ARBEITSGEMEINSCHAFT FÜR LEBENSMITTEL-, VETERINÄR- UND AGRARWESEN

SOIL ORGANIC MATTER

AND

ELEMENT INTERACTIONS

Austrian-Polish Workshop

Edited by

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Reviewed papers presented at the Austrian - Polish Workshop, given at the Polish Academy of Sciences in Vienna, April 20 – 21, 2005

CONTENT

PREFACE

The Austrian-Polish workshop "Soil Organic Matter and Element Interactions" took place in Vienna from April 20-23, 2005 and was the continuation of the workshop "Soil monitoring and soil protection", which was carried out in Lublin, Poland in 2002. The idea of having such meetings every two to three years - once in Poland, once in Austria – should be continued in the future.

At the meeting in Vienna, Polish and Austrian soil scientists exchanged their results on soil investigations, environmental pollution, soil classiffication, and remediation techniques, discussed the role of organic matter in soil in both countries and its importance in the future as well as problems of forestry and afforestation in Austria and Poland.

We would like to thank Prof. Marian Herman from the Polish Academy of Sciences in Vienna for providing the location of the workshop and accomodation. It was really an appropriate place for such a kind of meeting. We would like to thank also the head of the Association for Food, Veterinary, and Agriculture (ALVA) Doz. Dr. Gerhard Bedlan and the Austrian Agency for Health and Food Safety (AGES) for the support of the meeting and for the possibility to visit the AGES Institute for Soil Health and Plant Nutrition in Vienna.

We are especially grateful to Prof. Othmar Nestroy for organising and leading an interesting farm and field excursion, for his geological and geographical introduction to the workshop and for having been an excellent guide through the city of Vienna before and after the official meeting. All the speakers we would like to thank for the good presentations and careful preparations of the papers.

This brochure contains all presentations from the workshop in Vienna and focuses on the role of organic matter in soil and it`s interactions with nutrients and microelements. We do hope that this brochure provides a basis for understanding this special kind of research in Poland and in Austria and that it helps to intensify Polish-Austrian cooperation in this field of work.

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INTRODUCTION TO AUSTRIA -
A GENERAL GEOGRAPHIC SURVEY

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The Republic of Austria, which covers an area of 83,871 square kilometres, looks back at a most eventful history. It began with the first mention of "Ostarichi" in 996, which referred to an area between Amstetten – Krems – St. Pölten in Lower Austria. By the 16th century, under the rule of Charles V, Austria had developed into a large empire, where "the sun did not set". Now the country has dwindled to what remained from the Danube Monarchy after the Peace Treaties of St. German-en-Laye in 1919 and Trianon in 1920. The next outstanding events were the Austrian peace treaty of 1955 following World War II, and finally Austria's entry into the European Community in 1995.

No less eventfull and varied than the country's history are its geology, climate, physical geography, and landscape (Map 1 and Map 2)

Map 1. Physical map of Austria
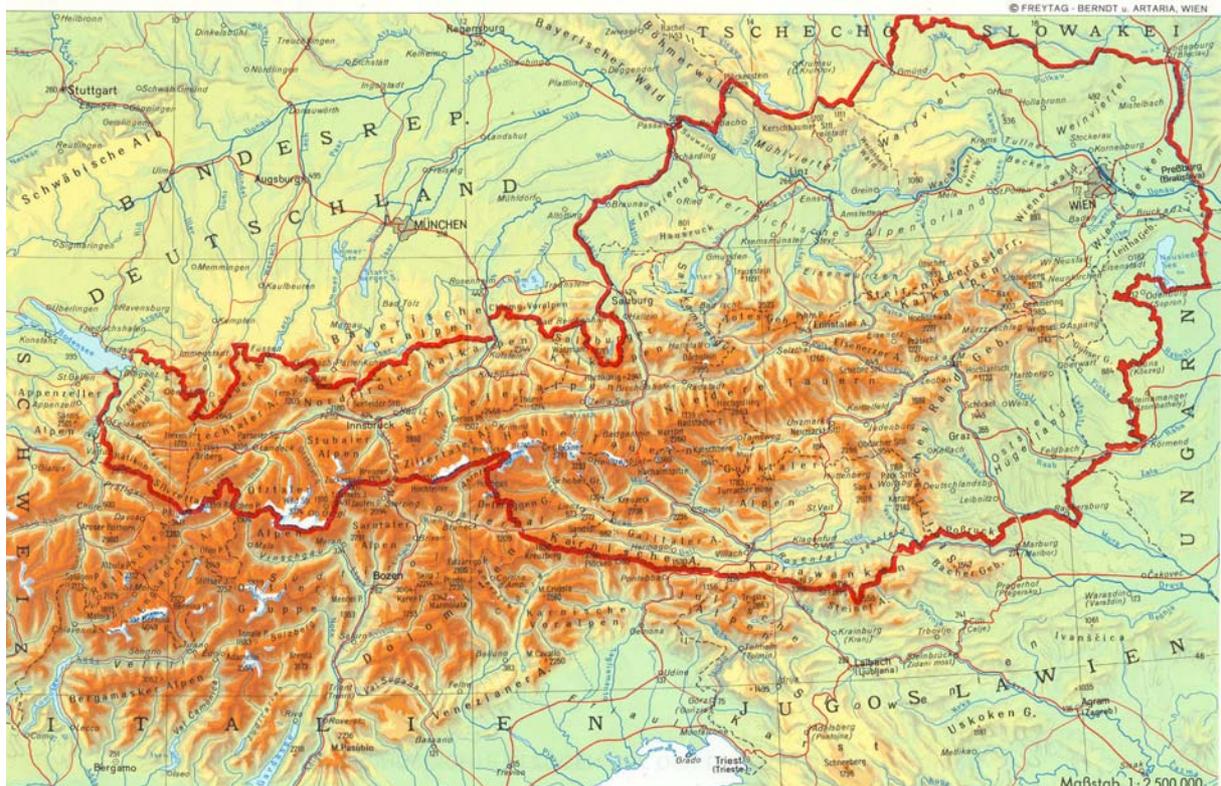
Map 2. Shares of different altitudes above sea-level in Austria
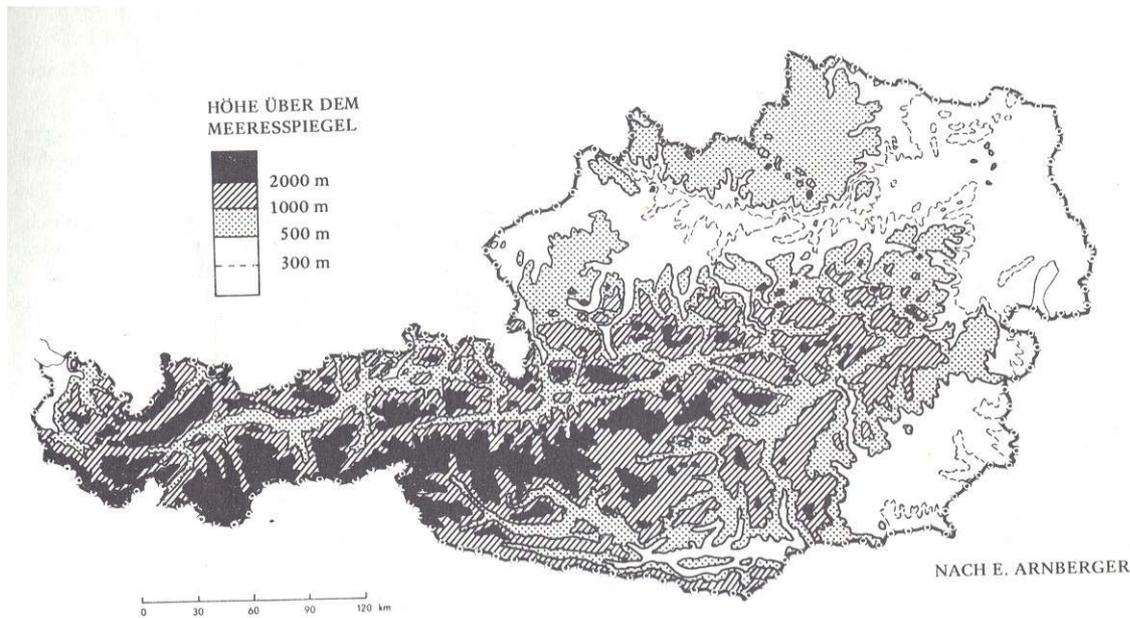
GEOLOGY AND GEOMORPHOLOGY OF AUSTRIA

About 10% of Austiran's area is taken up by the Variscan Massif (Moldanubian and Moravian Zones, see Map 3) ranging from 400m to 900m in altitude and with a moderate to strong relief, reaching 1,387m in maximum altitude. The Variscan Massif (the Bohemian Massif) consists of granite mainly in the west, while gneiss prevails in the east. Apart from some negligible exceptions such as Sauwald, Kürnberger Wald, Neustadtler Platte, and Dunkelsteiner Wald, this zone is bounded by the Danube to the south and the Manhartsberg hill to the east.

The dominant feature in Austria's geography are the Eastern Alps, which cover about 64% of the country's area. These can be divided into the flysch zone (about 5%), the Northern Calcareous Alps and the Graywacke Zone (about 22%), the Central Alps (about 33%) and, finally, the Southern Alps (about 4%).

This Alpine body is surrounded by the forelands (about 22%) to the north and south-east, and by several inner-alpine and pheripheral basins, accounting for about 4% in total, such as the basins of Vienna, Graz, Klagenfurt, Lungau, and Tullner Feld.

The Eastern Alps are lower and wider than the Western Alps and, also in constrast to these, do not consist of autochthonous massifs, but are the result of very complex nappe folding.

The Central Alps are separated from the flysch zone as well as the Calcareous Alps and the Graywacke Zone to the north by a series of longitudinal valleys and passes (Kloster valley, Arlberg, Inn valley, Gerlos pass, Salzach valley, Enns valley, Schober pass, Mur valley, Semmering, Schwarza valley). To the south, this boundary is essentially formed by the river

Drau, or a series of valleys composed of the Puster valley, the Drau valley, the Klagenfurt basin, and the Missling valley. The Central Alps show very rugged forms and reach high altitudes, especially in the western and central parts due to such rocks as resistant gneiss, granite, and mica schist, to name only a few. The highest peak is Grossglockner which is 3,797m above datum.

Map 3. Geological sketch map of Austria
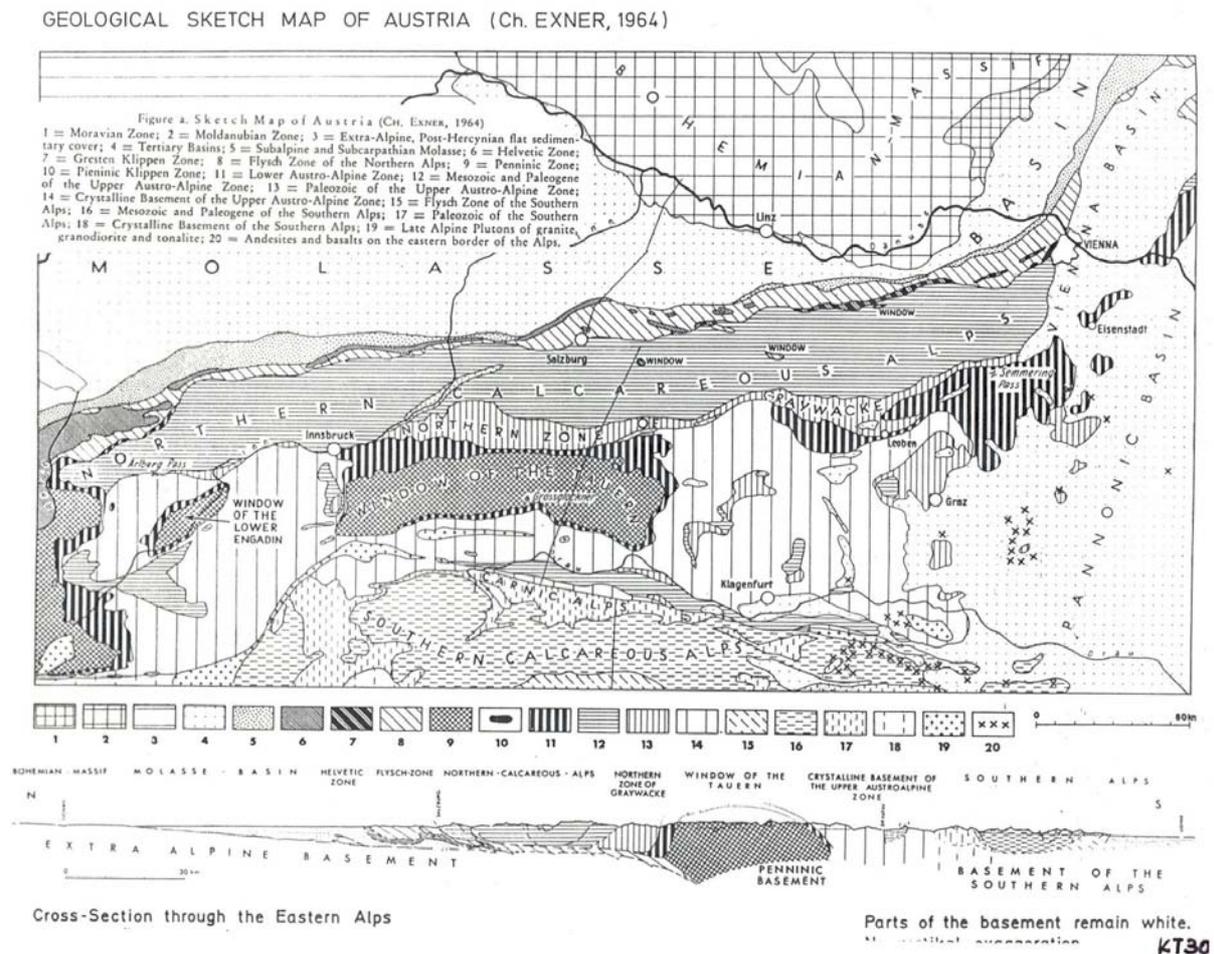
Lower, gentler, and green landforms ("Grasberge" or "grass mountains") characterise the Graywacke zone, which gained some importance in the past because of its magnesium, copper, and iron mines. This zone is adjacent to the Northern Calcareous Alps, which show plateau character in the east and sharp ridges in the west, reaching a maximum altitude of 3,038m (Passeierspitze).

South of the Periadriatic Suture follow the Southern Alps, which are composed partly of limestones and dolomites and partly of mica schists, and, in analogy to the Northern Calcareous Alps, also show partly plateau character.

