}$$

where al is albedo of soil surface, T_s is its temperature, ε is its emissivity. Albedo and emissivity of soil surface may be described by following equations [1]:

$$\varepsilon = 0.9 + 0.18\theta \tag{5}$$

$$al = \begin{cases} 0.35-\theta & 0.10 \le \theta \le 0.25 \\ 0.10 & 0.25 \le \theta \\ 0.25 & \theta \le 0.10 \end{cases} \tag{6}$$

where θ is volumetric soil water content.

H_s is heat exchanged due to air movements near soil surface, this air movements may be caused by wind or convection. Sensible heat flow may be described by following equation [1]:

$$H_s = \rho_a c_{pa} \frac{T_s - T_a}{r_a} \tag{7}$$

where ρ_a is a air density, c_{pa} is a heat special capacity of air, T_a is a temperature of air at some distance (2 meters) from soil surface and r_a is a aerodynamic resistance of air near soil surface. Value of r_a is evaluated by the following formula [1]:

$$r_a = \frac{(\ln(2/Z_o))^2}{0.16W_s} \tag{8}$$

where Z_o is so called roughness length, parameter which describes soil surface. Evaporation rate may be evaluated as follows [1]:

$$E = \frac{H_o - H_a}{1000r_a} \tag{9}$$

where H_a is a air absolute humidity at 2 meters and H_o is a air absolute humidity near soil surface.

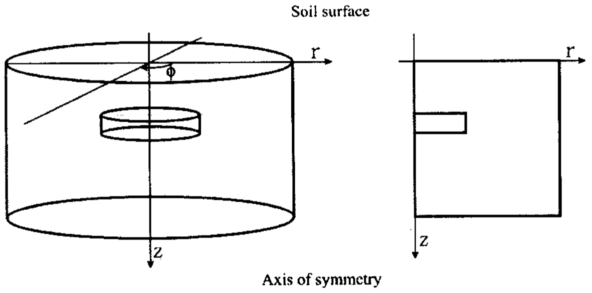

Fig.1. Real 3D problem geometry and its reduction to 2D

Boundary conditions on others boundaries are chosen as follows: at bottom of soil profile there are static thermal conditions assumed - temperature is constant, at left and right boundaries there is Neuman type boundary with no flow condition described by following equation:

$$\frac{\partial T}{\partial r}=0 \tag{10}$$

Model parameters. Results generated by the model are dependent on meteorological data and model parameters. In this model we have chosen five parameters which are:

soil volumetric heat capacity, cv
soil heat conductivity, lambda
roughness length, zo
volumetric moisture of soil profile, init_moisture
temperature at the bottom of soil profile, t11

GLOBAL SENSITIVITY ANALYSIS

Method description. It is important while working with any kind of model to know impact of each model parameters. One of technique which can be used to achieve this aim is a global sensitivity analysis. We are using Fourier Amplitude Sensitivity Test (FAST) which is one of variance based global sensitivity evaluation method. The other method which can give useful information about model parameters is scatter plot analysis.

Scatter plot analysis. There are five parameters describing the model. Depending on values of this parameters model gives different results. Temperature in soil profile calculated by model can be compared with temperatures measured in chosen points in soil profile. The Root Mean Square Error (RMSE) is a standard statistical measure how model calculated values fit into experimentally measured values. RMSE is defined as follows, where T_i^{meas} is temperature measured in *i*-th point, T_i^{simu} is temperature calculated by model in *i*-th point, *N* is a number of points where measured and simulated data are compared:

$$\sigma_{RMSE}=\sqrt{\frac{\sum_{i=0}^{N}\left(T_i^{meas}-T_i^{simu}\right)^2}{N-2}} \tag{11}$$

There is other often used based on σ_{RMSE} measure of model predictions, that is likelihood measure calculated by following equation:

$$w=\left(\frac{1}{\sigma_{RMSE}^2}\right)^n \tag{12}$$

To make scatter plots, model was run 9975 times for different parameter sets. This parameter sets were generated by using Monte Carlo technique where values of each of model parameter was randomly chosen with equal probability from predefined parameter range. Ranges of values for model parameters used in statistical experiment was chosen arbitrarily and are presented in Table 1.

Tab. 1. Initial range of model parameters

parameter	range
cv	$2*10^6 - 4*10^6$
lambda	1 - 3
zo	0 - 1
init_moisture	0 - 0.4
t11	5 - 9

For each parameter set model was run and σ_{RMSE} was calculated. Results of this calculations are presented at scatter plots below, where at x-axis are values of parameters for each parameter set and at y-axis is shown value of $(1/\sigma^2_{RMSE})^{1.5}$. The highest values of $(1/\sigma^2_{RMSE})^{1.5}$ the better model fits into measured data for given parameter set. For low values of $(1/\sigma^2_{RMSE})^{1.5}$ model fits poorly.

From scatter plots we can read some kind of information about influence of chosen values of model parameter on model run, which can be useful while model verification procedure . We can see for instance from figure 3 that predefined range for model parameter lambda is too wide. Good runs for model are grouped at values of lambda higher than 2. Also better runs of model are grouped in mid-range from $2.4*10^6$ to $3.6*10^6$ if we consider model parameter cv (figure 2). There is no special to say about parameters t11 and theta_init, figures 4 and 5 shows nothing interesting. But from figure 6 we can see that parameter zo has great influence on model predictions. We can see that independently from values of other parameters value of parameter zo determine if model runs good or not. Based in figure 6 we can constrict range to (0 – 0.1) for parameter zo which will be used for model validation.

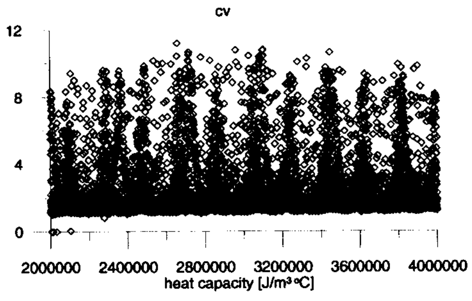

Fig.2. Measured soil profile temperature dependence on time

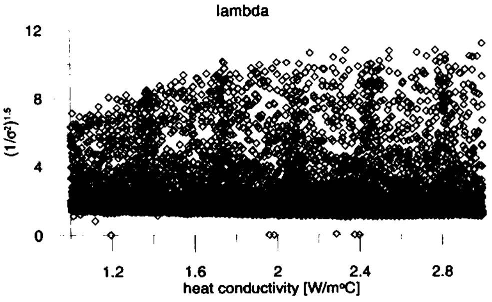

Fig.3. Measured soil profile temperature dependence on time

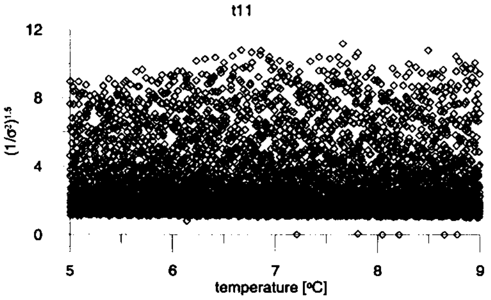

Fig.4. Measured soil profile temperature dependence on time

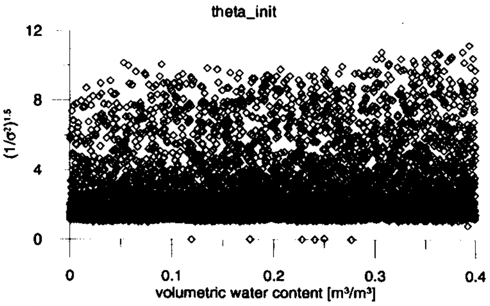

Fig.5. Measured soil profile temperature dependence on time

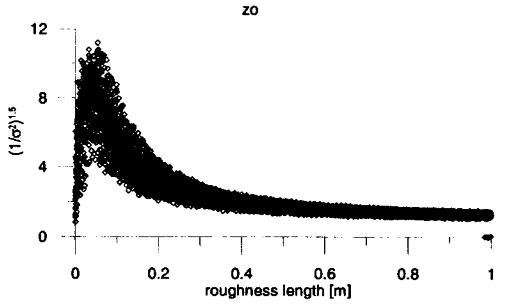

Fig.6. Measured soil profile temperature dependence on time

Model sensitivity indices. Data generated while model runs for different parameter sets may be used for evaluation of model global sensitivity indices. This indices was evaluated by SIMLAB 2 software, which can be run on data independently prepared. Below there are presented first order sensitivity indices and total sensitivity indices calculated for model parameters. As likelihood measure equation 12 was used with different values of parameter *n*. Commonly used in literature value of parameter *n* is 1.4.

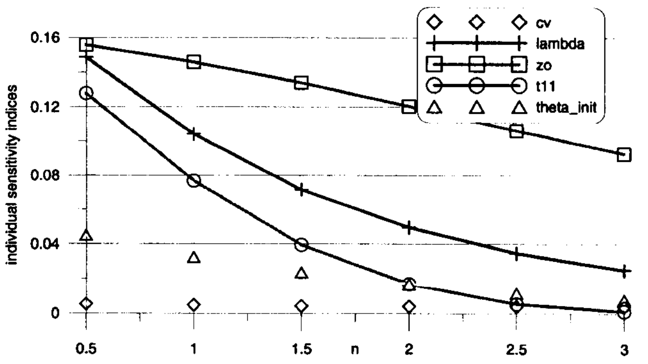

Fig.7. Individual sensitivity indices of model parameters

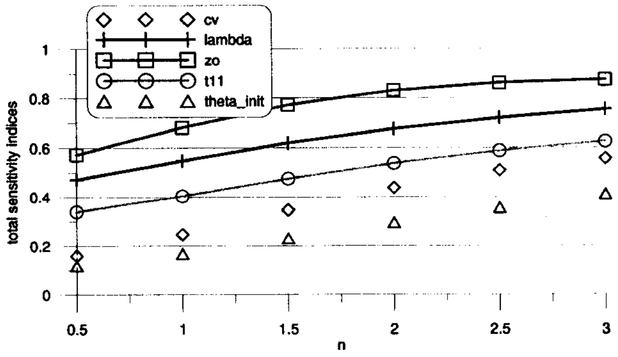

Fig.8. Total sensitivity indices of model parameters

We can see from both plots that impact of parameter zo on model runs is greater than other parameters. This was already shown by scatter plots. The other parameters which are determining model predictions are in order lambda, t11, cv and theta_init.

MODEL VERIFICATION

Verification procedure is based on searching such model parameters set for which model predictions of temperature are the same as temperature measured by experiment. Function commonly used for describing correctness of model predictions is σ_{RMSE} (RMSE). Such formulated validation procedure is in fact maximization/minimalization problem, and standard mathematical maximization techniques may be used here. Models used in environmental studies are particularly interesting while considering minimalization of the σ_{RMSE} in space of model parameters values, because model may fit into measured data good for different parameters sets. RMSE is not smooth function of model parameters. In such case there are two techniques which can be used for RMSE minimalisation: genetic algorithms or simulated annealing. For purpose of this work genetic algorithms were used, where aim function was defined as inverse of RMSE.

Verification experiment. Data for model calibration was measured in experiment carried in Lublin, Poland for two weeks from 20-11-2003. In this experiment air humidity and temperature near soil surface and at 2 meters, wind speed, incoming solar radiation and temperature at 12 depths to 0.5 m were measured. While data collection two instrumentation sets were used, standard agrometeorological weather station produced by EIJKELKAMP and equipment prepared in IA PAS [4] used for remote wireless soil and air temperature measurements. View of experiment field is shown in figure 9.

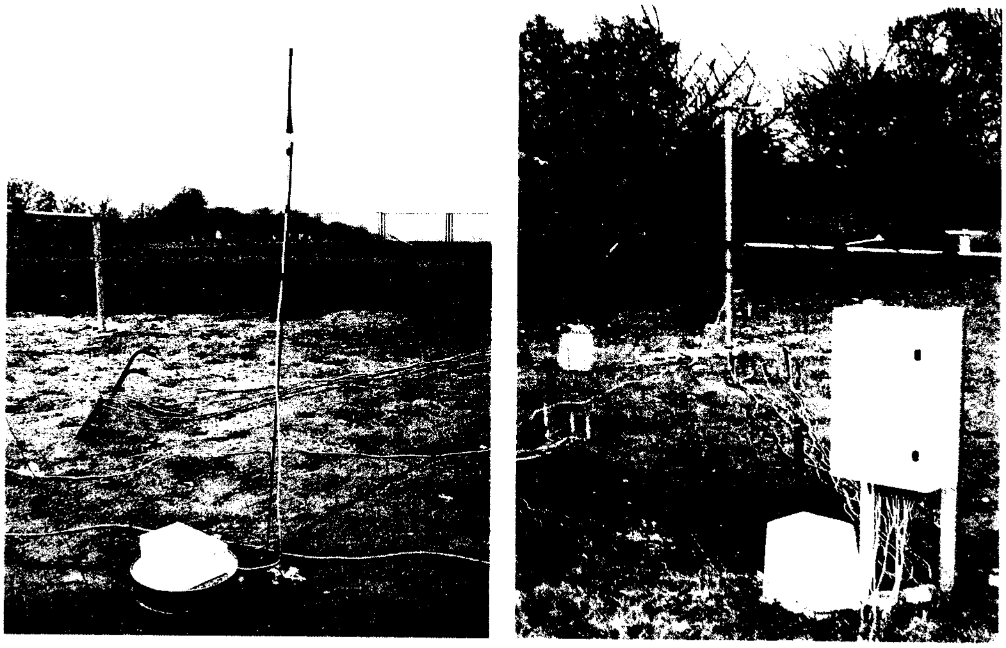

Fig.9. Experimental field

Results of verification. As a result of verification process we received model parameters for which model predictions are as close to measured data as it was possible. In this example σ_{RMSE} for validated model parameters equals 0.4207 and values of this parameters are presented in Table 2.

Tab.2. Validated model parameters

parameter	value
cv	$2.75685*10^6$
lambda	2.26869
zo	0.0400531
init_moisture	0.336791
t11	8.85522

There are changes in soil profile calculated by model for validated parameters shown in figure 10. Figure 11 shows data measured in experiment which were used for model verification.

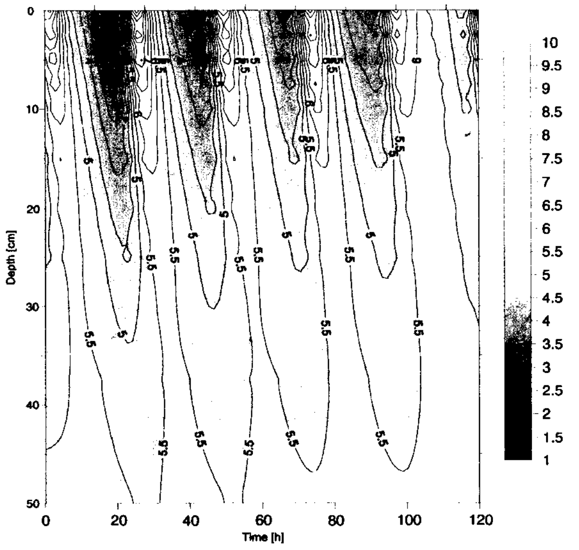

Fig.10. Simulated soil profile temperature dependence on time

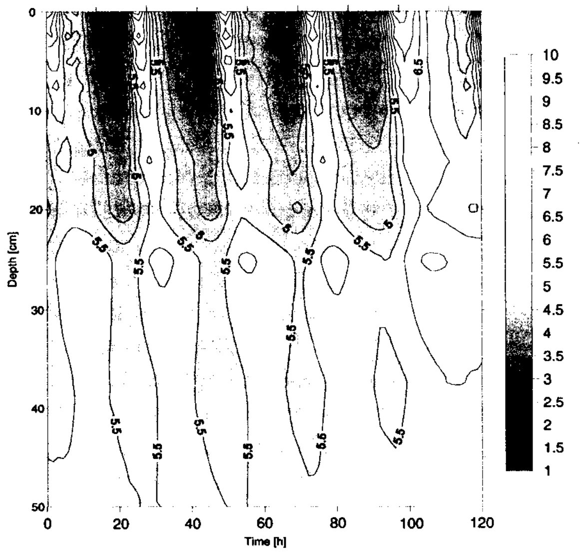

Fig.11. Measured soil profile temperature dependence on time

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DISSOLVED ORGANIC MATTER IN PHOSPHATE FERTILIZED MUCKS

Matyka-Sarzyńska D.

INTRODUCTION

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 loses its sorption abilities and gains more hydrophobic character. The mechanism of the above changes is called secondary transformation. As consequence of above process, muck formation take place. Different schemes have been introduced in the literature for the characterization of muck formations and of the degree of peat transformation. Okruszko (1976) suggested application of a three-point scale for this purpose and divided mucks into three categories: peaty mucks (Z_1), humic mucks (Z_2) and grainy, i.e. proper mucks (Z_3). Further, on the basis of the character of genetic layers and their thickness three stages of mucking process can be distinguished which are: Mt I - weak mucking, Mt II – moderate mucking, and Mt III – strong mucking. The above classification schemes are qualitative. However, quantitative approaches have also been developed to classify the degree of the secondary transformation of peats. Usually, such classifications are based on the numerical values of water adsorptivity, because the changes in peat mass under the influence of drying are manifested by the decrease of water holding capacity. According to Gawlik's (Gawlik, 1992) approach, the state of mucks transformation is characterized by the index of water holding capacity index, W_1. It expresses the relation between water capacity of the sample that had been previously dried in the temperature 105^{o}C (c) to water capacity of the sample in natural state (a). Adsorptive abilities (water capacity) of mucks was determined by centrifugal method with the rate of centrifugation equal from the equation: W_1=c/a and is given as decimal fraction. The value of 0,36 distinguishes non-transformed peat formations from fransformed. Mucks with the index of above 0,90 are completely degraded (Gawlik, 2000).

As the consequence of the secondary transformation, soil degradation and lost of fertility occurs. One of important factor of these phenomena can be release of organic matter.

SOIL ORGANIC MATTER

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 (Schnitzer and Khan, 1978; Wershaw, 1994).

Structure of humic substances

Humus is probably the most chemically and physically active component od soils but it is still the least understood. But nevertheless there are several general common features: the presence of an aromatic ring, nitrogen as an obligatory component and functional groups.

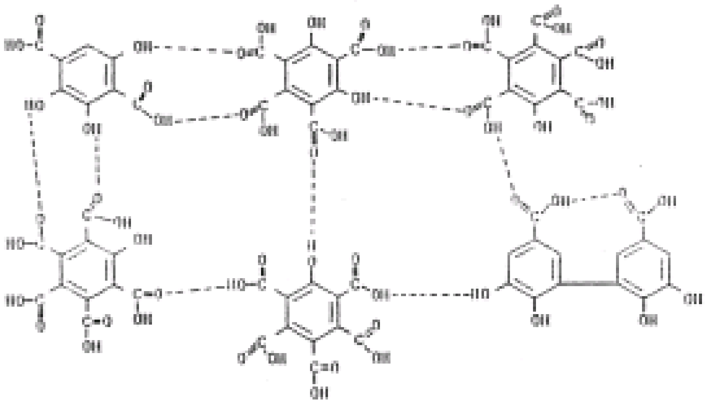

Fig.1. *Hypothetical structure of humic acids after Stevenson (1982).*

Historically humus (humic substances) can be divided into the following three main fractions: humic acids (HA), fulvic acids (FA) and humines. In this classification (Kononova, 1966), humic acid is soluble in strong base but precipitates at pH values less than 2; fulvic acid is soluble in both basic and acidic solution; humin is insoluble in both basic and acidic solutions. 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.

On surfaces of humic substances functional groups of acidic character dominate (OH and COOH). In general natural organic matter has a negative charge caused by the dissociation of its surface functional groups. Acidic functional groups of humic substances have very different acidic strength depending on the kind of the group and its locality. So, the number and acidic strength (dissociation constants) of functional groups constitute a primary characteristics of soil organic matter (Stevenson, 1982; Sposito, 1989).

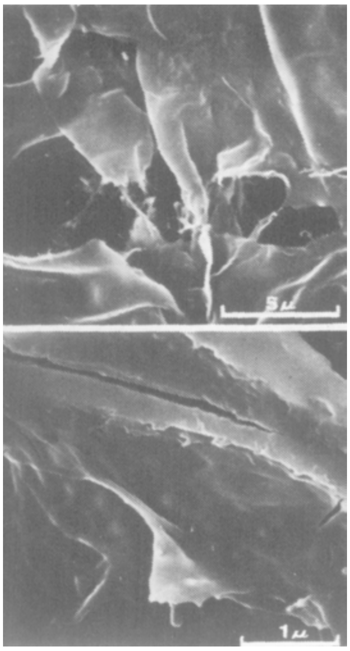

Fig. 2. *Scaning electron micrographs of FA at pH 8(Schnitzer and Khan, 1978)*

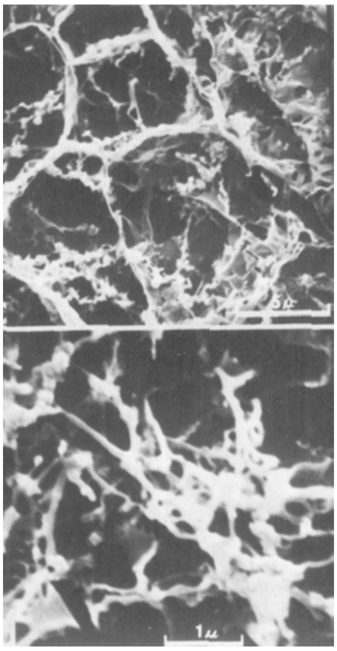

Fig. 3*. Scaning electron micrographs of HA at pH 8(Schnitzer and Khan, 1978)*

Function of organic matter in soil

The importance of humus as a major factor in controlling the physical and chemical properties of soils has long been recognized. The organic matter plays a significant role in cations exchange and can interact with inorganic anions (phosphorus) via polyvalent cations. So, humus has physical and physico-chemical function in that it promotes good soil structure (stability of aggregates of soil particles), thereby improving soil fertility, aeration, retention of moisture, buffering and exchange capacity of soils. Organic matter contributes to plant growth through not only its effect on the physical, chemical but also biological properties of the soil. It has: nutritional function in that it serves as a source of N, P for plant growth. Humus content is also important in maintaining biological function in soils. It affects the activities of microflora and microfauna organisms (Schnitzer and Khan, 1978).

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 (McDowell and Wood, 1984). 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.

PHOSPHATE

So far public concern about phosphates has concentrated mainly on phosphorus as plant nutrient (Addiscott and Thomas, 2000). Phosphates are also present in soil solution as the result of fertilizing and they can originate from sludge. The transfer of different forms of phosphate in drainage from agricultural soils to watercourses can contribute to water quality problems associated with eutrophication.

Forms of phosphate in the soil

All phosphate in the soil is there as phosphate (strictly as orthophophate), PO_4. Both organic and inorganic phosphates are to be found (table 1), but neither category is ever present to the dominant category in soils (Addiscott and Thomas, 2000).

Table 1. Some categories of phosphate in the soil (Addiscott and Thomas, 2000).

Category	Subcategory	Examples	References
Inorganic	Ionic	PO_4^{3-}, $H_2PO_4^-$, HPO_4^2-	Aslyng (1954)
	Mineral	Apatite, tinticite	Frossard et al. (1995)
Organic	Monoesters	Inositol hexaphosphate	Anderson et al. (1974)
	Diesters	Phospholipids	Newman and Tate (1980); Hawkes et al. (1984)
		Nucleic acids	Newman and Tate (1980); Hawkes et al. (1984)
	Biomass P	Microbial P	Brookes et al. (1982, 1984)
		Adenosine triphosphate	Jenkinson et al. (1979)
	Humic P		Tiessen et al. (1994)

Inorganic phosphate

Inorganic phosphate is found in a variety of insoluble forms, of which the commonest is apatite. This has the general formula $Ca_{10}X_2(PO_4)_6$, where X is OH^-. Calcium may be substituted by sodium or magnesium. The mineral apatite is the primary source of phosphate for plant life. It is need to keep in mind that orthophosphoric acid is tribasic and the first dissociation constant is very much greater than the second or third.

$$H_2PO_4 \Leftrightarrow 2H^+ + H_2PO_4^- \qquad K_1 = 9x10^{-3}$$

$$H_2PO_4^- \Leftrightarrow 2H^+ + HPO_4^2- \qquad K_2 = 6x10^{-8}$$

$$HPO_4^{2-} \Leftrightarrow 2H^+ + PO_4^{3-} \qquad K_3 = 1x10^{-12}$$

The proportions of the three orthophosphate ions depend on pH of the solution. Only all the dihydrogen phosphates are soluble in water. So, apatite-containg rock phosphate is most useful as a fertilizer when the soil has a pH of 6,2 or less.

Organic phosphate

Soil sorption capacity of organic matter towards anions has not been properly recognized. Organic matter does not sorbs phosphate directly in all circumstances, but it can strongly influence on sorption or desorption of phosphate by other soil components for example polyvalent cations. The oxides and hydroxides of iron and aluminium present on surfaces of organic compounds play an important part in the sorption of phosphate and finally can caused the coagulation of humic substances. Additionally, phosphate forms stable complexes with divalent inorganic cations. It is worth to remember that phosphate in acidic solution (pH below 6) can cause removal of organic matter to soil solution The existence of mobile organic phosphate which is not clearly defined from chemical point of view is also probable

CONCLUSION

Despite the importance of organic matter transfer caused by the presence of phosphate, it remains still poorly studied. More and more phosphates originated from anthropogenic sources are in waters, the problem of water pollution caused by phosphorus are still ignored. Understanding the behaviour of different P products in peat soils in conjunction with the role soil organic matter is an important advancement and could have important implications for use of P fertilizers.

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METHODS FOR AMELIORATING Na-SALINE SOILS AND COPPER POLLUTED ACID SOILS BY USING ORGANO-MINERAL WASTES

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INTRODUCTION

Na-saline soils and heavy metal polluted acid soils have to be ameliorated for improving their fertility. Different waste products could be applied as meliorative agents in dependence of their physico-chemical properties**.** Many reports concern the use of different waste products as soil amendments for improving soil chemical properties and plant growth (Munoz et al., 1994, Sajwan et al., 1995, Shamshuddin, 1998). Besides, the amelioration with waste materials allows an ecologically conformed utilization of the environmental pollutants.

The study performs theoretically elaborated and experimentally confirmed methods for amelioration of Na-saline soils and copper polluted acid soils by using organo-mineral wastes (Raychev et al., 2000; Raychev et al., 2001). The methods are patented (Raychev et all., 1999, 1999a). Colloid - chemical state of the soil adsorbent and its sensibility at external influences are in the base of a methodology scheme worked out by us. Its essence is the blockage of Na^+ and Cu^{2+} ions inside the soil by means of their incorporation in stabile organic-mineral formations.

By means of introduction of waste product $FeSO_4$ in saline soil conditions for hydroxycomplexes - type $Na_2[Fe(OH)_4]$ and $Na_5[Fe(OH)_8]$ are created. The local acidification activates the ion exchange between Na^+ and Fe^{n+}. Cation exchange capacity (CEC) of mineral colloids increases and the flocculation processes are facilitated after organic materials treatment that are enriched with stabile organic matter compounds (waste coal powder). The fenomenon is attended with the formation of negatively charged form of $Fe(OH)_3$. $Na_n[Fe(OH)_m]$ stabilization and Na^+ enclosure in the organic-mineral formations would decrease the level of the so called “salt barrier”.

The concentration and the form of amphoteric elements compounds present in the soil solution are governed mainly by its reaction. The pH determines the possibility of ionic forms of these elements to participate in various reactions as a function of its composition and charge. Full neutralization of the strongly acidic part of the soil adsorbent with bases at pH 6.0 does not practically allow for a presence of ionic forms of all amphoteric elements. This fact is the base of the commonly used methods of liming acid soils applied for the neutralization of plant-toxic soil acidity and for decreasing the toxic effect of heavy metal pollutants as well. Assumed is that at the pH 6.0 the mobility of amphoteric elements is minimized via precipitation of hydroxides. However, the liming effect is usually time-limited, mainly because of low sorption capacity of clay fraction occurring in acid soils.

In our previous works it was established that an addition of organic material having high humification degree (waste anthracite coal powder) increases significantly the effectiveness of liming of copper polluted acid soil (Raychev, 1997; Raychev and Arsova, 1998; Raychev et al., 1999). According to D. Orlov (1985) under these conditions (pH 5.0 to 6.0) a chelating of ionic forms of aluminum and heavy metal pollutant and a formation of heteropolar salts of free carboxylic groups of the humus acids (HA) and calcium ions of the lime material are likely to occur. The binding of amphoteric elements' cations by the anionic parts of such complexes eliminates their participation in ion-exchange reactions.

MATERIALS AND METHODS

I. Method for physico-chemical melioration of Na- saline soils

Amelioration of Na-saline soils is based mainly on a replacement of Na^+ ions with Ca^{2+} through gypsum or other hydrolytic acid salts ($FeSO_4$) application and leaching the products of the reaction out of the soil profile.

Basic disadvantages of the applied chemical amelioration is the necessity of construction of hydrotechnical installations and use of great water quantities for taking the soluble salts out of the root soil layer. The possibility of soluble humus compounds movements down the soil profile and the danger of subsoil water pollution appear to be a disadvantage from environmental point of view as well.

The meliorative approach proposed by us overcomes in a great extent the disadvantages mentioned above. Its essence is the blockage of Na^+ ions inside the soil. By means of introduction of $Fe(OH)_3$ in saline soil conditions for stabile hydroxy-complexes are created. The additional treatment with anthracite coal powder containing compounds with a high degree of humification (humic acids) encloses Na^+ in organo-mineral formations and decreases its toxicity.

Advantages of the method are the following: blockage of Na^+ ions inside the soil; decrease the soluble salt level and its toxicity for plants; minimizes the salt leaching out of the soil profile; enriches the soil with structure forming organic matter; minimizes the environmental pollution hazard; minimizes financial input due to no needs of hydromelioration.

II. Method for amelioration of copper polluted acid soils

Especially vulnerable object concerning the heavy metal pollution is acid reaction of soils. The mobility of toxic elements in the soil depends on the response of both pH medium and type of organo-clay interactions.

To eliminate the heavy metal toxicity under these conditions "liming" of such soils is used to apply. The lime meliorants are with high content of Ca and Mg and their application in the soil is in amounts calculated on the base for neutralizing the toxic soil acidity and decreasing the heavy metal mobility to non toxic extent for plants. In the case of copper polluted soils an organic materials (manure) are usually applied to decrease the copper toxicity. Liming leads to marked losses of lime materials because of leaching of bicarbonates in vertical and lateral water flow. The fact is caused by the low sorption capacity of the clay minerals in these soils.

The new method increases the effectiveness of the melioration of copper polluted acid soils trough the association of Cu^{2+} ions in stable organo-mineral formations that decreases its toxicity. This effect is achieved through a treatment of the acid soil with mixture from anthracite coal powder, containing compounds with a high degree of humification (humic acids) and lime product.

The advantages of the method are: decrease of copper ions toxicity through their association in stabile organo-mineral adsorption structures; improving the humus system quality; increase the amount of strongly bound Ca^{2+} ions in the new-formed organo-mineral formations; decrease of losses of lime materials; stabilization of the optimal soil pH value for a long period that leads to the increase of the meliorative effect; possibility for applying such meliorative approach on soils polluted with other toxic elements.