Thus, the Alpine body in Austria is about 525km long and 265km wide in the east and only 32km wide at the narrowest point in the west. The main range of the Alps extends over almost 200km, with altitudes above 2,000m, and is interrupted only by a few passes, such as Radstädter Tauern, Katschberg, and Brenner. So, it is not surprising that only about 39% of the country lies below an altitude of 500m. Some 30% is situated between 500m and 1,000m, and about 40% above 1,000m above datum (see Map 2).

The highest summit in Austria is Grossglockner (3,797m) and the highest permanent settlement is Rofenhöfe in the Ötz valley in Tyrol (at an altitude of 2,014m). The highest road connection over the Alps (during the summer season) is the Hochtor pass (2,014m). The lowest settlements are Illmitz and Wallern in the Seewinkel region in Burgenland, situated at 117m above datum, and the lowest area is Lake Neusiedl at 115m above datum.

CLIMATE CONDITIONS AND WATER REGIME

As to the country's macroclimatic conditions (see Map 4 and 5). I should like to mention that Autria lies within the transition zone between the strong oceanic influence to the west and the continental influence to the east. This is manifested by the temperature difference between summer and winter increasing, and the mean annual precipitation depths decreasing, towards the east.

Taking into account the additional influence of altitude and relief, we can subdivide the country into atlantic, continental (Pannonic), and alpine climates. The atlantic or oceanic climate is characterised by smaller temperature differences, moderately warm summers, and the absence of droughts, with the total annual precipitation depth usually reaching more than 1,000mm. Under the impact of the rain-carrying northerly and north-westerly winds, ascent rains on the northern slope of the Alps may raise the annual precipitation depth to as much as 2,000mm or more in such areas as the Bregenzerwald in Vorarlberg and the Salzkammergut. In the areas characterised by continental, or Pannonic, climate, precipitation reaches only some 600mm annually, with a minimum of only 450mm in dry years. Further symptoms in these areas are a drought in the summer and rigidity and bare frost in winter. Pannonic climate is considered to prevail in the Weinviertel region in the Carpatian foreland, the eastern part of the North Alpine Foreland, the Vienna and Tulln basins, and in northern Burgenland. In the Waldviertel region in north-western Lower Austria, the climate is of the Pannonic Highland type. The characteristics of the Illyric type of climate are a high thermal continentality showing submediterranean symptoms with a second precipitation peak in late autum and the absence of droughts. This climate prevails in the south-eastern Alpine foreland, in the

Map 4. Mean annual temperature in Austria (1961-1990)
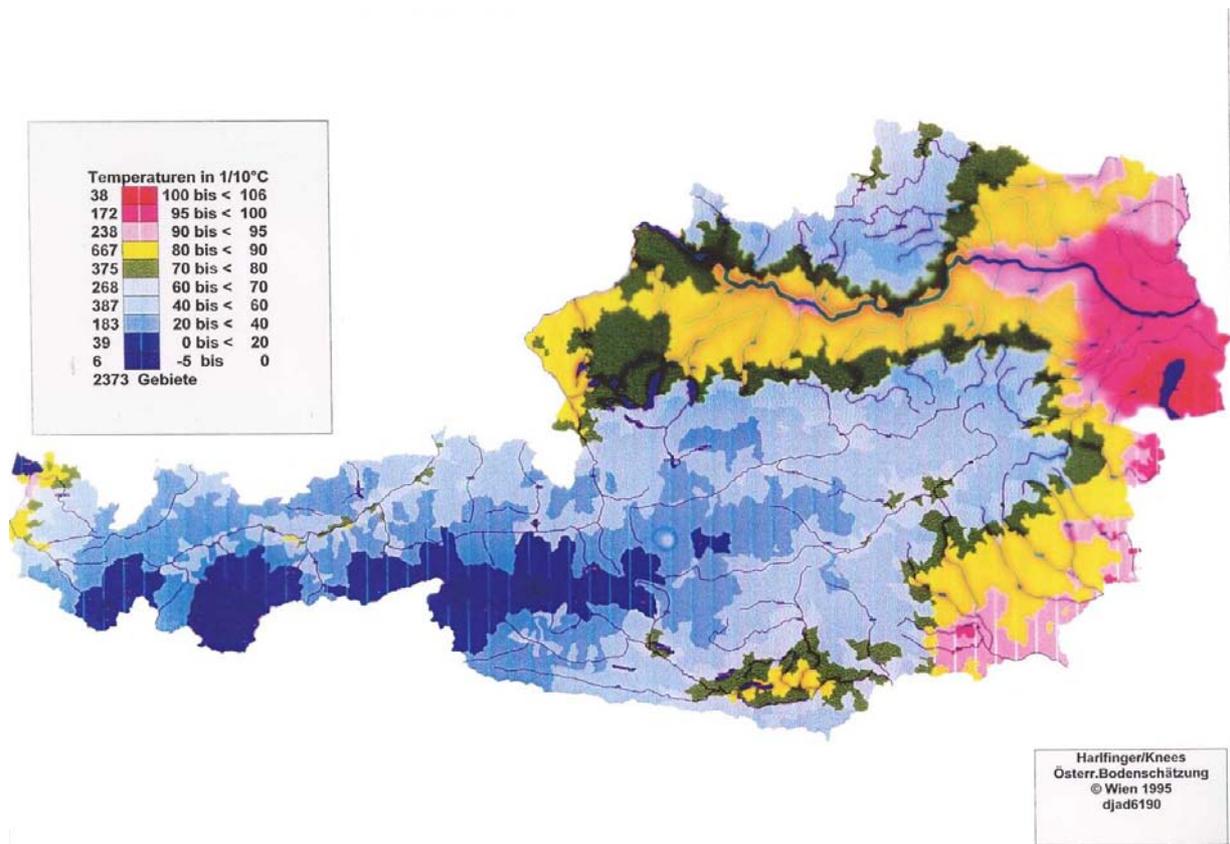
Map 5. Mean annual precipitation amount in Austria (1961-1990)
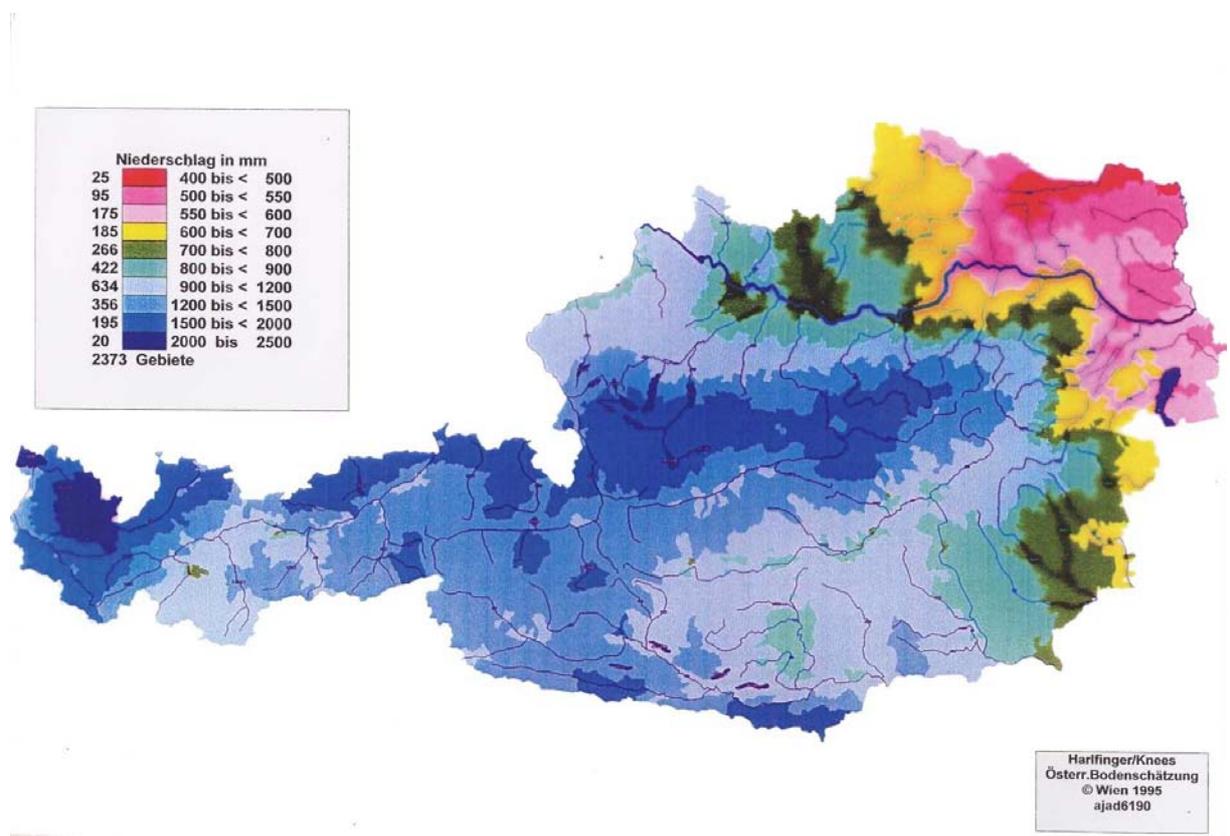
southern part of Styria, in the southern part of the Lavant valley and in the Klagenfurt basin in Carinthia.

The Alpine climate province is characterised by a strong dependence on the altitude and great differences between the peripheries and the inner zones. Characteristic features of these areas are generally short and cool summers, sudden weather changes, long winters rich in snow, foehn-wind in south-north trending valleys (Wipp, Ziller, partly Salzach, Gasteiner valleys), and inversion weather in winter (Lungau, Klagenfurt basin, Mürz valley, middle Enns valley). I should also mention the inner-alpine dry valleys, such as the upper Inn valley, the Kauner, Pitz, Ötz, lower Wipp, upper Möll, and upper Isel valleys, where the annual precipitation depth is not more than 800mm, or even as little as 650mm (for example, in the upper Inn valley). This is considered to be due to their being situated on the lee side of the mountains. On the other hand, ascent rains in the Northern Calcareous Alps and also in the Southern Alps may cause extreme annual precipitation depths, e.g. 2,700mm in the Karnische Alps in Carinthia.

Regarding the altitude limits for the natural vegetation, there are great differences between the west – more moist and cold – and the east – warmer and drier, as well as between the Central Alps (Silvretta, Samnaun, Ötztaler and Zillertaler Alps, Hohe and Niedere Tauern, Gurktaler and Seetaler Alps, the Styrian Fringe mountains) on the one hand and the foothills in the north (northern foothills, northern limestone and slate Alps) and the south (Karawanken and Karnische Alps, Gailtaler Alps) on the other hand. Likewise, we have found a hypsometric change in the plant associations with a temperature decrease of 6°C per 100m, along with a decrease in annual vegetation period. Considering these facts, we identify seven main vegetation zones in Austria: the Collin Zone (=planar-collin) until 250m to 400m in the foothills to the north and south (500m in the Central Alps), the Sub-montana Zone to between 350 and 500 (700)m, the Montana Zone to between 1500 and 2000m – this is also the limit of the continuous forest, the Sub-alpine zone to between 1800 and 2100 (2300m), the upper tree line and Krummholz Zone, the Alpine Zone to between 2500 and 2800m – the limit of continuous vegetation, the Sub-nival zone to between 2800 and 3100m, and the Nival zone – the zone of perpetual snow and/or glaciers above this limit.

A percentage of 96% of the Austrian territory drains to the River Danube, up to 3% to the River Rhine, and up to 1% to the River Moldava. The longest river is the Danube, the Austrian section being 350km long. This is followed by the Mur, which is 348km over its Austrian section, the Inn with 280km, the Enns with 254km, and the Salzach with 225km.

The substantial differences in water regime between the Austrian rivers are shown in Figure 1.

Figure 1. Middle amount of water of some Austrian rivers
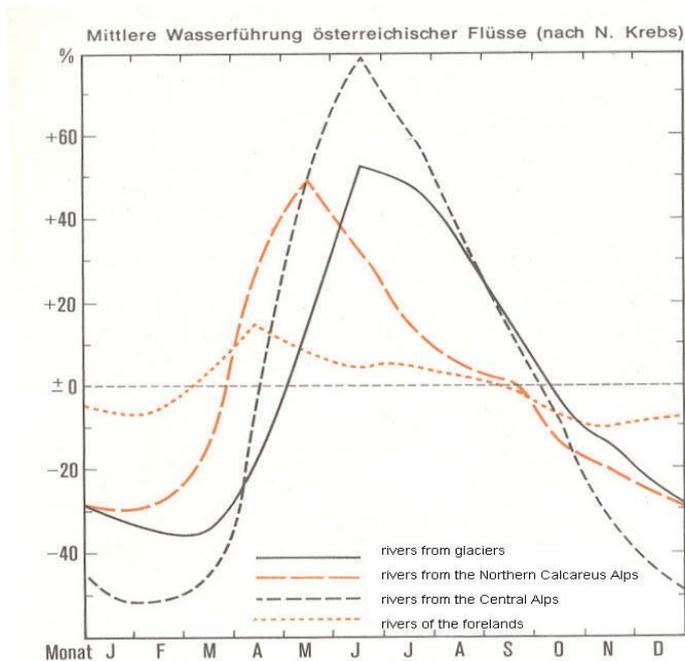
These rivers can be used as examples to demonstrate the considerable differences in the range of seasonal fluctuations in the water regime of Austrian rivers. Whereas the Inn at Kufstein shows a 500% difference between the month of maximum discharge and that of minimum discharge, there is a difference of only a little over 100% for the Danube in Vienna. Moreover, a characteristic of the River Inn is the fact that 55% of the total volume of annual flow occurs in June, July, and August, and only 7.5% in the months of December, January, and February.

Austria has about 5,200 natural lakes. The most important of them are Lake Constance (international water shared between Austria, Switzerland, and Germany) with a total area of 538.5km², Lake Neusiedl (the Austrian share being135km²), Attersee (45.9km²), Traunsee (24.5km²), Wörther See (19.3km²), Mondsee (14.2km²), Millstätter See (13.3km²), Wolfgangsee (13.5km²), and Ossiacher See (10.6km²).

SOILS OF AUSTRIA

As to the soil cover in Austria (see Map 6 and Figure 2), their most outstanding characteristic is the hypsometric change: Precipitation increases and temperature decreases as the altitude increases (on the whole, moister and colder in the west, warmer and drier in the east). Second in importance as a determining factor is the chemical composition of the parent material (substrate). Due to these and other factors, such as vegetation, animal activity, human influences, and time, we have a very large variability of soil types in Austria.