III. Waste products

The actuality of the two proposed methods is also conditioned by the presence of great amount of waste materials, which could catalyze the colloid-chemical interactions in the soil adsorbent. The properties of the tested in laboratory and pot experiments waste products allow their ecological application as meliorants for Na-saline soils and copper polluted acid soils. The following wastes are used:

A. Mineral wastes: ferrihydroxide from oxide copper ores leaching in the hydrometallurgical process in "Elshitza" mine, West Bulgaria; carbonates deposits from a power station, refinery near Burgas, East Bulgaria (product of lime decarbonization and water coagulation, containing 74.4% $CaCO_3$, neutralizing capacity 2200 meq.g^{-1}).

B. Organic wastes: Anthracite coal powder from "Svoge" coal mine, West Bulgaria, containing 85% humic acids; manure.

RESULTS AND DISCUSSION

I. Amelioration of Na – saline soil

On the basis of theoretical analysis of physico-chemical parameters of meadow sulfate-sodic solontchak-solonetz from the area of Belozem, Plovdiv region, South Bulgaria (surface horizon 0 - 20 cm electroconductivity χ = 4.97mS.cm^{-1}; pH (H_2O) 8.2; Na^+ = 5.0 mequ/100g; water soluble Na^+ = 10.2 mequ/100 g - in water extract with ratio soil : water = 1 : 5) a scheme has been worked out of the colloid-chemical state of its soil adsorbent (Fig.1).

The applicability of this theoretical model has ben estimated by means of biological test. The pots containing 3 kg of the soil (in four replications) with different combinations of the meliorates amendments were prepared according to the following scheme:

1. Original soil+NPK
2. Original soil+NPK+FeSO4 (18 t/ha), washing with water
3. Original soil+NPK+coal powder (anthracites - 20 t/ha)
4. Original soil+NPK+coal powder (anthracites - 40 t/ha)
5. Original soil+NPK+coal powder (anthracites - 60 t/ha)
6. Original soil+NPK+coal powder (lignites - 20 t/ha)
7. Original soil+NPK+FeSO4 (18 t/ha)+coal powder (anthracites - 20 t/ha)

8. Original soil+NPK+FeSO4 (18 t/ha)+coal powder (lignites - 20 t/ha)

The amount of NPK added to the soil was 600 mg N, 600 mg P and 725 mg K per pot. The dose of $FeSO_4$ was equvalent to the dose of gypsum and it was 18 g $FeSO_4x7H_2O$ per pot, added as a water solution.

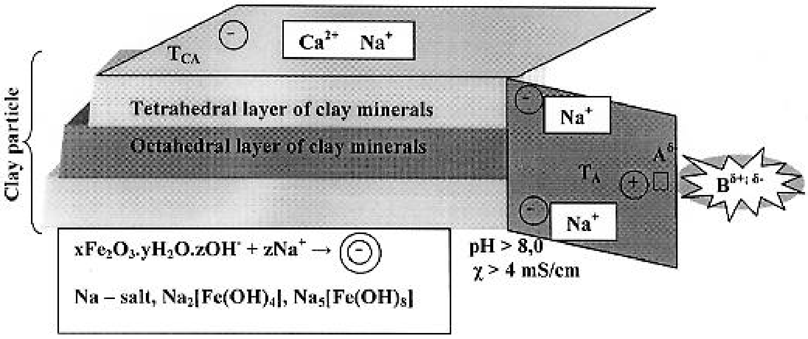


Fig. 1. *Colloid-chemical state of soil adsorbent in conditions of sulfate-sodic solontchak-solonetz. Abbreviations below Figure 2.*

The choice of organo-mineral meliorates (anthracite and lignite coals) is confirmed with the high content of organic components of humic type, their stability and sorption abbility as well as the availability of the materials.

The added agents were equilibrated with the soil at 80% soil water capacity and after soil from variant 2 were washed with amount of distilled water calculated from the formula of Volobuyev (1975). After the moisture of the washed soil decreased to 80% of soil water capacity, 50 seeds of alfalfa were seeded in every 8 variant pots, in four replicates. When the plants reached the 3rd leaf stage, part of them were removed and 25 plants were grown further. During plant growth the soil moisture was kept around 80% water capacity. Exchangeable Na was estimated in soils according to Bower (1950) method. The cuts were harvested in the beginning of flower stage. The yield of 4 cuts in dry matter is presented in Tab. 1.

The biomass yield from variant 2, accepted for standard, increases weakly. In all other variants treated with anthracite coal materials the increase is significant but the variant differences are insignificant. A rapid increase in biomass quantity was estimated after the third cut in variant 8 in comparison with variant 6 - treated with lignite coal dust only. An assumption could be made that after the preliminary treatment with $FeSO_4$ the excess of HA (with a high rate of humification) intensifies the processes of their flocculation with clay particles saturated with Fe^{n+} ions. Within coal dust application without preliminary iron-containing material treatment the electro-chemical charge of HS is activated (Fig.2).

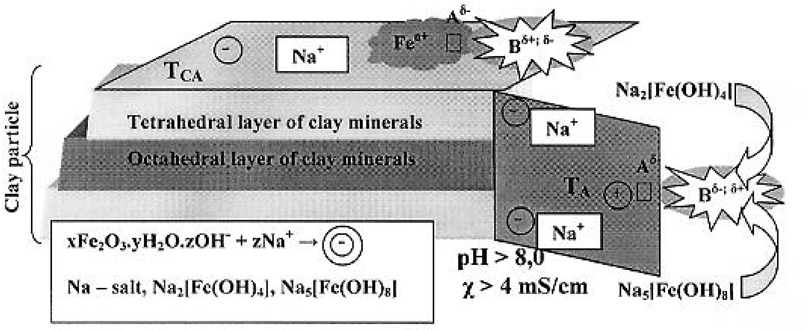


Fig. 2. *Colloid-chemical state of soil adsorbent in conditions of sulfate-sodic solontchak-solonetz after treatment with humic substances, enriched in cyclinuclear components*

Abbreviations for the Figures
T_{CA} *- capacity of strongly-acidic ionexchanger;*
T_A *- capacity of poor-acidic ionexchanger;*
δ *- electric charge of the organic macromolecules;*
Molecular configuration of humic substances is marked through:
A - the easily oxidated fraction of humus substances;
B - the difficulty oxidated fraction of humus substances.

The adsorption of part of Na^+ on the HS surface causes a step by step dissociation of $Na_n[Fe(OH)_m]$. The concentration of $[Fe(OH)_m]^{k-}$ increases and they might associate with the positively charged parts of the organic macromolecules. The limited Fe^{n+} quantities terminates the flocculation process towards their association with the lateral surfaces of the soil clay minerals.

The prolonged keeping of constant humidity within the experiment provokes a natural leaching of watersoluble salts (χ decreases under 1.55 $mS.cm^{-1}$ in all variants). This causes a twice decrease of exchangeable Na even in the control variant.The coal dust treatment decreases its content under 0.9 mequ/100g. After $FeSO_4$ treatment exchangeable Na has not been discovered. The Na watersoluble form quantities decrease in all variants more than 40 %. The exception are variants 1, 2 and 6 where no significant changes compared with the original soil has been discovered. pH decreases with 0.3 - 0.4 points at the end of experiment.

II. Amelioration of Cu – polluted acid soil

Two-year-long pot experiments were carried out with alfalfa grown on a light gray forest soil (Albic Luvisol) with the following physico-chemical characteristics: pH (H_2O) 4.8; exch. Al = 2.4 mequ/100 g; exch. $H_{8.2}$ = 8.5 mequ/100 g; exch.(Ca^{2+} + Mg^{2+}) = 16.8 mequ/ 100 g; CEC = 24.6 mequ/100 g. Soil pH was measured in water suspension 1:2.5. The exchangeable acidity (exch. Al) was determined titrimetrically after displacement of Al^{3+} ions by 1 n $CaCl_2$. The total acidity (exch. $H_{8.2}$) and exchangeable bases were determined, titrimetrically and complexometrically, respectively, after saturation of the soil sample with buffer solution (Na-acetate and K-maleinate, pH 8.2). Cation exchange capacity (CEC) was calculated by the sum of exch. $H_{8.2}$ and exch. bases (Ganev and Arsova, 1980).

Table 1. Yield of alfalfa depending on the applied meliorants in sulfate-sodic solontchak-solonetz (Belozem, Plovdiv) (LSD – the least significant difference)

Variants	Yield, dry weight (g.kg^{-1})				
	I cut	II cut	IIIcut	IVcut	∑
1. Original soil+NPK	no germination				
2. Original soil+NPK +$FeSO_4$ (18 t/ha), washing with water	0.9	0.7	1.8	0.8	4.2
3. Original soil+NPK +coal powder (anthracites - 20 t/ha)	1.1	2.0	6.9	7.8	17.8
4. Original soil+NPK +coal powder (anthracites - 40 t/ha)	1.3	2.2	8.2	9.0	20.7
5. Original soil+NPK +coal powder (anthracites - 60 t/ha)	1.4	2.2	9.2	9.3	22.1
6. Original soil+NPK +coal powder (lignites - 20 t/ha)	1.1	2.0	2.1	2.2	7.4
7. Original soil+NPK +$FeSO_4$ (18 t/ha) +coal powder (anthracites - 20 t/ha)	1.3	1.7	7.2	9.3	19.5
8. Original soil+NPK +$FeSO_4$ (18 t/ha) +coal powder (lignites - 20 t/ha)	1.0	1.9	5.9	5.8	14.6

The soil was polluted with 300 mg Cu kg^{-1} added as CuO (0.375 g.kg^{-1}). The soil pollution exceeded several times the permissible contaminant levels, which were 40 mg.kg^{-1} for Cu at pH 5.0. Waste carbonate deposit and coal powder were used as meliorants. In all treatments the amount of carbonate deposit was constant ($Ca_{opt.}$ = 0.23 g/100 g), calculated as the optimal liming rate of acid soils (Ganev, 1987) and the coal powder (B) was added according to the scheme:

- Control – polluted soils with Cu;
- $Ca_{opt.}$ – carbonate deposit added in an amount corresponding to the optimal liming rate ($Ca_{opt.}$ = 2.3 g/kg);
- K_1 – carbonate deposit (Caopt.) and coal powder (B_1) in a ratio 1:4 (Caopt.+ B_1= 2.3 g + 10 g per kg soil);
- K_2 - carbonate deposit ($Ca_{opt.}$) and coal powder (B_2) in a ratio 1:8 ($Ca_{opt.}$ + B_2 = 2.3 g + 20 g per kg soil);
- K_3 – carbonate deposit ($Ca_{opt.}$) and coal powder (B_3) in a ratio 1:12 ($Ca_{opt.}$ + B_3 = 2.3 g +30 g per kg soil);
- K_4 – carbonate deposit ($Ca_{opt.}$) and coal powder (B_4) in a ratio 1:16 ($Ca_{opt.}$ + B_4 = 2.3 g + 40 g per kg soil).

Experiments were conducted in three replications with 1.2 kg soil per pot and moisture 60% of the field capacity. Manure of 10 g.kg^{-1} was applied. A preliminary interaction between the soil additives was carried out in the course of two months.

The alfalfa cuts were harvested in the beginning of the blowing stage. The dry biomass from seven cuts was weighted (Table 2). Copper content in the biomass (I and II cuts) was determined by atomic absorption spectrometry (AAS) methods. Soil pH was measured in soil - water suspension 1:2.5 at the end of the experiment.

Soil pH was maintained in the optimal range (pH 5.8 - 6.2) during the treatment with the carbonate deposit, applied either separately ($Ca_{opt.}$) or in combination with the coal powder (K_{1-4}). Additional acidification (pH 4.4) was observed in the control variants in comparison to the initial soil pH value (pH 4.8) caused by the soil pollutant. Treatment with the highest coal powder content (K_4) soil pH showed a tendency of decrease (pH 5.8) in relation to the other combined treatments (K_{1-3}), most probably due to an insufficiency of carbonate deposit for neutralizing the acidic groups (-COOH) of the humic acids.

The biomass amount from the I cut was highest after the treatment with carbonate deposit and coal powder in a ratio 1:4 (K_1). The differences, however, between this amount and the amount obtained upon treatment with carbonate deposit ($Ca_{opt.}$) and the other combined products (K_{2-4}) were not significant. The treatment with the combined product K_2 (1:8) had a significant positive effect on the II cut production. A statistically significant maximal production from the next cuts (III – VII cut) was obtained at carbonate deposit and coal powder applied in a ratio 1:8 (K_2). A decrease of the biomass amount from all cuts was observed in the variants K_3 and K_4 containing 30 and 40 g coal powder per kg soil, respectively. The combined treatment K_2 had a maximal effect on the total alfalfa production ($\sum$) as well.

Table 2. Alfalfa production from seven cuts and soil pH depending on the organo-mineral treatments of acid soil polluted with Cu (LSD – the least significant difference)

Treatments	Soil pH (H_2O)	I	II	III	IV	V	VI	VII	$\sum$
		Dry weight g / 10 plants							
Control	4.4	1.46	1.24	0.87	0.63	0.39	0.74	0.72	6.05
Caopt.	6.0	2.28	2.23	1.70	1.76	2.26	3.00	2.90	16.23
K_1	6.1	2.38	1.98	1.50	2.00	2.53	4.55	4.00	18.94
K_2	6.1	2.19	2.60	1.75	2.17	2.87	4.83	4.97	21.38
K_3	6.2	1.87	1.64	1.22	1.38	2.12	3.17	3.01	14.41
K_4	5.8	1.97	1.55	1.22	1.33	1.73	2.90	2.82	13.52
LSD 1%		0.27	0.23	0.15	0.07	0.08	0.10	0.35	
0.1%		0.38	0.30	0.20	0.09	0.12	0.19	0.41	

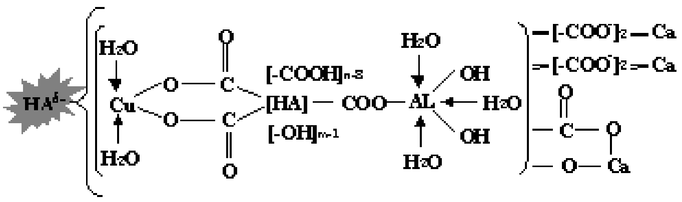
It could be assumed that the treatment with combined product K_2 of carbonate deposit and coal powder in a ratio 1:8 is the most appropriate for realizing a maximal effect on alfalfa productivity according to the proposed experimental scheme. Therefore, the amount of 2.3 g carbonate deposit and 20 g coal powder per 1 kg soil polluted with copper could be accepted as an optimal dose for plant growth, allowing also an ecological utilization of the waste products.

The copper content in the biomass from the I and II cuts decreased to almost normal limits (17 – 25 mg.kg^{-1}) after treatment with carbonate deposit and coal powder (Ca$_{opt.}$, K$_{1-4}$) compared to the control (35 –37 mg.kg^{-1}). There were not significant differences between copper content in alfalfa biomass upon treatment with carbonate deposit applied separately (Ca$_{opt.}$) and in combination with coal powder (K$_{1-4}$). The fact is due mainly to the soil pH buffered in the relatively stable optimal range during the whole vegetation excluding the possibility of some particular influence of the increasing coal powder amount on copper mobility.

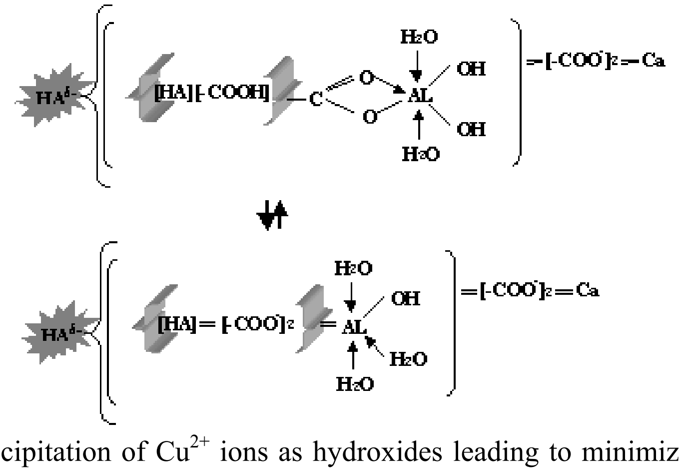
Therefore, the treatment of the heavy metal polluted soils with carbonate deposit and coal powder (Ca$_{opt.}$, K$_{1-4}$) causes an immobilization of Cu^{2+} ions because of their association in hydroxides and organomineral complexes at optimal soil pH.

The mechanisms of complex compound formation in K$_1$ – K$_4$ variants involve some reactions, which can be:

- Additional dissociation of formerly non-active acidic groups, which consume the relative excess of lime material and buffer the whole system at optimal pH according to the scheme:



Intra-molecular rearrangement of the anionic part of the complex heteropolar salt leading to formation of valence bound of phenolic hydroxyls and Al and coordination of oxygen of carbonyl group that increases chelating capacity of humic acids in respect to amphoteric cations:



- Precipitation of Cu^{2+} ions as hydroxides leading to minimization of their chelating by humic acids.

Which of these processes is dominant depends on the quantitative ratio between the lime material and coal powder.

CONCLUSION

Positive effect of tested methods on plant growth in pot experiments shows a need to extend the investigations under field experiment conditions and confirms the applicability of the wastes for amelioration of Na-saline soils and copper polluted acid soils. Advantages of the proposed methods were experimentally proved.

By using the organo-mineral wastes an ecological effect would be achieved due to an improvement of the soil physico-chemical characteristics and utilization of environmental pollutants such as the wastes actually are.

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ELECTRONIC CONFIGURATION AND TYPES OF BONDINGS IN THE CRYSTAL-CHEMICAL STRUCTURE OF CLAY MINERALS

Raytchev T., Atanassova I., Hajnos M.

ABSTRACT

This review presents some major characteristics of the crystal structure of clay minerals and the role of their electronic configuration in the formation of the colloid-chemical character of their active centers (areas). The clay minerals are considered as complex adsorption systems with colloidal structure, built of definite number of atoms bound with chemical bonds and therefore representing a unified multi-atomic quantum-mechanical system with multi-centre electronic orbitals with translation symmetry. The electronic configuration of the unified layers in the two-layer package in kaolinite and the bonds distribution in the T_d-coordination of Si and the O_h coordination of Al with the strongly electronegative ligands of O (respectively OH-groups) is discussed.

The proposed theory lies in the basis of a model for the distribution of some major colloid-chemical adsorption centers at the organo-mineral components of the soil colloids. It reflects the binding between the negatively charged colloids of the clay minerals and the humic substances from the one hand and the positively charged ionic and hydroxyl forms of the amphoteric elements, on the other.

INTRODUCTION

The highly stabilizing role of soil clays in modeling the structure of the soil adsorbent determines the importance of the colloid behavior of their major constituents in this process (Berry, L.G. et. al., 1987; Ganev, 1987; Ganev, S., 1990; 1971; Lazarov, D., 2001; Brindley & Brown, 1980; Tarasevich, J., 1988). Their high specific surface area and the presence of definite active centers contribute to sorption processes accompanied with changes in their structural – energetic condition.

In order to reveal the decisive role in the colloid-chemical behavior of the soil adsorbent, this review presents some major characteristics of the crystal structure of clay minerals and the role of their electronic configuration in the formation of the colloid-chemical character of their active centers (areas).

An emphasis is placed on their major differences and on this basis an attempt has been made to explain the major consequences of their impact on the character and the distribution of the adsorption centers. The clay minerals could be considered as complex adsorption systems with colloidal structure, built of a definite number of atoms bound with chemical bonds and therefore represent a unified multi-atomic quantum-mechanical system with multi-centre electronic orbitals possessing a translation symmetry.

BONDING CHARACTER IN THE STRUCTURAL PATTERN OF THE CLAY MINERALS AND SOURCES OF STRUCTURAL CHARGE

Clay minerals are secondary allumino-sillicates with a general formula $nSiO_2Al_2O_3.mH_2O$ and a characteristic mole ratio $SiO_2:Al_2O_3 = 2 \div 5$ depending on impurities and type and extent of isomorphism. Although some of the clay minerals are stable at very high temperatures, they can be also synthesized at ambient temperature, during various sedimentation processes, diagenesis [i] and weathering, as well as could be of biogenic origin, i.e. from mineralization products of plant residues.

Their common properties are the crystal layer structure, the colloid dispersion, the sorption characteristics and the presence of the constitutional water. Each group, however has specific behavior and importance in the formation and properties of the different soil types. On the basis of the structure of the crystal lattice of the majority of the clay minerals lie two structural patterns: Si-O-Si tetrahedral (T_d) and O-Al-OH octahedral (O_h). The alumino-sillicate minerals carry an electronegative charge, which determines the cation exchange properties. There exist two major sources for the origin of negative charges: (1) isomorphous substitution and (2) dissociation of exposed OH-groups.

(1) The permanent (pH independent) negative charge results from isomorphous substitutions or vacancies in the structure. Generally, Al^{3+} substitutes for Si^{4+} in tetrahedral coordination (T_d), and Mg substitute for Fe^{3+} or Al^{3+} in octahedral coordination (O_h). The isomorphous substitution takes place only with ions of comparable size, while the valency between substituted ions should not differ more than one unit. The chemical properties of the 2:1 clay minerals can differ in accordance with the position and quantity of structural charge. The structural charge is balanced by cations ("counterions") by or close to the clay mineral surface. The spatial distribution of the counterions actually affects the colloidal behavior of the clay minerals and one of the models describing the interfacial region is the *DDM (diffuse double-layer theory of Van Olphen)*.

(2) The appearance of OH groups on crystal edges or on exposed planes, can also give rise to negative charges. At high pH, these hydroxyls dissociate slightly and the clay surface acquires the negative charge of the O^{2-} ions. This type of charge is called variable or pH-dependant charge. The magnitude of the variable charge varies with pH and type of colloid.

Kaolinite and other 1:1 clay minerals usually have siloxane (Si-O-Si) surfaces on one basal plane and oxyhydroxide surfaces on other basal planes. Exposed hydroxyl groups can dissociate and play an important role in development of negative charge. Kaolinite also has subbasal hydroxyls surrounded by a network of oxygens from silicon tetrahedrons. However, due to electronic configuration of these octahedrons, the dissociation and consequent contribution to the overall negative charge of the subbasal hydroxyl groups may be rather small. There is some evidence (McBride, 1976; Lim, et.al., 1980) that kaolinites possess a small quantity of permanent charge and adsorb cations on planar surfaces.

Crystal-chemical nature of the structural units.

Tetrahedral layer (T_d)

In the tetrahedral structure Si atoms are surrounded by 4 O atoms. The binding between them takes place through overlapping of the innate sp^3-hybrid orbitals, resulting in the formation of 4σ-bonds (Fig.1).

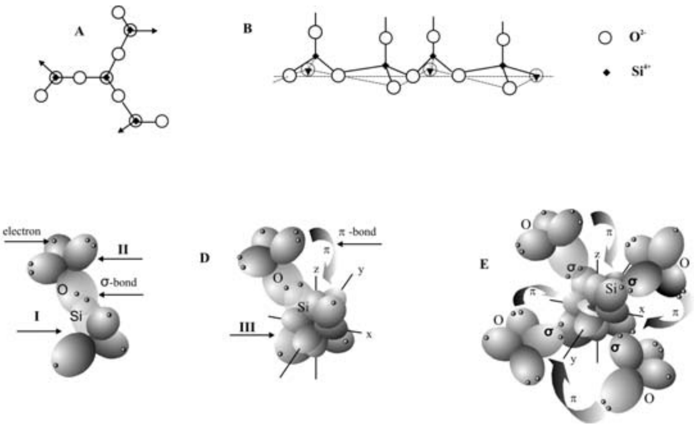

Fig. 1. *Formation of tetrahedral layer of clay minerals:*
A *– fragment of the hexagonal network of the repeating fragment with composition* $(Si_4O_{10})^{4-}$*;* ***B*** *– schematic representation of the basal surface, formed by the fragment* $(Si_4O_{10})^{4-}$*. With flashes are marked the ions of the oxygen, which belong to other structural fragment;* ***C*** *– formation of* ***σ****-bond between silicon and oxygen:* ***I*** *–* sp^3 *hybridisation of the silicon atom;* ***II*** *-* sp^3 *hybridisation of the oxygen atom;* ***D*** *– formation of the* ***π****-bond between silicon and oxygen:* ***III*** *– sterical configuration of the four* sp^3*-hybrid orbitals and two free d-orbitals* (d_z2; $d_x2_{-y}2$) *of the silicon;* ***E*** *– chemical bonds in a fragment of the tetrahedral layer.*

Since every O atom is bound to two Si atoms, its second sp^3-hybrid orbital is overlapped with the respective orbital of the neighboring Si atom. The other ready electron pairs on the remaining two hybrid orbitals additionally strengthen the σ-bonds through overlapping with free d-orbitals of the outer electron layer of Si.

This is the way of formation of donor-acceptor interaction and respectively π-bonding with the participation of the ready electron pair of the atom bonded to Si and Si free d-orbital[ii]. The formation of a π-bond strengthens the σ-bonds between Si and O and predetermines the stability of the tetrahedral structure of layer silicates.

Octahedral layer (O_h)

The other major construction element of layer silicates is composed of two layers tightly packed O atoms and OH groups and between them are situated the atoms of Al, Fe or Mg (Fig.2). The central cation is surrounded by 6 anions each situated on the top of O_h e.g. for the Al atom the formula is $[Al(OH)_6]^{3-}$. Since the anions belong to adjacent O_h the resulting net formed is called the "O_h layer". This type of structure is characteristic of the minerals gibbsite [$Al(OH)_3$] and brucite [$Mg(OH)_2$].

In the structure of gibbsite (Fig.2) the atoms of Al in the octahedral coordination leave six sp^3d^2-hybrid orbitals, thee of which possess one electron. The binding between the Al atoms and the OH-groups through σ-bonds is carried out through overlapping of the hybrid orbitals. There is also a possibility of leaving ready electron pairs of the O-atoms for a formation of a d_π-p_π-bonding and a realization of a π-bond (Fig.2).

With two orbitals of one O atom are formed two valent bonds: one with the H atom and another "resonance" bond with two atoms of Al. The rest two hybrid orbitals with ready electron pairs, and at suitable geometry could overlap with free sp^3d^2-hybrid orbitals of Al.

The mobility of the donor electrons and π-electrons allows their transition from one atom to another. This results in delocalization of the orbiltals, enveloping several atomic nuclei. Each of the O-Al- bonds might be presented as 1/2σ- and 1/2dπ-pπ-bond. The lack of symmetry of the charge centers predetermines also the realization of H-bonds between adjacent OH groups. Because of the accumulation of the above-mentioned phenomena, around the Al-OH motif a dipole field is formed whose influence is induced over the molecular field of the entire crystal lattice.

Electric neutrality of the package

The thermodynamic prerequisite for electric neutrality requires the compaction of one O_h layer and one T_d layer in an electroneutral package (Fig.3). The neutralization between the positive and the negative ion charges takes place through the adjacent intermediate layer of O and OH anions of the neighboring layers. Generally judged their condensation leads to the formation of mixed T_d-O_h packages and actually to formation of specific clay mineral structures. They can consist of two separate layers (two-layer structure or 1:1 type of minerals: kaolinite, dikite, halloisite), but also the O_h layer may be inserted between two T_d layers (three-layer structure 2:1 type of minerals: smectite, beidellite, muscovite, vermiculite, hectorite, etc.), Fig.3.

The electronic configuration of the unified layers in the two-layer package (e.g. in 1:1 minerals such as kaolinite) and the bonds distribution in the T_d-coordination of Si and the O_h coordination of Al with the strongly electronegative ligands of O (respectively OH-groups) has the following peculiarities:

- Increased electronic density in the outer surface planes relative to the inside of the package;
- Appearance of H^+-cations on the basal plane of the T_d layer in acid medium provokes the formation of H-O bonds;
- Formation of hydrogen bonds takes place also between adjacent OH groups on the basal plane of the Al-OH motif;

- Formation of inner structure bonding between the O_h-OH groups and the common to Si and Al oxygens;
- The σ-bond between the atomic orbitals of Al and O (sp^3d^2-sp^3) is weaker than the σ-bond Si - O (sp^3-sp^3);
- Formation of π-bonds strengthens the σ-bonds.

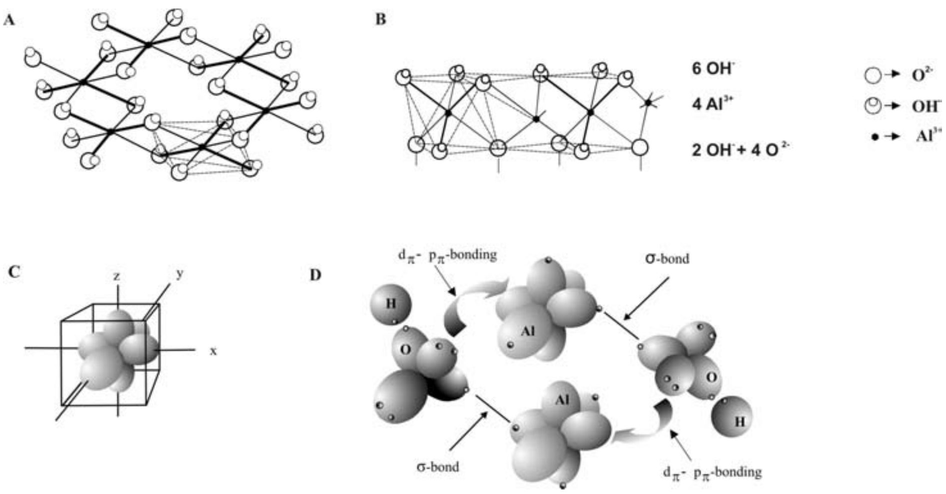

Fig. 2. *Formation of octahedral layer of clay minerals:*
A *– single layer from the structure of the gibbsite where Al occupied 2/3 of the octahedral positions;* ***B*** *– schematic representation of the basal surface, formed by the fragment* $Al_4O^4(OH)_8$*;* ***C*** *–* sp^3d^2*-hybridisation between one s-, three p- and two d-orbitals;* ***D*** *– formation of* ***σ****- and* ***π****-bond (*d_π*-*p_π *- bonding) between aluminium and oxygen in a fragment of the octahedral layer.*

CONSEQUENCES TO THE CRYSTAL SURFACE OF CLAY MINERALS

In order to clarify the participation of the clay minerals (e.g. kaolinite) in the formation of the soil adsorbent and its colloid and chemical behavior, some major consequences resulting from the character of the electronic configuration and the types of bonding on the crystal surfaces are important, i.e.:

- The decreased electronic density in the oxygen area on the basal plane of the T_d layer because of appearance of exchangeable H+-cations increases the polarity of H-O bonds and respectively the acidic character on the surface of the hexagonal rings.
- The delocalized multi-centre electronic configuration in the area of the hexagonal gibbsite layer on the O_h-plane creates non-symmetrical dipole field. Its characteristics are determined by increased electron density around OH-groups and the appearance of partial positive charge in the vicinity of Al atoms.

- The different length of Si-O-Al bonds may cause a change of the T_d coordination and the presupposed allowed angle of Si-O bond orientation, and may lead to geometry deformations in the crystal structure. A possible consequence is a shift of the ideal hexagonal symmetry formed by inclination of the oxygens towards the gibbsite layer with following deformation of the T_d layer. This is a reflection of the appearance of the partial charges both in the area of T_d bonded with Si oxygens and in the vicinity of the octahedral Al.

Some peculiarities in the behavior of soil clays in real conditions are probably consequences of the influence of such deformation effects.

The presence of colloid hydroxyl forms of some polyvalent cations on the strongly acidic planes of the clay minerals in acid soils might be a result of the above-mentioned speculation in addition to structural defects in the crystal structure caused by isomorphous substitution in the lattice. The presence of heterovalent isomorphism Mg^{2+} - Al^{3+} in the surface and near surface octahedral AlO (OH) planes leads to a stronger polarization of the OH groups bonded to Al and Mg and respectively increases the acidity of these groups.