Map 6. Austrian Soil Types, after J. Fink, 1958
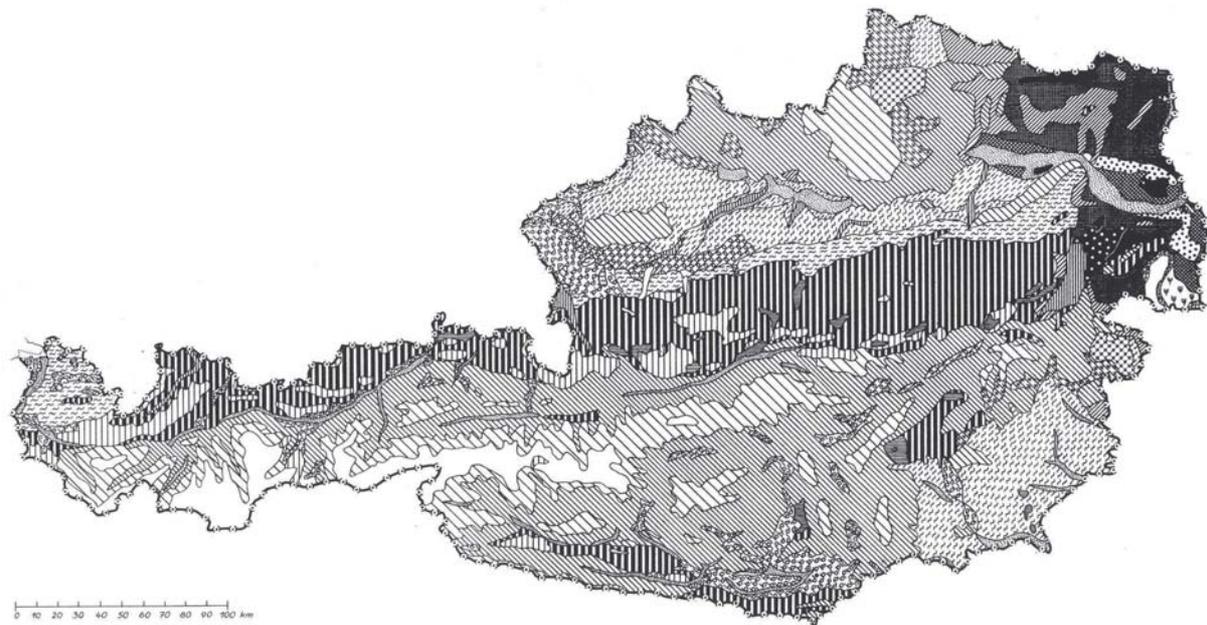
Figure 2. Legend for the Austrian Soil Map after J. Fink, 1958, Austrian Soil Classification 2000, and WRB 1998.

Bodentypenkarte von Österreich

Legende
1. Originallegende nach J.Fink 1958
2. Legende nach der Österreichischen Bodensystematik 2000
3. Legende nach World Reference Base for Soil Resources, 1998

1. Auböden im Allgemeinen
2. Carbonatfreier Grobmaterial-Rohboden, Carbonathaltiger Grobmaterial-Rohboden
3. Haplic Fluvisols, Eutric Fluvisols

1. Schilf- und Moorböden
2. Dy, Niedermoor
3. Dystric Histosols, Eutric Histosols

1. Salzböden im Allgemeinen
2. Solontschak-Solonetz, Solonetz, Solontschak
3. Calcic Solonchaks, Haplic Solonetz

1. Ehemalige Anmoore, tschernosemähnlich („Smonitza")
2. Carbonathaltige Feuchtschwarzerde, Carbonatfreie Feuchtschwarzerde
3. Gleyic Chernozems

1. Ehemalige Anmoore über Schotter
2. Anmoor, Carbonathaltige Feuchtschwarzerde
3. Eutric Histosols

1. Tschernoseme, wechselnd mit Lößrohböden
2. Carbonathaltiger Tschernosem, Carbonathaltiger Kultur-Rohboden
3. Haplic Chernozems, Eutric Leptosols, Leptic Calcisols

1. Tschernoseme über Schotter
2. Carbonathaltiger Tschernosem
3. Siltic Chernozems

1. Kalkfreie Tschernoseme aus Flugsand
2. Carbonatfreier Tschernosem
3. Haplic Kastanozems

1. Rendsinen auf Kalkschotter
2. Mullartige Rendzina
3. Rendzic Leptosols

1. Rendsinen auf Kalkstein, untergeordnet terra fusca
2. Mull-Rendzina, Kalkbraunlehm
3. Rendzic Leptosols, Cromic Luvisols

1. Terra fusca, untergeordnet Rendsinen
2. Kalkbraunlehm, Mull-Rendzina
3. Chromic Luvisols, Rendzic Leptosols

1. Anfangsbodenbildungen im Kalkgebiet
2. Carbonathaltiger Grobmaterial-Rohboden, Carbonathaltiger Feinmaterial-Rohboden
3. Calcaric Leptosols, Leptic Calcisols

1. Braunerden aus Löß, wechselnd mit Lößrohböden
2. Carbonathaltige Braunerde, Carbonathaltiger Kultur-Rohboden
3. Calcaric Cambisols, Eutric Leptosols

1. Parabraunerden aus Löß
2. Rezente Parabraunerde, Relikt-Parabraunerde
3. Calcic Luvisols

1. Vergleyte Parabraunerden und Pseudogleye aus Löß, Staublehm und Schlier
2. Vergleyte Rezente Parabraunerde, Typischer Pseudogley
3. Gleyic Luvisols, Dystric Planosols

1. Pseudogleye in der Flyschzone
2. Typischer Pseudogley, Typischer Stagnogley, Hangpseudogley
3. Dystric Planosols

1. Bindige Braunerden, zum Teil vergleyt
2. Carbonatfreie Braunerde, Vergleyte Carbonatfreie Braunerde
3. Haplic Cambisols, Gleyic Cambisols

1. Leichte Braunerden
2. Carbonatfreie Braunerde
3. Haplic Cambisols

1. Magere Braunerde und podsolige Braunerden aus Kristallin
2. Carbonatfreie Braunerde, podsolige Carbonatfreie Braunerde
3. Dytric Cambisols, „Podzolic" Cambisols

1. Podsolige Braunerden aus Sandstein und Schotter
2. Podsolige Carbonatfreie Braunerde
3. Dystric Cambisols, „Podzolic" Cambisols

1. Podsolige Braunerden, wechselnd mit alten Verwitterungsdecken
2. Podsolige Carbonatfreie Braunerde, Reliktpseudogley
3. „Podzolic" Cambisols

1. Vorwiegend alte Verwitterungsdecken (typologisch Pseudogleye und Braunlehme)
2. Reliktpseudogley, Kalkbraunlehm
3. Planosols, Chromic Luvisols

1. Semipodsole und Podsole
2. Semipodsol, Podsol
3. „Podzolic" Cambisols, Haplic Podzols

1. Anfangsbodenbildungen im Kristallingebiet (und Gletscher + größere Seen)
2. Carbonatfreier Grobmaterial-Rohboden, Carbonatfrei Feinmaterial-Rohboden
3. Umbric Leptosols

The scale of the map permitting, I have tried to give an overview of soil distribution in Austria, using the Austrian Soil Classification of 2000 and the WRB of 1998. In the region of Pannonic climate, in the north-eastern part of Austria, we have found, on loess material, Calcic Chernozems and Calcaric Regosols, Arenic Regosols and Anthropic Regosols, accompanied by Haplic Phaeozems, and Calcaric Cambisols at higher levels. In the Seewinkel region, the eastern area of Lake Neusiedl, we have found several sites with Carbonatic Solonchaks and Haplic Solonetz, but normally a mixture between these two soil types. In the Alpine foreland to the north and south-east, we have found dominant Haplic and Dystric Luvisols, Gleyic Cambisols in the northern foreland, and Gleyic Cambisols and Luvic and Haplic Planosols in the south-eastern foreland. The Bohemian Massif is characterised by a dominance of Dystric and Skeletic Cambisols, Haplic Umbrisols, and Haplic Podzols. Besides these types, we have found a number of Dystric and Eutric Histosols. In the flysch zones, we have found many kinds of Planosols and Histosols, occassionally Hayplic and Gleyic Podzols. In the limestone and dolomite regions of the Alps in the north and south, there are many kinds of Calcaric, Lithic and Rendzic Leptosols, occasionally interrupted by Palaeosols, such as Chromic Cambisols. In the Central Alps, there is a dominance of Dystric Cambisols and Humic Leptosols and Leptic Umbrisols, and very rarely Haplic Podzols and Dystric Histosols. Large valleys and basins are covered with colluvial soils (on the fringes), many kinds of Calcaric and Dystric Fluvisols in the rivers, and Eutric and Dystric Gleysols as well as Histosols at stagnant sites. In addition, we have found many sites where Terric or Hortic Anthrosols have developed through long and strong human influence.

SPECIAL STATISTICAL DATA OF AUSTRIA

Out of Austria's total area of 83,870.95km², 31,400km² is agricultural land. Out of this, 14,042km² is arable land, 0.556km² vineyards, about 14,000km² are alpine pastures, and about 43,200km² are forests. In socio-economic terms, this involved in 1999: 215,224 agricultural and forestry holdings with an average area of 34.9 hectares, of which 80,046 run by full-time farmers (corresponding to 37%, with an average area of 36.6 hectares), 127,441 holdings run by part-time farmers (that is, 59%, with an average area of 13.8 hectares), and 7,737 legal entities (corresponding to 4% with an average area of 366.2 hectares). In Austria we have a very large number of organic farmers: 19,056 holdings with an average area of 31.5 hectares.

In 1999, 335,728 tractors, 13,834 combine harvesters, and 3,809 beet harvesters were in use. In 2003, the cereals and meat supply balance was 97% and 110%, respectively, and in 2002 the yields per hectare amounted to 5.06 tonnes of wheat and 10.21 tonnes of corn maize,

67.19 tonnes of sugar beet, and 2.600,000 hectolitres of wine. Irrigated land comprised about 4,000 hectares. Agriculture accounts for only 2% of the gross domestic product.

Agriculture and forestry went through a radical structural change after World War II and again after the country's joining the EU in 1995. Our country had to change its agrarian policy. So we have focused on two objectives: high production and productivity levels combined with the preservation of rural land and soil. Every farmer is now obliged to maintain agricultural fertility to survive against international competition, while preserving cultural landscapes, especially in alpine areas.

Between 1951 and 1983, about 1 million people left the agriculture and forestry sector. But this has not only been compensated by mechanisation and rationalisation, but it has even be possible to raise the level of national self-sufficiency by increasing productivity in all the domains of agriculture and forestry, despite the continuous decrease in land under agriculture and forestry (in an amount of as much as 10 hectares per day).

The total number of residents in Austria was 8.032,926 in 2003 (annual average). Out of these, 3.184,117 were employees. The agrarian sector employed 26,337, that is 0.8%; trade and industry 867,036, that is 27.3%, and the service sector 2.176,996, that is 68.4%.

About 21% of the gross national product comes from the industrial sector, 27% from trade and other services. Industry is still concentrated in the traditional areas. One of the main industrial centres is Vienna including the Vienna basin with a wide range of different industrial establishments to satisfy the needs of the large population centre. Another important industrial zone lies in upper Styria, in the Mur and Mürz valleys, with mainly steel works and other metal industries. Further south, there is the industrial area of Graz, the provincial capital, with metal industry, a very modern car cluster, and electrical industries.

A third industrial area lies within the triangle formed by Linz, Wels, and Steyr in Upper Austria. Their dominant branches of industry are steel, metal, chemistry, paper, and cellulose. Other industrial sites are found south of Salzburg, in the lower Inn valley, and in the Rhine valley in the province of Vorarlberg, with Dornbirn being a centre of textile and garment industries.

Great importance is attached to tourist trade in Austria. In 2002, tourist trade accounted for about 16% of the gross domestic product. There were 18,611 million foreign tourists and 117.966 million overnight stays (9.741 million in private homes), of which 31.619 million by Austrians and 86.347 million by guests from abroad. This brought an income of about

11,237.000 million dollars. Winter accommodations and relatively cheap bed-&-breakfast accommodations (about one-third) are on the increase.

Austria has excellent transport facilities. The Austrian Federal Railways, comprising 5,656 kilometres of track (of which 3,526km is electrified), carried 183.700,000 passengers and 82.220,000 tonnes in 2002. In 2003, 297.239,000 tonnes of goods were transported by road and 10.737,000 tonnes by inland ships. A further increase in river transport is expected after the opening of the Main-Danube Canal as an important Central European waterway.

In 2003, the dense network of motorways, highways, federal roads, and provincial roads was used by a stock of 5.505,927 motor vehicles, of which 4.054,308 private cars and station cars, and 326,087 heavy goods vehicles.

A number of well equipped airports serve the civil aviation system. The Vienna-Schwechat airport with its two runways (a third one being under discussion) accounts for 84% of Austria's total commercial air transport, with 16.344,253 passengers and 273,064 regular landings and take-offs. Other airports are in the provincial capitals: Salzburg (1.224,624 passengers), Graz (835,450 passengers), Innsbruck (675,076 passengers), Linz (588,765 passengers), and Klagenfurt (310,906 passengers).

Modern Austria, a small country with a great history, is both well equipped with state-of-the-art industries and is self-sufficient in terms of agriculture.

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THE ROLE OF ORGANIC MATTER IN ADSORPTION PROCESSES

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SUMMARY

Soil organic matter has a major influence on the adsorption properties of soils. The objective of the present work was to quantify the possible impact of soil management in this respect.

We examined especially the impact of different fertilisation of arable land on the sorption properties for selected organic compounds (polar and apolar substances) and heavy metals (Cd, Cu, Zn). We used from two long-term field experiments. One is the Ultuna long-term experiment in Uppsala/Sweden, set up in 1956, the other one is a long-term microplot field experiment, located in Styria/Austria, set up in 1962. Comparison of the distribution coefficients (K_D) reveals significant differences in the adsorption behaviour of organic compounds as well as of heavy metals between the investigated soils. In the Ultuna experiment, for instance, the amount of adsorbed Cu on soil with permanent pasture was twice compared with the plots which were treated as fallow. Heavy metal adsorption in differently treated plots can be predicted mainly by pH, soil organic carbon and the cation exchange capacity. In case of organic compounds, local molecular properties related to the charge distribution around specific functional groups govern the sorption behaviour of the investigated substances. It could be clearly shown that soil management has a significant impact on the sorption properties of agricultural soils for organic and inorganic compounds. The quantity and quality of soil organic matter as well as specific molecular properties of the sorbed ions and compounds are of distinct importance in this respect.

KEY WORDS: adsorption, heavy metals, organic pollutants, soil organic matter, soil management

INTRODUCTION

For many pollutants soil acts as the main sink within our environment. Organic compounds and heavy metals interact with clay minerals, soil organic matter, microbes and plant roots, which influence their medium- and long-term behaviour in the ecosystem. Soil also represents a potential source of pollutants entering the food chain via plant root uptake or by leaching and subsequent groundwater contamination. Predictions of sorption properties of soils are not easy due to their highly heterogeneous nature both in mineral constituents and soil organic matter. The origin, composition and content of the organic matter have an important impact on the sorption behaviour of the soil for organic compounds and heavy metals. The content and quality of organic matter of agricultural soils is related to farming practices including manuring. Thus, changes in farming practices over time will change soil organic matter, which consequently will also influence the adsorption behaviour for pollutants. The present paper investigates the sorption mechanisms of organic compounds and heavy metals onto soils and soil fractions from two long-term field experiments and model soils, respectively. This approach has the advantage that the impact of changes in soil organic matter characteristics can be followed quite easily, because mineral matter is less influenced by management during the observation period of a few decades.

MATERIAL AND METHODS

Soils from two long-term field experiments were used for the sorption studies. Eight treatments from the field experiment in central Sweden (Uppsala) and three from Austria (Styria, Gumpenstein). As organic compounds we selected naphthalene derivatives (naphthalene, 1-naphthol, 1-naphthylamine, 1-hydroxy-2-naphthoic acid, 1,4-naphthoquinone), comprising a wide range of functional groups and relative simple structures allowing the application of molecular modelling tools. Copper, zinc and lead were used for the adsorption experiments with metals. The heavy metals are characterised by different ionic sizes, oxidation states and electronegativity and differing ecological relevance in soil systems. Concerning the two long-term field experiments we concentrated our efforts on basic soil properties for further investigations. The organic substance of the two experiments was characterized by means of FT-IR spectroscopy. The eight treatments from Uppsala were analysed additionally by cross-polarization magnetic angle spinning (CPMAS) ^{13}C nuclear magnetic resonance (NMR). Soil particle size fractionation was performed with the three treatments from Gumpenstein receiving the soil fractions coarse sand, fine sand, silt and clay.

Another approach was the use of quantum-chemical methods as available in the program packages Hyperchem 7.0 and GAUSSIAN03 in the soil science field. Different molecular descriptors of organic compounds like K_{OW}, electrostatic potential or charge distribution were calculated and correlated with the results from the various sorption experiments.

RESULTS AND DISCUSSION

The impact of fallow, organic and mineral fertilizer amendments and landuse (grassland versus arable land) on changes in soil organic matter quantities and characteristics was investigated in detail as basis for the interpretation of the adsorption studies. Results of these investigations are presented elsewhere (Antil et al., 2005, 2005a; Gerzabek et al., 2005; Kirchmann et al., 2004).

Organic substances

A general trend of increased adsorption on smaller particle size fractions (coarse sand to fine sand to silt to clay) can be observed (Novoszad et al., 2005a). This can be related to both the increasing surface of the clay fraction and the increasing organic carbon content of the clay fractions. The KD-values for coarse sand ranged from 0.5 to 6.3, higher values could be found for clay ranging from 6.6 to 85.1. Although the adsorption on silt particles is decreased in comparison to adsorption on clay particles, the silt fraction with a percentage of 48% of the bulk soil represents the main sink for hydrophobic organic compounds in our case. In this study we also attempted to compare the adsorption behaviour of the bulk soil with that of the corresponding soil particle size fractions. For that purpose the estimated KD values were calculated using both the relative amount of each particle size fraction (coarse sand, sand, silt and clay) and their respective KD values. Prediction of the adsorption seems to be possible and shows a small underestimation, although a good correlation between the estimated and measured KD was obtained. Total adsorption of 1-naphthol and 1-naphthylamine was stronger than adsorption of naphthalene, 1-hydroxy-2-naphthoic acid and 1,4-naphthoquinone. The only observation of the adsorption patterns obtained from the bulk soil does not necessarily give an insight in the mechanisms related to the different functional groups of the HOCs. Adsorption on fractions and especially on the silt and clay fractions points to the major interaction mechanism. The soil with higher carbon content, animal manure (3.6 %) adsorbs more strongly 1-naphthylamine, 1-naphthol and 1-hydroxy-2-naphthoic acid than the fallowed soil (2.6 %) and the soil treated with mineral fertilizer

(2.4 %). The most important fact seems to be the possibility of the organic compounds to build hydrogen bonds and electrostatic interactions with the mineral surface. Sorption increased in the following order: 1,4-naphthoquinone < naphthalene < 1-hydroxy-2-naphthoicacid < 1-naphthol < 1-naphthylamine. This pattern can be also clearly seen in other studies. The three compounds with hydrogen atoms in their functional groups behave antithetically to 1,4-naphthoquinone and naphthalene. 1,4-naphthoquinone and naphthalene show a quite significant adsorption related to the organic carbon content of the soils.
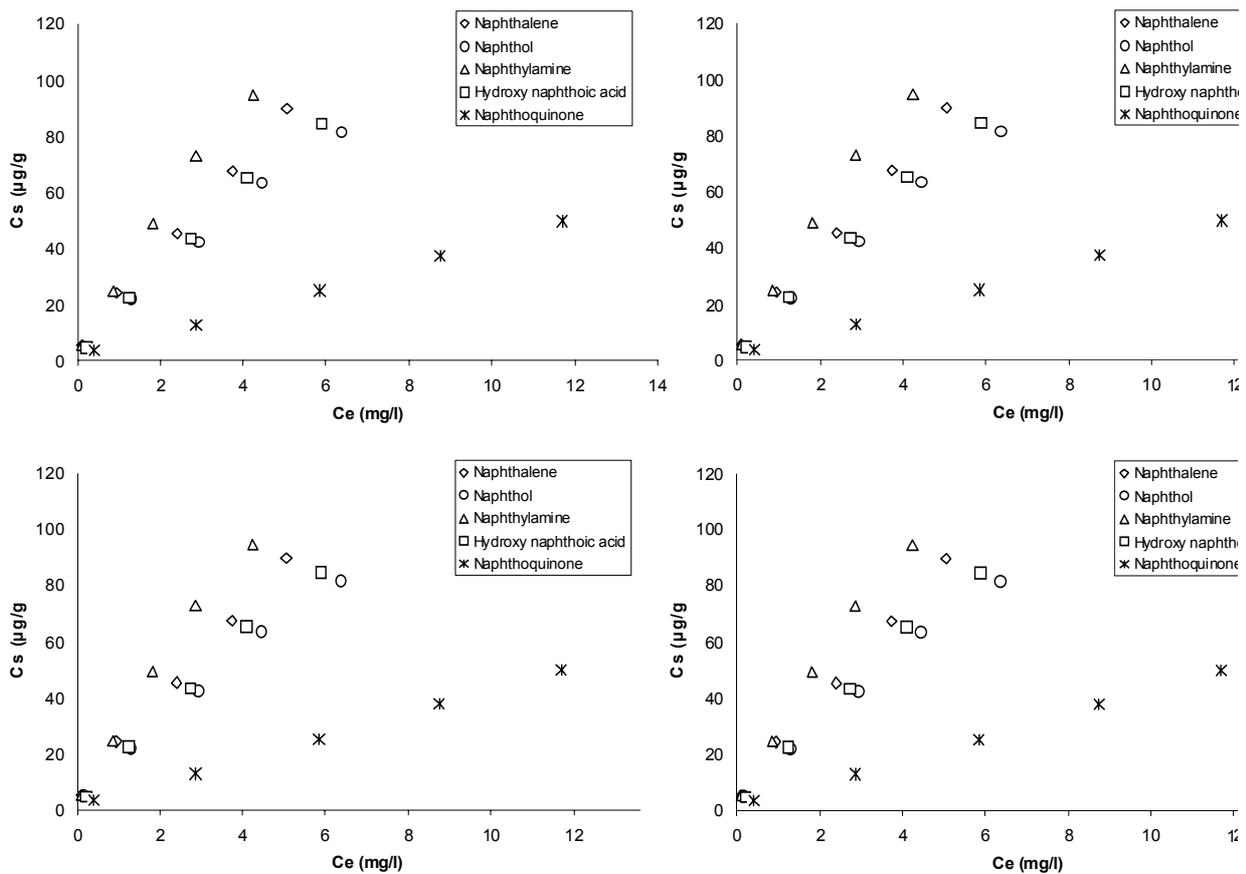
Figure 1. Adsorption isotherms of naphthalene derivatives on soil of different treatments (Novoszad et al., 2005)

For the other compounds the adsorption increases in that way as the mineral surface is less coated with organic soil material which is the case for soils with lower organic carbon content. This pattern is highly pronounced for 1-naphthylamine and 1-naphthol for the clay fraction and also the silt fraction, but not for the sand fractions. Clay mineral moieties, therefore, seem to be more attractive for electrostatic interactions compared to soil organic matter moieties. The impact of the clay and silt fraction, with a total content of more than

50%, on the adsorption behaviour of the bulk soil gives an explanation for the inherent results for the bulk soil. Particularly outstanding is the very high adsorption of 1-naphthylamine on the clay fraction of the soil treated with mineral fertilizer. The primary mechanism responsible for this strong sorption of aromatic amines on soils is the cation exchange of the protonated organic species with inorganic cations on minerals and soil organic matter. Cation exchange dominates especially as pH shifts to lower values, the amine speciation in aqueous phase shifts from the neutral to the protonated species. This effect can be observed with the clay fraction of the soil treated with mineral fertilizer. The long-term treatment results in a low pH of 4.4 and thus an increasing Kd-value for 1-naphthylamine up to 85.1. This study indicates that the mineral phase seems to offer more binding sites for molecules with hydrogen atoms in their functional groups when the surface is not coated with soil organic matter.

Besides the adsorption behaviour of the differently treated soils, molecular properties of naphthalene derivatives influence the sorption mechanisms (Figure 1). 1-naphthylamine was adsorbed at larger amounts than the other derivatives in all treatments, with a median KD-value of 10.4, followed by 1-naphthol (7.2), naphthalene (5.5), 1-hydroxy-2-naphthoic acid (5.1) and 1,4-naphthoquinone (2.1) (Novoszad et al., 2005). This shows that the functional groups have a major impact on the sorption behaviour of naphthalene derivatives. These functional groups lead to various octanol-water coefficients (KOW) which can be used to appraise the adsorption potential. 1,4-naphthoquinone with the lowest KOW value of 1.7 sorbs least, but there is no satisfactory correlation with the other compounds. 1-naphthol (KOW = 2.9), naphthalene (3.3) and 1-hydroxy-2-naphthoic acid (3.3) showed nearly equal adsorption behaviour. 1-naphthylamine with the second lowest KOW value of 2.2 adsorbs most. It is obvious that the octanol-water coefficient alone does not represent a reliable parameter for the prediction of the adsorption behaviour. Another explanation can be provided by the electrostatic potential. It is well accepted that soil surfaces are mainly negatively charged because of humic acids and clay minerals. Negative charges on soil matrix and the charges of the compoundss seem to influence the adsorption mechanisms. Especially negative electrostatic potential moieties might interfere the binding between compound and soil surface. Naphthalene (KD median = 5.5) without any functional group does not show any region of negative electrostatic potential. 1-naphthol (KD median = 7.2) shows one negative region but also a pronounced positive region around the hydrogen of the OH-group, which might lead to a higher adsorption compared with naphthalene. 1-hydroxy-2-naphthoic acid

(5.1) has also negative moieties and one extended positive at the position 3. 1-naphthylamine (10.4) sorbs most, which seem to be caused by the protonation effect. The positive charge is located around the nitrogen atom, thus affecting the adsorption behaviour highly. 1,4-naphthoquinone (2.1) has two negative moieties caused by oxygen, which might make it more difficult to sorb on the negative charged soil surface and lead to low KD values.

Heavy metals

Experimental batch sorption experiments were conducted using a standard procedure for heavy metals (OECD guideline 106). Initial heavy metal concentrations ranged from 40 to 200 mg/l. Freundlich equations (KF, 1/n) were suitable to describe the adsorption and desorption of the metals with $R^2 > 0.92$ (Lair et al., 2005). Comparison of the distribution coefficients revealed significant differences in the sorption behaviour of heavy metals between the investigated soils. In the Ultuna experiment, for instance, the amount of adsorbed Cu on soil with permanent pasture was twice as high as on the plot which was treated as fallow. In all plots, Cu was adsorbed most and strongest, followed by Zn and Cd. Cd-ions were weakly bonded and were released at high amounts. Generally, adsorption coefficients of the soils in the Ultuna experiment increased in the following order: sewage sludge < fallow < inorganic fertiliser without N < green manure < peat < Ca(NO3)2 < animal manure < permanent grassland. Results demonstrate that soil pH value was the main factor controlling the behaviour of heavy metals in soil altered through management. Furthermore, the amount of the organic carbon in the soils significantly influenced the sorption behaviour. Heavy metal adsorption in differently treated plots can be predicted mainly by soil pH, the content of the soil organic carbon and the cation exchange capacity of the soil. These results were supported by additional ad- and desorption measurements on physical soil fractions, by sequential extraction procedures as well as column experiments, which were done with soils of the Gumpenstein experiment (Lair et al., 2005a). In this long-term experiment the soil management using animal manure lead to a higher adsorption of the selected heavy metals as compared to the soils amended with slurry+straw or NPK mineral fertilizers over long time periods. Ratios between KF values of the particle fractions (clay : silt : fine sand :coarse sand) reach up to almost 14:5:1:1 for Cu, 12:4:1:1 for Cd and 24:3:1:1 for Zn in the different sites of the Gumpenstein experiment, showing that the origin of soil organic matter and an increasing role of mineral adsorption with decreasing carbon contents influence the sorption behaviour.

Results allow us to quantify the influence of different farming practices on the sorption properties of soils for Cu, Cd and Zn. Further these results provide a data set to gain more information about active adsorptions sites in soils and they support theoretical sorption models on soil matrices.

ACKNOWLEDGEMENTS

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LOW MOLECULAR WEIGHT AND HIGH MOLECULAR WEIGHT ORGANIC ACIDS FOR THE COMPLEXATION OF SOME ELEMENTS IN SOIL

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SUMMARY

The aim of the present research was to evaluate the influence of citric acids and humic acids on the solubility of aluminum, zinc and cadmium ions and their toxicity for pea plants.