Aluminum, for instance initially plays the role of a central atom in the O_h layer of the package. In the gibbsite structure, each hydroxide ion is situated above the two cations and above the respective cavity. Its oxygen is oriented towards aluminium, and the hydrogen towards the outermost coordination relative to Al. All this results in the change of the angle of hydroxyl ions position relative to the gibbsite surface. Such geometry will pull up the proton to the bridge oxygen (Si-O-Al) between the two layers of the package. Because of the orientation effect and the induced interactions, a hydrogen bond is formed. That's why prerequisites occur for local shrinking of the O_h layer, followed by the reciprocal reaction also in the T_d layer of the package. In strongly acidic medium the H^+ ions can easily migrate inside the crystal lattice. Their hydrolytical attack may be directed both to the surface OH-groups[iii], and towards the bridge oxygens between the atoms of Al and Si. The hydrolysis process of Al (having a central place in the octahedral) leads to accordingly hydroxyl- and aqua- complexes of Al[iv]. Its coordination in the lattice structure is disturbed and allows movement of the complexed forms towards the negatively charged centers of the basal planes.

The actual presence of these colloid forms of Al in the cavities of the crystal structure and in the vicinity of its initial coordination center maintains the level of its partial positive charge. This charge is transmitted (induced) on the outer crystal surfaces. The comparatively higher dimensions of this colloid may cause inner tension in the structure and appearance of secondary deformations in its geometry. Its "emerging" on the basal plane will neutralize part of the negative charges and respectively will decrease the cation sorption capacity and facilitate the package interaction[v].

Consequently positively charged zones may appear also on the basal plane of the T_d layers, as a result of the destructive role of acidification and the following "emerging" of colloid forms of Al for neutralization of part of the negatively charged geometric centers. The behavior of the hydrolyzed forms of the transition elements on the surface of allumino-sillicates probably also depends on similar geometric deformations. It was shown (Atanassova and Ilieva, 2003) that the pH-dependant specific sorption (basied on the discrepancy between Cu^{2+} adsorbed/Ca^{2+} desorbed shifted to the lower pH (< 4) with increasing Cu concentrations and specific sorption with kaolinite was recorded even at pH 3.6. The surface of kaolinite exhibited a higher affinity for Cu (log K_d values of the distribution coefficient) with increasing pH than the smectite and vermiculite surfaces (Atanassova I., 1995)

Fig. 3. *Formation of the combined package of kaolinite (A) and montmorilonite (B) and chemical bonds between silicon-oxygen and alumo-hydroxylic layers (C).*

The exchangeable Cu on the smectites may exist as aqua complex such as Cu $(H_2O)_6^{2+}$ but also as a hydroxo-complex $CuOH^+$. This specific sorption indicates a stepwise dehydration (McBride, M. and M. Mortland, 1974), which in turn facilitates the shrinking of the ions in the hexagonal cavities and occupying free O_h pozitions. This results in the in layer charge reduction and impossibility for further resolvation.

Therefore, in some cases the geometric position of the OH groups should open the space above the Al atoms in their O_h coordination, thus increasing their susceptibility to cationic attack and facilitating the isomorphic substitution. Such interactions induce considerable changes in the ion-exchange properties of clay minerals. The lower sorption capacity of the O_h surfaces relative to the T_d ones and the smaller distance between the packages of clay minerals such as kaolinite can be explained with the above mentioned arguments.

CONCLUSIONS

The specific electronic configurations influence the acidic properties of the basal Si-O-Si planes of the clay minerals. These properties are formed through the negative charges derived from heterovalent isomorphism in the crystal lattice. The weakly acidic ion exchange positions (variable charges) originate from ionizing OH-groups pertinent to Al-OH surfaces.

Adsorption properties on the clay minerals are a function of the density and distribution of centers of different origin over the entire surface. Part of them occupy separate sections of the alumino-silicate crystal lattice and possess a comparatively regular geometric configuration characteristic of the clay type. The appearance of amorphous structures on the crystal planes cause the formation of the so called zones with colloidal nature (rather different from the regular “geometric” types of zones), which in turn can migrate both inside and outside the clay structure.

The partial neutralization of clay minerals inherent charge and the appearance of positively charged portions favor the “bridge” binding of the clay minerals with the humic substances. This binding may possess both: (1) “point-like character”, in case of a strict geometric distribution of the bonds with the polyvalent cations and the appearance of H-bonds and (2) “zone-like character” as a result of the electrostatic interaction between colloids having alternative electric charge.

These views are on the basis of a model (Raychev, T., et al., 2001a, b) for the distribution of some major colloid-chemical adsorption centers on the organo-mineral components of the soil colloids. This model relies on the standpoint for the possible binding between the negatively charged colloids of the clay minerals and the humic substances from the one hand and the positively charged ionic and hydroxyl forms of the amphoteric elements, on the other in the form of a “sandwich-like” charged colloid structures.

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[i] Geological process of transformation of sedimentation products into rocks.

[ii] The presence of free d-orbitals of Si leads to compexation and attaining of a maximum coordination number. In some cases sp^3d^2-hybridization and coordination number 6 is attained.

[iii] Accompanied by formation of H_2O and H_3O^+.

[iv] $[Al(OH)]^{2+}$; $[Al(OH)_2]^+$; $[Al(H_2O)_6]^{3+}$ etc.

[v] With some preconditions, it may be speculated that a complexation process takes place between the central ion with colloidal nature (coordination number is difficult to determine) from one hand, and from another the OH and/or O ligands belonging to the basal and/or edge surfaces of soil clays.

PHYSICO-CHEMICAL ASSESSMENT OF HUMUS SYSTEM STABILITY

Raytchev T., Filcheva E., Sokolowska Z.

SUMMARY

This paper performs discussions on the possibilities of differential-thermal analysis and method of thermal-oxidize destruction for establishing the connection between stability and genetic peculiarities of formed humus substances. These considerations are based on both, published papers and commonly used extraction procedures, detrmining humus composition. It is shown how bio-chemical transformation course of organic substances reflect on the dynamic character of new-formed organic compounds, their colloid-chemical behavior and the relationship between oxidize stability and principle different functions in formation of soil microstructure. The paper performs the priority of thermal analysis in investigation of individual nature of humus substances with different genesis without preliminary extraction from soil. This method independently with no other analytical methods gives only qualitative idea about the principle participation of the individual components in the structure of the soil adsorbent.

Priority of proposed fractional scheme and elaborated analytical method of the oxidation-thermal destruction of humus substances consist in the possibility for identification of the components during their decomposition. The problem connected with changes of their natural state is solved by analysis of samples in their native state.

The proposed fractional scheme gives an information on the behaviour and structural features of the groups of soil humus substances, carbon content and the oxidation state of different fractions by analysis of samples in their native state. The possibility for application of data obtained is in a great importance for studies on colloid-chemical state and stability of soil adsorbent, and as indicators of anthropogenic impacts on the ecological media of its formation.

INTRODUCTION

Recent investigations on the improvement the efficiency of commonly used meliorating agents to neutralize toxic soil acidity and possibilities for elimination some difficulties in connection with their application, allow to develop new approaches for rehabilitation of productive and ecological functions of agricultural lands in regions, polluted with heavy metals. (Raytchev, 1996; Arsova and Raichev, 2000; 2001; Raytchev et al., 1999; 2001a,b; 2002). The base of these assumption states complex formation with soil organic matter; chemical sorption on the iron- and aluminum oxides with high specific surface; coordination in octahedral Al-Si minerals and admixed occlusion (Chouldjian 1978; Filcheva 1976; Atanassova 1993, McBride 1981; Hodgson 1965; Boldyrev 1983; Charlot 1969;

Friedrichsberg 1984; Ganev 1990; Jozefaciuk et al. 1992; Orlov 1985; Shnitzer 1991).

The positive result of model testing put the question about quality of the organic components of the proposed organo-mineral meliorants. One of the requirements is the addition of organic material (OM) having high degree of humification ("maturity"). Nevertheless the question is discussible, it is considered that organo-mineral complexes of heavy metals with humus compounds in the initial stage of humification in some cases increase elements solubility with alkalization the media. This is ground to study the relationship between structural stability and steric features of organic compounds as components of soil organic matter and to discuss the possibilities of the methods applied for this purpose.

Principal different functions of humus substances in formation of soil micro structure are defined of genesis of soil adsorbent and conditions for its formation.. The quality of humus system is a result of natural selection during the biochemical transformation of death plant and animal residues in the soil. The result of this process is grouping in different according to their stability fractions, which reflect the genetically features. This is a ground of commonly used schemes for their identification and distributions in groups and classes on their general signs (Orlov, 1985; Schnitzer, 1991; Kononova, 1966; McKeague, 1986; Stevenson, 1982**)**.

The main disadvantage of extractable methods is creation conditions for changing the structural fragments of humus substances and destruction of their native status. The nature of strongly bound humus fraction with mineral phase, which can not be extracted with conventional methods, could not be clarified. Extraction procedure takes 15-20 hours for contact between soil sample and extracting reagents. Filtration and additional operations complicate and slow up the analytical process. This way it creates circumstances for interactions between alkali extracts and atmospheric CO_2. These are only the reasons why the soil organic matter composition has only the informative character regarding participation of its separated components in colloid-chemical structure of soil adsorbent.

Data of thermal analysis relatively well present the individual nature of humus substances with different origin. On the base of distinguished three structural units: aliphatic, aliphatic-cyclic and cyclic could evaluate the degree of aromatization and thermo stability of the constructed components (Orlov, 1974, 1985). Standpoints of the most investigators, concerning processes of humification and humus accumulation, give grounds to accept the thermal analysis as appropriate one for analyzing the genesis of humus system and evaluation of its peculiar components. Analysis of the extracted humus substances limited its significance. This is a reason to develop a comparative study on the possibility that method to be applied for measuring reliable data analyzing soil samples in their native state. (Raytchev et al., 1984a, 1984b; Raytchev, 1996).

MATERIALS

Samples of surface horizons of leached smolnitza (Vertisol, FAO), leached chernozem (Haplic Chernozem), grey forest soil (Haplic Luvisol), light grey forest soil (Eutric Planosol) were analysed. The studied soils are related to the different taxonomy units and varied in humus content, particle size distribution, pH and CEC. Four types of treating were studied: no preliminary treatment; treated by H_2O_2; saturated with humus substances; treated by H_2O_2 and humus substances. Thermal destruction of humic acids got: after straw decomposition (3 and 12 months); coal and studied soils was traced out (Kononova, 1966).

The investigated soils form the descending order as follows: Vertisol > Haplic Chernozem, Haplic Luvisol > Eutric Planosol, as a rezult of aromatic share in the soil organic matter. The thermal analysis of the soil samples in natural state comperatively well shows the correlation between stability and genetical features in the structure of the humus system. In the progress of the oxidazability the thermal stability increases.

RESULTS AND DISCUSSION

On the base of the rate of oxidation and thermal stability soil organic matter of both soils Eutric Planosol and Vertisol could assign to the opposite types of plants transformation: initial stage of humification and maximal aromatization, respectively. High bio-chemical activity leads to braking off the peripheral chains from the molecules of humic acids and accumulation of the most stable components. Fulvic acids, which are more available to microorganisms, decrease. Podzolic soils, characterized with lower bio-chemical activity, consist humic acids enriched with peripheral chains and fulvic acids with carbon. This reflects to the ratio Ch/Ch. Analiysis of more number of soil samples from the main soil types of Bulgaria confirm the genetic affiliation and evaluation nature. The humus system form the order (Table 1)

Table 1. Ratio(A/B) between low -(A) and high temperature (B) fractions of humus substances in the studied soils

Soil Type (FAO, 1997)	A / B
Eutric Planosol	2.0
Haplic Luvisol	1.4
Luvic Phaeozem	1.2
Chromic Luvisol	1.0
Haplic Chernozem	0.8
Eutric Vertisol	0.6

Well-expressed relationship between stability and genetic features in the humus structure is grounds to accept thermal analysis as an appropriate one in analyzing components of soil organic matter with no preliminary extraction, followed by destruction of soil samples. It could be accepted that during thermo destruction a fractionation accomplished, but the identification of their structural components is complicated or even impossible. This needs a preliminary extraction and analyzing of humus substances where the disadvantages of the applied methods and changes of the native state of the studied samples are occurred. Thermal analysis combined with appropriate chemical methods of investigation allow to establish a relationship between genesis and evolution level of humus fraction and their specific participation in creation of colloid-chemical structure of soil adsorbent (Duchaufour, 1968, 1972). Stereo features are formed in the initial stages of decomposition of death plant and animal residues, included in the solid phase of their bio-chemical transformation. Components of soil organic matter, which are not involved in these processes, are refereed to this phase. Intermediate products, formed during the elementary parallel, induction, and sequential reaction catalyze the following ones namely between main sources of humus substances and natural humus substances. Their different thermo destruction and constant synthesis started in each stage of destruction leads to formation of semiliquid phase. It contains products, released by enzymes, and which have high activity and colloid-chemical properties. It could presume that an intermediate phase originates contained biological mixture of substrate and enzymes in different state of biochemical commitment. (Figure1).

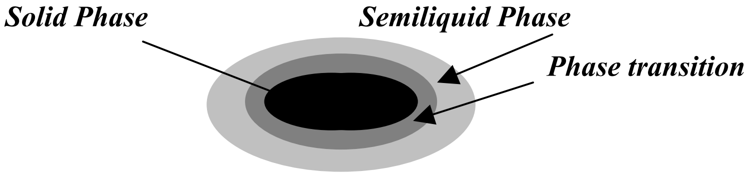

Fig. 1. *Scheme of dynamic three phase distribution of soil organic matter components included in the biochemical transformation*

When export of intermediate product absence, favorable conditions for parallel reactions of synthesis are created. This leads to formation of specific humus substances and corresponding destruction. Domination of mineralization processes will exclude the carbon mass out of the system and this would transmit a subside type of the wave character of common cycle of the transformation. In chemical point of view, group of unstable organic compounds (its content changes fast) contains unspecific compounds, hydrocarbons, polypeptides, lipids, chlorophyll, and pigments. It could be expected that microorganisms consumed it as source of energy and reserve of nutrients. Humic acids, fulvic acids, lignin and polysaccharides are referred to more stable substances.

It is necessity to indicate, that simple static concept of molecular structure is not applicable for humus macromolecules. This concept have to be accepted in wider significance i.e. including not only process of their formation, but their different dynamic behavior. This is not a chance, it is an integral characteristic of biomolecules, that determine its dynamic structure and biological function. The most important steric features of these high moleculer formations are connected with flexibility of the chain. The last one decreases with enhancing with both, number of the polar groups and size of the steric net. This property is of great importance, allowing formation of "clatrate" compounds, where molecules are bounded mechanically, thanks to its steric configuration. Elasticity and high activity of the organic fragments facilitate formation of stable adsorption - solvate layers on the mineral colloids' surface, constructed the organo-mineral nucleus of soil adsorbent. New organic molecules could be sorbed on this stabilized organo-mineral layer via polyvalent ions and surfaces with polymerized units with highly performed aromatic character are formed.

The investigation on kinetic of oxidazable thermodestruction shows that the progress of that process depends on the stability of the components corresponding to their structural features. The results obtained give a reason to define two hidhly differentiated humus fractions according to their thermal stability marked as A and B. Fraction A includes mainly organic compounds with aliphatic structure enriched in -OH, -COOH and other functional groups. These can be connected to the aromatic compounds as well. It is the most dynamic part of the humus and organic substances received into the soils. The humus substances of fulvic type enriched in -OH and -COOH groups as well as the organic substances which components are in the initial stage of humification are included in fraction A. Because of its instability and specific susceptibility to the changes in the environment this fraction gives a dynamic character of the properties of the colloidal soil formations. The degradation of fraction A needs relatively low energy. Fraction B is formated mainly by aromatic compounds and components of the humus compounds with maximal degree of aromaticity. If the conditions for their formation are changed, part of its components could be stabilized and the other part - disintegrate to more unstable components. The latest one gives the possibility to natural transfusion from one to another combination. Formation of organo - mineral compounds and the high oxidation state stabilises fraction B to biodegradation. This fraction is structural formation and stabilized colloid-chemical state of soil adsorbent. Their typical representatives are humin (unextractable carbon) and compounds that are in the composition of anthracite. More energy is needed to destroy fraction B.

On this base a method for realization the fractional scheme was develop. The defects of the extraction methods and the limitations in the thermal analysis are avoided by study the kinetics of the process analysing samples in their native state.The analysis during the destruction reduce the risk of changes in their native state. (Raytchev, 1996; Raytchev T. et al., 1993). Comparative study was carried out in order to clarify its possibility. Samples of surface horizons of leached smolnitza (Vertisol, FAO), grey forest soil (Haplic Luvisol, FAO), light grey forest soil (Eutric Planosol, FAO) and coal were analysed (Raichev, 1992). The studied soils are related to the different taxonomy units and varied in humus content, particle size distribution, pH and CEC. These samples are analyzed according to the method of Kononova-Belchikova (Kononova, 1966) and ratio between fraction of humic and fulvic acids was determined. .

Thermogravimetric data and energetic parameters show strong correlation with proportion of their alifatic and aromatic components. On this base the investigated soils form well distinguished evolutional order reflected the intramollecular differentiation of the organic components in humus composition

Using DTA method the proportion between low- and high temperature fractions: A and B was measured. Data obtained were compared with ratio CA/CB, where CA = organic carbon content of labile fraction and CB organic carbon content of high oxidize fraction (Table 2).

Table 2. Parameters of soil organic matter

	Soil			
	Light grey forest soil (Umbric Planosol)	Grey forest soil (Chromic Luvisol)	Leached smolnitza (Peleutric Vertisol)	Coal
C (I), %	0.99	1.03	1.88	38.4
C (II),%	1.09	1.04	1.75	
T_M, ^0K	381.7	379.5	380.4	380.4
C_A, %	0.81	0.75	1.13	10.3
C_B, %	0.18	0.28	0.75	28.1
C_A/ C_B	4.5	2.7	1.5	0.4
C_f/C_h	4.2	1.9	0.3	
C_h/C_f	0.24	0.54	3.26	
w, %	-10.1	-0.5	6.9	
$F = \frac{172.414}{100 - W(\%)}$	1.565	1.716	1.836	
humus, %	1.71	1.78	3.23	
humus, % (F)	1.55	1.77	3.45	
N* N**	0.100* 0.096**	0.120 0.112	0.150 0.130	

Abbreviations: C (I) - C content in sample, corresponding to CO_2 measured during destruction process; C (II) - C content in sample, measured as CO_2, released as a result of reduction of the oxidizing agent excess; N* - N content (Kjelhdal method), measured after ending the destruction; N** - N content (Kjelhdal method), measured after destruction

The adequateness of proposed fractional scheme is proved via similar results obtained, analyzing samples applied methods mentioned above (Raichev, 1992).

An additional indication for application of this method in the condition of Na salinity is absence of high oxidized components in the humus system, specific for sodium-sulfuric solonchak-solonetz (Plovdiv region). This is in correspondence with its genesis - alkali reaction does not allow formation of stable organic structure and humus substances are presented as soluble sodium fulvates.

CONCLUSIONS

The dynamic character of new-formed organic structures in the biochemical transformation of organic substances in soils reflected on their colloid-chemical behavior. Their flexibility and high activity facilitate construction of organo-mineral nucleus of soil adsorbent. The different state of chemical commitment between organic fragments and mineral colloids determine connection between oxidizing stability and functional specificity. This is in the grounds of the common schemes and methods for identification and distribution groups and classes on the base of their common features.

Their main disadvantage could be generalized as creation conditions for changing of their structural fragments and destruction of their native state. The nature of strongly bound humus fraction with mineral phase, which can not be extracted with conventional methods, could not be clarified. Thermal analysis, if not combined with other analytical methods, cannot answer the questions about the principal contribution of the individual components of humus substances in forming the soil adsorbent's structure. Proposed fractional scheme and analytical method for its realization allow parametric of humus compounds concerning its carbon content, degree of oxidation and qualitative participation of structural determined part of humus in the soil adsorbent. During this fractionation differentiated transfer coefficients *organic carbon-humus* are obtained. Identification of the components during destruction is one of the main advantage of this scheme, thanks to the less changes in their native state.

Application of the results obtained using described methods for analyzing of humus system is of a great importance for studying colloid-chemical behavior and stability of soil adsorbent, and for indication of changes, connected with natural and anthropogenic impacts on the ecological media of its formation.

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RAINFALL IMPACTING ENERGY ON SOIL WITH VEGETATION COVER

Rousseva S.

Vegetation, being the most important component of ecosystems, reduces the erosion rate by weakening the impact and intensity of rainfall, by increasing the resistance to water flow through the enlarged by plants hydraulic roughness, by decreasing the total amount of water available to transport sediment and by changing the drop-size distribution of rainfall. Considering the present state of knowledge on role of vegetation during rainfall event, a mathematical model is developed to relate the impacting energy of rainfall on soil covered with vegetation to rainfall and vegetation characteristics. The developed model is illustrated by estimates of the impacting energy of 30 mm rainfall of intensity 30 mm h^{-1} on four crop types: wheat, maize, alfalfa and apple orchard. The soil erosion impact is assessed for the period May – August considering the highest probability of erosion events for this period of year. Estimates using the proposed equation are proved to be reliable by comparing them with assessments of an already approved model for calculating the kinetic energy of the leaf drainage. The approach is applied for the purposes of a geographic information system for soil erosion risk assessments on the territory of Bulgaria at a scale of 1: 100 000 based on the USLE approach.

INTRODUCTION

In order to develop sustainable systems of agriculture that satisfy the present and the future needs of the mankind, there must be reliable information on the constraints and potential of the land resources. The UNEP Project GLASOD (GLobal Assessment of SOil Degradation) recognized erosion by water as the most important soil degradation type, representing more than a half of all soil degradation.

Soil erosion by water refers to a series of processes leading to soil depletion and export of sediment. It takes place through three main processes: (i) mechanical disruption, slaking, compaction, dispersion and detachment of soil particles, aggregates and clods from the soil mass due to the impact of raindrops and the overland flow; (ii) movement of detached material by gravity or by overland flow and (iii) deposition. Planning for soil and water conservation measures requires knowledge of the relations between the driving forces that cause loss of soil (e.g. the erosivity of rainfall, the slope of the land, the erodibility of soil) and the factors that help to reduce such loss (e.g. the plant cover, the conservation practices and measures, the soil resistance).

Vegetation, being the most important component of the ecosystems, modifies the impact of rain on soil. Vegetative canopy influences soil and water losses by changing the impact and intensity of rainfall, the resistance to water flow through the enlarged by plants hydraulic roughness, the total amount of water available to transport sediment and the distribution of throughfall (Haynes, 1940; Morgan, 1980). It has been known at least since 1916 that plants intercept and transmit rainwater down their stems (Kiesselbach, 1916) and at least since 1948 that vegetation canopies change the drop-size distribution of rain and that splash detachment under canopies is different from that on a bare soil (Chapman, 1948). For the time being, it has been known that vegetation affects the rainfall impact on soil through storing rainwater on leaves and branches (intercepted store), transmission of rainwater down the leaves, branches and stems to the ground (steam flow) and transformation of the rainwater to water drops drained from the leaves (leaf drainage).

In spite of numerous observations and recorded measurements of interception store, stem flow and leaf drainage, few have attempted to describe the relationships between vegetation properties and soil erosion processes. Merriam (1973) suggested an exponential relationship to model the volume of the interception store depending on the rainfall volume. De Ploey (1982,1984) developed a general model for the stemflow phenomena on grasses and trees, which was subsequently modified by Van Elewijck (1989a, b) for field crops. Thus, the volume of stemflow was modelled as a function of the temporary intercepted by vegetation rainfall and the average acute angle of the plant leaves and branches to the plant stems. Based on numerous studies, Brandt (1989) showed that drop sizes of leaf drainage were sensitive neither to rainfall intensity nor to the canopy structure or leaf characteristics. He suggested that normal distribution of water drops with a mean diameter between 4.52 and 4.95 mm and a standard deviation between 0.79 and 1.3 mm might adequately simulate the leaf drainage. Brandt (1990) estimated the impacting energy of the modified by vegetation rainfall as a function of the effective height of the plant canopy. From all these studies, the variables important in controlling the vegetation effects on the rainfall impact on soil can be identified as: rainfall intensity, duration of rainfall, canopy cover, plant height, size and orientation of leaves, and development of canopy.

The aim of this lecture is to present a deterministic approach for estimating the impacting energy of rainfall on soil with vegetation cover depending on the plant growth stage. Application of the approach for soil erosion risk assessment is demonstrated as well.

CONCEPTS

Considering the present state of knowledge about the role of vegetation during rainfall event, the net volume of the rainfall (*NR*) at any moment (*t*) after the start of rain can be considered as a sum of four portions: (1) rainfall directly reaching the soil (*DR*); (2) rainwater intercepted by the vegetation (*IR*); (3) rainwater reaching the ground through flow down the leaves and stems (*SF*) and (4) rainwater reaching the ground as modified by the vegetation rainfall (*MR*) (Rousseva, 2000): that is conceptually presented (Fig.1).

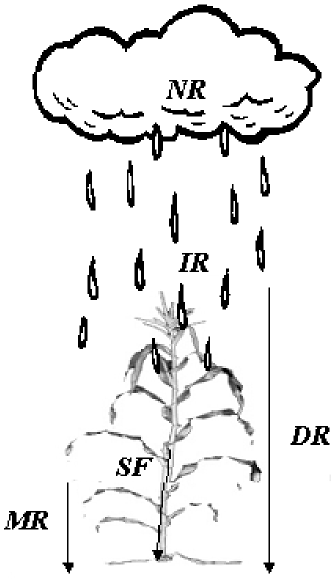

Figure 1. *Conceptual presentation of the net volume of the rainfall (NR) as a sum of four portions: (1) rainfall directly reaching the soil (DR); (2) rainwater intercepted by the vegetation (IR); (3) rainwater reaching the ground through flow down the leaves and stems (SF) and (4) rainwater reaching the ground as modified by the vegetation rainfall (MR)*

If so, one can write:

$$NR(t) = DR(t) + IR(t) + SF(t) + MR(t). \qquad (1)$$

With respect to soil erosion, *IR* and *SF* do not directly contribute to soil detachment. Hence, the net rainfall impacting energy on soil with vegetation cover (KE_{imp}) should be considered for *DR* and *MR*:

$$KE_{\mathrm{imp}}(t) = KE_{\mathrm{DR}}(t) + KE_{\mathrm{MR}}(t). \qquad (2)$$

To resolve equation (2), we should take into account the following relationships.

- $DR(t)$ is proportional to $NR(t)$ with coefficient of proportionality equal to the portion of the soil that is not protected by the vegetation canopy:

$$DR(t) = (1\text{-}c)\, NR(t)\ ; \qquad (3)$$

- the model of Van Elewijck (1989a, b), modified by Morgan et al. (1998) for the stemflow is:

$$SF(t) = 0.5\ (TIF) \cos\alpha\ ; \qquad (4)$$

- the sum of $IR(t)$ and $SF(t)$ is actually the temporary intercepted by vegetation rainfall (*TIF*):

$$TIF(t) = IR(t) + SF(t)\ ; \qquad (5)$$

- the model of Merriam (1973) for the interception store is:

$$IR(t) = IR_{\max}\,\{1 - \exp[-\,DR(t)/IR_{\max}]\}. \qquad (6)$$

Substituting equations (3), (4), (5) and (6) in equation (1), resolving it for MR(t) and taking into account that:

$$EK_{\mathrm{MR}}(t) = 0.5\ V^2\, MR(t)\ , \qquad (7)$$

$KE_{\mathrm{DR}}(t) = (1\text{-}c)\, KE_{\mathrm{rain}}(t)$, (8)

we obtain an equation for estimating the impacting energy of rainfall on soil with vegetation cover at any moment (t) after the start of rain:

$$EK_{\mathrm{imp}}(t) = (1\text{-}c)EK_{\mathrm{rain}}(t) +$$

$$0.5(1\text{-}0.5\cos\alpha)V^2 \int_0^t \{cDR(t') - IR\max\{1 - \exp[-DR(t')/IR\max]\}\}dt', \quad (9)$$

where: $EK_{\mathrm{imp}}(t)$ is the impacting energy of rainfall on soil with vegetation cover, J m^{-2}; $EK_{\mathrm{rain}}(t)$ is the impacting energy of rainfall on bare soil, J m^{-2}; c is the crop cover, expressed as a portion of the ground area covered by vegetation canopy ($1 \geq c \geq 0$); α is the average acute angle (degrees) of leaves and branches to the plant stem; V is the fall velocity of the drops dripping from the vegetation on the soil, m s^{-1}; DR is the volume of rainfall, mm; $IR_{\max}$ is the maximum volume, mm, of the interception store for particular crop or vegetation cover.

Equation (9) is applied to estimate the impacting energy of 30 mm rainfall of intensity 30 mm h^{-1} on four types of agricultural plants: wheat, maize, alfalfa and apple orchard for the period May – August when the highest probability of erosion events exists (Rousseva, 2000). The input parameters needed for resolving equation (9) were set in accordance with data from measurements presented in different literature sources as follows:

- impacting energy of the simulated rainfall was set as 30.278 J m^{-2} mm^{-1} (Rousseva et al., 2000);
- average monthly portions of ground covering (c) by wheat, maize, alfalfa and apple orchard (8 x 8 m) were calculated from the decadal measurements by Roshkovan (1988) for May, June, July and August;
- drop fall velocity (V) was evaluated after Laws (1941), considering average diameter of dripping from vegetation drops of 4.8 mm (Brandt, 1989) and effective height of fall (H_{eff}) – 75 % of the vegetation height. Average monthly heights of wheat and maize were calculated from the measurements by Daskalov et al. (1994) for May, June, July and August, and these of alfalfa and apple trees were set according to Morgan et al. (1998);
- values of the maximal volume of the interception store (IR max) for mature wheat, maize, alfalfa and apple orchard according to Morgan et al. (1998) were considered for the maximal vegetation cover gained by particular plant and reduced in accordance with the values of c;
- Values of the average acute angle of plant leaves and branches to the stem were set according to Morgan et al. (1998).

Table 1 shows the values of the input parameters for calculating the energy of impact on soil with vegetation cover according to equation (9). Listed input values describing the alfalfa and apple ecosystems are mean values for the whole period May – August since these do not vary much during this period (Roshkovan, 1988) considering mature plants. Alfalfa mowing has been neglected in these estimates. It is assumed that wheat is harvested by the end of July while the fields covered with wheat have not been ploughed yet in August. Data, presented in Table 1, show that the values characterizing the vegetation effects on the impact of rainfall on soil can vary in broad ranges not only with respect to the type of vegetation but with respect to the growing stage as well. Thus, strong variability of both estimates of the impact energy and the parameters controlling the impact energy can also be expected.

Table 1. Values of the input parameters for equation (9): c is the crop cover; α is the average acute angle of leaves and branches to the plant stem; H is the height of vegetation; V is the fall velocity of the drops dripping from height of $0.75H$; IR max is the maximum volume of the interception store for particular crop or vegetation cover.