Both, low and high molecular weight organic acids seems to be great binding agents for the Al, Zn and Cd-ions complexation and for the decreasing of their toxicity for the plants. However, there are two points, which should be taken into consideration:

- the ratio of binding agent : metal ions

- the origin of humic acids, which influences their structure and chemical composition and this should be analysed by NMR techniques.

KEY WORDS: aluminium, heavy metals, citric acid, humic acids, metal uptake

INTRODUCTION

The most important effect that the presence of organic matter produces in the soil is susceptibility to form complexes between functional carboxyl and phenol groups and aluminum (Sposito, 1989; Fox et al., 1990). This statement refers to high-molecular-weight organic acids of not-totally recognized structure (humic and fulvic acid) and to low-molecular-weight acids like for example citric acid. It appears that citric acid can form permanent soluble complexes with Al and has influence on chemical status of the soil and plants (Sposito, 1989; Stevenson, 1994; McBridge, 1994).

Mobilty of heavy metals in the environment influences the increase of their accumulation in plants, which is a serious problem for living organisms. Organic matter greatly contributes to the changes of particular forms of toxic elements in soils. This changes depend on environmental pH and chemical properties of elements themselves (Sparks, 1995; Stevenson, 1994). According to Sposito (1989), reactivity of organic matter components depend on their multi-functionality, molecule charge and structural flexibility. In opinion of Evangelou et al.,

(1999), bonds between organic matter and heavy metals may be formed on a base of ionic exchange (out-spere complexes) and ligand or coordination bond exchange (inner-sphere complexes).

The aim of present research was to evaluate the influence of citric acids and humic acids on the solubility of aluminum, zinc and cadmium ions and their toxicity for pea plans.

MATERIAL AND METHODS

Four water culture experiments were set up in plastic pots of 4 dm^3 capacity on modified Knopp`s medium.) (Brauner and Bukatsch, 1987). Basic medium contained following salts:

$Ca(NO_3)_2$	1,0 g $\cdot$ dm^{-3}	H_3BO_3	550 mg $\cdot$ dm^{-3}
KNO_3	0,25 g $\cdot$ dm^{-3}	$MnCl_2$	350 mg $\cdot$ dm^{-3}
KCl	0,12 g $\cdot$ dm^{-3}	$CuSO_4 \cdot 5H_2O$	50 mg $\cdot$ dm^{-3}
$MgSO_4 \cdot 7 H_2O$	0,25 g $\cdot$ dm^{-3}	$ZnSO_4 \cdot 7 H_2O$	50 mg $\cdot$ dm^{-3}
2% $C_6H_5FeO_7 \cdot H_2O$	1 $cm^3 \cdot dm^{-3}$		

In serie I and II aluminum was added as calcium chloride in the amounts of 27 mg $\cdot$ kg^{-1} and 54 mg $\cdot$ kg^{-1}. In order to complex free aluminum ions citric acid was used for both aluminum levels in the mole ratio Al : citric acid – 1 : 1 and 1 : 0.5.(serie I). Two amounts of humic acid (100 mg $\cdot$ dm^{-3} and 200 mg $\cdot$ dm^{-3}) were used for both levels of aluminum (serie II).

Zinc and cadmium ions were added as nitrates at the amounts of 150 mg Zn $\cdot$ dm^{-3} and 3 mg Cd $\cdot$ dm^{-3}. In the experiments with heavy metals (series II and IV) three types of humic acids (HA) were used: artificial preparation from Aldrich company and two natural humic acids extracted from lessive soil and chermozem soil according to Konanowa (1968). The amount of all HA were 200 mg $\cdot$ dm^{-3}.

After 14 days of common pea's growth and development, harvest of plant biomass was made separating above ground parts from roots. Then, fresh matter of above ground parts was weighed, roots were measured and after drying, dry matter of above ground parts and roots was weighed. After grinding of dried samples, their digestion in concentrated sulfuric acid with 30% H_2O_2 addition, was performed (Ostrowska et al., 1991).

RESULTS AND DISCUSSION

The influence of citric acids and humic acids on the aluminium solubility and toxicity

An addition of citric acid to the solutions with Al decreased by half the content of solubel aluminium at both levels (Tab. 1).

Table 1. Citric acids as low molecular weight organic acids and aluminium

Changing of	Al - 1			Al - 2		
	Solution with Al	C.A. : Al 1 :1	C.A. : Al. ! : 0.5	Solution with Al	C.A. : Al 1 :1	C.A. : Al. ! : 0.5
mg Al /dm^{-3}	26,6	17,3	14,2	56,6	20,7	12,7
pH	4,3	5,0	4,4	4,0	4,7	4,2
Dry matter of plants [g / pot]	5,30	6,00	4,80	3,00	3,15	2,57
Dry matter of roots [g / pot]	1,70	3,10	1,60	1,15	1,75	1,00
Al in roots [%]	0,07	0,10	0,04	0,11	0,67	0,44
Al in above ground parts [%]	0,02	0,02	0,02	0,03	0,04	0,03

C.A. – citric acid;   Al-1 - addition of Al – 27 mg / dm^{-3};   Al – 2 – addition of Al – 57 mg / dm^{-3}

In both cases the pH values of the solution increased about 0,7 units in relation to the objects with free aluminium ions. Application of citric acid on the level lower by half than the amount of aluminium ions resulted in complexing more of free aluminium ions even though the pH of the studied solution did not increase as markedly as it did at the mole ratio of Al : citric acid of 1 : 1 (Tab. 1). The results presented here, show a significant role of the citric acid in complexing free aluminium ions even if the pH-change of the solution is only slight.

The amount of 100 mg and 200 mg of humic acid was enough for the reduction of 27 and 57 mg of Al per dm-3 solution, respectively (Tab.2). Zhu Xiaoping et al (1994) and Stępniewski et al. (1994) claimed that ability of organic compounds, especially aromatic organic compounds, to complex Al ions is decidelly higher than in the case of any other inorganic ligands.

The amounts of dry mass of the plant parts above ground as well as dry roots mass were higher, than the ratio of citric acids : aluminium ions were 1 : 1 at both levels of toxic aluminium. It was observed, that higher level of aluminium ions needed higher level of humic acids for the increase of dry mass of both parts of plants (Tab. 2). Weryszko-Chmielewsk et al., (1997) found that the level of free aluminium ions had a fundamental influence not only

on the plant growth and development, but also on their morphological and anatomical changes.

Aluminium in plant samples was mainly gathered in the roots in which it´s concentration was sometimes almost 3 times higher than in the above ground parts (Tab. 1 and 2).

Table 2. Humic acids as high molecular weight organic acids and aluminium

Changing of	Al - 1			Al - 2		
	Solution with Al	H.A –200 + Al	H.A.-100 + Al.	Solution with Al	H.A –200 + Al	H.A.-100 + Al.
mg Al /dm^{-3}	26,6	1,0	0,48	56,6	2,1	5,9
pH	4,3	6,0	6,3	4,0	6,3	6,1
Dry matter of plants [g / pot]	5,30	4,10	7,20	3,00	7,80	5,60
Dry matter of roots [g / pot]	1,70	2,00	3,60	1,15	3,90	3,30
Al in roots [%]	0,07	0,01	0,01	0,11	0,34	0,26
Al in above ground parts [%]	0,02	0,02	0,01	0,03	0,01	0,01

Despite that, aluminium content in the above ground parts of the studies plants also reached considerably higher values. It could have been the result of taking whole citric-aluminium chelates by the plants, even the effect has been also observed in the objects with humic acid use for the complexation of Al ions.

The influence of natural and artificial humic acids on zinc and cadmium solubility and toxicity

Significant changes of soluble zinc and cadmium contents under the influence of natural and artificial humic preparations were recorded (tTab. 3 and 4). The greatest decrease of Zn^{2+} ion concentration was found at the presence of artificial humic acid preparation by Aldrich company, then in object where humic acids extracted from degraded chernozem (Tab. 3). No general changes of Zn^{2+} ion content in the solution after application of humic acids extracted from lessive soil were recorded. All three humic preparations significantly affected the decrease of Cd^{2+} ions in solution (Tab. 4), however, the greatest (6-fold) decrease of cadmium ions was recorded using natural humic preparation extracted from degraded chernozem.

Table 3. Natural and artificial humic acids and zinc

Changing of	Solution with Zn ions	Artificial H.A. Aldrich	Natural H.A. lessive	chernozem
mg Zn / dm^{-3}	62,5	44,0	63,0	59,5
pH	5,0	5,2	5,1	5,5
Dry matter [g / pot]	0,38	0,34	0,34	0,24
Dry matter of roots [g / pot]	0,09	0,09	0,10	0,08
Zn uptake by roots [μg / plant]	147,3	155,5	192,2	181,6
Zn uptake by above ground parts [μg / plant]	322,6	243,2	295,7	241,2

Discussed changes of free zinc and cadmium ions in solution were caused by complexing with organic compounds used towards heavy metals (Sposito, 1989; Alloway, 1990; McBride et al., 2000). However, the action varied for both ion types and depended on preparation applied. Artificial preparation (Aldrich) significantly decreased the amounts of free Zn^{2+} and Cd^{2+} ions, and two natural humic preparations significantly decreased the content of free cadmium ions. Preparation extracted from chernozem decreased the amount of free zinc ions, but to a lesser extent than that produced by Aldrich company. It seems that both metals were bonded to organic matter in different ways, but Zn-HA-Aldrich binding was more specific and probably of inner-sphere type (Evangelou et al., 1999), and cadmium showed obviously higher affinity to all types of organic matter, which is consistent with opinion of some authors (Gorlach and Gambuś, 1991), however, all Cd-HA bounds were non-specific and probably of outer-sphere type (Evangelou et al., 1999).

Table 4. Natural and artificial humic acids and cadmium

Changing of	Solution with Cd ions	Artificial H.A. Aldrich	Natural H.A. lessive	chernozem
mg Cd / dm^{-3}	0,96	0,60	0,30	0,16
pH	5,5	5,8	5,6	6,0
Dry matter [g / pot]	0,35	0,97	0,50	0,49
Dry matter of roots [g / pot]	0,14	0,39	0,16	0,16

Cd uptake by roots [μg / plant]	31,5	36,8	13,2	10,7
Cd uptake by above ground parts [μg / plant]	9,69	7,20	7,32	9,15

In presence of zinc and cadmium in the solution dramatic decrease of dry matter of above ground parts as well as dry matter of roots was recorded (Tab. 3 and 4). No changes of root dry matter in discussed "humic-zinc" objects were observed (Tab. 3). Analysis of "cadmium-humic" objects (Tab. 4) shows obvious quantitative increase of common pea's bio-mass both of above ground parts and roots. However, the greatest changes took place in object where humic acids by Aldrich company were added to Cd ions. Many authors agree that the presence of organic matter in an environment affects the change of heavy metal's toxicity (Gorlach and Gambuś, 1991; Spiak, 1998; Badora, 2002).

Zinc uptake was the lowest at the presence of HA-Aldrich. Obvious decrease of zinc accumulation in above ground parts of tested plants due to natural and artificial humic acids was found, while the best effects were achieved for HA-Aldrich and for HA-chernozem (Tab. 3). Elevated cadmium ions uptake by roots of tested plants at the presence of HA-Aldrich (Tab. 4) took place. The other humic preparations clearly decreased Cd^{2+} uptake by the plant's roots. All applied preparations reduced cadmium ion concentration in above ground parts of common pea (Tab. 4).

It would be another mechanism explaining different action of natural and artificial humic preparations towards the reduction of zinc and cadmium toxicity at tested plants. It was found that the ratio of aluminum to the complexing organic acid was significant and most effective when it was 1 : 1. Varied influence of natural and artificial humic acids on binding of free zinc and cadmium ions in medium was observed, which might have resulted from : (i) different sorption capacity and multi-functionality of tested preparations; (ii) different chemical properties of cadmium and zinc ions, and (iii) varied ratios of preparation : metal ion.

CONCLUSIONS

1. Citric acid as low molecular weight organic acid in both doses (1 : 1 and 1 : 0.5) decreased more than 1.5 times aluminum concentration in the water solution at both

aluminium levels. The ratio of C.A : Al = 1 : 1 was the most optimal for the increase of dry matter of roots and above ground parts of plants.

2. It was observed an increase of Al concentrations in roots at Al-2 level. However, because of the presence of binding agent no Al toxicity was found for the plants.

3. The presence of humic acids as high molecular weight organic matter in both doses (200 and 100 mg $\cdot$ dm^{-3}) decreased Al concentrations at both levels more than 10 times in the water solution. It was observed the greatest influence on the increase of dry matter of roots and parts of plants above ground, if the amounts of humic acids exceeded more than 3 times aluminium concentration in the solution.

4. The presence of artificial and natural humic acids reduced Zn and Cd concentrations in the water culture solution. However, the increase of roots- and above ground parts dry matter of investigated plants was most efficient by using Aldrich humic acids.

5. There was observed the lowest zinc-ion uptake by pea roots in the presence of artificial Aldrich humic acids. Humic acids extracted from chernozem reduced mostly Cd-ion uptake by tested plants.

6. Both, low and high molecular weight organic acids, seems to be great binding agents for the Al, Zn and Cd-ions complexation and for decreasing their toxicity for plants.

   However, two points should be taken into consideration:

   - the ratio of binding agent : metal ions

   - the origin of humic acids, which influences their structure and chemical composition, and this should be analysed by NMR techniques.

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CHANGES OF THE CONTENT OF TOTAL AND EXTRACTABLE FORMS OF CADMIUM (Cd) IN SOIL AFFECTED BY ORGANIC MATTER AND LIME

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SUMMARY

The aim of the study was to estimate changes in the content of total and extractable cadmium content in the soil treated with sewage sludge from dairy plant and waste lime from sugar factory. Besides organic fertilization with FYM, application of sewage sludge and other organic wastes into soils is proposed in Poland to maintain positive organic carbon balance and stand or even increase soil fertility. The usage of sewage sludge and other wastes compels to carry out investigations on biogeochemistry of heavy metals in the soil. The total (aqua regia) and extractable (1 mol HCl $\cdot$ dm^{-3}) content of heavy metals in soil and materials used in field experiment was determined by atomic absorption spectrometry (AAS) using Hitachi apparatus Z – 8200. The part of extractable form of cadmium from total content in the soil was depended on liming. The application of sugar factory lime elevated Cd extractability in soil from all objects: control, sludge and FYM

INTRODUCTION

Besides industrial dust and transport pollution, application of wastes and sewage sludge for soil fertilization, usage of phosphorus and multi-components artificial fertilizers containing phosphorus and liming are important source of cadmium (Cd) in agrisystems. Positive balance of organic carbon in soil affects continuous renovation of active fractions of humus substances which can bind heavy metals. Metal ions can also be bound by living soil microorganisms which appear in huge amounts after organic matter application into the soil (Baldesent et al., 1988). Metals can be kept in this case by their incorporation into microbial cells and binding by bacterial exudates, especially by amino acids which can also be excreted by plant roots. Heavy metals bound by low molecule weight excreted amino acids may be taken up by microorganisms cells and root hair of plants causing higher accumulation of the

elements in cultivated plants (Paustian et al., 1992). The complexity of soil reactions and transformations is the reason why it is so difficult to predict metal bioavailability and mobility. It depends on interplay of forces between different elements of soil ecosystem.