Vegetation	c	α^{o}	H (m)	V (m s^{-1})	$IR_{\max}$ (mm m^{-2})
Apple orchard	0.55 [a]	10 [b]	5 [b]	7.44 [d]	0.50 [b]
Maize-May	0.02 [a]	10 [b]	0.15 [c]	0.50 [d]	0.02 [e]
Maize-June	0.25 [a]	65 [b]	0.6 [c]	2.75 [d]	0.24 [e]
Maize-July	0.6 [a]	65 [b]	1.8 [c]	4.96 [d]	0.56 [e]
Maize-August	0.85 [a]	65 [b]	2.4 [c]	5.53 [d]	0.80 [b]
Wheat- May	0.7 [a]	85 [b]	0.65 [c]	2.92 [d]	2.30 [e]
Wheat-June	0.9 [a]	85 [b]	0.9 [c]	3.57 [d]	3.00 [b]
Wheat-July	0.8 [a]	85 [b]	0.75 [c]	3.20 [d]	2.66 [e]
Wheat-August	0.06 [a]	0 [b]	0.05 [c]	0.00 [d]	0.00 [e]
Alfalfa	0.85 [a]	60 [b]	0.6 [b]	2.76 [d]	2.80 [b]

[a] Average monthly values calculated from decadal measurements by Roshkovan (1988); [b] According to Morgan et al. (1998); [c] Average monthly values calculated from weekly measurements by Daskalov et al. (1994); [d] According to Laws (1941); [e] Calculated in accordance with the values of c, considering the values cited by Morgan et al. (1998) for the maximal vegetation cover gained by particular crop.

Figures 2, 3 and 4 illustrate some results from the application of equation (9). Fig. 2 demonstrates the capability of equation (9) of distinguishing between different types of vegetation and growing stages. Fig. 3 shows the estimated percentage portions of rainwater directly reaching the ground (*DR*), modified by the vegetation canopy (*MR*), reaching the ground through flow down the leaves and stems of the plants (*SF*) and intercepted by plants (*IR*). The total amount of rainfall is 30 mm and the intensity is 30 mm h^{-1}. These estimates represent the role of maize and wheat against rainfall in dynamics during the period with high risk of erosion. The data presented in Fig. 2 show that the relative portion of rainwater that directly reaches the ground in maize fields gradually decreases throughout the studied period. The actual values of *DR* estimates, corresponding to the discussed relative percentages are 29.4, 22.5, 12.0 and 4.5 mm m^{-2} respectively for May, June, July and August. These decreases are mostly due to both the increases of the volume of rainwater modified by the vegetation (respectively 0.8, 5.7, 13.8 and 19.5 mm m^{-2}) and of the stemflow (respectively 0.1, 1.5, 3.7 and 5.2 mm m^{-2}). Wheat protection role shows similar, but less expressed trends. Discussed changes in the role of maize and wheat to protect soil from rainfall are reasonable and stay in conformity with the modifications of the plant characteristics during the growth of plants for the period of consideration (Table 1).

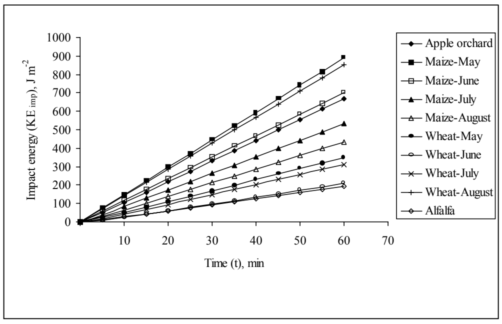

Fig. 2. *Impacting energy of simulated rainfall with intensity of 30 mm h^{-1} calculated according to equation (9) for different plants and months with high erosion risk.*

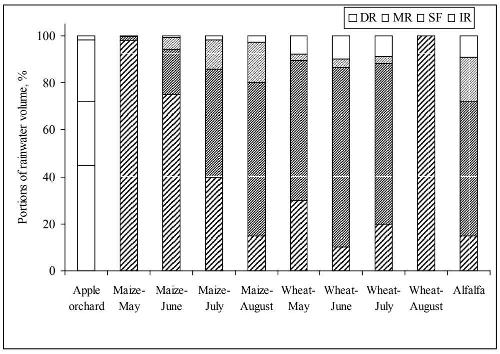

Fig. 3. *Estimated percentage portions of rainwater: directly reaching the ground (DR), reaching the ground as modified by the vegetation (MR), reaching the ground through flow down the leaves and stems (SF) and intercepted by the vegetation (IR), for months with high erosion risk. The amount of rainfall is 30 mm and the intensity – 30 mm h^{-1}.*

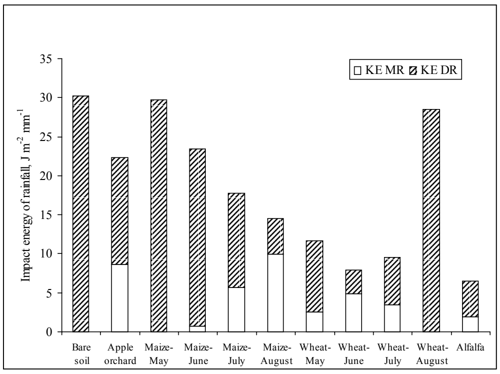

Fig. 4. *Estimated impacting energy of direct (DR) and modified (MR) rainfall with depth of 30 mm and intensity 30 mm h^{-1} for different plants and months with high erosion risk.*

Estimated net impact energy of the 30 mm rainfall with intensity 30 mm h^{-1} is shown in Fig. 3. Lowest energy of impact is observed for alfalfa ecosystem (6.45 J mm^{-1} m^{-2}), followed by wheat ecosystem in June (6.95 J m^{-2} mm^{-1}), July (10.39 J m^{-2} mm^{-1}) and May (11.62 J m^{-2} mm^{-1}). The energy of impact for apple ecosystem is 22.3 J m^{-2} mm^{-1} and for maize ecosystem gradually decreases from 29.7 J m^{-2}

mm^{-1} in May to 14.5 J m^{-2} mm^{-1} in August. Obviously, the rainfall realises almost all its kinetic energy for soil detachment for maize ecosystem in May (98 %) and wheat ecosystem in August (94 %). The portion of rainfall kinetic energy realised for soil detachment varies broadly, depending on the type of vegetation: from 21.3 % for alfalfa to 73.6 % for apple orchard. With respect to the crop growth stage, these values range from 77.4 % in June to 47.8 % in August for maize, and from 26.1 % in July to 38.4 % in June for wheat. The contributions of the direct rainfall and the rainfall modified by vegetation to the net impact energy are changed also depending on the crop growth stage and the type of vegetation (Fig. 2). Percentage contribution of the direct fall to the impact energy varies between 38.3 to 78.1 % for wheat and from 31.4 to 99.9 % for maize, depending on the crop growth stage, while the direct fall contribution for alfalfa is 70 %, and for apple orchard – 74 %.

RELIABILITY

The reliability of the approach for assessing the rainfall impacting energy on soil with vegetation canopy cover was estimated comparing the KE_{MR} values calculated with equation (9) for wheat, maize, alfalfa and apple orchard for the period April – August with the respective values calculated according to an already approved model for calculating the kinetic energy of the leaf drainage as:

$$KE_{\mathrm{MR}} = 15.8\,(H_{\mathrm{eff}})^{0.5} - 5.87 \qquad (10)$$

The mean of the differences between the values of KE_{MR} calculated by these two approaches is 0.77 J m^{-2} mm^{-1} and it has not been found to be statistically significant as proved by t-test ($p = 0.014$). These findings are well visualised in Fig. 5 showing the KE_{MR} estimates according to eq.(10) versus these calculated by eq. (9).

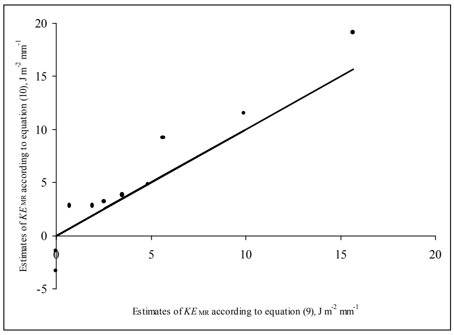

Fig. 5. *Estimated impact energy (KE_{MR}) of modified-by-vegetation rainfall according to equation (13) versus respective estimates by equation (9). Straight line represents 1:1 coincidence.*

Fig. 5 shows well also one disadvantage of the estimates of equation (10): the values of KE_{MR} at effective height of vegetation lower than 0.13 m are negative. Obviously, the equation proposed in this study does not show such disadvantage, assigning close to zero but still positive values of KE_{MR}.

APPLICATION

The model for estimating the rainfall impacting energy on soil with vegetation canopy cover was applied for the purposes of a geographic information system for soil erosion risk assessments on the territory of Bulgaria at a scale of 1: 100 000 based on the USLE approach (Rousseva, 2002; Lazarov et al., 2003). The concept of the USLE cover and management factor (C) is presented as:

$$C = \sum_{k=1}^{7} (EI_{30} \sum_{j=1}^{m} \sum_{i=1}^{n} \frac{A_{\mathrm{C}\,ijk}}{A_{ijk}}) \tag{11}$$

$$C \propto \frac{A_{\mathrm{C}}}{\mathrm{A}} = F_{\mathrm{C}} \frac{EK_{\mathrm{Cimp}}}{EK_{\mathrm{Rimp}}} \quad , \tag{12}$$

where: A and EK_{Rimp} are the soil loss and the rainfall impacting energy for bare soil; Ac and EK_{Cimp} are the soil loss and the rainfall impacting energy for a specific vegetation; EI_{30} is the rainfall erosivity factor; F_{C} is a constant characterizing the specific vegetation.

Equation (9) can be written as:

$$\frac{EK_{\mathrm{C\,imp}}}{EK_{\mathrm{R\,imp}}} = 1 - c + \frac{0.5V^2 n(1 - 0.5\cos\alpha)(cP - IR_{\max})}{EK_{\mathrm{rain}}}, \tag{13}$$

Substitution of Equation (13) into Equation (12) results in a formula, which is convenient for calculating the C-factor of a specific vegetation with a canopy cover c, fall velocity of the drops dripping from the vegetation on the soil V, average acute angle (degrees) of leaves and branches to the plant stem α and maximum volume of the interception store for particular crop or vegetation cover $IR_{\max}$.

Values of the constant F_{C} have been calculated for the main field crops and perennials (Tab. 2) using a regression analysis of two data sets – calculated proportions of impacting energies according to equation (12) and values of the C-factor obtained by long-term field plot measurements (Rousseva, 2002).

Table 2. Values of the constant F_{C} of Eq (12) for main agricultural plants

Plant	F_{C}	Plant	F_{C}	Plant	F_{C}
Maize	45	Tobacco	7.5	Alfalfa	250
Sunflower	45	Potatoes	7.5	Vineyard	6.5
Sugar beet	35	Wheat	175	Orchard	50

Values of mean monthly canopy cover (c), effective plant height (H_{eff}), average acute angle (degrees) of leaves and/or branches to the plant stem (α), maximum volume of the interception store ($IR_{\max}$), fall velocity of the drops dripping from the vegetation on the soil (V) were set as shown in Tab. 3 for the main field crops and perennials (Rousseva, 2002) in accordance with data from measurements presented in different literature sources. C-factor values were calculated for wheat, maize, sunflower, potatoes, tobacco, beats, alfalfa, vineyards and orchards using equations (12) and (13) with respect to rainfall erosivity monthly distributions for each of the 47 agro-ecological regions distinguished on the country's territory.

Table 3. Values of the input parameters of Equation (9) for estimating monthly proportions of the impacting energies for the main agricultural plants

Parameter	Month						
	IV	V	VI	VII	VIII	IX	X
	Wheat grown on non eroded and slightly eroded soils						
c	0.65	0.80	0.92	0.73	0.22	0.00	0.00
H, m	0.36	0.66	0.86	0.76	0.05	0.00	0.00
H_{eff}, m	0.27	0.50	0.65	0.57	0.04	0.00	0.00
V, m/s	1.40	3.80	5.97	5.13	0.00	0.00	0.00
α	85.00	85.00	85.00	85.00	0.00	0.00	0.00
$\cos\alpha$	0.09	0.09	0.09	0.09	0.00	0.00	0.00
IR_{max}	0.80	0.99	3.00	0.90	0.00	0.00	0.00
	Wheat grown on moderately and severely eroded soils						
c	0.46	0.56	0.64	0.51	0.16	0.00	0.00
H, m	0.25	0.47	0.60	0.53	0.05	0.00	0.00
H_{eff}, m	0.19	0.35	0.45	0.40	0.04	0.00	0.00
V, m/s	1.00	2.18	2.58	2.39	0.00	0.00	0.00
α	85.00	85.00	85.00	85.00	0.00	0.00	0.00
$\cos\alpha$	0.09	0.09	0.09	0.09	0.00	0.00	0.00
IR_{max}	1.49	1.83	2.10	1.67	0.00	0.00	0.00
	Maize grown on non eroded and slightly eroded soils						
c	0.00	0.07	0.45	0.57	0.74	0.23	0.00
H, m	0.00	0.15	0.60	1.80	2.40	2.40	0.00
H_{eff}, m	0.00	0.11	0.45	1.35	1.80	1.80	0.00
V, m/s	0.00	0.50	2.75	4.96	5.53	5.53	0.00
α	0.00	10.00	65.00	65.00	65.00	65.00	0.00
$\cos\alpha$	0.00	0.26	0.42	0.42	0.42	0.42	0.00
IR_{max}	0.00	0.07	0.49	0.62	0.80	0.25	0.00
	Maize grown on moderately and severely eroded soils						
c	0.00	0.04	0.27	0.34	0.44	0.14	0.00
H, m	0.00	0.11	0.42	1.26	1.68	1.68	0.00
H_{eff}, m	0.00	0.08	0.32	0.95	1.26	1.26	0.00
V, m/s	0.00	0.40	2.29	4.23	4.84	4.84	0.00
α	0.00	10.00	65.00	65.00	65.00	65.00	0.00
$\cos\alpha$	0.00	0.26	0.42	0.42	0.42	0.42	0.00
IR_{max}	0.00	0.04	0.29	0.37	0.48	0.15	0.00

Table 3. Continued.

Parameter	Month					
	IV	V	VI	VII	VIII	IX	X
Sunflower							
c	0.00	0.11	0.62	0.94	0.82	0.10	0.00
H, m	0.00	0.18	0.54	1.80	2.00	2.05	0.00
H_{eff}, m	0.00	0.14	0.41	1.35	1.50	1.54	0.00
V, m/s	0.00	0.55	2.58	4.96	5.17	5.22	0.00
α	0.00	40.00	40.00	40.00	40.00	40.00	0.00
$\cos\alpha$	0.00	0.77	0.77	0.77	0.77	0.77	0.00
$\mathrm{IR}_{\mathrm{max}}$	0.00	0.22	1.20	1.80	1.58	0.19	0.00
Tobacco							
c	0.10	0.33	0.75	0.67	0.53	0.42	0.05
H, m	0.05	0.30	0.53	0.67	0.68	0.68	0.68
H_{eff}, m	0.04	0.23	0.40	0.50	0.51	0.51	0.51
V, m/s	0.15	0.93	3.33	4.25	4.70	4.70	4.70
α	30.00	30.00	30.00	30.00	30.00	30.00	30.00
$\cos\alpha$	0.87	0.87	0.87	0.87	0.87	0.87	0.87
$\mathrm{IR}_{\mathrm{max}}$	0.24	0.79	1.80	1.61	1.27	1.00	0.12
Potatoes							
c	0.00	0.11	0.25	0.40	0.51	0.38	0.00
H, m	0.00	0.25	0.30	0.40	0.50	0.50	0.00
H_{eff}, m	0.00	0.19	0.23	0.30	0.38	0.38	0.00
V, m/s	0.00	1.00	1.68	2.18	2.39	2.39	0.00
α	0.00	40.00	40.00	40.00	40.00	40.00	0.00
$\cos\alpha$	0.00	0.77	0.77	0.77	0.77	0.77	0.00
$\mathrm{IR}_{\mathrm{max}}$	0.00	0.19	0.44	0.72	0.90	0.68	0.00
Sugar beet							
c	0.00	0.01	0.36	0.89	0.95	0.80	0.44
H, m	0.00	0.20	0.50	0.80	0.80	0.80	0.50
H_{eff}, m	0.00	0.15	0.38	0.60	0.60	0.60	0.38
V, m/s	0.00	0.55	2.39	3.33	3.33	3.33	2.39
α	75.00	75.00	75.00	75.00	75.00	75.00	75.00
$\cos\alpha$	0.26	0.26	0.26	0.26	0.26	0.26	0.26
$\mathrm{IR}_{\mathrm{max}}$	0.00	0.01	0.23	0.56	0.60	0.51	0.28
Alfalfa 2-3 years							
c	0.62	0.83	0.77	0.86	0.76	0.73	0.71
H, m	0.60	0.90	0.70	0.90	0.70	0.60	0.50
H_{eff}, m	0.45	0.68	0.53	0.68	0.53	0.45	0.38
V, m/s	2.76	3.57	3.07	3.57	3.07	2.76	2.39
α	60.00	60.00	60.00	60.00	60.00	60.00	60.00
$\cos\alpha$	0.50	0.50	0.50	0.50	0.50	0.50	0.50
$\mathrm{IR}_{\mathrm{max}}$	1.95	2.70	2.51	2.80	2.28	2.38	2.31

Table 3. Continued.

Parameter	Month						
	IV	V	VI	VII	VIII	IX	X
Orchard 8x8 with 60% maximal canopy cover							
c	0.12	0.21	0.52	0.62	0.60	0.46	0.31
H, m	5.00	5.00	5.00	5.00	5.00	5.00	5.00
H_{eff}, m	3.75	3.75	3.75	3.75	3.75	3.75	3.75
V, m/s	7.44	7.44	7.44	7.44	7.44	7.44	7.44
α	15.00	15.00	15.00	15.00	15.00	15.00	15.00
cos α	0.97	0.97	0.97	0.97	0.97	0.97	0.97
IR_{max}	0.10	0.17	0.42	0.50	0.48	0.37	0.17
Orchard 8x8 with 35% maximal canopy cover							
c	0.07	0.12	0.29	0.35	0.34	0.26	0.18
H, m	5.00	5.00	5.00	5.00	5.00	5.00	5.00
H_{eff}, m	3.75	3.75	3.75	3.75	3.75	3.75	3.75
V, m/s	7.44	7.44	7.44	7.44	7.44	7.44	7.44
α	15.00	15.00	15.00	15.00	15.00	15.00	15.00
cos α	0.97	0.97	0.97	0.97	0.97	0.97	0.97
IR_{max}	0.08	0.15	0.36	0.43	0.42	0.32	0.22
Orchard palmette							
c	0.20	0.31	0.49	0.55	0.51	0.40	0.30
H, m	2.50	2.50	2.50	2.50	2.50	2.50	2.50
H_{eff}, m	1.88	1.88	1.88	1.88	1.88	1.88	1.88
V, m/s	5.62	5.62	5.62	5.62	5.62	5.62	5.62
α	15.00	15.00	15.00	15.00	15.00	15.00	15.00
cos α	0.97	0.97	0.97	0.97	0.97	0.97	0.97
IR_{max}	0.18	0.28	0.44	0.50	0.46	0.36	0.27
Vineyard with 35 % maximal canopy cover							
c	0.08	0.20	0.31	0.35	0.27	0.20	0.14
H, m	1.00	1.00	1.00	1.00	1.00	1.00	1.00
H_{eff}, m	0.75	0.75	0.75	0.75	0.75	0.75	0.75
V, m/s	3.78	3.78	3.78	3.78	3.78	3.78	3.78
α	60.00	60.00	60.00	60.00	60.00	60.00	60.00
cos α	0.50	0.50	0.50	0.50	0.50	0.50	0.50
IR_{max}	0.11	0.29	0.44	0.50	0.39	0.29	0.20
Vineyard with 24 % maximal canopy cover							
c	0.06	0.14	0.21	0.24	0.19	0.14	0.10
H, m	1.00	1.00	1.00	1.00	1.00	1.00	1.00
H_{eff}, m	0.75	0.75	0.75	0.75	0.75	0.75	0.75
V, m/s	3.78	3.78	3.78	3.78	3.78	3.78	3.78
α	60.00	60.00	60.00	60.00	60.00	60.00	60.00
cos α	0.50	0.50	0.50	0.50	0.50	0.50	0.50
IR_{max}	0.08	0.20	0.30	0.35	0.27	0.19	0.14

The data in tables 4 and 5 show that the approach applied for assessing the cover and management factor has resulted in reasonable estimates of values for the main field crops and perennials grown on the territory of Bulgaria.

Table 4. Mean, minimal and maximal values and standard deviations of the crop and management factor (C) of the main field crops estimated for 47 agro-ecological regions distinguished on the territory of Bulgaria.

Crop / Parameter	Wheat	Wheat*	Maize	Maize*	Sunflowe	Tobacco	Potatoes	Beats	Alfalfa
Mean	0.22	0.28	0.39	0.50	0.32	0.71	0.69	0.34	0.07
St.Dev.	0.05	0.04	0.06	0.04	0.05	0.08	0.03	0.05	0.02
Minimum	0.12	0.16	0.27	0.42	0.20	0.51	0.62	0.22	0.04
Maximum	0.32	0.34	0.52	0.59	0.44	0.84	0.75	0.44	0.10

* For eroded lands

Table 5. Mean, minimal and maximal values and standard deviations of the crop and management factor (C) of vineyards and orchards estimated for 47 agro-ecological regions distinguished on the territory of Bulgaria.

Canopy / Parameter	Orchards			Vineyards	
	8x8m c*=0.35	8x8m c=0.60	Palmette	c=0.35	c=0.24
Mean	0.42	0.30	0.39	0.64	0.70
St.Dev.	0.08	0.04	0.06	0.05	0.03
Minimum	0.24	0.21	0.26	0.54	0.62
Maximum	0.58	0.39	0.51	0.74	0.77

* Canopy cover

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BEHAVIOUR OF FREE Fe AND Mn COMPOUNDS ALONG DEPTH OF SOME LUVISOLS FROM SOUTH ROMANIA AND NORTH BULGARIA

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ABSTRACT

Distributions of free Fe and Mn along depth of soils indicate the intensity and duration of weathering and soil - forming processes. The purpose of this paper is to compare the distributions of dithionite, oxalate and pyrophosphate extractable forms of the free Fe and Mn along depth of some Luvisols from South Romania and North Bulgaria. The results show, that the modern processes affecting mainly the mineral part of soils in Brun - rocast Luvic tipic from South Romania and Dark grey forest and Grey brown forest soils from South Bulgaria are lessivage, migration, complex formation, crystallisation. They are best expressed in the first soil. The soil from South Romania and the Grey brown soil from North Bulgaria differ in the processes that have occurred during the earlier stages of soil development. The first one was developed under better expressed humid conditions and higher moisture (due to higher level of ground waters), the second soils - on old parent materials under dryer conditions. It resulted in the more stable crystallised Fe form, accumulated in the Bt horizons with red colour (5YR).

INTRODUCTION

Studies on the distributions of free Fe and Mn along depth of soils are required, since they are results of weathering and soil - forming processes. Their content is higher than that of Al, since the released Al from the primary minerals is mostly included in the clay minerals, The extractable forms of the free Fe and Mn reflect more clear the soil processes. Dithionite, oxalate and pyrophosphate extractable compounds are different soil constituents. The oxalate extractable are the free poorly ordered compounds of Fe and bound with them free compounds of Mn, the dithionite extractable of Fe - the sum of poorly ordered and crystalline forms, the pyrophosphate - bound with organic matter compounds of Fe and Mn. Their depth functions illustrate the type and stages of different soil processes that have occurred in soils. The purpose of this paper is to compare the distributions of dithionite, oxalate and pyrophosphate extractable forms of the free Fe and Mn along depth of some Luvisols from South Romania and North Bulgaria.

MATERIALS AND METHODS

Objects of the studies were profiles of the following soils: from South Romania - Brun - roscat Luvic tipic from Branesti, developed under old oak forest (Profile 1); from North Bulgaria (Pleven region) - Dark grey – brown forest from Grivitza village, developed under oak forest (Profile 2); Grey - brown forest from Slaviany village, developed under oak forest (Profile 3a) and cropland (Profile 3). These soils are formed from loess deposits at similar climate conditions. The data of pH, content of clay fraction (separated by the method of Kachinsky, 1958) and total content of Fe_2O_3, Al_2O_3 and Mn of the studied soils are given in Table 1.

Table 1. pH and content of total Fe_2O_3, Al_2O_3 and clay fraction

Horizon and Depth, Cm	pH (H_2O)	Clay * %	Fe_2O_3 %	Al_2O_3 %	Mn mg.kg-1	Colour
Profile 1, Brun - roscat Luvic tipic, Albic Luvisol[1] South Romania, under oak forest						
A_0 0 - 4	5.3	24.8	3.50	10.58	2002	10YR 5/3
AE 4 - 24	4.8	20.0	3.81	11.28	781	10YR 6/3
EB 26 - 44	5.0	24.0	4.14	10.04	907	10YR 6/3
B_1t 44 - 80	5.2	34.3	5.41	12.93	693	7.YR 4/4
B_2t 80 - 130	5.4	30.0	5.32	13.75	869	7.5YR 5/6
B_3t 130 - 160	6.2	28.6	5.15	13.61	803	7.5YR 6/6
Ck 160 - 200	7.8	22.0	4.40	17.78	775	10YR 6/6
Profile 2, Dark grey forest, Luvic Phaeozem[1], North Bulgaria, under oak forest						
Ah 0 - 12	5.7	27.9	4.72	9.37	1056	10YR 4/1
A 18 - 37	5.1	28.6	5.15	11.72	1068	10YR 3/2
B_1t 37 - 66	5.9	34.0	5.86	11.49	888	7.5YR 4/2
B_2t 66 - 92	6.5	30.4	6.58	13.00	876	7.5YR 3/2
B_3t 92 - 112	6.0	24.4	.15	12.62	684	10YR
Ck 112 – 150	7.3	-	5.15	9.82	648	
Profile 3a **, Grey - brown forest, Haplic Luvisol[1], North Bulgaria, under oak forest						
A_1l 0 - 10	5.3	27.0	4.30	11.42	985	7.5YR 4/2
A_2l 10 - 30	5.5	29.5	4.71	12.95	750	5YR 4/6
B_1t 30 - 50	5.3	45.3	6.53	16.99	700	5YR 4/4
B_2t 50 - 75	5.5	41.6	6.27	16.56	635	5YR 4/5
Profile 3, Grey - brown forest, Haplic Luvisol[1] , North Bulgaria, cultivated						
A_1p 0 - 12	5.5	30.8	4.60	8.87	900	10YR 4/3
A $_2$p 12 - 22	5.1	31.2	4.64	12.81	935	10YR 4/3
AB 22 - 32	5.4	26.2	5.03	10.76	988	10YR 3/3
B_1t 32 - 62	5.5	37.4	6.15	12.08	692	5YR 3/4
B_2t 62 - 90	5.9	30.7	5.79	12.35	474	5YR 3/4
Ck 0 - 135	7.8	17.1	5.03	10.93	740	7.5UR 4/4

1 – according to FAO Legend; * -particle size < 0.001 mm. ** -data of Koinov et al., 1998. Confidence intervals at P 0.95 are: total Fe_2O_3 - 0.46% of soil mass; total Al_2O_3 - 1.45% of soil mass; total Mn - 69 mg/kg soil mass.

Total content of the elements was determined by acid dissolving (HF + $HClO_4$) of the soil samples (particle size < 0.001 mm). The content of their dithionite, oxalate and pyrophosphate extractable forms were determined according to the method of Mehra - Jackson (1960), Tamm (1934) by Arinoushkina (1970) and Bascomb (1968), respectively. Concentrations of selected elements in the obtained solutions determined by atomic absorption method (AAS) are given in Table 2.

Table 2. Content of free Fe and Mn forms along depth of the studied profiles (% of total).

Horizon and Depth (cm)	Fe_d %	Fe_o %	Fe_c %	Fe_p %	Mn_o %	Mn_p %
Profile 1, Brun - roscat Luvic tipic, Albic Luvisol[1], South Romania, under oak forest						
A_o 0 - 4	52.57	21.71	30.86	16.28	75.52	56.74
AE 4 - 24	42.52	23.62	18.9	13.38	87.58	32.65
EB 26 - 44	29.47	16.18	13.29	9.66	81.32	22.04
B_1t 44 - 80	15.90	14.79	1.11	7.39	75.32	24.22
B_2t 80 - 130	9.96	13.72	0.00	6.39	59.38	21.63
B_3t 130 - 160	9.32	11.46	0.00	4.85	66.50	16.44
Ck 160 - 200	10.45	10.45	0.00	2.27	48.74	6.19
Profile 2, Dark - grey forest, Luvic Phaeozem[1], North Bulgaria, under oak forest						
Ah 0 - 12	25.21	8.26	18.95	5.72	79.54	15.05
A 18 - 37	25.43	9.70	15.73	5.04	62.92	33.70
B_1t 37 - 66	27.64	9.21	18.43	2.38	61.26	17.56
B_2t 66 - 92	22.34	7.90	14.44	2.27	56.16	3.65
B_3t 92 - 112	24.39	6.50	17.89	1.30	70.17	0.58
Ck 112 - 150	22.59	3.30	19.29	0.77	37.96	0.61
Profile 3a *, Grey brown forest, Haplic Luvisol[1], North Bulgaria, under oak forest						
A_1l 0 - 10	33.26	12.79	20.47			
A_2l 10 - 30	30.57	11.46	19.11			
B_1t 30 - 50	31.39	7.96	23.23			
B_2t 50 - 75	32.54	7.97	25.06			
Profile 3, Grey brown forest, Haplic Luvisol[1], North Bulgaria, cultivated						
A_1p 0 - 12	-	19.06	-	7.20	66.12	13.5
A_2p 12 - 22	29.550.	13.13	16.42	4.74	59.45	6.3
AB 22 - 32	40.35	15.0	24.85	5.36	68.61	7.4
B_1t 32 - 62	35.77	13.17	22.60	4.22	60.98	2.5
B_2t 62 - 90	35.40	10.36	25.04	2.93	70.01	1.5
Ck 90 - 135	39.16	4.77	34.39	0.99	46.75	1.3

1 – according to FAO Legend; d, o, p - dithionite, oxalate and pyrophosphate extractable, c - crystalline; * - data of Koinov et al, 1998. Confidence intervals at P 0.95 are: Fe_d - 0.07% of soil mass; Fe_o and Fe_p - 0.06% of soil mass; Mn_o and Mn_p - 61mg/kg soil mass.

RESULTS AND DISCUSSION

Since the studied Brun - rocast Luvic tipic soil from South Romania (Profile 1) and Dark grey forest (Profile 2) and Grey brown forest soils from North Bulgaria (Profile 3a - under forest; 3 - from cropland) are developed on the similar parent materials (loesslike deposits) in the similar climate conditions (mesic-ustic), the results of: pH, distribution of clay fraction (< 0.001 mm) along depth, textural differentiation, total content of Fe_2O_3 and Al_2O_3 are close (Table 1). The distributions of the latter oxides along depth correspond to that of the clay fraction. Mn is more soluble and less included in the clay mineral lattices than Fe and Al, i.e. its behaviour is different.

Total Mn maximums in the studied soils are observed at the surface horizons, because it is a biogenic element. With soil development stages these accumulations at the upper parts of the profiles are getting clearer in most Bulgarian soils (Jokova and Boyadjiev, 1993, 1998; Jokova, 1994). Exceptions are cinnamonic soils developed on calcareous parent materials under thermoxeric climate conditions from South Bulgaria. The enrichment in Mn of the surface horizon is best expressed in Profile 1 (under old oak forest), due to the more advanced stages of Mn release and migration upward.

Pyrophosphate extractable Fe and Mn free compounds (Fe_p and Mn_p) are mainly bound with organic matter substances (Bascomb, 1968), i. e. the complexes of these elements are stable at pH 10 of the solution. The results show that they are accumulated in the surface horizons and gradually decrease with depth of the studied profiles (Table 2). These compounds are a main form of the transport of these elements. Compared with the soil profiles from North Bulgaria - (both developed under forests) and the profile from the arable land - the soil profile from South Romania developed under old forest is richer in these extractable forms. The part of the bound Mn from the total content is higher than the respective part of Fe ($Mn_p > Fe_p$). According to Petrova and Shishkov (1998) the studied soil from South Romania is richer in organic matter with higher degree of humification than the soil from Grivitza village, North Bulgaria (Profile 2). It is due to the high content of Mn (Table 1). Because of its oxidising power this element contributes to the higher ratios between humic and fulvic acids (Jokova, 1994)

The studied oxalate extractable compounds are mainly poorly ordered hydroxides of Fe and bound with them Mn ones (Fe_o and Mn_o), resulting from modern processes that have occurred in these soils. The upper parts of the profiles are richest in Fe_o and Mn_o (wherein weathering processes are the most active) and their content decreases with depth. The amounts of these forms are highest in Profile 1, but the differences in other profiles are less expressed than the differences in the pyrophosphate extractable forms. Mn is more easily reducible than Fe and reflects more strongly the reduction conditions. There are minimum's of the depth functions of Mn_o, corresponding to Bt_2 horizons of Profiles 1 and 2, as well as to B_1t horizon of Profile 3 (from the cultivated area). They are due to the higher moisture (caused by the high texture) and Mn reduction. The obtained Mn^{2+} compounds are more soluble and migrate to the lower and upper horizons. At Ap_1 horizon of the latter profile a second maximum is appeared at the boundary between arable layer and less permeable underling one. These minimum's of Mn_o (or of the total Mn) observed in the soil solum are chemical criteria of gley processes (Jokova, 1994).

The dithionite extractable Fe compounds Fe_d (method of Mehra - Jackson) are nearly the sum of the poorly ordered and crystalline forms. Coarser well crystallised oxides (magnetite, hematite) are not completely soluble in the dithionite - citrate - bicarbonate solution (DCB), but they are attacked by the oxalate one (Vodyanitskii, 2002, 2002). High temperatures and low moistures favourite the gradual crystallisation of Fe hydroxides with age. Therefore, the differences $Fe_c = Fe_d - Fe_o$ nearly express the content of the crystalline forms in some soils. They are rather indicative to the temperature and moisture regimes and the stages of weathering and soil - formation. They are a feature of old processes (Alexander, 1985).

Fe_d content is highest in the upper part of Profile 1, which drastically decreases along depth. It is due to the higher level of ground waters appeared during the earlier stages of soil development. It is confirmed by the carbonate concretions (a relict feature of gley processes) at the low part of that profile. The higher moisture had caused the reduction conditions and absence of extractable Fe crystalline forms (Fe_c) in DCB reagent. Maybe under such conditions magnetite has been formed (Lindsay, 1979). It is not dissolved by the DCB reagent (pH 7.3) and dissolved by the more aggressive oxalate reagent (pH 3.2). In the profiles from North Bulgaria Fe_d content decreases gradually along the profiles. The Bt horizons of the Profile 2, 3 and 3a are richer in Fe_d and Fe_c than the respective horizons of Profile 1. It is due to the lower moisture during the earlier stages of that soil development on older parent materials. The crystalline Fe forms are more stable and accumulated in the profiles.

The highest contents of Fe_d and Fe_c in the Bt horizons of Grey brown forest soil have resulted in the red soil colour (5YR). These soils are transitional between Brocan - rocast of South Romania and cinnamonic soils from South Bulgaria (Koinov et al, 1998).

CONCLUSIONS

The distributions of the dithionite, oxalate and pyrophosphate extractable forms of Fe and Al along depth of the studied Luvisols are indicative to the processes that have occurred. in the soils. The modern processes concerning the mineral parts of soils in the Brun - rocast Luvic tipic soil from South Romania and Dark grey forest and Grey brown forest soils from North Bulgaria are lessivage, migration, complex formation, crystallisation. They are best expressed in the soil from South Romania.

The soil from South Romania and the soils from North Bulgaria differ in the processes have occurred during the earlier stages of soil development. The first one developed under conditions of higher moisture, due to high levels of ground waters, the second soils - on old parent materials under dryer conditions. It resulted in the more stable crystallised Fe form, accumulated in the Bt horizons, They are distinguished by the red colour (5YR).

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PSYCHROMETRIC WATER POTENTIAL METER OF POROUS BODIES – DESCRIPTION OF A PROTOTYPE

Skierucha W.

ABSTRACT

The paper presents the design and performance of 8-channel thermocouple psychrometer for the measurement of water potential in porous bodies. The availability of advanced electronic components of high accuracy and microcontroller supervision enables to build a simple and reliable device to be used in water potential determination in the range up to –0.2 MPa and possibly higher. The device uses the psychrometric sensors available from the vendors. The presented meter can easily be adapted in automatic soil status monitoring stations.

Keywords: water potential, Peltier psychrometer, soil status monitoring

INTRODUCTION

The relation between water potential and relative humidity is theoretically expressed by the equation:

$$\Psi = \frac{RT}{V_w} \ln \frac{e}{e_0} \tag{1}$$

where: Ψ is the water potential in Pascal, R is the universal gas constant (8.3143 $J \cdot mol \cdot K^{-1}$), e/e_0 is the relative humidity expressed as a fraction, T is the absolute temperature (K), V_W is the molar volume of water ($1.8 \cdot 10^{-5}$ $m^3 \cdot mol^{-1}$). Since the publication of Spanner (1951) on the measurement of the water potential using Peltier effect, thermocouple psychrometers are widely used for measuring water potential of soils and plants.

The Peltier and Seebeck effects are two physical phenomena describing the psychrometric method of water potential measurements. The Peltier effect happens when a thermocouple junction is cooled or warmed by passing an electrical current through it in different directions. The Seebeck effect consists in the current flow in the loop of two dissimilar wires connected together when the junctions are at different temperatures.

PSYCHROMETRIC METER AND SENSORS

The construction of a typical psychrometer and its connection to the prototype meter are presented in Fig. 1. Very fine chromel and constantan wires (25 µm diameter - so that cooling of this junction will not significantly change the temperature of the larger reference junction) form the welded thermocouple used for the measurement of the equilibrium relative humidity/water potential.

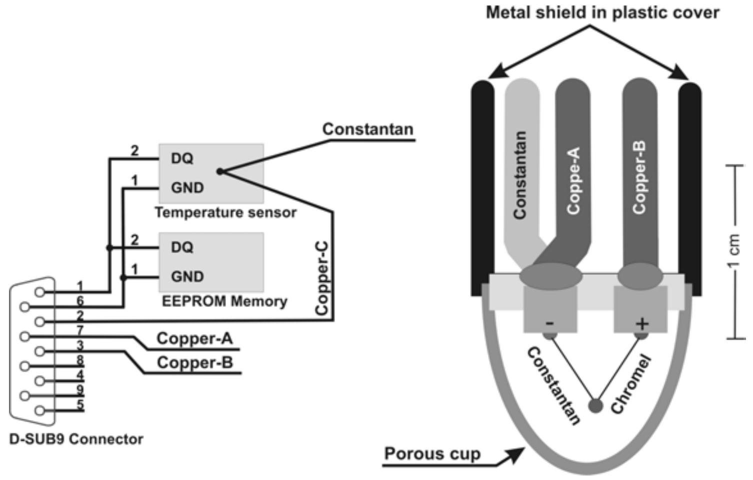


Fig. 1. *Peltier Psychrometer sensor with porous ceramic thermocouple shield (Wescor, 1998) and the meter connector with installed electronics for cold junction compensation and storage of the sensor individual parameters*

Two copper wires, Copper-A and Copper-B, allow feed the fine Constantan/Chromel thermocouple junction with appropriate cooling current and then making the readout of psychrometric voltage difference associated with the water potential. Copper-C/Constantan thermocouple junction is used for the readout the psychrometric sensor temperature. The cold junction compensation of this thermocouple is done by the measurement of its temperature by means of semiconductor temperature sensor, Dallas DS18B20 (Data Sheet available on www.maxim-ic.com). This very convenient 12 bit temperature sensor measures with ±0.5°C accuracy and 0.0625°C resolution and is integrated with digital circuity responsible for 1-Wire communication with the master microcontroller. The Copper-C/Constantan reference junction is thermally connected with DS18B20 by means of a special adhesive of small thermal resistance. The junction and the body of the DS18B20 temperature sensor are fixed together by epoxy resin to increase the thermal inertia of the whole construction that is placed in the housing of the D-SUB9 connector. Inside this there is also another 1-Wire device Dallas DS2430A EEPROM memory, connected in parallel with the DS18B20 temperature sensor. Each psychrometer sensor may have its characteristic parameters, i.e. DS18B20 temperature correction, thermocouple cooling coeficient (Campbell and Campbell, 1973), probe unique identification number, written to the EEPROM memory so as to increase the accuracy of the measurement and for the sensor identification.

The fine Constantan/Chromel welded junction is covered with a porous cup (or ultrafine weave stainless steel screen shield) that provides necessary cover while allowing the internal air to equilibrate with the ambient.

The main difficulties to overcome in the construction of the planned device are twofold: the resolution and stability of the readout device has to be very high (below 50 nV) in order to allow the measurement of relative humidity in the range of 99.99-95% with the acceptable accuracy. This has been solved by the selection of modern electronic analog and digital components. The other difficulty is to to keep the measuring Constantan/Chromel junction at the same temperature as the reference junction. From Eq. (1), the change of the vapor pressure ratio of about 0.01 at 25˚C corresponds to about 1.4 MPa difference in water potential. It would be therefore necessary to limit the change in reference junction temperature to about 0.001˚C to maintain precission of 0.01 MPa (Bingham et al, 1971). This is especially challenging for measurements in field conditions. The most critical range is close to 100% humidity corresponding with the soil water potential range adequate with natural conditions of plants growth.

The measurement cycle consists of few steps that are controlled by the microcontroller and electronic circuitry of the meter. These steps may vary according to the water potential to be measured, temperature, accuracy needed and time of measurement. Optimization of measurement process with respect to different restrictions may lead to various measurement procedures. The measurement sequence, taking place to determine psychrometric water potential value is as follows (Fig. 2):

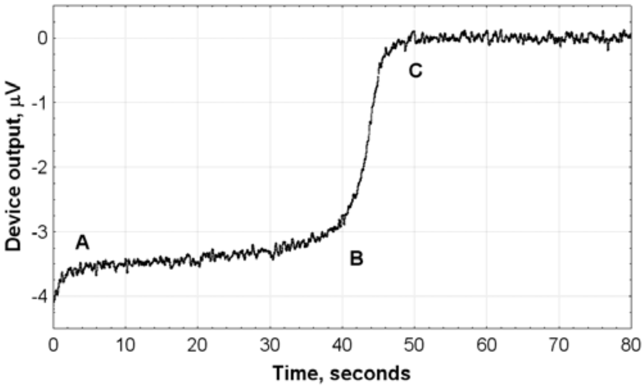


***Fig. 2**. Output of the thermocouple psychrometer.*

1) The fine Constantan/Chromel thermocouple should not have water condensed on the fine wires. This is assured by passing the appropriate value warming current across through the junction and then, after stopping the current, the junction should attain temperature equilibrium with the air space surrounding it. Also the air space must be in temperature and vapour equilibrium with the sample to be measured.
2) The Peltier cooling current is passing through the fine Constantan/Chromel thermocouple junction. The magnitude and duration of cooling current must be sufficient to cool the junction below the dew point temperature of the equilibrated air. When the temperature of the junction is below the dew point, water condenses on the junction from the surrounding air. The Peltier current

is discontinued and the thermocouple output voltage starts to be monitored (Fig. 2, point A). During the evaporation of water condensed on the thermocouple junction its temperature does not change rapidly (part A-B in Fig. 2). This temperature, called the wet bulb depression temperature, depends of relative humidity of the air surrounding the sensor. The wet bulb depression lasts until all water evaporates from the junction and the thermocouple temperature returns to the ambient (part B-C in Fig. 2).

The schematic picture of the prototype thermocouple psychrometer is presented in Fig. 3.

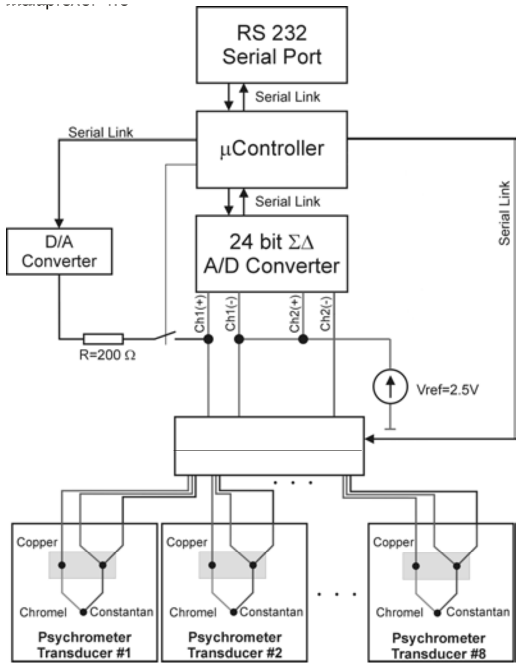


***Fig. 3**. Prototype of thermocouple psychrometers*

The meter is controlled from PC compatible computer, by the application program written in Visual Basic, equipped with RS232C asynchronous serial port for sending commands and receiving raw data. The raw data received from the meter consists of several hundreds three byte long data points representing values of voltage drop on the fine wires Constantan/Chromel or the thick wires Copper-A/Constantan thermocouples.

The input multiplexer enables to connect up to eight thermocouple sensors to the Analog Devices AD7730 24-bit Sigma-Delta Analog to Digital (Data Sheet available on www.analog.com). This is a very flexible device with a programmable gain input amplifier (PGA) for bipolar input ranges from ±10 mV to ±1.25 V or unipolar input ranges from 20 mV to 2.5 V. The presented meter is set for ±10 mV bipolar mode that enables to sample the input voltage with 1.2 nV resolution. This is theoretical value, impossible to achieve in practice because of noise introduced by the measurement system. The device has a digital filter with the nodes that can be configured for 50 Hz for European and 60 Hz for American areas. The internal circuitry includes system and device calibration registers enabling to make corrections for zero and gain drifts. Each subsequent measured value is automatically corrected for the device zero and gain drift. System calibration requires manual switching of the meter input to the system ground and selected range voltage. The presented meter uses the device calibration before recording each response from the psychrometer sensor.

The 8-bit Digital to Analog (D/A) converter with the output voltage swing 0-5V, current limiting resistor R, the switch and the low noise, precision 2.5V reference, Vref, are applied to control the value of warming or cooling current that is injected into the Constantan/Chromel junction. The both converters and the multiplexer are controlled by means of a three wire fast synchronous serial link from the microcontroller PIC 16F876 (Data Sheet available on www.microchip.com).

The input values of the D/A converter in the range of 128-255 results in the warming current flowing in one direction, while the input values from the range 0-127 results in the cooling current flowing in opposite direction across the Constantan/Chromel junction. The current resolution is about 0,39 mA and the maximum value about 7 mA. The cold junction compensation of Copper-A/Constantan thermocouple that measures the temperature of the Psychrometer sensor is done by the measurement of its temperature Ti (Fig. 3).

The value of cooling current has to be determined experimentally so as to receive the temperature depression and the corresponding voltage swing in the fine Constantan/Chromel measuring junction somewhere in the middle of the 80 seconds time period when this voltage is sampled by A/D converter. The voltage of the measuring thermocouple is sampled with the frequency of 50 Hz, giving 4000 data points consisting of 3-byte words that are sent to PC computer by serial asynchronous link for further processing.

CALIBRATION OF THE PROBES

The calibration of the psychrometric sensors is performed by immersing them into the solutions of NaCl of known water potential (or relative humidity). The relationship between water potential and molality is presented after Lang (1967) in tabularized form (Tab. 1). The containers filled with NaCl solutions were placed in a water bath of constant temperature 25±0.3ºC. There is an influence of temperature on the psychrometer readout reported in Brown (1970).

The examples of calibration readouts from the same probe for different NaCl solutions are presented in Fig. 4. When molality of the NaCl solution decreases, the cooling time necessary for vapor condensation on chromel-constantan thermocouple decreases, too. To condense vapor on the thermocouple sensor inserted in 1.2 mole NaCl solution it is necessary to provide 7 mA current for 50 seconds while for the 0.2 mole solution the cooling time is 4 seconds and current value 5 mA. For each solution presented in Fig. 4 the effect of evaporation of water condensed on the thermocouple is distinctive and is represented by fast voltage change. The higher molality of the solution, the lower is relative humidity of the air inside the shield of the sensor and the bigger is the voltage drop on the thermocouple.

Table 1. Relation between molality, water potential and relative humidity for NaCl solutions at 25°C (Lang, 1967)

molality	**water potential in MPa at 25°C**	**relative humidity**
0.05	-0.234	0.998
0.10	-0.462	0.997
0.20	-0.915	0.993
0.40	-1.823	0.987
0.60	-2.744	0.980
0.80	-3.682	0.974
1.00	-4.640	0.967
1.20	-5.620	0.960

The applied cooling time is in direct proportion with the time necessary for the water to evaporate from the cooled junction. This phenomenon can be used also in water potential analysis.

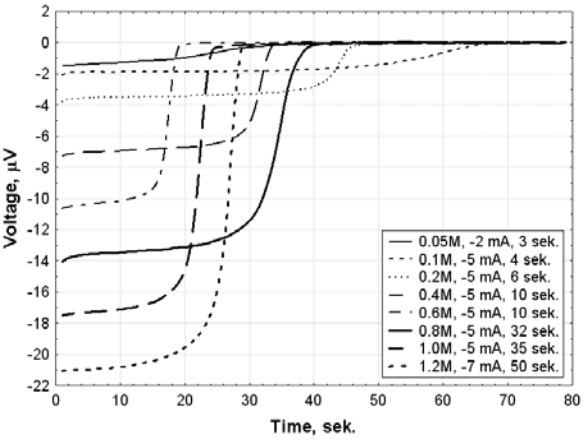
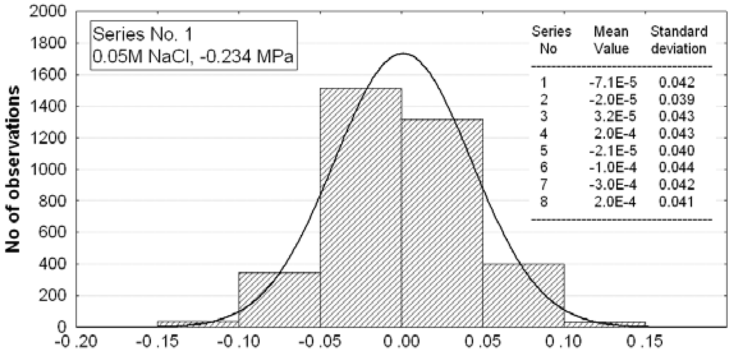


***Fig. 4**. Voltage generated by presented Peltier psychrometer as a function of time for different NaCl solutions representing different water potentials (each curve is generated for specific cooling current in the Constantan/Chromel junction)*

The current and time values in the legend in Fig. 4 refer to the cooling current flowing across the Constantan/Chromel junction for the defined time. The chosen values depend on molal concentration of the particular NaCl solutions used for calibration. The voltage representing temperature equilibrium state is zero in Fig. 4.

Actually this value differs from zero because the distance from the Chromel/Constantan fine thermocouple to the input of the A/D converter includes connections of different wires generating thermocouple voltages themselves. Therefore the data in Fig. 4 are adjusted to take account the zero drift of the system. This is done by subtracting the average value of 100 last points from each point of the curve. If the whole measuring system is in stable temperature state when the measurement process takes place, the only change of the output curve will result from the temperature depression caused by evaporation of wet thermocouple junction.

Each curve from Fig. 4 is a fitted trend line into the observed data points calculated as a moving average from ±50 points. This smoothing procedure is not necessary for low water potentials, but for water potentials above –0.4 MPa the interpretation of the curve is more reliable because of the scatter of collected data.



Series No	Mean Value	Standard deviation
1	-7.1E-5	0.042
2	-2.0E-5	0.039
3	3.2E-5	0.043
4	2.0E-4	0.043
5	-2.1E-5	0.040
6	-1.0E-4	0.044
7	-3.0E-4	0.042
8	2.0E-4	0.041

Fig. 5*. Distribution of the meter error between the observed voltages (series No. 1) and the corresponding values from the fitted ±50 points moving average.*

The resolution of the presented meter is determined from the distribution of error calculated as the difference between the observed and the fitted values, using the ±50 points moving average. The histogram of this error is presented in Fig. 5.

For the psychrometric sensor inserted into the 0.05 molal solution of NaCl (the corresponding water potential is 0.234 MPa) the mean value of the error is close to zero and the standard deviation, describing the noise produced by the meter and the sensor, is about 0.04 μV. The readout is repeated seven times for the same psychrometric sensor and similar values of error distribution are reported.

The calibration function of a psychrometric sensor as the relation between the device readout and examined water potential is presented in Fig. 6. The straight trend line shows that calibration can be simplified to only two-point measurement. The calibration formula presented in Fig. 6 refers only to the specific psychrometric sensor. Each sensor should be calibrated independently to obtain as high accuracy of measurement as possible. The total number of eight psychrometric sensors (type PST-55 from Wescor Inc., with ultrafine dutch weave stainless steel screen shield) were calibrated on NaCl solutions, according to the procedure described above. All the sensors had linear characteristic similar to the one in Fig. 6, although the slope differed slightly from 3.5 to 3.7 μV/MPa at 25ºC.

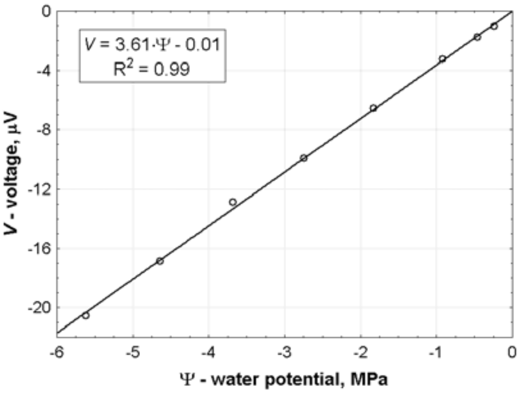


Fig. 6. *The calibration function as a trend line for a Peltier psychrometer sensor*

CONCLUSIONS

The presented thermocouple psychrometer is a convenient computer controlled device that enables the user to measure water potential simultaneously from up to eight sensors. The collected data may be analyzed using various statistical tests as they have numeric form. The flexible construction of the meter enables the user to treat the sensor with heating and cooling currents of various values so as to determine the water potential in the range –6 to –0.2 MPa that correspond to the relative humidity range from 0.96 to about 0.998. The presented device can be applied not in soil physics for water potential determination, but also in building industry or food industry to determine properties of tested materials in the relative humidity range of 95-100%.

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ANALYSIS OF THE MECHANICAL PROPERTIES OF PEA STEMS (*PISUM SATIVUM L.*)

Skubisz G., Święcicki W., Łabuda H.

INTRODUCTION

In recent years, studies were undertaken with the aim of determining the strength characteristics of pea stems (Skubisz 2002, Skubisz at al. 2001). Pea plants have a strong tendency to lodging. Although plant breeders achieved considerable success in breeding pea cultivars with enhanced productivity, they now aim at breeding new cultivars, more resistant to lodging (Boros and Sawicki 1997, Święcicki and Wiatr 2001). It is a known fact that plant resistance to lodging is closely correlated with the mechanical properties of their stems (Skubisz 1982, Skubisz 2001). Studies on the mechanical properties of plant stems and black currant shoots show the occurrence of inter-cultivar differences (Dunca 2003, Skubisz 2001, Skubisz at al.2001, Skubisz and Tys 1987).

A review of the literature of the subject indicates that the strength properties of pea stems are related to the content of a cell wall component – ksyloglucan – in the lower part of the stems (Cutillas-Iturralde and Lorence 1997). Other studies showed the relation of the mechanical properties of plants to cellulose (Rusin 2002, Speck at al. 1996a,Vincent 1992) and to the content of cellulose and lignin (Skubisz 2001).

In the study the authors determined the mechanical parameters of the stems of pea cultivar in the process of bending. At the same time, in the course of the plants ripening, an analysis was made of the variability of those parameters along the stem length. Other parameters determined included the stem wall thickness and cross-section surface area. Also, an assessment was made of the relation between the geometrical parameters and the mechanical properties of pea stems. The study was made on pea cultivars susceptible and resistant to lodging, to allow the determination of inter-cultivar differentiation.

The aim of the study was to demonstrate the inter-cultivar differences of pea cultivar on the basis of absolute values of the mechanical parameters of their stems.

PLANT MATERIALS AND METHOD

The mechanical properties of pea stems were expressed by means of stem rigidity, modulus of elasticity, and the maximum bending stress. The study was performed for narrow-leaf cultivars (*afila*) – Piast and Brutus (resistant to lodging) and Komandor (susceptible to lodging), and a cultivar with leaf-type morphology – the Rola (susceptible to lodging). Pea seeds originated from the collection resources of the Polish Pea Gene Bank, and the plants were grown on the experimental plots of the Academy of Agriculture in Lublin. Plants were sampled from the field at full pods and at full ripeness. A representative sample consisted of 30 plants. The strength characteristics of the pea stems were obtained in the static test, in which an Instron strength tester was used to determine - within the force range of elastic strain - the stem rigidity (EI) and the modulus of elasticity (E), and at the moment of maximum bending force application to the stem – the maximum bending stress (σ_{max}) (Skubisz 2002). At the same time, measurements were taken of the outer (Φ_z) and inner (Φ_w) stem diameter at the point of bending. The diameter values were necessary to determine the moment of inertia (I) and the index of strength (W), and to evaluate the stem wall thickness (G) and the stem cross-section surface area (S). In order to determine the variability of the mechanical properties on the stem length, the measurements were taken at five points on the stem length. The first measurement point was located close to the root (about 2 cm above). The stem was divided into five equal sections, from the root upwards. The measurements were taken on stem sections of standardized length. The results are presented in Table 1 and Table 2 as well in Figures 1 through 4.

RESULTS

A characteristic variability of the mechanical parameters was observed on the length of the pea stems (Table 1 and Table 2).

The study showed that the parameters reach their extreme values. Rigidity had the lowest values at the root of the plant. Then its value increased steadily up along the length of the stem, and then lowered again at the plant top. Especially high values of stem rigidity were characteristic for plants resistant to lodging. The elasticity of pea stems reached its minimum in the middle of the stem length. High values of the modulus of elasticity were observed close to the root and, only slightly lower, at the plant top. It was found that the maximum bending stress provided a similar interpretation of the pea stem strength. However, the values of the maximum bending stress varied within a much narrower range of variability on the stem length.

The study showed that the pea cultivars under analysis differed in the strength of their stems. The Piast (an earlier cultivar from 1995, selected for comparison with results for the new cultivars) and Brutus cultivars were characterized by much higher values of the mechanical parameters as compared to the Komandor cultivar. At the same time it was found that the Rola cultivar was characterized by high values of stem rigidity. The correlation coefficients showed a significant relationship between the mechanical parameters and the stem wall thickness and the stem cross-section surface area. The study showed significant correlation coefficients and a directly proportional dependence of stem rigidity on the stem wall thickness and cross-section area, the values of the correlation coefficients being as follows: Piast $r_{0.05}$ = 0.53 – 0.65, Brutus $r_{0.05}$ = 0.48 – 0.68, Komandor $r_{0.05}$ = 0.63 – 0.70. Those relations for the Rola cultivar were low, at $r_{0.05}$ = 0.21 – 0.42. A negative correlation was found between the modulus of elasticity and the maximum bending stress, and the geometric parameters analyzed – Piast $r_{0.05}$ = -0.42 to -0.70, Brutus $r_{0.05}$ = -0.44 to –0.70, Komandor $r_{0.05}$ = -0.29 to –0.52, Rola $r_{0.05}$ = -0.41 to –0.70.

Table 1. Mean values of assignment parameters of the cv. Piast, Brutus, Komandor and Rola stems during of the full pudding (x - average , W - coefficient of variability).

		Assignment parameters				
Measurement points on the length	Statistic parameter	$EI \cdot 10^3$ Nmm^2	$E \cdot 10^2$ MPa	σ_{max} MPa	G mm	S mm^2
		Phenological phase				
		Full pudding				
Cultivar		PIAST				
1	x	2.1	4.2	8.6	0.58	4.9
	W	59	41	34	14	18
2	x	6.6	3.4	5.5	0.85	10.6
	W	33	46	37	20	28
3	x	7.5	3.0	5.5	0.96	12.8
	W	30	48	28	20	31
4	x	7.1	2.7	4.6	0.96	12.9
	W	29	49	22	23	29
5	x	6.2	4.0	5.8	0.78	9.5
	W	29	37	20	22	34
Cultivar		BRUTUS				
1	x	3.4	3.0	6.5	0.57	6.7
	W	51	51	35	33	44
2	x	5.5	1.2	2.9	0.96	15.5
	W	43	39	31	22	31
3	x	6.9	1.3	3.1	1.02	17.9
	W	32	61	31	26	34
4	x	7.6	1.4	3.1	1.06	18.2
	W	26	52	27	21	26
5	x	5.9	2.5	5.1	0.80	11.1
	W	36	41	28	23	32
Cultivar		KOMANDOR				
1	x	2.2	1.4	3.6	0.67	8.2
	W	43	34	34	36	40
2	x	3.2	0.9	2.5	0.71	11.3
	W	41	41	40	30	35
3	x	4.4	0.9	2.4	0.82	13.9
	W	37	38	32	29	33
4	x	5.0	1.0	2.4	0.85	14.4
	W	55	37	37	32	36
5	x	3.7	1.6	3.7	0.70	9.6
	W	56	47	38	32	40
Cultivar		ROLA				
1	x	5.3	4.0	6.4	0.87	9.4
	W	32	64	22	22	29
2	x	6.4	1.9	3.5	1.03	15.1
	W	24	64	32	20	29
3	x	7.1	1.8	3.6	1.06	15.5
	W	26	50	28	19	28
4	x	6.7	2.1	4.0	1.02	14.6
	W	33	55	25	26	37
5	x	6.2	3.8	5.9	0.86	10.3
	W	41	50	23	29	38

The above findings concern the Piast and Brutus cultivars. It was also found that the mechanical parameters of the stems of cultivars resistant to lodging had a weak correlation with the stem wall thickness. The correlation coefficients concerning the relation between the modulus of elasticity and the maximum bending strain, and the stem wall thickness of ripe stems of the Komandor and Rola varieties, were insignificant.

Table 2. Mean values of assignment parameters of the cv. Piast, Brutus, Komandor and Rola stems during of the full ripeness (x - average, W - coefficient of variability).