On the other hand, the uptake of toxic heavy metals by living organisms mostly occurs by exposure to dissolved species – biologically or ecologically active or available forms of elements. Thus the concentration of heavy metals in soil solution is of prime importance. These fractions of toxic metals are affected by soil parameters such as pH, the mineral clay, organic matter content, redox potential and others. It is well known that soil organic matter (SOM) can immobilize toxic elements by precipitation, chelate ring formation, adsorption or (bio)transformation. Soil acts as a sort of buffer which influences the impact of toxic elements. Buffering in this sense can be described as storage of elements without a direct effect of heavy metals on the toxicity experienced at contaminated sites.

Unfortunately, organic carbon content in arable soils has been imbalanced for many years, especially after economical and political changes in Polish economy. The application of organic materials, mainly farm yard manure (FYM) decreased in this period due to a reduction in the number of animals. Also the decrease of the share of papilionaceous crops and perennial grass mixture in crop rotation in Polish agriculture influences organic carbon balance in soils. The loss of carbon in arable land which results from agriculture practices has serious consequences for both physical and chemical soil properties (Mc Laughlin et al., 1999).

The application of organic matter as a FYM, green manure, sewage sludge and others organic wastes into soils is proposed in Poland as a method of maintenance positive organic carbon balance and stands or even increases soil fertility. The usage of sewage sludge and other wastes compels to carry out investigations on biogeochemistry of heavy metals in the soil.

The aim of the study was to estimate changes in the content of total and extractable cadmium content in the soil treated with sewage sludge from dairy plant and waste lime from sugar factory.

MATERIAL AND METHODS

The six experimental treatments, without organic fertilization – control, FYM, sewage sludge under liming and no liming conditions were established on brown soil (Dystric Cambisols acc. to FAO):

1. Without liming and organic fertilization

2. Without liming, FYM 35 t · ha^{-1} (175 kg N · ha^{-1})
3. Without liming , sludge 22 t · ha^{-1} (176 kg N · ha^{-1})
4. Lime 5 t · ha^{-1} , without organic fertilization
5. Lime 5 t · ha^{-1} , FYM 35 t · ha^{-1} (175 kg N · ha^{-1})
6. Lime 5 t · ha^{-1} , sludge 22 t · ha^{-1} (176 kg N · ha^{-1}).

The dose of sewage sludge was comparable to the N dose applied with 35 t · ha^{-1} FYM, i.e. 175 kg N · ha^{-1}and it allowed to draw a direct comparison of both organic fertilizers. The sewage sludge contained higher concentrations of P, Ca, N, and Na than FYM. None of heavy metals exceeded the maximum value in the sewage sludge, therefore it can be used for fertilization. Three years after beginning of field experiment soil samples from 0 – 20cm layer were taken for laboratory investigations.

The total content of nutrients and some heavy metals in soil and materials used in field experiment was determined, after digestion of samples in aqua regia. Extractable forms of heavy metals were determined in solution 1 mol HCl · dm^{-3} with soil extraction ratio 1:10. The content of cadmium in phosphorus fertilizers was determined in HCl extractant used for digestion of phosphorus and multi-component fertilizers containing phosphorus and originating from five domestic factories. Measurements were carried out by AAS-Spectrometer using Hitachi apparatus Z – 8200, with flame or graphite furnace version depending on Cd concentration in solutions.

RESULTS AND DISCUSSION

Among heavy metals occurring in phosphorus and multi-component fertilizers containing phosphorus, cadmium is of the greatest interest, because the metal mostly affects human's health. Other heavy metals occurring in those fertilizers have been neglected up to date. Among phosphorus fertilizers originating from Polish factories (Filipek, Kwiecień, 2004), the highest cadmium contents were found in granulated triple superphosphate (36.60 mg Cd · kg^{-1}, i.e. 183 mg Cd · kg^{-1} of P) of fertilizer (Tab. 1). In a case of multicomponent fertilizers, the highest cadmium amounts were found out in fertilizer mixture "Fruktus 2" (214 mg Cd · kg^{-1} of P).

Table 1. Statistical estimation of variation of cadmium content in phosphorus and multicomponent fertilizers produced in Poland

Characteristics	Phosphorus Fertilizers	Multicomponent fertilizers
Mean	9.35	5.44

Median	3.55	3.85
Geometric mean	4.94	3.71
Variance	183.68	20.34
Standard deviation	13.55	4.51
Standard error	5.53	0.77
Minimum value	1.40	0.20
Maximum value	36.60	18.30
Range	35.20	18.10
Coefficient of variation	144.95	82.89

Although recorded levels of cadmium in fertilizers (about 140 mg Cd $\cdot$ kg^{-1} of P by 2006) proposed in all members of European Union (Cupit et al., 2002), it is not a threat of pollution of agricultural production area with heavy metals, particularly with cadmium, in present situation (about 8 kg P $\cdot$ ha^{-1} $\cdot$ year^{-1}). Fertilizer industry still searches for technological solutions that would diminish the content of unnecessary elements, e.g. cadmium, in fertilizers, but at present, only production of phosphorus fertilizers from high-quality phosphate rocks may efficiently reduce the pollution (Górecka H., Górecki H., 2000; Górecki H. et al., 1992).

The European Union countries determined limits of cadmium contents in phosphorus fertilizers, which will be achieved finally in 2015 (Cupit et al., 2002). The limits are restraints, which can enhance phosphorus fertilizers manufacturing costs. Proposed limits of Cd in P-fertilizers are as follow:

- 60 mg Cd $\cdot$ kg^{-1} P$_2$O$_5$ (140 mg Cd $\cdot$ kg^{-1} P) to 2006
- 40 mg Cd $\cdot$ kg^{-1} P$_2$O$_5$ (90 mg Cd $\cdot$ kg^{-1} P) to 2010
- 20 mg Cd $\cdot$ kg^{-1} P$_2$O$_5$ (45 mg Cd $\cdot$ kg^{-1} P) to 2015

Proposal of cadmium content limits in phosphorus fertilizers in Poland (Tab. 2) is comparable to EU proposition stand on 2010 year. The proposal is two fold lower than effective being ones for present.

Table 2. Proposal of trace elements content limits in fertilizers in Poland (Filipek, 2003)

Fertilizers	Units	Cd	Pb
Phosphate	mg $\cdot$ kg^{-1} P mg $\cdot$ kg^{-1} P$_2$O$_5$	110 48	140 62
Calcium limes	mg $\cdot$ kg^{-1} CaO mg $\cdot$ kg^{-1} Ca	8 11	200 280

The content of cadmium in materials used in field experiment: sewage sludge from dairy, sugar factory waste lime, and manure, respectively 1.0, 0.3 and 0.4 mg Cd · kg^{-1} did not exceed allowed values in wastes exploited to land amelioration and fertilization and did not increase the content of extractable cadmium in soil.

Table 3. Effect of organic fertilization and liming on the content of extractable cadmium in soil [mg Cd · kg^{-1}]

Liming - A	Organic fertilization - B			Means – A
	Control - 0	Sludge	FYM	
Control - 0	0,09	0,10	0,11	0,10
Lime - 1 Kh	0,14	0,14	0,12	0,13
Średnie B	0,11	0,12	0,11	

LSD p-0.05: Factor A -   0,02*
            Factor B -   0,03
            Interaction A × B - 0,05
Explanations: FYM – farm yard manure, LSD – less significant differences

The content of extractable (in solution 1 mol HCl · dm^{-3}) cadmium (Tab. 3) in soil was slightly differentiated and varied from 0.09 mg Cd · kg^{-1} in double control treatment – without liming and organic fertilization – to 0.14 mg Cd · kg^{-1} of soil limed and treated with sludge.

Table 4. The content of the total [mg Cd · kg^{-1}] and the share (in %) of extractable cadmium in soil

Liming - A	Organic fertilization - B		
	Control - 0	Sludge	FYM
Control - 0	0.44 (20.5)	0.52 (19.2)	0.48 (22.9)
Lime - 1 Kh	0.45 (31.1)	0.54 (25.9)	0.48 (25.0)

The percentage of extractable cadmium in Cd total in soil given in brackets (Tab. 4) varied from 19.2 to 31.1%. Soil liming with sugar factory waste lime increased cadmium solubility

substantially in spite of higher pH values. Many authors (Ericsson, 1989; Laegreid et al., 1999) argue that solubility of the most of heavy metals diminish in soils with lower pH.

Table 5. Average Cd loads in agriecosystems of Poland [Filipek, Domańska, 2002]

Specyfication	Years	
	1970-1990	1990-2002
Cd input (mg Cd · ha^{-1} · year^{-1})		
P fertilizers	3000,0	900,0
Manure	1000,0	600,0
Atmospheric deposition	1100,0	1000,0
Total	5100,0	2500,0
Cd output (mg Cd · ha^{-1} · year^{-1})		
Crops	1200,0	1200,0
Leaching*	400,0	400,0
Total	1600,0	1600,0
Accumulation (input-output)	3500,0	900,0
Increase of Cd concentration in top layer of soil (mg Cd · kg^{-1})		
	0,0012	0,0003

*- from [Mc Laughlin, Singh, 1999]

On the other hand liming and application of organic matter into the soil enhance microbial activity and decomposing of nitrogen organic compounds. Ammonia and ammonium cation NH_4^+ in aerated conditions can be oxidized to nitrates (V) NO_3^-, which activates metal solubility, especially divalent cations (Baldesent J. et al, 1988).

Taking into consideration the average concentration of cadmium in the top layer of soil (0.4 mg Cd · kg^{-1}) and the increase of Cd concentration in arable horizon of soil in 1970-1990 (Tab. 5), when about 50 kg of phosphorus (P_2O_5) and 200 kg NPK · ha^{-1} · y^{-1} were used, we can conclude that it may take about 300 years, to double Cd-content in the soil. At present, when the level of the use of phosphorus fertilizers is about 17 kg of phosphorus (P_2O_5) it would take more than 500 years.

CONCLUSIONS

1. Among phosphorus fertilizers originating from Polish factories, the highest cadmium contents were found in granulated triple superphosphate (36.60 mg Cd · kg^{-1}, i.e. 183 mg

Cd $\cdot$ kg^{-1} of P)and in multicomponent fertilizer mixture "Fruktus 2" (18.30 mg Cd $\cdot$ kg^{-1}, i.e. 214 mg Cd $\cdot$ kg^{-1} of P).

2. The content of extractable (in solution 1 mol HCl $\cdot$ dm^{-3}) cadmium in soil was slightly differentiated and varied from 0.09 mg Cd $\cdot$ kg^{-1} in double control treatment – without liming and organic fertilization – to 0.14 mg Cd $\cdot$ kg^{-1} of soil limed and treated with sludge.

3. The share of extractable form of cadmium in total content of Cd in the soil was depended on liming. The application of sugar factory lime elevated Cd extractability in soil from all objects: control, sludge and FYM

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EFFECT OF ORGANIC MATTER ON THE AVAILABILITY OF ZINC FOR WHEAT PLANTS

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SUMMARY

The objective of the study was to investigate the effect of soil organic matter on the availability of zinc for plants. The experiment material consisted of a set of 156 soil samples from Lower Silesia and another set of 45 soil and plant samples collected from wheat fields. All samples were tested for Zn content. Soil zinc was assayed using four methods: DTPA, EDTA, 0.1 M HCl and 1 M HCl. Based on the analysis of the correlation coefficients for organic matter vs. soils zinc (Zn_S) it was found that stronger extractants such as 1 M HCl or 0.1 M HCl extract much more organic matter-bound zinc than do EDTA or DTPA. The analysis of correlation coefficients of organic matter vs. zinc availability index (Zn_P/Zn_S) showed that organic matter restricts the availability of zinc for plants and this should be taken into consideration for the determination of threshold values for soil zinc. Furthermore, ranges of Zn contents of soil optimum for wheat relative to organic matter content when assayed using the DTPA, 0.1 M HCl and 1 M HCl methods were presented in the study.

KEY WORDS: zinc, availability, soil extraction, organic matter

INTRODUCTION

There is no doubt that zinc is bound by organic matter (Dabkowska-Naskert, 2003; Kabata, 1990; Kabata, 2000; Lityński, 1982; Tisdale, 1985). However, the effect of organic matter on the availability of Zn for plants has not been sufficiently explained. Organic matter (OM) can be both a source of Zn or it can reduce Zn availability through binding it in organic compounds unavailable for plants. In the literature, there are reports on both the enhancing and the inhibiting effect of OM on the solubility of Zn and its availability for plants.

Antoniados and Alloway (2002) demonstrated that an addition of OM to soil resulted in an increased uptake of Zn by ryegrass. They summed up their report by concluding that organic matter increased Zn solubility and its availability for plants. In the study of Almas et al., (2000) addition of organic matter increased the solubility of soil Zn through the formation of organic-Zn complexes. According to Impellitteri et al., (2002) organic matter caused a certain increase in Zn solubility but only under very high pH. Catlet et al., (2002) found that the binding of Zn^{+2} ions by OM has a significant impact on the solubility of Zn in the soil. Most probably, those ions are absorbed by OM at the pH of up to 8.4, being precipitated as minerals at higher pH.

Contrary to the previous studies Shumann et al., (2001) found that under excess soil Zn an addition of OM substantially lowered Zn availability for plants. Likewise, Tisdale (1985) and Lityński (1982) emphasized that application of fresh manure could cause zinc availability to decrease.

It can be supposed that the lack of relationship between soil organic matter and zinc availability found by some investigators is the result of the stimulating and the inhibiting effect of organic matter on the uptake of zinc by plants canceling each other. A case in point can be the study of Kashem and Singh (2001) who showed that a 4% addition of organic matter failed to influence the level of zinc uptake by rice plants.