		Assignment parameters				
Measurement points on the length	Statistic parameter	EI · 10^3 Nmm^2	E ·10^2 MPa	σ_{max} MPa	G mm	S mm^2
		Phenological phase				
		Full ripeness				
Cultivar		PIAST				
1	x	3.5	5.8	11.9	0.63	6.2
	W	49	44	39	24	34
2	x	6.0	2.8	4.6	0.82	10.6
	W	32	34	44	20	46
3	x	7.8	2.4	4.3	0.81	12.3
	W	27	41	40	13	55
4	x	8.0	2.3	4.2	0.82	11.8
	W	30	40	25	19	46
5	x	6.4	3.9	7.3	0.71	10.2
	W	29	38	34	20	35
Cultivar		BRUTUS				
1	x	3.6	6.4	10.0	0.67	5.9
	W	45	42	30	27	36
2	x	6.1	2.9	4.7	0.84	10.8
	W	37	51	28	16	21
3	x	7.0	2.0	4.4	0.85	12.8
	W	33	40	25	17	23
4	x	8.1	2.2	4.5	0.77	12.0
	W	38	30	25	19	25
5	x	5.5	3.9	5.7	0.73	8.5
	W	39	46	38	19	26
Cultivar		KOMANDOR				
1	x	2.2	4.4	6.8	0.64	5.4
	W	35	39	26	20	34
2	x	3.3	2.5	3.9	0.66	8.0
	W	34	59	36	20	29
3	x	3.8	2.0	3.5	0.66	8.5
	W	42	43	29	21	31
4	x	3.9	2.3	3.8	0.66	8.5
	W	44	43	24	20	29
5	x	2.7	3.8	5.8	0.60	5.9
	W	42	44	35	17	24
Cultivar		ROLA				
1	x	4.9	3.9	6.8	0.71	8.4
	W	47	55	32	16	29
2	x	5.7	2.3	4.6	0.72	10.5
	W	33	49	25	13	22
3	x	6.4	1.7	3.6	0.74	11.8
	W	38	48	30	14	20
4	x	5.8	1.7	3.7	0.73	11.0
	W	37	64	35	18	25
5	x	5.5	3.5	4.9	0.68	8.7
	W	41	56	38	14	28

Analysis of the mechanical parameters between the points of measurement showed significant differences between the first and second, third, fourth and fifth points (Fig. 1-3).

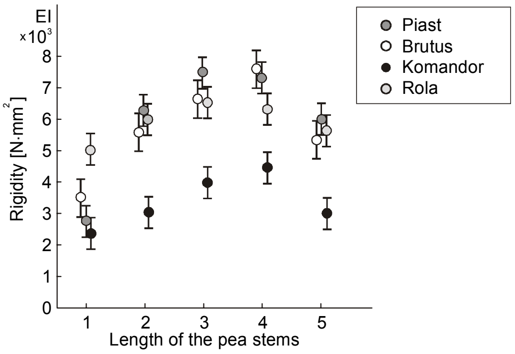

Fig. 1. *Mean values and the 95% Tukey HSD intervals of EI stems for experiment points on the length of the pea stems (1..5 points on the length of stem from the root to the tip for complete filling pod and full ripeness).*

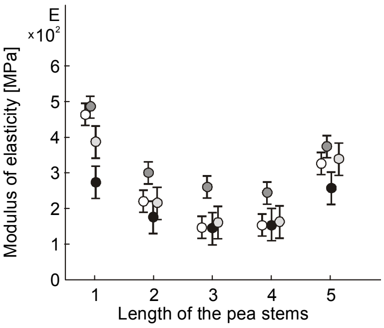

Fig. 2. *Mean values and the 95% Tukey HSD intervals of E stems for experiment points on the length of the pea stems. Explanations as in Fig.1.*

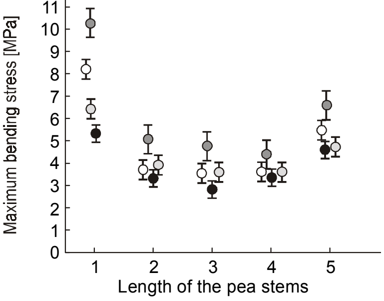

Fig. 3. *Mean values and the 95% Tukey HSD intervals of σ_{max} stems for experiment points on the length of the pea stems. Explanations as in Fig.1.*

At the same time, homogeneous groups were observed which, as a result of variance analysis performed, did not show significant differences in rigidity, modulus of elasticity and maximum bending strains. This was true, most frequently, of the second, third and fourth sections of the stems. Review of the literature confirmed differentiation of the mechanical properties on the length of stems of cereals (Skubisz 1982), rape (Skubisz 2001), herbal plants (Speck at al 1996a) and flax (Gawda 1997).

The study showed that in spite of the variability of the mechanical properties observed on the length of pea stems, homogeneous groups occurred which, as a result of variance analysis performed, did not show significant differences in rigidity, modulus of elasticity and maximum bending strains. This was true, most frequently, of the second, third and fourth sections of the stems.

The study helped to know the strength characteristics of the stems of the pea cultivars under analysis. Variance analysis was used for statistical evaluation of the results (Fig. 4).

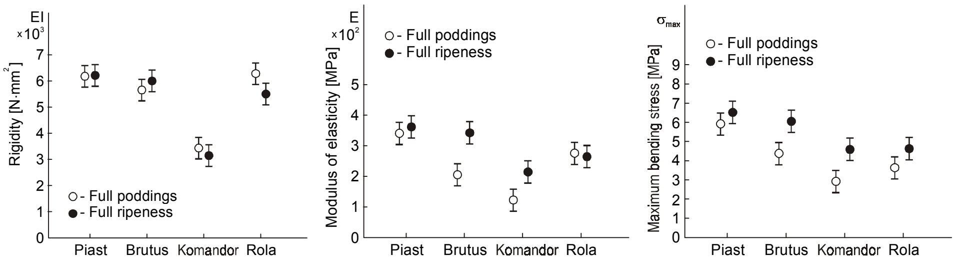

Fig. 4. *Mean values and the 95% Tukey HSD intervals of EI, E and σ_{max} stems for cultivars of the pea.*

The analysis showed the significance of the inter-cultivar differences, on the basis of the stem rigidity, modulus of elasticity, and the maximum bending stress alike. That fact substantiated the close correlation between the mechanical properties of pea stems and the resistance of pea plants to lodging.

The study showed differences between the pea cultivars. Similar findings had been obtained in earlier studies on the Piast and Agra cultivars (Rusin 2002), which showed that the strength characteristics of pea stems demonstrate inter-cultivar differentiation. The results obtained permit the formulation of the following conclusions:

CONCLUSIONS

The pea cultivars under analysis differed in the strength of their stems.

Stem rigidity, modulus of elasticity and maximum bending stress showed inter-cultivar differentiation.

The Piast and Brutus cultivars are characterized by much higher values of their mechanical properties as compared to the Komandor cultivar.

The Rola cultivar is characterized by high values of stem rigidity.

In the middle of the stem length, rigidity reaches its maximum value, while the modulus of elasticity and the maximum bending stress attain their minima.

Characteristics of the mechanical properties of the Piast and Brutus cultivars correlate with the stem wall thickness and the stem cross-section surface area.

It was shown that the strength characteristics of pea stems remain closely correlated with the resistance of the pea plants to lodging.

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METHODS AND MODELS FOR DETERMINATION SOIL HYDROPHYSICAL CHARACTERISTICS

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

INTRODUCTION

For the description of physical processes taking place in the soil-plant-atmosphere system 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 (pF curve, hydraulic conductivity, diffusivity, etc.) characterising the investigated object. Most of the models of water movement in soil profile use the moisture retention curve, coefficient of saturated hydraulic conductivity and the relationship between coefficient of unsaturated hydraulic conductivity and soil water contents or soil water potential. Also soil hydrophysical characteristics plays a key role in creation of plant growth conditions. They determined water availability for plant root system and water movement with chemicals to the deeper layers of soil profile. The knowledge of soil water hydrophysical characteristics is necessary for the study of some processes in the soil such as infiltration, drainage, solute movement and water availability for plants as well as for a description and prediction of water and solute transport processes, to quantify the effects of a land use and soil management on the soil structure related processes. The spatial distribution of water characteristics in the soil is also an important factor in the investigations of plant cover and hydrological changes caused by climate change. For this reason, important efforts are therefore being undertaken to elaborate and develop methods and models for soil water characteristics determination.

DETERMINATION OF SOIL WATER RETENTION CURVE AND HYDRAULIC CONDUCTIVITY

Measurement of static retention curve

The water retention curve is a basic static hydrophysical characteristic of soil, described by the dependence between soil water content (moisture) (mass or vol.) and soil water potential (J m^{-3}, pF). Water retention curve is determined in laboratory, using low and high pressure chambers (classic apparatus – LAB 0123, Model 1000, 1500 and 1600, 700-123 MANIFOLD, SOILMOISTURE Corp., Santa Barbara, California, USA). Usually moisture-potential characteristics are measured between saturation and wilting values, *ie* pF 0 – pF 4.2 (0.1-1500 kJ m^{-3}).

Determination of hydraulic conductivity coefficient and dynamic retention curve

Unsaturated hydraulic conductivity is one of the most important physical soil characteristics. Applying TDR techniques [1, 2] and the instantaneous profile method (IPM) the measurement of hydraulic conductivity coefficient *k(ψ)* and also dynamic retention curve *θ(ψ)* has become much faster and effective. It was demonstrated, that this method gives accurate results for various initial and boundary conditions applied to the soil sample. The instantaneous profile method (IPM) rest on simultaneously measurements of water content and water potential dynamic in the process of drying or wetting the soil column.

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

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

Alternatively the flux can be calculated from the equation:

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

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

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

Using this method it is possible to determine relationship between hydraulic conductivity coefficient and water potential (Fig. 1) and so called dynamic retention curve (Fig. 2).

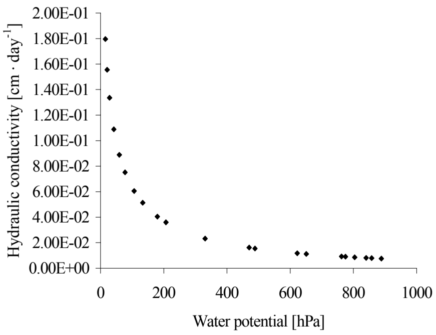

Fig.1. Hydraulic conductivity coefficient as a function of water potential

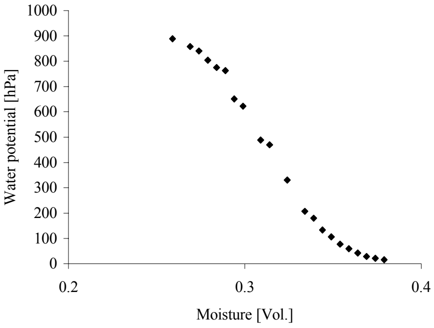

Fig. 2. Dynamic retention curve

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

Estimation of the retention curve

In the Institute of Agrophysics, Polish Academy of Sciences, a database of hydrophysical properties of Polish arable soils was created [5], containing, between others, the information about physical properties of the soils, the water retention curves and the values of water conductivity coefficients under different values of soil water potential. Therefore, a possibility was created to study the impact of chosen soil physical parameters on the value of the water content and water conductivity coefficient under chosen soil water potential values.

The measurements of the water retention curve and the water conductivity coefficient in saturated and unsaturated zones are time and labor consuming and require a specific instrumentation. Therefore, a general tendency exists to evaluate those characteristics with acceptable accuracy with the use of elaborated physical, mathematical and statistical models and algorithms. The investigations, performed in this direction have resulted in creation of numerous models and algorithms, which enable to evaluate the water retention curve and the values of the coefficient of water conductivity. A large group of these models are pedotransfer functions. Therefore in the Institute of Agrophysics PAS in Lublin, the model of retention curve was elaborated, based on the following equations of multiple regression [4]:

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

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

$$\theta_p = b_0 + b_1 Y_1 \tag{5}$$

for the water potential values higher then pF 2.7 (490 hPa), where: θ_p is the predicted water content [g g^{-1}], Y_1 - the specific surface area [m^2g^{-1}], Y_2 - the mean weight diameter of particles [mm], Y_3 - the bulk density [g cm^{-3}] and the parameters b_0, b_1, b_2, b_3 are the regression coefficients. Elaborated model was validated using Obtained correlation coefficient for validation of this model (Fig. 6.) is R = 0.87.

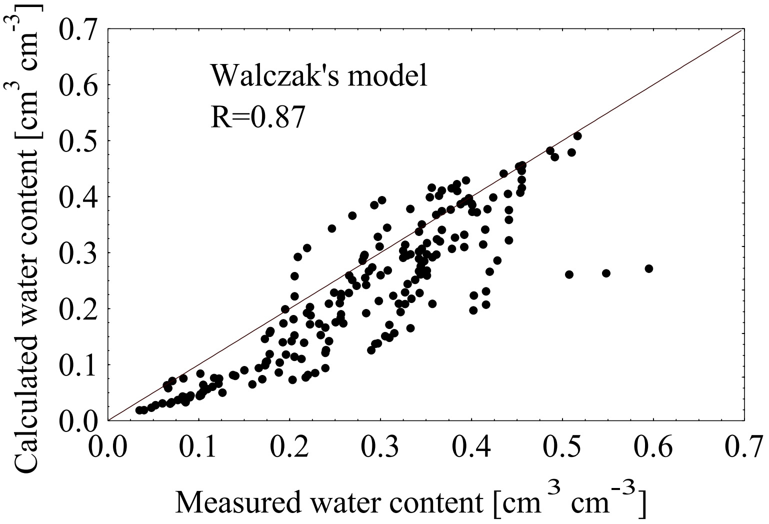

Fig. 6. *Validation of the model: measured and calculated water content*

Estimation of the hydraulic conductivity coefficient

The impact of chosen soil physical parameters on the value of the water conductivity coefficient under chosen soil water potential values was investigated [3]. The following values of the soil water potential were taken for the statistical analysis and the respective pF values: pF 0 (0.98 hPa); pF 1 (9.8 hPa); pF 1,5 (31 hPa); pF 2 (98 hPa); pF 2,2(155 hPa); pF 2,5 (310 hPa); pF 2,7 (490 hPa) ;pF 3 (980 hPa).

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

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

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

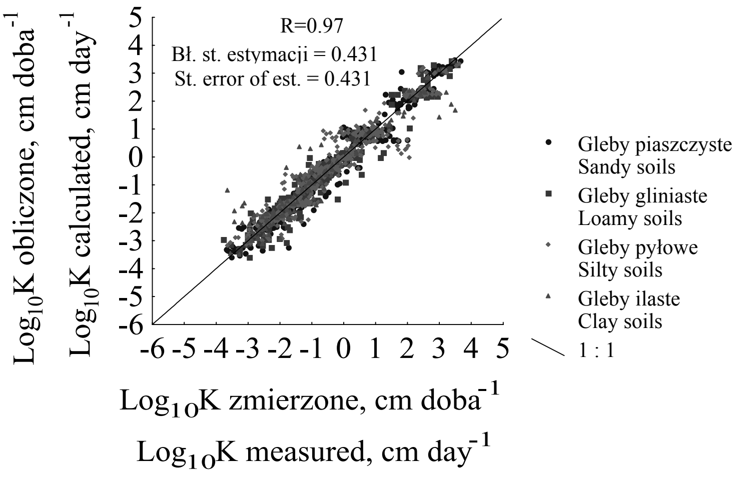

Fig. 7. *Validation of the model: measured and calculated values of logarithm of hydraulic conductivity coefficient*

Obtained correlation coefficient for validation of this model (Fig. 7.) is R = 0.97.

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TRANSPORT OF GASES THROUGH *BRASSICA NAPUS CV.* IN LABORATORY MEASUREMENTS

Stępniewska Z., Przywara G.

ABSTRACT

The aim in this paper was to shown a response of the rape plants (*Brassica napus* cv.) on aeration status in root zone after irrigation with waste water. As an indicators of soil aeration conditions the redox potential (Eh) was used. Experiments were performed in growth chambers in a plexi pots filled with *Eutric Histosol* material from the Ap horizon. Each pot was containing with the soil packed to a bulk density 0.65 Mg m^{-3} . Aeration conditions were differed by increasing soil waste water content up to full saturation.

After 4 days of growth under different aeration conditions the availability of oxygen to root zone were change Eh from 550-450 to -165 mV. An increase of methane and carbon dioxide fluxes , due to hypoxia after 4 days of irrigation of *Eutric Histosol* with waste water, on the level 0.01 $dm^3m^{-2}h^{-1}$ and 2,3 $dm^3m^{-2}h^{-1}$ respectively to waste doses was observed. In two days after irrigation ethylene in composition of tested gases was found and show the flux 0,003 $dm^3m^{-2}h^{-1}$ and tendency to growing up with.time.

INTRODUCTION

An essential negative consequence of soil flooding is a oxygen deficiency in the submerged plant tissues. Development of soil hypoxia induces evolution of higher amounts of carbon dioxiode and of smaller amounts of other gases such as, molecular hydrogen and H_2S, ethylene and methane (Gliński and Stępniewski, 1985, Marschner 1986). Plant adaptation to soil hypoxia includes a series of interconnected reactions directed to supply oxygen to the tissues and preservation of homeostasis (Monk et al., 1984; Chirkova, 1988; Crawford and Braendle, 1996).

In connection with the specificity of the effect of hypoxia on plants of special interest are compensatory changes connected with transformations of respiration pathways. Under oxygen deficiency most plants exhibit intensification of glycolysis. Main products of anaerobic metabolism are lactate (Xia and Saglio, 1992) and ethanol (Crawford, 1977, Monk et al., 1984; Chirkova, 1988). Under prolonged and deep hypoxic stress the formation of ethanol proceeds. Accumulation and transformation of this phytotoxic products are connected with functioning of alcohol dehydrogenase. Activity of this enzyme under root or under general anoxia increases significantly. (Crawford and Baines, 1977; Chirkova, 1988).

Unspecific plant response to the action of different in nature stress factors including hypoxia appear to be reactive oxygen species (ROS), which induce lipid peroxidation (LPO), destruction of pigments and cell structures (Elstner, 1982; and Halliwell, 1984). The plants possess the defense system against oxidative destruction. It constists of low molecular antioxidants (ascorbic acid, glutathion and others) and enzyme detoxificators of ROS such as superoxide dismutase – glutathione reductase, ascorbate peroxidase, and others (Larson, 1988). The resistance of plant to extreme temperatures, salinity, drought and other stress factors is connected with the free proline content in the plant tissues as one of the typical mechanisms of biochemical adaptation functioning in the plants (Gliński and Stępniewski, 1985).

The aim in this paper was to shown a response of rape plants (*Brassica napus* cv.) on aeration status in root zone after irrigation with waste water. As indicators of soil aeration conditions the redox potential (Eh) was used. The experiments were performed in growth chambers in which plexi pots filled with *Eutric Histosol* material from the Ap horizon were put. Fitotron camera with programming system for light intensity and differentiation of root zone temperature was used..

METHODS

The fresh *Eutric Histosol* (32,9 % of organic carbon and 0,39 % of total nitrogen, pH 7.4) containing 21% water from the Ap horizont of Tyśmienica river meadow (Poland) was taken. After sieving (through a 2 mm sieve) was placed into plexiglass pots (20cm high and 3cm in diameter), moistened to full water capacity with urban waste water after second step of purification.

Table 1. Chemical and physical parameters of purified urban waste water used for irrigation of *Eutric Histosol* (Kotowski, 1998).

Parameters	Unit	Range
pH	-	6,47-8,41
ChZT	g O_2 m^{-3}	30,1-56,3
BZT_5	g O_2 m^{-3}	8,3-22,6
$N\text{-}NH_4$	g N m^{-3}	1,1-7,1
$N\text{-}NO_3$	g N m^{-3}	20,2-38,4
N-tot	g N m^{-3}	22,3-43,6
$P\text{-}PO_4$	g P m^{-3}	3,1-6,8
P-tot	g P m^{-3}	3,7-7,0
Na^+	g Na m^{-3}	24,3-69,4
K^+	g K m^{-3}	11,8-27,7
Ca^{2+}	g Ca m^{-3}	59,7-95,2
Mg^{2+}	g Mg m^{-3}	12,6-19,7
SO^{2-}	g SO_4 m^{-3}	43,6-116,3
Cl^-	g Cl m^{-3}	67,8-121,6
Zn	mg Zn m^{-3}	18-800
Cu	mg Cu m^{-3}	6-198
Pb	mg Pb m^{-3}	7-96

In spring time rape seedlings (*Brassica napus* cv.) were taken from cultivated field and transported to laboratory in the stage of 5-6 leaves and placed into plexiglass pots and subjected to growth at experimental conditions. A moisture conditions in the range 0 –15 kPa by differentiation of waste water doses were received. Under control conditions distilled water instead of waste water was added. Each combination was triplicates.

Upper part of tested plants was hold at 40% of air humidity and 100W m^{-2} in a 16h of fotoperiod at 23^{o}C. Measurements of soil redox potential (Eh) as well as gases samples for gas chromatograph analysis every 1 hour during experiment were done.

RESULTS

The experiment performed at 23^{o}C in *Eutric Histosol* shown increase of methane concentration up to 0.01 dm^{3}m^{-2}h^{-1} in the plexigalass cameras covering planted *Brassica napus* after four days of irrigation with waste water. At the same time methane concentration at control conditions non excided 0.001 dm^{3}m^{-2}h^{-1}. When temperature of rizosphere zone was kept at 6 and 14^{o}C differences of air composition in compare to the control was non observed (Fig.2).

Contemporary with methane emission increase of carbon dioxide up to 2.3 dm^{3}m^{-2}h^{-1}was noted at 23^{o}C after two days of soil flooded with waste water while at control conditions remain on the level below 1 dm^{3}m^{-2}h^{-1}.

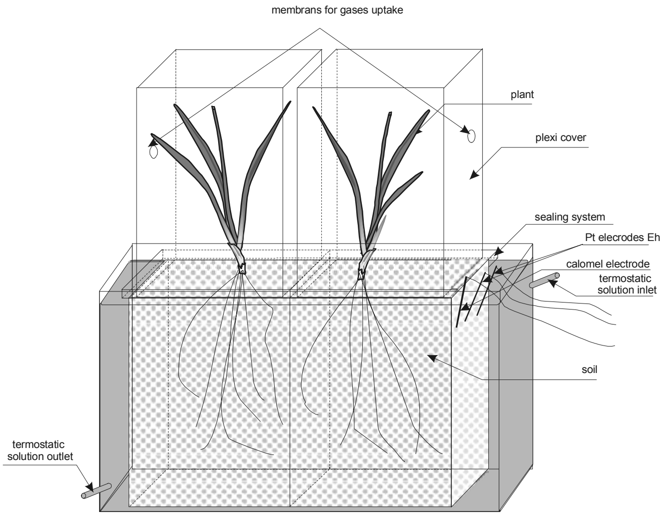

***Fig.1**. Plexiglass set-up used for experimental plant growth*

Tendency to increase of $C0_2$ concentration was observed in the combination performed at 14^{o}C (Fig.3). Presence of ethylene in a composition of analysed gases as a result of waste water treatment at 23^{o}C the was found. Ethylene flux was increase up to the end of experiment when obtained 0.003 dm^{3}m^{-2}h^{-1} (Fig.2).

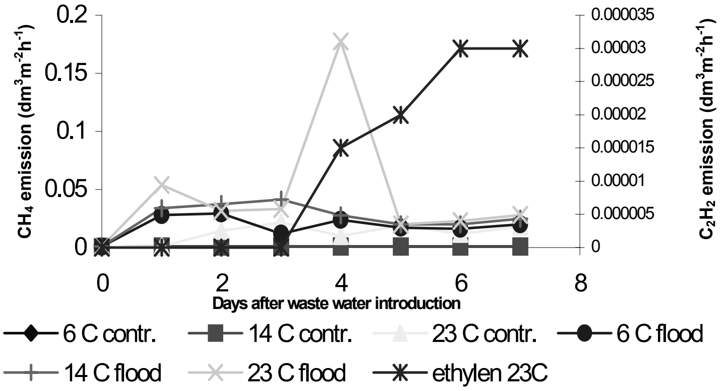

Fig.2. *Dynamic of methane and ethylene fluxes after irrigation of Eutric Histosol with waste water after second step of purification.*

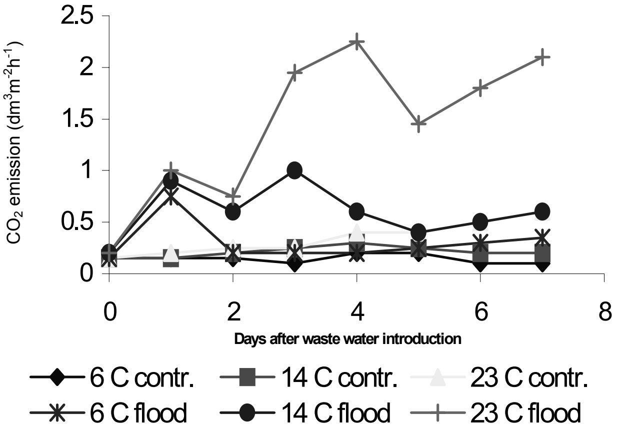

Fig.3. *Dynamic of carbon dioxide flux after irrigation of Eutric Histosol with waste water after second step of purification.*

CONCLUSIONS

Irrigation of rape plant with waste water during summer time effects on oxygen transport in rizosphere. As a consequence of cells root metabolism in anaerobic conditions changes in composition of released gases in upper part of plants were observed.

Even short time as 3-4 days of quite saturated soil conditions involved formation of new gases as methane and ethylene. Intensity of their fluxes to atmosphere are connected with temperature in root zone, and at 6 ^{0}C that is stabilised on the control level.

Contemporary increase of carbon dioxide concentration indicate on deep hypoxic stress increasing with flooded time when to survival under unfavourable conditions plants develop metabolic adaptation as glycolysis and fermentation.

There are several papers indicating that released gases in anaerobic soil conditions are going on rather from vegetated surface than non-vegetated surfaces, what indicate on active transport of gases from soil or sediments to troposphere. Our experiment confirm an active interface between internal gas phase of root and its of potential significance in the loss of methane or carbon dioxide to the atmosphere.

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DYNAMIC OF TWENTY-FOUR HOURS METHANE EMISSION FROM THE LAKE MOSZNE IN THE POLESKI NATIONAL PARK (EAST PART OF POLAND)

Stępniewska Z., Szafranek A.

ABSTRACT

Methane is an important greenhouses gas, which can be formed in wet soil or in the lake sediment. Process of methanogenesis require low redox potential and high content of easy decomposed organic matter and that conditions occur in lakes bottom.

The aim of this paper was to show dynamic emission of methane from the lake Moszne during twenty–four hours observation. The Lake Moszne which has 17.6 ha area and maximal depth 2.5 m is situated in Łęczyńsko-Włodawskie Lake District in the east part of Poland. It is one of the natural lakes in this region which has small anthropogenic influences. That lake bottom characterizes rich content of humus and organic matter, it is surrounded by peat and overgrown by plants and forest. Organic matter flows down from peat to lake and cause turbidity of water and the water is faintly stir.

During the summer (in middle of July 2002) air samples were taken by twenty four hours. The summer season was selected because characterizes much higher emission of methane than cold season during the year. In order to estimate of methane emission from tasted lake samplers of released air were collected inside chamber located by shore lake on the surface of water. Formed gasses were taken from chamber by syringe and next analysed by gas chromatograph with flame ionisation and temperature capture detectors. It was affirmed that concentration of methane in collected, during the twenty-four hours, air samples ranged from 3.5 % to 56.6 %.

This results showed that investigation lake is a serious sours of methane, where emission was determined on the level 13.3 kg CH_4 ha^{-1} day^{-1}.

INTRODUCTION

Methane is an important greenhouse gas, which like carbon dioxide and nitrous oxide contributed in climate changes. The tropospheric lifetime of methane is about 7 years and it absorbs radiation in the 3 to 4 μm and 7 to 8.5 μm wavelength range. Methane concentration in atmosphere is estimated as 1.8 ppmv (part per million by volume) and increase about 0.5% to 1% per year. It is also consider the most abundant reactive trace gas in the troposphere, its reactivity is important to both tropospheric and stratospheric chemistry (Huttunen, 2001, Singh, 2000, Wuebble, 2002). For that reasons it has been reported in about 20% participation to the greenhouse effect.

Process of methanogenesis occurs under anaerobic conditions and the presence organic compounds with participation methanogenic microbial communities. Methanogens consume H_2 formatted in intermediate fermentation of organic acids and alcohols and gaining energy by reducing CO_2 and the methyl groups of methanol, methylamines and acetate to CH_4. About 70% of the methane is formed from acetate and 30% of remaining from carbon dioxide and hydrogen. Gaining in this way energy methanogens use for their own cell maintenance and growth (Kettunen, 1999, Lay, 1996, Reeve, 1997). In the presence of O_2 released of CH_4 can be consumed by methanotrophic bacteria (Huttunen, 2001)

Methanogenic degradation of organic matter in lake sediments occurs in a wide range of temperature including psychrophilic to extreme thermophilic conditions. An exponential dependence of methane production rate was found between 2 and 30 ˚C (Nozhevnikova, 1997).

Emission of methane depends from the season of the year. During the winter, when lake surface is cover by ice and water is not stirring, gasses emission to the atmosphere is diminished. During the open water period lakes can release CH_4 into the atmosphere. For that reasons there are often large CH_4 emission in the summertime, where the production of CH_4 can be favoured by high amounts of easily degradable organic matter and in the O_2 deficient sediment (Huttunen, 2003).

Methane emission from lake sediments occurs in two ways: molecular diffusion throughout bubbles and by plants. Air channels in plants and roots simplify methane emission from vegetated sites and also transmit oxygen into soil profile (Bazhin, 2001, Yu, 1997). Plants with roots immersed in waterlogged soil in order to maintain root function and survival must transport oxygen from atmosphere down to the roots. Plants characteristic for waterlogged environments are adapt to anoxic condition by equipped in aerenchyma with large intercellular air space in root, which facilitates transport of gas phase to the roots and from them (Watson, 1997).

The rate of methane emission depends also on the concentration of methane in the bubbles which are formed on the bottom of the lake and next migrated to the lake surface and atmosphere (Bazhin, 2004). Lakes, swamps, peatlands are great source of methane emission and amounts to half the methane flux into the atmosphere from various source and contributes 15% to the greenhouse effect (Cao, 1998, Edwards, 1998).

Methane emission from wetlands is correlated significantly with the mean water table level. Vascular plants regulate the CH_4 emission from peatlands by substrate supply from primary production and also by transporting CH_4 throughout aerenchymatous tissues into the atmosphere (Huttunen, 2003).

METHODS AND MATERIALS

The dynamics of methane emission from the Moszne lake were led during summer (in the middle of July 2002). The lake Moszne has 17.6 ha area and maximal depth 2.5 m. It is situated in Łęczyńsko-Włodawskie Lake District in the east part of Poland. It is natural lake surrounded by muddy plants, swamps and natural pine forest. Remains of plants flows down to bottom of the lake and cause rich content of humus and organic matter. In sediments at the bottom where anaerobic conditions are presented occurs process of methanogenesis.

Air samples were taken from the surface and from the shore of the lake during period of twenty-four hours. Samples were collected in two kinds of chambers. On the surface of the lake by the shore first chamber were located (Fig.1) and at the beginning of measurement was completely fill by water and second (Fig 2.) on the soil on shore of the lake was situated. The first chamber was made of plastic and had load in order to preserve it before emerge from water. The second chamber was consist of two parts: base made of metal, which lower edge was located on the depth 5 cm in the ground and plastic lid tightly connected with base by seal with water coat. Gasses samples were taken in three replications. In each case with takeing gas samples measurements of temperature both in the lake water as in soil were performed. Lake water and soil temperatures were tested by thermometry constructed for soil measurements.

Gasses samples from the lake and air samples emitted from shore were taken by syringe with needle by rubber plugs on the surface of the chambers and collected in deaerated and air-tight glass vials. Samples were analysed by using of gas chromatograph with flame ionisation and temperature capture detectors.

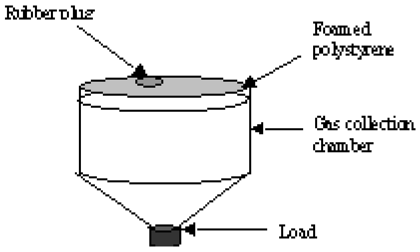

***Fig 1**. Scheme of gasses collection chambers from the lake surface*

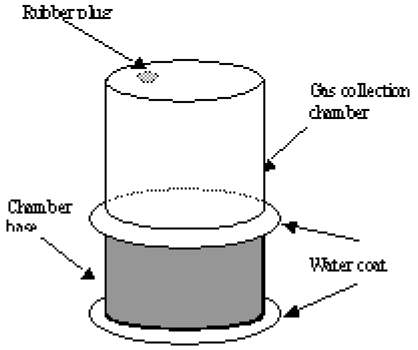

***Fig 2**. Scheme of gasses collection chambers from the lakes shore.*

RESULTS AND DISCUSSION

Dynamic of CH_4 concentration in gasses samples taken from sediments layer of the lake and shore as a function of time is presented in Fig. 3. and 4.

That figures shown that methane emission was not constant during measurement period in both sites. Level of methane emission during the night and the day from float chamber was differ, nightly emission equalled about 47,7 % of total twenty-four hours emission. In the case standing chamber emission during the night was significantly lower than during the day and amounted 88 % of twenty-four hours emission.

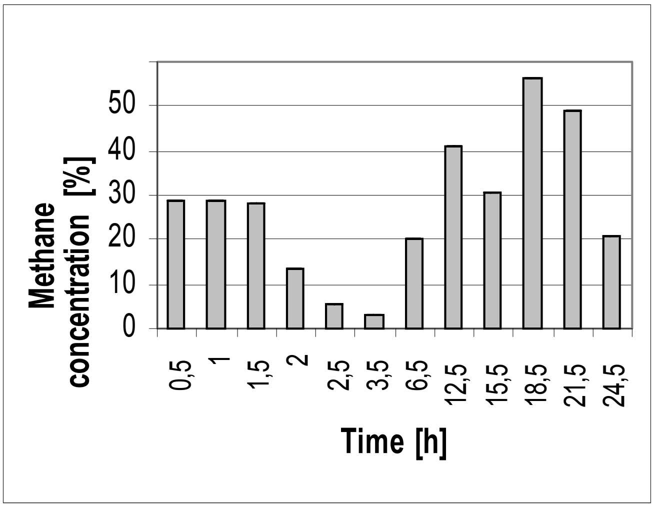

Fig. 3. *Daily of methane concentration in gas samples released from the lake surface.*

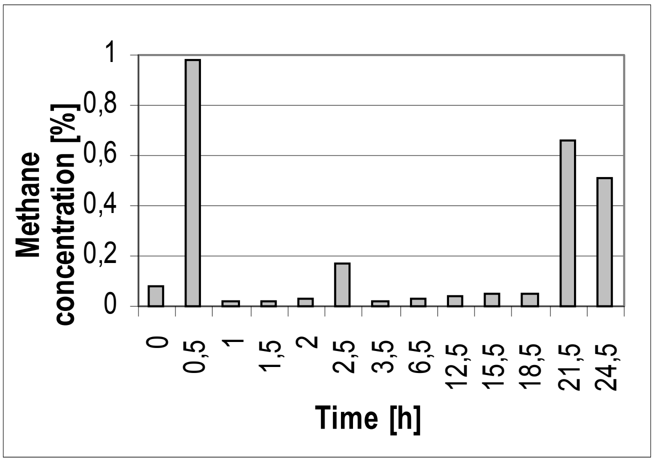

Fig. 4. *Daily of methane concentration in gas samples emitted from the lake shore.*

Statistically significant difference between CH_4 emission and time of experiment in both case were found ($p<0.00005$). Relation between CH_4 concentration and the lake water and soil temperature are presented in Fig.5. and Fig.6. In each case positive correlations, meaning that increase of temperature in littoral zone caused increase of methane emission.

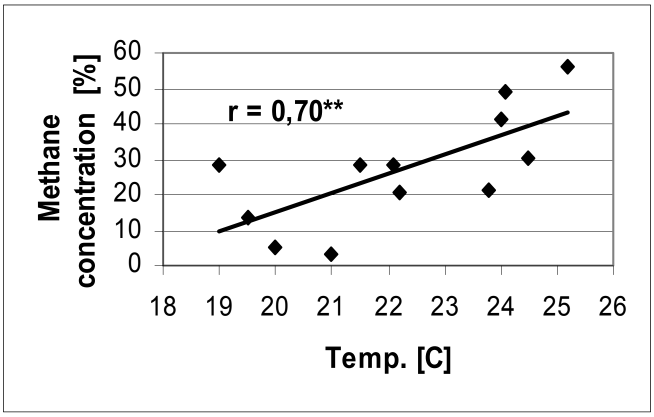

Fig. 5. *Methane concentration as a function of the lake water temperature (in littoral zone).*

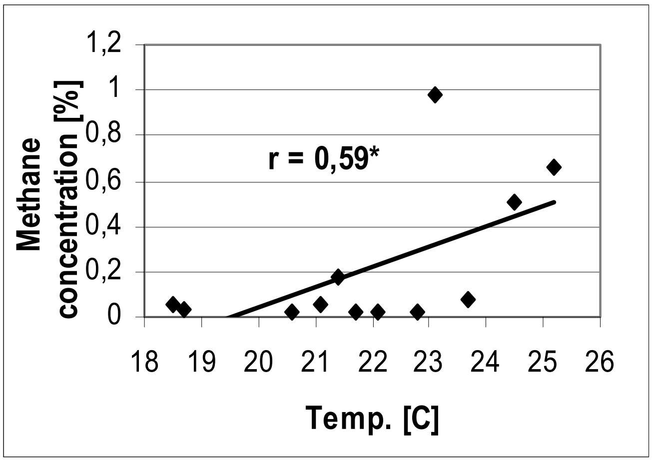

Fig. 6. *Methane concentration as a function of soil temperature (lake shore).*

Daily mean measured values of methane concentration in air samples taken from two measurement sites presents Tab. 1. It was affirmed, that methane concentration in air samples released from the lake surface, in the wide ranged from 3.5 % to 56.6 %. In the chamber situated on the shore considerable lower of CH_4 content values amounted from 0.022 to 0.656 %, what consists maximally only 1.2% compare to gas emission from lake sediment. When formed methane is transported to the soil surface it might be oxidized then finally emission from the peats is considerable lower then from lakes.

Table 1. Concentration of CH_4 with time; mean value ±L SD (95% half interval of confidence). Mean values followed by the same letter are not significantly different at 5% level.

Time [h]	Methane [%]	
	lake surface	lake shore
0.0	-	$0.077 \pm 0.139_a$
0.5	$28.56 \pm 0.43_e$	$0.976 \pm 0.171_c$
1.0	$28.46 \pm 0.61_d$	$0.022 \pm 0.139_a$
1.5	$28.46 \pm 0.61_d$	$0.024 \pm 0.171_a$
2.0	$13.69 \pm 0.61_b$	$0.026 \pm 0.171_a$
2.5	$5.34 \pm 0.61_b$	$0.175 \pm 0.140_a$
3.5	$3.35 \pm 0.61_a$	$0.024 \pm 0.140_a$
6.5	$20.48 \pm 0.61_d$	$0.029 \pm 0.171_a$
12.5	$41.15 \pm 0.61_g$	$0{,}045 \pm 0.140_a$
15.5	$30.39 \pm 0.61_f$	$0.05 \pm 0.139_a$
18.8	$56.39 \pm 0.35_h$	$0.054 \pm 0.139_a$
21.5	$48.76 \pm 0.61_g$	$0.656 \pm 0.140_b$
24.5	$21.12 \pm 0.61_d$	$0.508 \pm 0.140_b$

It was estimated that up to 90 % of methane produced in peatlands can be consumed by methanotrops during its transport to the surface and next to the atmosphere (Macdonald, 1998). Results presented by other authors obtained from measurement leaded on eutrophic lake Postilampi in Finland indicated highest methane concentration in emitted gasses on the level 55.5-69.2% (Huttunen, 2003).

This results showed that investigated lake district is a serious source of methane, particularly in littoral zone very modified by temperature. Emission during summertime was estimated on the level 13.3 kg CH_4 ha^{-1} day^{-1} from the surface of the tested lake and showed the maximum at 56 % level from the volume sample whilst the minimum at 3.3 %.

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REDOX RESISTANCE OF SOILS ENRICHED WITH NITRATES

Stępniewska Z., Szmagara A., Ostrowski J.

ABSTRACT

The addition of nitrates to soil in case of lack of oxygen leads to their consumption as electron acceptor in denitrification process. Therefore the presence of nitrates under anaerobic conditions can affect buffering of redox status in soil. Reduction of nitrates, connected with N_2O emission, appears when the amount of oxygen in soil is totally exhausted and the water displaces the air in porous medium. After reducing all available nitrates the soil redox potential decreases below 400 mV (at pH=7).

The aim of this work was to and to determinate how an addition of nitrates affects the redox resistance of amended soils on the example of a large set of soils.

The selected soil samples of various properties come from arable layer of 171 mineral soil profiles, belong to different soil units.

Both the control samples flooded only with distilled water and enriched with a nitrates solution up to 100 kg $N\text{-}NO_3^- \cdot ha^{-1}$ (between 22 and 33 μg $N \cdot g^{-1}$) samples were incubated at the constant temperature 20°C±1°C.

The nitrates addition caused increase of t_{400} values by 0,5 day in the case of over 41% of tested soils and from 1 to 5 days for about 13% of soils as compare to control samples. In the 32% of soils did not found any significant changes in redox resistance after addition of 100 kg $N\text{-}NO_3^- \cdot ha^{-1}$, whereas in about 13% was observed the negative effect. The difference between initial values of Eh for enriched and control samples ranged from 0 - 50 mV for over 55% of soil samples and from –50 mV to 0 for about 40% of tested soils.

INTRODUCTION

Nitrates introduced into the soil with fertilizers, mainly in spring, are rapid taking through plants. Excess of no assimilated nitrates are leached to groundwater due to high solubility in water or undergone changes in chemical and microbiological processes.

Denitrification process, which proceeds in anaerobic conditions, is a source of 70-90% of N_2O emission from soils and land use practices, known as a greenhouse gas. The N_2O concentration in atmosphere is established on the level of 314 ppbv, increase about 0,2% per year and its estimated emission is equal 7 Tg year^{-1} (Khalil, 2002). It was showed that N_2O emission is correlated with soil redox potential. The beginning of N_2O emission from the light textured soils was observed at 400 mV, while in the heavier textured soil below 400 mV (Włodarczyk *et al.*, 2003).

Theoretically, nitrates can also be bounded into sorption soil complex, nevertheless Polish soils are characterized by very low sorption complex to anions.

Redox potential (Eh) is an aeration parameter characterising the complex of total redox transformations occurring in the soil. A progressive decrease of redox potential occurs when soils are flooded because oxygen is only sparingly soluble in water and diffuses about 10^4 times more slowly in water than in air. In these conditions proceeds in turn reduction of molecular oxygen, nitrates, oxides of manganese and iron, sulphates and carbon dioxide presented in soil solution (Schlesinger, 1997). The humic substances presented in soil also can effect on redox properties and redox transformations in soil, especially for iron reduction (Struyk and Sposito, 2001).

Stability of redox potential in the environment can be describe by soil feature called "soil redox resistance" which is defined as the time, at which in the water saturated soil the redox potential decreases to the value of 400 mV corresponding to the beginning of the nitrate decomposition (t_{400}) or to 300 mV (t_{300}) characteristic to the beginning of reduction of manganese and iron oxides (Gliński *et al.*, 2000).

Nitrates are not only used as an electron acceptor for anaerobic oxidation of iron but also for oxidation of organic substrates and hydrogen (Ratering and Schnell, 2001). In addition, they can be used for anaerobic ammonium oxidation process (anammox) (Van de Graaf *et al.*, 1995). Nitrates can also be produced in the oxic microsites from ammonium in nitrification process.

The aim of this work was to and to determinate how an addition of nitrates affects the redox resistance of amended soils on the example of a large set of soils.

MATERIALS AND METHODS

For laboratory experiments, surface horizons of soil samples have been selected from the Bank of Mineral Soils of Poland gathered in the Institute of Agrophysics of Polish Academy of Sciences in Lublin (Gliński *et al.*, 1991). The soil samples were taken from 171 soil profiles representing 25 units of typical mineral arable soils covering the territory of Poland (Table 1).

Tested soils were air-dried and sieved (1 mm sieve), and then 30-g samples were placed in 100-ml beakers and enriched with 30 ml of potassium nitrate solution adequate to dose 100 kg $N\text{-}NO_3^-ha^{-1}$, taking initial content of nitrates into consideration (Stępniewska *et al.*, 2003). The same amount of distilled water was added to control samples. Samples were incubated at $20^oC \pm 1^oC$ in darkness (Heraeus) open to the air.

The Eh values were measured in soil suspension by pH/redox meter (CPI-551 ELMETRON) equipped with platinum electrodes 0,5 x 4 mm and calomel reference electrode. The first measurements were performed after 3 hours, and next one in following days until the redox potential, both in control and sample enriched with nitrates, received values below 200 mV. Before each a series of measurements every platinum electrode was calibrated in Michaelis buffer (at Eh = 168 mV). The placed Eh values are means from measurements carried out with three platinum electrodes (Gliński and Stępniewski, 1985).

Table. 1. Studied soil units and number of tested soil samples.

No.	Soil unit	No. of soil samples
1	Rendzin Leptosols IB 1a	7
2	Rendzin Leptosols IB 1b	5
3	Haplic Phaeozem	4
4	Haplic Luvisols and Dystric Cambisols - loose sands	41
5	Haplic Luvisols and Dystric Cambisols – light loamy sands	10
6	Haplic Luvisols and Eutric Cambisols – loamy sands	4
7a	Haplic Podsols – loamy sands	12
7b	Eutric Cambisols – loamy sands over loams	16
8a	Haplic Podsols – light loams	13
8b	Eutric Cambisols – light loams	12
9a	Haplic Podsols – medium loams	11
9b	Eutric Cambisols – medium loams	11
10	Eutric Cambisols and Haplic Luvisols – heavy loams	5
11	Eutric Cambisols and Haplic Luvisols – non uniform loams	7
12	Haplic Luvisols and Distric Cambisols – gravels	11
13a	Haplic Podsols – hydrogenic silts	4
13b	Eutric Cambisols – hydrogenic silts	4
14	Haplic Luvisols and Eutric Cambisols – loess	8
15	Haplic Luvisols and Eutric Cambisols – clays	7
16	Haplic Luvisols and Eutric Cambisols – loams and skeleton loams	4
17	Haplic Luvisols – loams	16
18	Haplic Luvisols and Eutric Cambisols – clays	3
19	Haplic Luvisols and Eutric Cambisols – silts	3
20	Eutric Fluvisols – loams and silts	4
21	Distric Fluvisols – sands	4
22	Distric Fluvisols – sands	3
23	Mollic Gleysols – dev. from loams and silts	11
24	Mollic Gleysols – dev. from sands	7
25	Terric Histosols	5
	Total	171

RESULTS AND DISCUSSION

The charts showing changes of the Eh value in time were obtained on the base of Eh measurements. Here, the rate of change in the soil redox potential was soil specific. It depended on the original content of soil oxidant and reductants.

The differences between initial Eh values (after 3 hours of incubation) for enriched and control samples ranged form 0 to 50 mV for over 55% and from – 50 mV to 0 for about 40% of studied soils.

The values of t_{400} and t_{300} were received from the Eh graphs respectively for control and nitrate enriched each sample. The shapes of curves were very different for every investigated soil. The examples of Eh dynamic during incubation of soils originated from various soil units are presented on Fig. 1 (a, b, c).

The values of t_{400} for control samples on presented charts were rather small, about 0 to 0,5 of day, and in samples enriched with nitrates this values were on similar level (Fig. 1a and Fig. 1c) or reached even over 3 days (Fig. 1b).

Between the t_{300} values of control samples of presented soils we can report some variability, 0,875; 2,625 and 0,875 on Fig. 1a, 1b and 1c, respectively. The high differences are shown in t_{300} values of enriched samples. For soil presented on Fig. 1a t_{300} reached more than 7 days, and 8,5 days and over 2 days for soils on Fig. 1b and Fig. 1c.

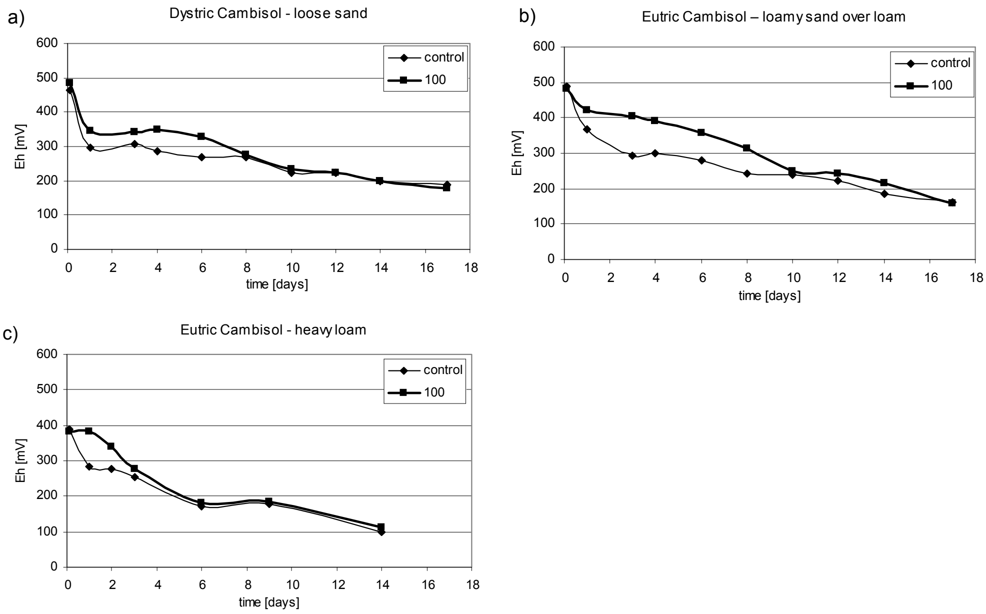

Fig. 1. *Dynamics of Eh changes during incubation at 20^oC of: a) loose sand (Dystric Cambisol) No. 4, b) loamy sand (Eutric Cambisol) No. 7b and c) heavy loam (Eutric Cambisol) No. 10, at the control and enriched with nitrates (100 kg N-NO$_3^-$ ha^{-1}) conditions.*

The effect of nitrates doses on the rate of nitrates reduction was determined on the basis of calculated differences between t_{400} values of enriched ($t_{400\text{-}100}$) and control soil samples ($t_{400\text{-control}}$) of investigated soils (171 soil samples). It was found that about 32% of examined soils did not show any changes in redox resistance after enrichment with nitrates, for over than 41% of soils t_{400} values increase by 0,5 of day. In the case of 13% of soil samples negative effect of enrichments was observed. In the same number of soils the addition of nitrates caused the increase of t_{400} values by more than 0,5 of day until even 5 days (Fig. 2).

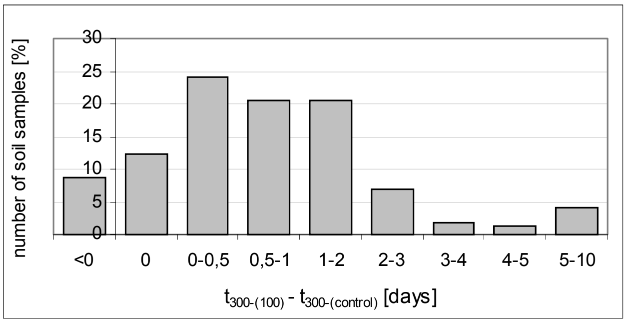

Fig. 2. *Histogram of soil enriched and control samples number in relation to changes of t_{400} (n = 171).*

In order to determination of difference between the time of nitrates reduction in control and enriched samples, t_{300} values, respectively $t_{300\text{-}(100)}$ and $t_{300\text{-(control)}}$ from 0 to 8 days and from 0 to 14 days were found. Division groups between the values of $t_{300\text{-}(100)}$ and $t_{300\text{-(control)}}$ are presented in Fig. 3.

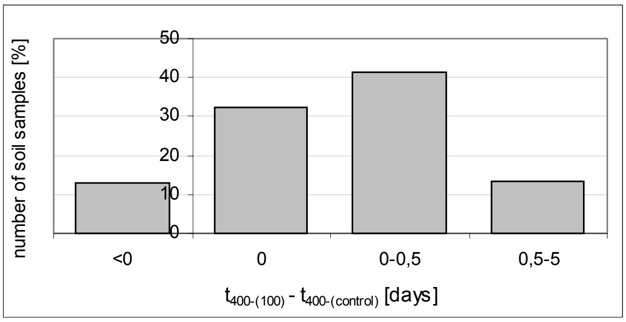

Fig. 3. *Histogram of soil enriched and control samples number in relation to changes of t_{300} (n = 171).*

In the case of almost 9% of soils the consumption of nitrates in the first step of anaerobic condition occurred faster in enriched samples than in control samples, in about 12% did not observed any differences, but in the most of soils (79%) differences ranged from 0,5 of day even up to 10 days.

In studies of other authors (Picek *et al.*, 2000) indicated the effect of glucose, as an energy source for microorganisms, on rate of redox transformations in soils. The Eh value in glucose-amended sandy clay loam soil decreased from +627 mV to –44 mV within 24h and fell to –306 mV after 48h, while in the unamended soil the Eh decreased only slightly.

The significant correlation between redox potential and organic matter in determined in forest soil (texture silty to silty-clayey) (r= - 0868) as well as relationship between redox potential and nitrates concentrations was found by Brettar *et al.*, 2002. In our investigations this relation was not confirmed.

Another experiment performed with the two paddy soil suspensions (texture silt loam and clay loam) amended with potassium nitrate to provide 50 $\mu g\ N{\cdot}g^{-1}$ about one month was required to undergo to redox potential in range +400 mV to –300 mV. The two upland soil suspensions (texture loamy sand and silt loam) with the same amendment of nitrates were required about two months to reach such level of redox potential (Yu *et al.,* 2001).

From the environmental point of view stability of nitrates, as mineral fertilizer, is important for plants but their excess of nitrates in waters (rivers, lakes) can provide to eutrophication. Not assimilated by plants nitrates can be transformed to nitrous oxide, very harmful greenhouse gas that contribute to partial destruction of the ozone layer in the stratosphere. The beginning of N_2O emission from the light textured soils was observed at 400 mV, while in the heavier textured soil below 400 mV (Włodarczyk *et al.*, 2003).

Moreover, increase of redox capacity on the nitrate level inhibits reduction of the compounds of iron or manganese and sulphate (Greene *et al.*, 2003).

CONCLUSIONS

Model investigations of redox resistance performed at 20°C on the soil samples representing 25 units of arable soil profiles enriched with nitrates (up to the level 100 $kg{\cdot}ha^{-1}$) allowed us to state that:

1. Nitrates present at the first period of incubation (3 hours) differed the Eh values for ±50 mV of enriched and control samples from each other.
2. The amendment of soil samples with nitrates caused the delay of nitrates reduction by 0,5 of day in the case of over 41% of examined soil samples, by over than one day in 13% (maximally delay is 5 days), no effected in 32%, and in 13% showed negative effect.
3. The t_{300} values of control samples ranged from 0 to 8 days (for all tested soil material), and for nitrates enriched samples ranged from 0 to 14 days.
4. The amendment effect of nitrates on redox resistance was found in 79% of all tested soil material. The highest effect of added nitrates, i.e. differences between t_{300} of enriched and control samples, ranged from 0,5 of day even up to 10 days.

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ENZYME ACTIVITY IN THE SOIL CONTAMINATED BY CHROMIUM (III, VI) FORMS

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ABSTRACT

Soil biological properties are influenced by heavy metals. Chromium compounds can have detrimental effect on soil microorganisms and their enzymatic activity, which responds for soil fertility. Therefore enzyme activities can be considered effective indicators of soil quality changes resulting from environmental stress or management practices. Between them dehydrogenase is considered an indicator of overall microbial activity because it occurs intracellulary in all living microbial cells, and it is linked with microbial redox processes. Catalase activity has been related to both the number of aerobic microorganisms and soil fertility. Whilst soil phosphatase activity plays a major role in mineralization process and is crucial in decontaminating of terrestrial environment polluted by organophosphate pesticides.

The aim of the experiment was to tested the influence of Cr (III) and Cr (VI) compounds on dehydrogenase, catalase and phosphatase activity of selected mineral soil. Soil sample was taken from the bank of Polish soils, gathered in the Institute of Agrophysics of the Polish Academy of Sciences. The air dry soil was amended with Cr (III) in the form of $CrCl_3$ and with Cr (VI) as a $K_2Cr_2O_7$ in the concentration range from 0 to 20 mg dm^{-3}.

It was stated that soil enzymatic activity decreased with the increase of chromium concentration. Only in the soil samples amended with Cr (VI) salt at the range 2-5 mg dm^{-3} an initial increase of phosphatase activity was found. The supplement of Cr (III) caused reduction of enzymatic activity to 55–90% with reference to samples without enrichment. Results suggest the negative effect of chromium contamination on the activity of soil enzymes.

INTRODUCTION

Heavy metals are common in human activity and constitute a serious health risk because they easily accumulate in soils, water and organisms. Chromium is one of the heavy metals located in the soil. It is very specific kind of metal, because the environmental and biological behavior of chromium depend most of all on its oxidation state (Welp, 1999, Cervantes, 2001, Stewart, 2003, Tokunaga, 2003). Chromium is known to exist on all oxidation states from 0 to VI, however the two most common oxidation states found in the environment soil are: Cr III and Cr VI. These two forms are different in charge, physicochemical properties, and chemical and biochemical reactivity. The anionic Cr (VI) is considered to be highly mobile in soils, while the Cr (III) cation is believed to be significantly less mobile (Cervantes, 2001, Stewart, 2003). Although, Cr (III) is generally thought less harmful than its oxidized form, it may be of concern due to its potential to be oxidized to Cr (VI) (Welp, 2001, Tokunaga, 2003).). Chromium compounds are stable in the trivalent state and occur in nature in this state in ores, such as ferrochromite, whilst chromium (VI) is usually produced from antropogenic sources (Cervantes, 2001).

Soil enzyme activities are considered to be sensitive to pollution and have been proposed as indicators of soil degradation (Trasar-Cepeda, 2000, Ledin, 2000). Studies of enzyme activities provide information on the biochemical reactions occuring in soil (Dąbek-Szraniawska, 1996, Stewart M.A., 2003).

Dehydrogenase is considered an indicator of overall microbial activity because it occurs intracellulary in all living microbial cells, and it is linked with microbial redox processes (Camina, 1998, Welp, 1999). Dehydrogenases play a significant role in the biological oxidation of soil organic matter by transferring protons and electrons from substrates to acceptors (Brzezińska, 2001).

Catalase is an intracellular enzyme found in all aerobic bacteria and most facultative anaerobes, but absent in obligate anaerobes (Trasar-Cepeda, 1999, Anderson, 2002). Catalase activity in the soils is thought as an indicator of aerobic microbial activity and has been related to both the number of aerobic microorganisms and soil fertility (Guwy, 1999, Trasar-Cepeda, 1999).

Phosphatases are among the enzymes, which transform P from non – available, organically bound forms into phosphate ions, that can be absorbed by microorganisms and plants (Baum, 2003). Acid and alkaline phosphatase catalyse the hydrolysis of various phosphate–containing compounds and act as transphosphorylases at acid and alkaline pH_s, respectively (Kramer, 2000). Phosphatase enzymes can be a good indicator of the organic phosphorus mineralization potential and biological activity of soil (Kramer, 2000).

The aim of the experiment was to test the influence of Cr (III) and Cr (VI) on dehydrogenase, catalase and phosphatase activity of selected mineral soil.

MATERIALS AND METHODS

The experiments were performed in laboratory conditions on the Eutric Cambisol-loam soil taken from the bank of soils, situated in the Institute of Agrophysics of the Polish Academy of Sciences. The main characteristics of investigated soil are presented in Tab.1. The air dry soil samples were enriched with solution of Cr (III) in the form of $CrCl_3$ and with Cr (VI) as $K_2Cr_2O_7$ in the concentration range from 0 to 20 mg dm^{-3}. Non–amended soil samples were used as a control.

Table 1. Characterization of the soil material

Soil	Granulometric composition [%]							
Eutric Cambisol - loam	Depth, cm	1-0.02	0.02- 0.002	<0.002	t_{300}	t_{400}	OM [%]	pH
	20 - 25	75	22	3	9	3	2,19	5,86
	85 - 90	77	10	13	12	3	1,25	5,91

Dehydrogenase activity was determined by Casida et all method (1964) with use TTC (2,3,5-triphenylotetrazolium chloride). Soil, (6 g), was placed in 50 ml glass flasks, where 1 ml 3% aqueous solution TTC, 120 mg $CaCO_3$ and 4 ml distilled water were added. The soil samples were incubated for 20 hours in thermostatic chamber at 30 C. After incubation the soil samples were extracted with ethanol, and filtered. Absorbance was measured by means of HITACHI UV-VIS U-2001 spectrophotometer at 485 nm.

Phosphatase activity was determined using the method of Tabatabai and Bremner (Tabatabai, 1969), according to one gram of soil was placed in a 50 ml centrifuge tube with 25 ml of toluene, 4 ml of MUB – phosphate (pH 6.5 for acid and pH 11 for alkaline phosphatase) and 1 ml of 15 mM p-nitrophenyl phosphate solution. After one hour incubation to every soil samples 1 ml of 0.5 M $CaCl_2$ and 1 ml of 0.5 M NaOH were added. The contents of tubes were immediately filtered. Absorbance was measured by means of HITACHI UV-VIS U-2001 spectrophotometer at 400 nm

Catalase activity was assayed by Johnson and Temple method (Johnson, 1964). Soil, (2 g), was placed in a 125 ml Erlenmeyer flask with 40 ml of distilled water, 5 ml 30% H_2O_2 and was shaken for 20 min. Next, 5 ml 3N H_2SO_4 was added. The tube contents were filtered and immediately titrated by 0.1N $KMnO_4$.

All determinations of enzymatic activities were performed in triplicate, and all values reported are averages.

RESULTS

Realized laboratory experiments showed that exist the relationship between soil enzymatic activity and Cr concentration in the soil environment. The highest enzymatic (dehydrogenase, phosphatase, catalase) activity in the control samples without Cr contamination were noted. Higher values of enzymatic activity of controls were caused by biotic and abiotic natural processes which took place in the soil. Excess of chromium forms in the soil disturb homeostatic metabolism of microbes, what reflect their enzymatic activity.

The influence of Cr (III) and Cr (VI) compounds on soil dehydrogenase activity is presented in Fig.1. Dehydrogenase activity showed a tendency to decrease with increase of chromium concentration. The lowest concentrations of both Cr (III) and Cr (VI) at the level 2 mg dm^{-3} reduced soil dehydrogenase activity to 51 and 66%, respectively. Meanwhile the highest Cr (III) and (VI) addition at the level of 20 mg dm^{-3} limited enzymatic activity to 6% and 15%. These results are compatible with observations of Welp (1999) and Trasar –Cepeda et all. (2000). As a consequence of analysing Fig. 1. it is possible to say that Cr (III) forms caused stronger inhibition of activity of soil microorganisms, than more dangerous Cr (VI) forms.

One possible explanation for this fact is that more dangerous form of Cr (VI) was reduced to less toxic form of Cr (III) by microorganisms living in the soil.