The objective of the study was to determine the relationship between organic matter content of the soil and the availability of zinc for wheat plants based on the collection of soil and plant samples. The determination of zinc content ranges of the soil optimal for wheat, taking into consideration the organic matter level of the soil was supposed to be the final outcome of the study. Another goal of the study was to investigate the extent to which common extracting solutions such as 0.1 M HCl, 1 M HCl, EDTA and DTPA extract Zn bound to organic matter.

MATERIAL AND METHODS

The study material was made up of two sample sets: 156 soil samples collected from arable soils (set I) and 45 soil and plant samples collected from fields under winter wheat (set II). Wheat plants were sampled at the shooting stage (7/8). Both sample sets were from the province of Lower Silesia.

In soil samples of both sets determinations were made of organic carbon using Tiurin's method. Subsequently, organic matter (OM) was calculated using the conversion factor of 1.724.

In 156 soil samples Zn and the remaining microelements were determined using four methods: specific method (IUNG, 1980), 1 M HCL (Gembarzewski and Korzeniowska, 1996), DTPA (Lindsay and Norvell, 1978), EDTA (Lakanen and Ervio, 1971). Zn, Cu, Fe and Mn were determined using the AAS method and B and Mo were assayed calorimetrically. Specific assays were different for each microelement: 0.1 M HCl for Zn, hot water for B, 0.43 M HNO_3 for Cu, $MgSO_4+Na_2SO_3$ for Mn, $(NH_4)_2C_2O_4+(COOH)_2$ for Mo.

Only zinc was assayed in set II of 45 soil samples. Zinc assays of soil material were identical as those performed for set I. In the plant material, Zn was determined using the ASA method following dry mineralization.

The description of the two sample sets was shown in Tables 1 and 2.

Table 1. Contents of organic matter and microelements (%) extracted from soil with extractants studied (mg·kg^{-1}) in the set of 156 soil samples – mean values and value ranges

Trait	Extraction method			
	1 M HCl	Specific	EDTA	DTPA
Zn	12.0 (3.8-45.0)	7.4 (1.4-33.8)	4.8 (1.5-23.7)	3.8 (0.8-12.9)
B	1.27 (0.10-4.34)	0.43 (0.09-1.36)	0.36 (0.02-1.600)	0.39 (0.02-1.50)
Cu	4.5 (1.2-14.8)	3.7 (1.1-13.4)	1.7 (0.5-6.6)	1.0 (0.2-4.0)
Fe	1184 (462-4100)	x	68 (1-390)	35 (1-252)
Mn	198 (42-1105)	70 (9-216)	55 (8-750)	27 (2-105)
Mo	0.274 (0.027-1.100)	0,113 (0,017-0,440)	x	x
OM	2.9 (0.9-7.5)			

x – unavailable,

Table 2. Description of the set of 45 samples from soils under wheat

Item	Mean content and range
Organic matter (%)	2.0 (0.8-4.1)
fraction <0,02 mm (%)	29.7 (8-54)
pH in KCl	5.7 (3.9-7.4)
Zn in 1 M HCl (mg·kg^{-1})	9.6 (4.4-33.0)
Zn in 0,1 M HCl (mg·kg^{-1})	6.1 (1.8-21.2)
Zn in EDTA (mg·kg^{-1})	3.4 (1.5-8.0)
Zn in DTPA (mg·kg^{-1})	3.8 (1.7-11.5)
Zn in plant (mg·kg^{-1})	24.3 (15.0-44.2)

RESULTS AND DISCUSSION

Simple correlation between OM content and Zn content in soil as assayed using four different methods was calculated for sample set I (156 samples). For comparison, correlations for the remaining microelements were calculated as well (Tab. 3). The high positive correlation coefficients for the specific method and for 1 M HCl indicate that Zn forms bound to OM undergo extraction using those methods. It is true for other microelements as well. The

weaker extractants EDTA and DTPA extract microelements from organic compounds to a much lesser degree which is indicated by the low coefficients or by the absence of significant correlation. Similar results for EDTA were obtained by McGrath et al., (1988). Negative correlations for B and Fe extracted by DTPA give evidence that OM may interfere with extraction of these micronutrients using DTPA. It is possible that the specific extractants and 1M HCl extract too much Zn, B and Cu whereas DTPA extracts too little B and Fe in terms of the potential uptake by plants.

The analysis of the correlation shows a close relationship between Zn and OM. In addition, B and Cu are strongly bound to organic matter, Mn and Mo showing a weaker affinity. Likewise, Kabata (1999) states that Cu, B and Zn are strongly bound to organic matter whereas Mn is the most weakly bound.

Table 3. Simple correlation coefficients between organic matter content and microelement contents in soil for the set of 156 soil samples

Micro element	Extraction method			
	Specific	1 M HCl	EDTA	DTPA
Zn	+ 0.467***	+ 0.536***	ns	+ 0.210**
B	+ 0.570***	+ 0.687***	ns	- 0.477***
Cu	+ 0.526***	+ 0.671***	+ 0.268**	ns
Fe	X	+ 0.485**	ns	- 0.372***
Mn	+ 0,283***	+ 0,338***	ns	ns
Mo	Ns	ns	x	x

x–not available, ns–non-significant correlation, significance level: *< 0,05, **<0,01, ***<0,001

The 45 samples of set II, alongside with the analyses of the soil material, were also analyzed for Zinc content of the wheat plants that had grown on those soils (Table 2). It allowed the calculation of not only the correlations between OM and zinc content in soil but also between OM and zinc content of wheat plants. Since no significant correlations were obtained between OM and plant Zn, correlations were calculated between OM and Zn availability indexes (Table 4). The Zn availability index was expressed in terms of the ratio of Zn content in plant to Zn content in soil (Zn_P/Zn_S).

Table 4. Simple correlation coefficients between OM content and Zn content in soil (Zn_S), and between OM content and availability indexes (Zn_P/Zn_S) for the set of 45 samples collected from wheat fields

Method	Zn_S	Zn_P/Zn_S
1 M HCl	+ 0.704***	- 0.648***
0,1 M HCl	+ 0.740***	- 0.695***
EDTA	+ 0.327*	ns
DTPA	+ 0.644***	- 0.564***

ns – non-significant correlation, significance level: * < 0,05, ***<0,001

As in sample set I, high correlation coefficients between OM and Zn content in 1 M HCl, in 0,1 M HCl, and in DTPA show that those solutions extract organic matter-bound Zn (Table 4). The negative correlation coefficients between OM and the availability index point to a negative impact of OM on Zn availability to plants – the more OM is in the soil the lower the Zn_P/Zn_S index is. Furthermore, the negative coefficients for Zn_P/Zn_S versus positive for Zn_S, warrant the supposition that the tested solutions, with the exception of EDTA, extract much larger amounts of Zn from organic matter than wheat is capable of taking up. The results are in agreement with the opinion by Tisdale et al., (1984) that organic matter increases the solubility and extractability of Zn which does not always go hand in hand with increased uptake by plants. It suggests the need to take into consideration OM content while determining the thresholds of Zn content assayed using 1 M HCl, 0,1 M HCl or DTPA.

As a further stage of this study, optimum ranges for Zn content in soil for wheat as dependent on OM content in soil were calculated (Table 5). Simple regression equations calculated based on sample set II were used for the purpose:

- for 1 M HCl: $Zn_P/Zn_S = -0.923$ OM + 5.118, $R^2 = 47\%$, P<0,0000,

- for 0.1 M HCl: $Zn_P/Zn_S = -2.106$ OM + 10.163, $R^2 = 48\%$, P<0,0000,

- for DTPA: $Zn_P/Zn_S = -1.797$ OM + 11.515, $R^2 = 32\%$, P<0,0000,

where: Zn_P –Zn content in plant in mg·kg^{-1}, Zn_S – Zn content in soil in mg·kg^{-1}, OM – organic content in soil in %, n = 45.

Based on the papers of Bergmann and Jones (Bergman, 1992; Jones et al., 1991), the range from 20 -70 mg·kg^{-1} was taken as the optimum Zn content of winter wheat plants.

Table 5. Optimum Zn content in soil (mg·kg^{-1}) for the growth of winter wheat relative to organic matter level in soil

Method	OM content in soil (%)			
	0.5-1.5	1.6-2.5	2.6-3.5	3.6 -4.5
1 M HCl	4.8-16.7	6.1-21.4	8.5-29.8	14.0-49.0
0.1 M HCl	2.5-8.7	3.4-11.8	5.2-18.2	11.5-40.2
DTPA	2.1-7.2	2.5-8.8	3.3-11.4	4.6-16.2

According to Table 5 the required content of soil Zn increases with the increase in the percent content of organic matter. The optimum Zn content in soil obviously also depends on the Zn assay used. The highest Zn contents were obtained using 1 M HCl, and the lowest using DTPA which is due to different amounts of Zn extracted using those methods.

CONCLUSIONS

Since no correlation was found between organic matter and Zn content in plants neither positive nor negative impact of OM on Zn availability for wheat plants could be unequivocally stated. It may be supposed that the effects cancelled each other. The proposed increase of optimum Zn contents in soil along with the increase in OM content is the result of the amounts of organic matter-bound Zn extracted by the solutions tested being higher than the amounts that wheat plants were able to take up. The allowance for OM content is, to a degree, a correction to make up for the imperfection of the extractants used.

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SOIL ORGANIC MATTER IN THE CZECH REPUBLIC

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INTRODUCTION

Soil organic matter contributes to soil productivity through various processes and mechanisms e.g. providing nutrients after decomposition, increasing the soil's cation exchange capacity, building soil structure and buffering the soil against rapid changes in pH. Organic matter content in soils of Czech Republic is about 2 – 3%. The quantity of carbon stored in soils is highly significant; soils contain approximately three times more carbon than vegetation and twice as much as that which is present in the atmosphere. Various environmental factors, not at least human dependent land management, can significantly affect the dynamic equilibrium of the soil carbon pool. Predictions if future carbon pools will change must be made with caution. It is also well known that effects of land management practice on soil carbon may not be measurable for twenty years.

Dynamics changes of soil organic matter can be best studied by long–term field experiments. Such field experiments show that there is a direct linear relationship between the quantity of carbon added to soil as organic matter and the amount of carbon accumulated in the soil. However, the dynamic of soil organic matter is complex and the factors controlling the flux of carbon will interact unequaly at each site. The problem is, that in the Czech Republic and in other countries are not sufficient number of long - term field experiments.

METHODIC OF OBSERVATION

Next possibility to obtain data on soil carbon content are results from database Basal Agricultural Soil Monitoring System (BSMS) of the Central Institute for Supervising and Testing in Agriculture (CISTA). This system is in operation since 1992. At present, BSMS consists of 190 monitoring plots in basal system and 27 monitoring plots in subsystem of contaminated plots (established in 1996) is interfaced with monitoring in protected areas in Czech Republic.

Basal soil monitoring system

Each monitoring plot is defined like rectangle 40 x 25m (1000 m^2) and is determined by geographical co-ordinates.

Monitoring plots were chosen according following principles:

- to keep a ratio of occurrence of soil types in Czech Republic
- to keep a ratio of representation of types of soil cultivation,
- to keep even location of monitoring plots in regions,
- soil pollution (for choosing of contaminated plots).

The base sampling period is 6 years but specific parameters are sampled every year. Usually four samples are taken from topsoil and subsoil.

Figure 1. Location of monitoring plots

Lokalizace pozorovacích ploch bazálního monitoringu zemědělských půd
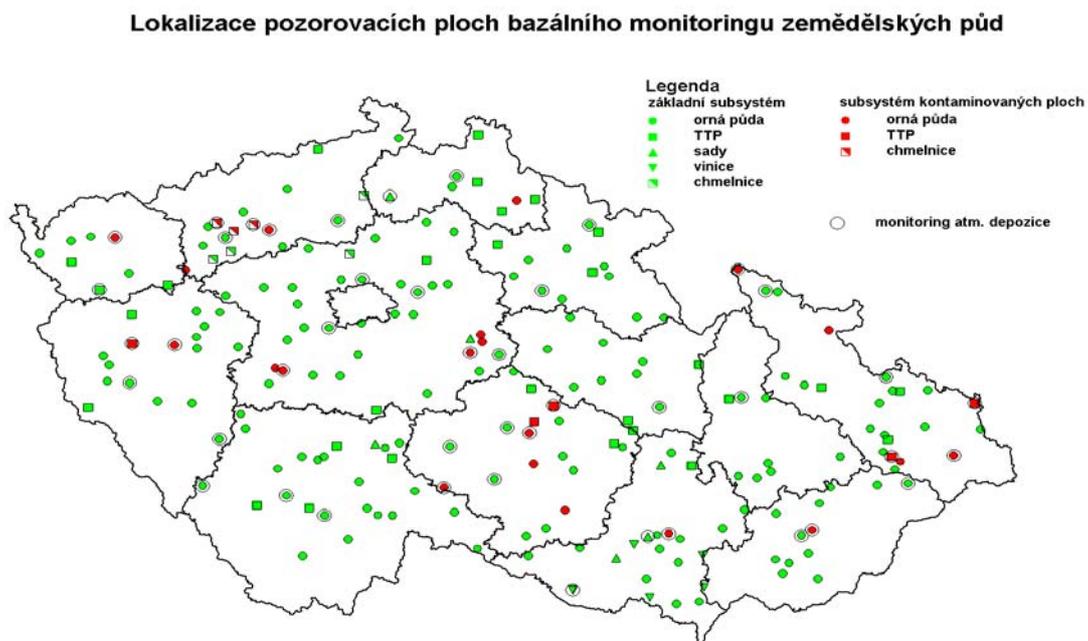
RESULTS AND DISCUSSION

There were selected 89 monitoring plots in arable soils for observation of organic matter. The analytical data result from the period 1992 – 2001 resp. 2002 and 2003 ("grant task").

Soil organic matter quantity

The statistical parameters of soil organic matter quantity show that the content and differences of soil organic matter is related to soil types and some soil texture parameters. It is also

shown, that correlation exists between particle size distribution and content of organic matter (Tab. 1).