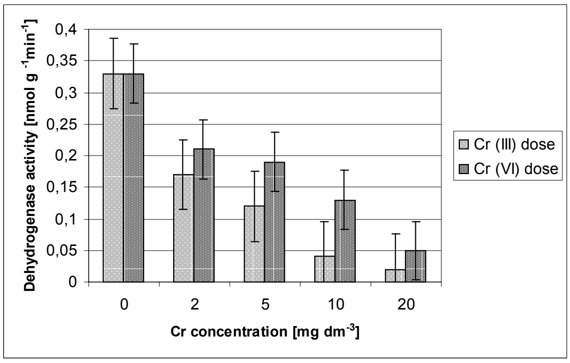

Fig. 1. *Changes in the soil dehydrogenase activity at different dose of Cr (III) and Cr (VI) amendment*

The effect of Cr on soil acid and alkaline phosphatase activity are shown in Fig. 2. Both enzymatic activities displayed a linear drop in the soil samples amended both with Cr (III) and Cr (VI) forms. However, acid form of phosphatase seemed to be more resistant to Cr contamination than its alkaline counterpart.

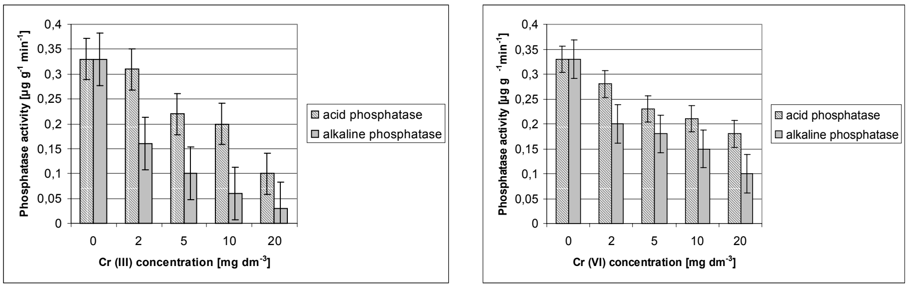

Fig. 2. *Changes in the soil phosphatase activity at different dose of Cr (III) and Cr (VI) amendment*

Moreover, it was stated that Cr (III) compounds are responsible for stronger inhibition of soil phosphatase activity. Cationic form of Cr (III) exerts a significant influence on soil enzymatic activity (Stewart et all., 2003). The risk imposed by Cr (III) form is connected with its ability to be oxidized to Cr (VI) salts (Fendorf, 1995). The lowest values for phosphatase activity as an effect of 20 mg dm^{-3} Cr (III) and Cr (VI) addition were observed, whilst the highest after 2 mg dm^{-3} of both Cr (III) and Cr (VI) doses were found. As a consequence of 20 mg dm^{-3} Cr (III) concentration acid phosphatase activity was inhibited for 70% and alkaline to 90% in relation to the control. Whereas, the same Cr (VI) concentration level caused 54% drop of acid kind of the enzyme and 30% for the alkaline phosphatase.

Changes in the soil catalase activity in the environment contaminated by Cr forms are presented in Fig. 3. Catalase activity seemed to be also sensitive to presence of chromium in the soil. Even the smallest doses of Cr at concentration 2 mg dm^{-3} inhibited 50% of enzymatic activity. In the samples, which were enriched with higher Cr concentration (5, 10, 20 mg dm^{-3}) activity of catalases were inhibited in 70-80%.

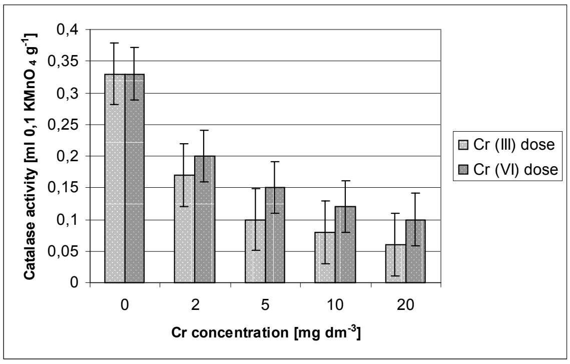

Fig. 3. *Changes in the soil catalase activity at different dose of Cr (III) and Cr (VI)*

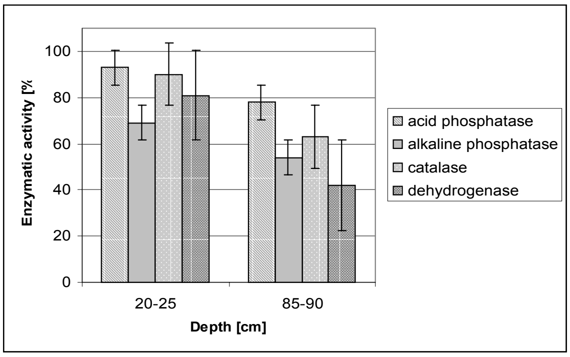

Fig. 4*. The effect of depth in soil profile on soil phosphatase, catalase and dehydrogenase activity in the Eutric Cambisol without Cr contamination*

The effect of depth of soil profile on soil dehydrogenase, phosphatase and catalase activity is shown in Fig. 4. Every kind of enzyme demonstrated diminishing trend as the depth of soil profile is growing. The highest values of enzymatic activity achieved their maximum at surface layer (20-25 cm) and were reduced at subsoil (85-90 cm).

This phenomenon was connected with humus placing, quantity of which decreasing in the deeper layers. Moreover, in the surface layer the optimum conditions for living of microorganisms occurred.

An appointed ecological doses ED_{50}, when it is possible to observe 50% drop of enzyme activities are presented in a Tab. 2.

Table 2. Estimated values of ED_{50}

Type of Enzyme	ED_{50} for Cr (III) [mg dm^{-3}]	ED_{50} for Cr (VI) [mg dm^{-3}]
Dehydrogenase	2.0	4.5
Acid phosphatase	8.5	18.8
Alkaline phosphatase	2.0	4.7
Catalase	2.0	5.6

It was calculated that ED_{50} for Cr (III) came to 2.0 mg dm^{-3} for both dehydrogenases, catalases as alkaline phosphatases. However, in the case of acid phosphatase 50% drop of enzymatic activity at the level of 8.5 mg dm^{-3} was noted. Meanwhile, for Cr (VI) ED_{50} values ranged from 4.5, 4.7 to 5.6 mg dm^{-3} for dehydrogenases, alkaline phosphatases and catalases, respectively. Acid modification of phosphatase seemed to be the least sensitive on Cr (VI) contamination, because 50% fall of enzymatic activity as a result of 18.8 mg dm^{-3} was estimated.

SUMMARY

The study showed that, chromium pollution in the soil environment have a strong negative effect on soil enzymatic activity. Chromium is a dynamic element that has many industrial uses and as a consequence can be found throughout the environment.

Both Cr (III) as Cr (VI) forms have ability to reduce soil enzymatic activity. Activity of dehydrogenases, phosphatases and catalases seemed to be very sensitive to Cr presence in the soil. Stronger inhibition of enzymatic activity was found for Cr (III) than for Cr (VI) in cation and anion forms. Although, Cr (III) is generally considered to be less harmful for different organisms, but in soil conditions it may be of concern due to its ability to accumulate in some soils (Fendorf, 1995, Stewart, 2003). It was confirmed that enzymatic activity reached maximum values at surface layer, where higher content of organic matter is responsible for the most favourable conditions for living of microorganisms.

Investigations about enzymes activities can be important for soil pollution in a heavy metals test. Presence of heavy metals in the soil environment is very disadvantageous for their activity and proper soil functioning.

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ASSESSMENT OF NITRATE LEACHING UNDER DIFFERENT NITROGEN SUPPLY OF IRRIGATED MAIZE

Stoicheva D., Kercheva M., Koleva V.

ABSTRACT

The study estimates nitrate leaching under different nitrogen supply of irrigated maize grown on Fluvisol as monoculture. The NLEAP (Nitrate Leaching and Economic Analysis Package) model application allowed to join the information obtained during the long-term field experiment of irrigated maize and to assess the character of seasonal and year-to-year dynamics of drainage and nitrate leaching. The sequential runs with the event-by-event time scale of the NLEAP model were performed for the period 1972-1990 and additional validation test was run for 2001 and 2002. The reliability of NLEAP model was tested in regard to the volume of water drained out of 1m soil layer, soil water storage and residual soil nitrogen in some of the experimental years. Year-to-year variation in the drainage flow was significant. The coefficient of variation among the measured values for the long-term period was 43% for non-fertilized variant, and about 60% for the different N treatments, and among the simulated values for the same period it is about 50-60%. The average NLEAP simulated drainage were 87, 70 и 76 mm for the non-fertilized, reduced and optimum treatment, respectively.

Annual quantity of simulated leached nitrate-nitrogen was less than 40 kg/ha for the whole period (1972-1990) under non-fertilized variant. It is above 40 kg N/ha very rare (less than 10% of the years) under reduced nitrogen treatment and nearly half of the years under optimum N treatment (V_3).

INTRODUCTION

The probability distribution of nitrate leaching out of the root zone is an important predictive tool for groundwater contamination risk analysis. Susceptible to leaching are coarse textured soils with medium to high water permeability. Usually, the influence of climate on water percolation and hence on the leached nitrate quantities is considered either for the particular years or as the average for long-term period representing steady-state situation (Stoichev, 1997; Koleva, 2002). High annual variability of precipitation restricts to some extent the predictive capacity of the so called representative years. On the other hand long-term average climate data significantly underpredict the depth of leaching (Thomas and Southard, 2002). These are the reasons for using long-term records of MTO data on daily basis for simulating the influence of climate on percolated water and respectively on nitrate leached.

Most of the experimental studies have been focused on nitrate concentration in leached water out of the root zone as an indicator for nitrogen loads under specific crop-soil-agrotechnical activities combinations. Different type of lysimeters have been used in the experimental studies on soil nitrogen and water losses in the country (Stoichev, 1974, 1997; Petrova, 1979, 1985; Dinchev, 1983). Despite the criticism to the lysimeters in regard to their accuracy for determination of drainage water volume, they have produced an important information about drainage water chemical composition under different anthropogenic loads. The necessity for monitoring of vulnerable to nitrate contamination regions, also suggests the implementation of indirect methods for assessment of the drained water quantities and leached nitrate in variety of climate conditions and anthropogenic loading.

Nitrate leaching simulation models have been applied in Bulgaria since the end of 1990s (Stoichev et al.,1998, 2001; Popova et al., 1999). The NLEAP (Nitrate Leaching and Economic Analysis Package) model (Shaffer et al., 1991) was tested for simulating nitrate leaching in different case studies: crop rotation under rainfed conditions, tomato growing under intensive irrigation and manuring in household garden, irrigated corn experiments (Stoichev et al., 1998; Stoichev et al., 2001).

The aim of this study was to assess the leached nitrate-nitrogen under different nitrogen supply of irrigated maize on Fluvisol over a number of years using long-term experimental data and NLEAP simulations.

MATERIAL AND METHODS

Site and experimental layout

Long-term experiment with irrigated maize grown as monoculture was set up in 1972 (Stoichev, 1997) at the field station of the Nikola Poushkarov Institute of Soil Science in the village of Tsalapitsa (lg=24°35’ E, lat= 42°14’ N, alt.=180 m) situated on Maritsa River watershed, Southern Bulgaria. The soil of the experimental field is defined as sandy clay loam and classified as Fluvisol according to FAO soil classification (FAO Soil Map, 1997). Soil properties of Fluvisol used as input data for NLEAP simulations are presented in Table 1.

Table 1. Soil properties of the Fluvisol in the village of Tsalapitsa used as input data for NLEAP simulations.

Parameter	0-30 cm	30-90 cm
Organic matter, %	0.70	0.49
pH in H_2O	6.0	6.4
CEC $cmol_{(c)}.kg^{-1}$	20.6	23.7
BD, $Mg.m^{-3}$	1.55	1.49
AWHC, v/v	0.155	0.150
WP, v/v	0.140	0.160

Experimental layout consists of plots with 200 m^2 size in six replications. In the design are included two N treatments (V_5 and V_3) and a non-fertilized control (V_1). For treatment (V_3) nitrogen rates were calculated to fully compensate nitrogen uptake by plants biomass and since 1975 an average rate of 232 $kg.ha^{-1}$ (a.s) for this treatment has been applied. For the other treatment V_5 was applied 50 %

reduced rate from the amounts of treatment V_3 (116 kg.ha^{-1}), which was defined as optimum with respect of N uptake. The ammonium nitrate fertilizer was applied spread - 2/3 of the rate before sowing and the remaining 1/3 was incorporated at the time of the 10-11 leaf phenological phase.

Modified Ebermaier-Shilova type of lysimeters (0.11 m^2) (Stoichev, 1974) were installed under each treatment at 1 m soil depth in three replications for collecting the leachate volumes. The main difference of this type of lysimeter compared to lysimeters with disturbed soil and monolith field lysimeters is that the contact plate was cut into the soil profile without disturbing the overlaying soil layers (Figure 1). Leachate volume was collected monthly in plastic containers at the bottom outlet of each lysimeter. Data for the period 1981-1998 were used for evaluation of space variability of drained water and for a test of NLEAP model performance.

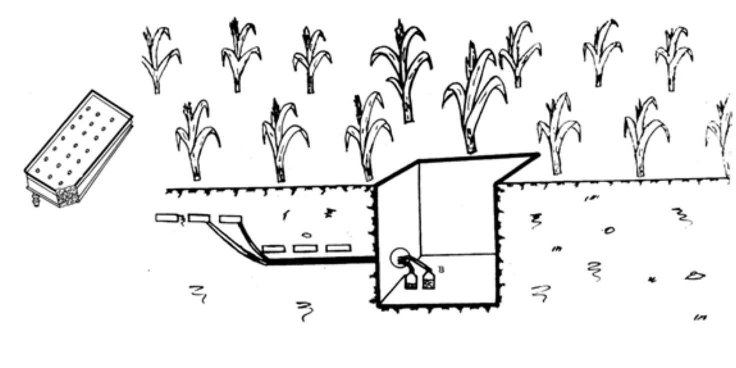

Fig. 1. *Modified Ebermaier-Shilova type of lysimeters*

Irrigation was applied by means of sprinklers scheduled so as to keep water content around field capacity and ensure a non-deficit water regime for crop growth. The applied scheduled sprinkler irrigation (96-400 mm) and the precipitation (98-444 mm) fully compensated the real evapotranspiration sums (432 -605 mm) for the vegetation period.

Data acquisition for NLEAP simulation

NLEAP model developed for quantitative estimate of nitrate leaching and risk assessment for groundwater pollution (Shaffer et al., 1991). The soil profile in the model is separated in two layers - upper 0-30.5 cm (1ft), and lower from 30 cm soil depth till rooting depth boundary. In this study the lower boundary was set to 91.5 cm (3 ft), which is close to the depth of the Ebermayer lysimeters. In the case of non-deficit water regime this should not lead to significant overestimation of water and hence nitrogen losses (Kirkova, 1996). Drainage (WAL-water available for leaching) is calculated after each precipitation and irrigation event using equations:

- for upper layer: $WAL_1=Pe-ET1-(AWHC-St_1)$
- for lower layer: $WAL=WAL_1-ET2-(AWHC2-St_2)$,

where ET is evapotranspiration, Pe is effective precipitation, AWHC is available water holding capacity, St is available water storage at the end of the previous time step. Indices 1 and 2 refer to upper and lower layer, correspondingly.

The leached nitrate-nitrogen (NL, kg/ha) depends on soil nitrate-nitrogen available for leaching (NAL) and is computed by an exponential relationship with soil layer porosity (POR) and water available for leaching (WAL):

$NL_l=(NAL_l).\{1-\exp[(-1.2)(WAL_l)/POR_l]\}$

$NAL=NAL_2+NL_l$

$NL=(NAL).\{1-\exp[(-1.2).(WAL)/POR]\}$

The nitrate-nitrogen content available for leaching in the upper and lower soil layers are calculated from nitrogen balance as follows:

$NAL_l=N_f+N_p+N_{rsd}+N_n-N_{plt}-N_{det}-N_{oth}$

$NAL_2=Nrsd_2-Nplt_2$,

where N_f is NO_3-N added to the soil from fertilizers, N_p is NO_3-N added from precipitation and irrigation, N_{rsd} is residual NO_3-N in the soil layer, N_n is NO_3-N produced from nitrification of ammonium-N, N_{plt} is NO_3-N uptake by the crop, N_{det} is NO_3-N lost to denitrification, N_{oth} is NO_3-N lost to runoff and erosion. The equations used for calculation each term are described in (Shaffer et al., 1991).

The daily climate data were obtained from the nearest MTO station in Plovdiv (Meteorological annual references, 1972-1984) and from the MTO station of the Nikola Poushkarov Institute of Soil Science in Tsalapitsa for the period after 1985. The grass reference evapotranspiration was calculated by a modified Penman equation (Doorenbos and Pruitt, 1984). The long-term records of MTO data were loaded into the NLEAP user database. As it is shown on Figure 2, the average precipitation totals for vegetation and post vegetation periods for 1972-1990 are close to that for 1991-1998, so the first one could be considered as representative for today's climate. Last years - 2001 and 2002 are characterized with less than average October-April precipitation and greater rainfall during maize vegetation period.

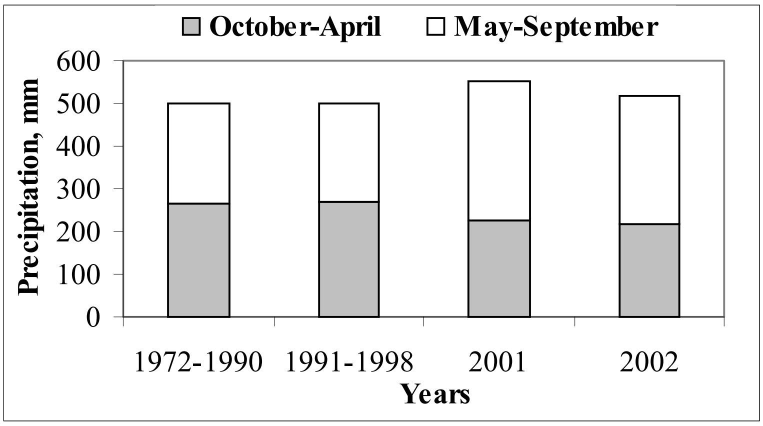

Fig. 2. Precipitation totals for the studied years and periods.

The sequential runs with the event-by-event time scale of the NLEAP model were performed for the period 1972-1990 and additional for 2001 and 2002 using actual information for climate (daily precipitation, monthly air temperature and grass reference evapotranspiration); agrotechnics; irrigation and fertilization management, yields (Stoyanov and Donov, 1996). The parametrization of the NLEAP model for this field experiment was described in Stoichev et al. (2001). It concerned nitrogen uptake by corn, maximum yields, proportions of corn development phases for all treatments. The initial date for sequential runs was 1 January for the period 1971-1990, 27.11.2000 - for 2001 and 2.02.2002 for 2002. The calculated values for nitrogen and soil water content on the last day of the previous year were used as initial data for the 1 January in sequential mode. In 2001 and 2002 runs actual sample data were used as initial values.

Statistical analysis and evaluation were made by using STATGRAF software.

RESULTS AND DISCUSSION

In this study the reliability of the NLEAP model is tested regarding to drainage water for the period 1981-1989, and to soil water storage and residual soil nitrogen in 2001 and 2002. The great space variability of measured drained water among the three lysimeter replications under non-fertilized variant (control) is shown on Figure 3. The standard deviation of replicates for the period 1981-1998 in each treatment is about 20-30 mm in average. This leads to the absence of statistically proved difference between the treatments.

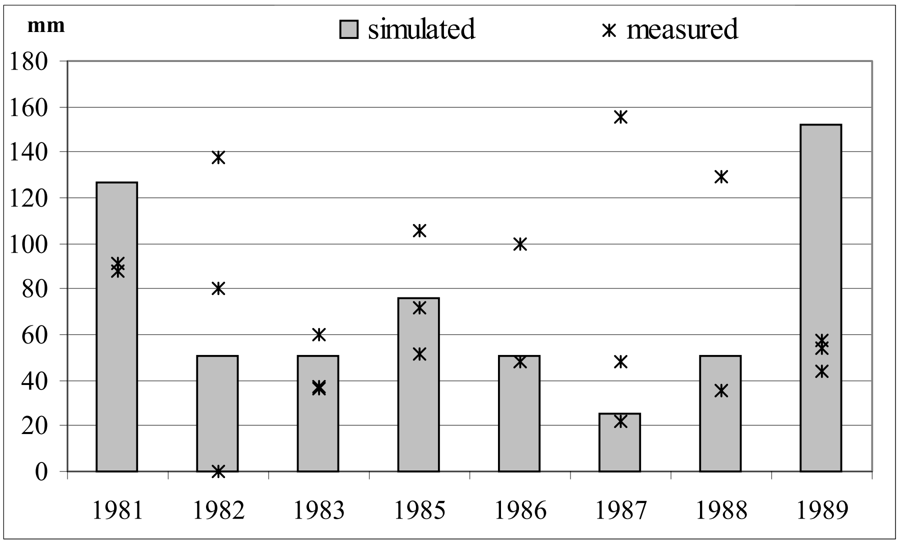

Fig. 3. *NLEAP simulation and measured annual drainage water (mm) at 1m soil depth under non-fertilized control*

Similar results were established at the beginning of the experiment and were the reason to average the drainage water values of all 9 lysimeter replications (Stoichev, 1974, 1997). The explanation of these results could be the great space variation of hydrological properties of the Fluvisol and unequal distribution of the applied irrigation as well as the increased soil evaporation of non-fertilized variant due to the lower leaf area index (LAI). Therefore in some field studies the differences in cumulative evapotranspiration under low and high nitrogen supply are not so significant (Nielsen and Halvorson, 1991). On the other hand the influence of nitrogen fertilization on the quantities of drained water is related to the crop transpiration coefficients and the water use efficiency. It was proved that any stress that reduces photosynthesis would reduce transpiration (Goudriaan and van Keulen, 1979; Tanner and Sinclair, 1983; Jones et al. 1986).

Average annual values of collected in lysimeters drainage under control variant (V_1) and optimum (V_3) treatment for the whole experimental period (1972-1998) are close to each other – about 50 mm, while under the treatment with 50% reduction of fertilization rate (V_5) it is 70 mm (Table 2).

Table 2. Mean long-term values of measured and simulated drainage flow at 1 m soil depth under different nitrogen supply of irrigated maize.

Treatments	1972-1998	1972-1990	
	mean	mean	
	measured	measured	simulated
V1	47	56	87
V5	69	86	70
V3	50	62	76

NLEAP simulated drainage quantities for the years of simulation (1972-1990) are 87, 70 и 76 mm in average for the treatments V_1, V_5 and V_3, correspondingly. Year-to-year variation in the drainage volume is also significant. Among the values measured for the period 1972-1990 the coefficient of variation (Cv) is 43% for non-fertilized, and about 60% for the N treated variants, and among the simulated values for the same period it is about 50-60%. Statistical summaries (maximum and percentiles) of simulated monthly sums of drainage flow (mm) at 1m depth for the period 1972 – 1990 are presented on Figure 4. The distribution of monthly values shows that in half of the years no drainage flow is observed.

Statistical summary of simulated annual leached nitrate-nitrogen under different nitrogen supply for the period 1972-1990 is presented on Figure 5. Annual quantity of leached nitrate-nitrogen is less than 40 kg/ha for the whole period (1972-1990) under non-fertilized variant. It is above 40 kg N/ha very rarely (less than 10% of the years) under reduced N treatment (V_5) and nearly half of the years under the optimum treatment (V_3). The year-to-year variations in non-fertilized and reduced N treatments are small due to the small quantities of nitrogen available for leaching.

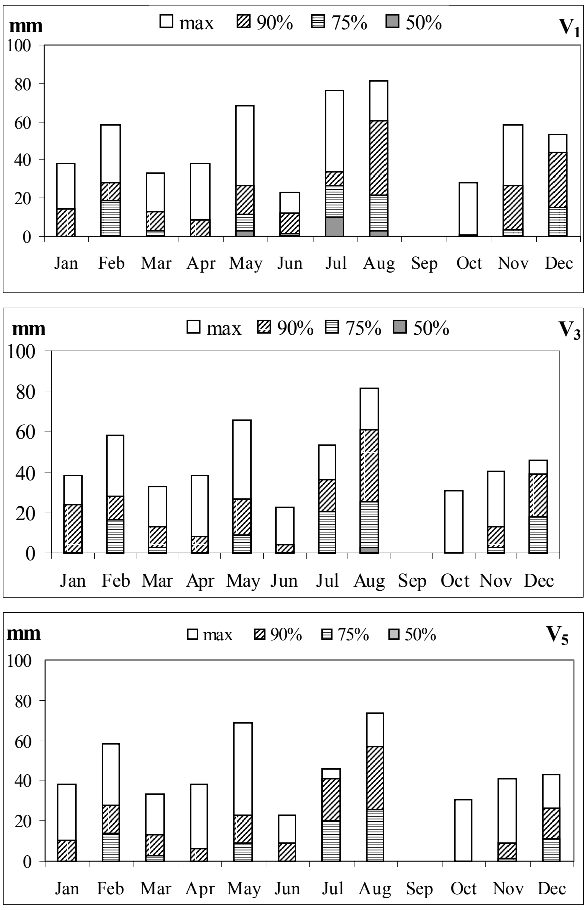

***Fig. 4**. Statistical summaries (maximum and percentiles) of simulated monthly sums of drainage water (mm) at 1m soil depth for the period 1972–1990.*

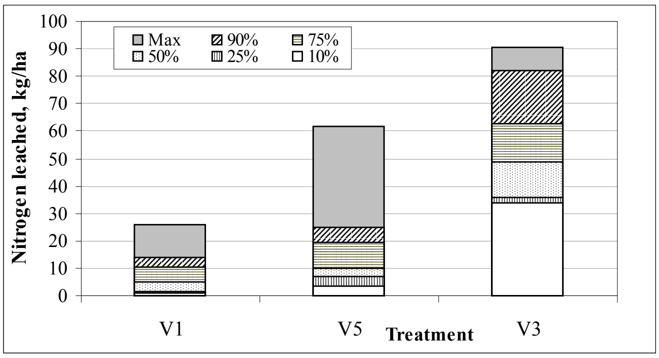

***Fig. 5.** Statistical summaries (maximum and percentiles) of simulated annual sums of leached nitrate-nitrogen at 1m soil depth for the period 1972 – 1990.*

Validation test with data obtained in 2001 and 2002 shows that better coincidence between measured and simulated residual soil nitrate-nitrogen have been achieved in the first year (Table 3). At the end of October the model predicts significantly higher values of NO_3-N available to leaching than the measured ones. One of the possible explanation is the high values of ammonium nitrogen, which suggests the occurrence of denitrification process.

Table 3. Input, measured and NLEAP simulated residual soil NO_3-N (**kg.ha^{-1}**) in Fluvisol. (Nov. 2000-Oct. 2002)

Treatments	Soil layer, cm	27.11.2000	28.04.2001		2.02.2002	28.10.2002	
		Input	Meas.	Simul.	Input	Meas.	Simul.
V_1 ($N_0P_0K_0$)	0-30	60	65	53	40	8	9
	30-90	60	123	94	72	14	74
	0-90	120	188	147	112	23	81
V_5 ($N_{10}P_5K_0$)	0-30	80	68	66	49	19	9
	30-90	60	105	102	125	52	140
	0-90	140	174	168	174	70	149
V_3 ($N_{20}P_{15}K_0$)	0-30	123	78	85	46	16	9
	30-90	67	119	115	180	131	95
	0-90	190	198	200	225	147	104

It was found good coincidence between measured and simulated quantities and seasonal distribution of drainage water in both years (Figure 6, Table 4). The exception is one-month delay of simulated drainage flow in April 2001. The quantities of leached nitrate-nitrogen is also close to that under N treatments (Table 4). Overestimation of simulation is observed under non-fertilized variant in both years.

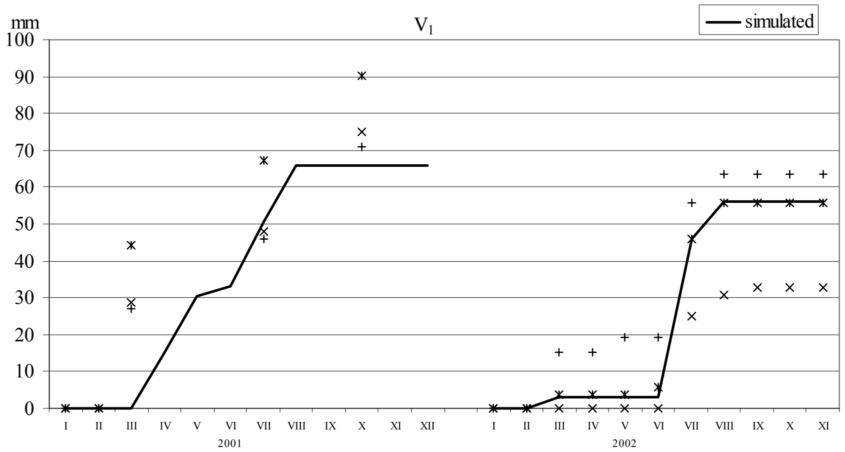

Fig. 6. *Accumulated drainage water (measured * and simulated-) under non-fertilized variant in 2001 and 2002.*

Table 4. Measured and predicted annual drainage quantity (LP) and leached nitrate-nitrogen (NL).

		Dec.2000-Nov.2001			Feb.2002-Nov.2002		
		B_1	B_5	B_3	B_1	B_5	B_3
LP, mm	Meas.	79±10	65±12	73±17	51±16	55±33	84±56
	NLEAP	64	56	56	53	43	41
NL, $kg.ha^{-1}$	Meas.	12	25	40	5	25	44
	NLEAP	28	31	39	21	31	39

During 2001 and 2002 the simulated drainage quantities vary between 40 and 65 mm - less than the average. Although similar as the annual quantities (Table 4), the drainage water and hence the leached nitrate-nitrogen have different seasonal distribution (Figure 7). In 2001 they are almost equally distributed in April, May, July and August, while in 2002 the leaching is concentrated in July due to the heavy precipitation within this month and the irrigation performed at the end of June.

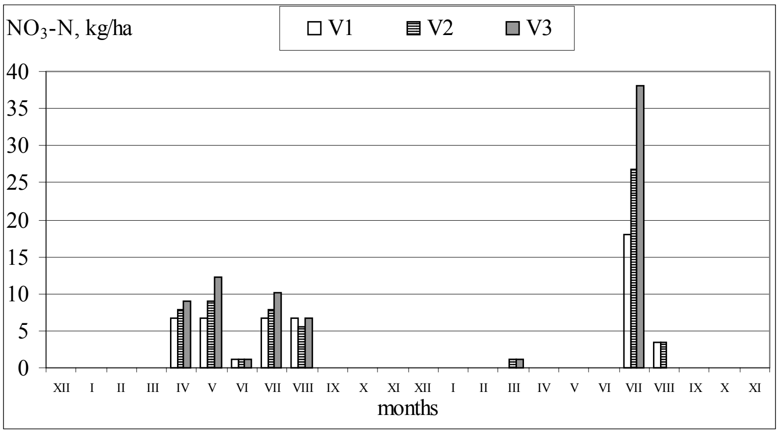

Fig. 7. NLEAP simulation of leached nitrate-nitrogen under different fertilization treatments of irrigated maize in 2001 and 2002 in Tsalapitsa.

During the summer period irregular distribution of precipitation and the applied irrigation scheme are the most significant factor for leaching occurrence because soil water content at the beginning of vegetation is usually close to the soil field capacity.

CONCLUSION

Simulation with NLEAP model allows to join the information obtained during long-term field experiment with irrigated maize on Fluvisol in Southern Bulgaria and to assess the character of seasonal and year-to-year dynamics of nitrate leaching under today's climate and different nitrogen supply. The model gives reliable results regarding the influence of climate conditions and anthropogenic loads on the leached nitrogen and could be used as predictive tool for the risk analyses in vulnerable regions.

Acknowledgement

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