Table1. Content of soil organic matter related to the main soil type and texture classes

Phaeozem

Soil type	C_{ox}	Texture class	C_{ox}
Average	2,44	loamy- sandy	
Medián	2,23	sandy-loamy	
Minimum	1,65	loamy	1,90
Maximum	3,41	clay-loamy	2,57
Count	4	loamy- clay	3,41

Cambisol

Soil type	Cox	Texture class	Cox
Average	1,57	loamy- sandy	1,40
Medián	1,42	sandy-loamy	1,45
Minimum	0,77	loamy	1,40
Maximum	3,19	clay-loamy	
Count	64	loamy- clay	

Chernozem

Soil type	Cox	Texture class	Cox
Average	1,72	loamy- sandy	
Medián	1,60	sandy-loamy	1,72
Minimum	0,71	loamy	1,61
Maximum	2,02	clay-loamy	
Count	20	loamy- clay	

Luvizem

Soil type	Cox	Texture class	Cox
Average	1,28	loamy- sandy	
Medián	1,28	sandy-loamy	1,20
Minimum	0,98	loamy	1,33
Maximum	1,47	clay-loamy	
Count	13	loamy- clay	

Fluvizem   Cox

Soil type	Cox	Texture class	Cox
Average	1,75	loamy- sandy	1,38
Medián	1,70	sandy-loamy	1,45
Minimum	1,05	loamy	1,79
Maximum	2,51	clay-loamy	2,08
Count	20	loamy- clay	

Pseudogley

Soil type	Cox	Texture class	Cox
Average	1,71	loamy- sandy	
Medián	1,67	sandy-loamy	1,41
Minimum	1,16	loamy	1,96
Maximum	3,13	clay-loamy	
Count	17	loamy- clay	

Gley soil

Soil type	Cox	Texture class	Cox
Average	1,56	loamy- sandy	
Medián	1,76	sandy-loamy	1,16
Minimum	1,16	loamy	1,57
Maximum	3,08	clay-loamy	
Count	11	loamy- clay	

Rendzina

Soil type	Cox	Texture class	Cox
Average	1,35	loamy- sandy	
Medián	1,33	sandy-loamy	
Minimum	0,79	loamy	
Maximum	1,62	clay-loamy	
Count	4	loamy- clay	

Brown soil

Soil type	Cox	Texture class	Cox
Average	1,33	loamy- sandy	1,05
Medián	1,24	sandy-loamy	1,29
Minimum	0,87	loamy	1,30
Maximum	3,35	clay-loamy	1,1
Count	39	loamy- clay	

Regosol

Soil type	Cox	Texture class	Cox
Average	0,89	loamy- sandy	
Medián	1,02	sandy-loamy	
Minimum	0,50	loamy	
Maximum	1,15	clay-loamy	
Count	5	loamy- clay	

Soil organic matter quality

Quality of organic matter depends on character of humus-accumulated material and condition of humification. Organic matter is determined as organic carbon. The relationship of Carbon and Nitrogen determines the value of the material or at least indicates what management adjustments need to happen to make the amendment valuable in building soil quality. The relationship is expressed as the Carbon: Nitrogen ratio (C:N). Young immature crop plants may have a C:N of 15 :1 and on the other end of the spectrum is sawdust with 200:1. The C:N ratio of soil organic matter is usually about 10 - 12 :1, higher values indicate worse quality of humus.

Figure 2. Development of average content of C_{ox} and N_{tot} and their carbon/nitrogen ratio in arable soils in Czech Republic

	1992	2001	2002	2003
N tot	0,149	0,151	0,151	0,155
Cox	1,462	1,463	1,553	1,607
C:N	9,807	9,670	10,273	10,336
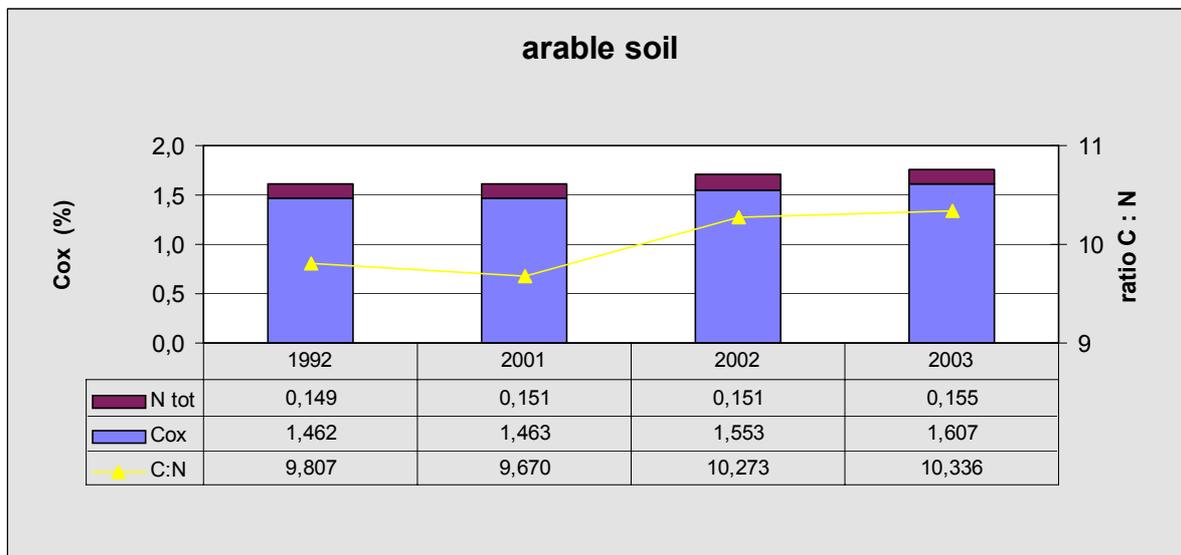
Figure 3. Average content of C_{ox} and N_{tot} and the carbon/nitrogen ratio in main soil types of the Czech Republic

	RM	LM	HM	RA	GL	KM	PG	ČM	FM	ČA
Ntot	0,10	0,12	0,14	0,13	0,15	0,16	0,17	0,16	0,16	0,21
Cox	0,89	1,28	1,33	1,35	1,56	1,57	1,71	1,72	1,75	2,44
C:N	9,13	10,31	9,33	10,29	10,46	10,08	10,25	10,72	10,71	11,38
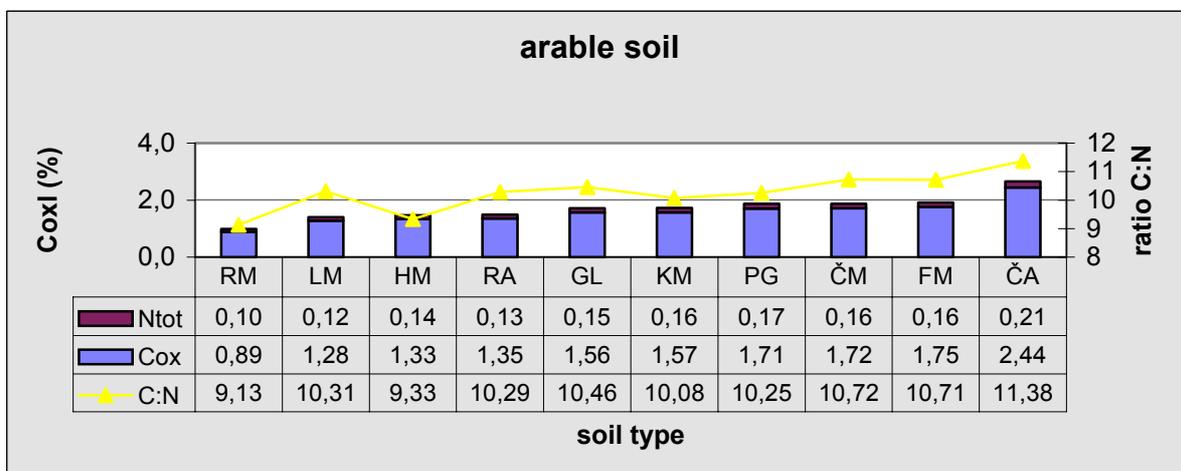
CONCLUSIONS

From the results of BSMS it can be concluded:

- Content of soil organic matter depend on soil type and soil texture
- Content of soil organic matter in main soil type and soil texture correspond with soil organic matter in long-term field experiments
- Content of soil organic matter in Czech republic is stabile and has increasing tendency
- Organic matter quality (ratio C:N) has been slightly raised

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EFFECT OF DIFFERENT FERTILIZATION SYSTEMS ON ORGANIC CARBON CONTENT OF A LIGHT SOIL FROM SOUTH-WEST POLAND

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SUMMARY

The impact of a 32-year application of different fertilization schemes on total organic carbon content of a light soil was investigated in this study. Soil samples were taken from a long-term field trial located in Jelcz-Laskowice (South-west Poland). Eight rotation cycles were carried out, including following fertilization schemes: 1) no fertilization, 2) farmyard manure (FYM), 3) mineral fertilization, 4) ½ FYM + ½ mineral fertilization, 5) FYM + ½ mineral nitrogen.

It was observed that crop management under Norfolk rotation without any fertilization, or with crop-adjusted mineral fertilization only, maintained a stable organic carbon content in the soil. FYM applied alone or with mineral fertilizers caused an increase in organic carbon content.

KEY WORDS: organic carbon, long-term trial, light sandy soil, FYM fertilization, mineral fertilization

INTRODUCTION

Different crop management practices, including fertilization, results in gradual conversion of soil properties that affect soil fertility. The evidence thus far indicates that exclusively mineral fertilization applied over long time leads to adverse changes in many physico-chemical properties of the soil. That negative impact can be alleviated by introducing regular organic fertilization and liming. One of the major characteristics of soil fertility is the organic matter content. Different opinions on the impact of fertilization on this soil parameter frequently result from too short duration of investigations. Given the inconsistency of the changes in soil organic matter as observed over a few years' periods (Lopez-Bellido et al., 1997; Toth and Kismanyoky, 2000) the conclusions should be based on data from long-term trials.

The objective of the study is to compare the effects of different fertilization systems, mineral, organic and combined mineral and organic, applied over a 32-year period on the content of organic matter of a light sandy soil.

MATERIAL AND METHODS

The experiment material originated from a long-term field trial which was set up at the IUNG Experiment Station at Jelcz-Laskowice in south-western Poland near the city of Wroclaw. The long term precipitation average for the area is 570 mm, annual average temperature is 8.5^0C and the length of growing season is 228 days. The trial was set up on a Haplic Luvisol. The crops were rotated under 4-year Norfolk system: root crops (potatoes or beets), spring crops (barley or oats), legume (clover, lupine or peas), winter crops (wheat or rye). Catch crops were grown after winter small grains: mustard, sunflower or legume and cereal mixture. The plots (100 m^2) were laid out as a Latin square design with 5 replications and were assigned to the following fertilization treatments:

1 - no fertilization,

2 - farmyard manure at 600 dt $^.$ ha $^{-1}$ applied to a root crop every fourth year,

3 - mineral fertilization at a rate equivalent to the amount of NPK supplied by FYM spread over 4 years,

4 - ½ of the FYM application every fourth year and mineral fertilizer NPK at a rate equivalent to ½ of FYM application spread over 4 years,

5 - an application of 600 dt $^.$ ha $^{-1}$ of FYM to a root crop every 4th year and mineral nitrogen at a rate equivalent to ½ of FYM application spread over 4 years.

Mineral fertilization was applied according fertilizer recommendation created by Institute of Soil Science and Cultivation in Pulawy, Poland.

Eight 4-year rotation cycles were run. After the termination of the 6th rotation investigations were started to determine the effect of liming on the improvement of physico-chemical properties of the soil. To this end the plots were divided into two equal parts, one which was left unlimed and the other was limed every four years based on neutralization of one level of hydrolytic acidity. Each year soil samples were collected from the arable layer after the harvest. The samples were analyzed for the pH$_{KCl}$, content of macronutrients, micronutrients and for organic carbon using Tiurin's method (Tiurin, 1931). The results were subjected to ANOVA and the differences were tested for significance using Tukey's test at p<0,05.

RESULTS AND DISCUSSION

The content of organic carbon in the soil, regardless of the fertilization system used, varied fairly substantially over the successive rotation cycles which is shown in Figure 1. The variations were due to variable crop yields and variable amounts of crop residues depending on the crop. Likewise, other investigators emphasize the impact of the crop and crop residues on the level of organic carbon in the soil (Sainju et al., 2002; Yang et al., 2003).
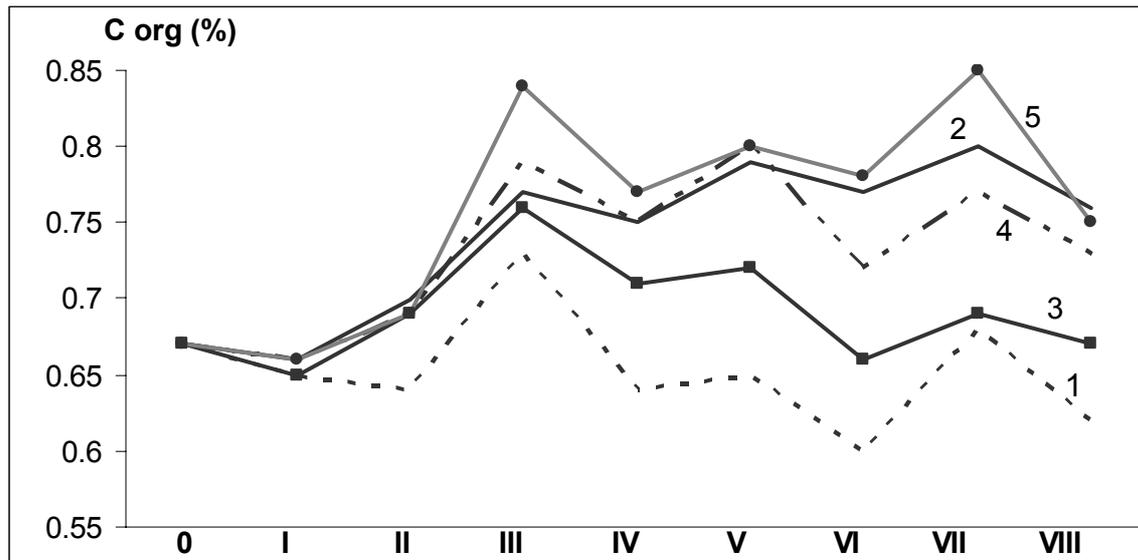
Figure 1. Organic carbon concentration in soil depending on fertilization in successive rotations (0-initial concentration, I-VIII – values for the last year of every 4-year rotation): 1. control, 2. FYM, 3. NPK, 4. ½ FYM +1/2 NPK, 5. FYM + ½ N

After 4 years of the study (1st rotation) the C_{org} content of the soil in all treatments was close to that found in the non-fertilized soil (Fig. 1). After the 2nd rotation (8 years) there was an increase of C_{org} which was equally for all fertilization systems. In the next period a fertilization system-dependent increase of organic carbon content occurred.

Average C_{org} contents calculated for the whole 32-year long study period varied depending on fertilization treatment used (Table 1). All fertilization systems showed an increase of the total organic carbon content related to the control. The smallest increase occurred in the NPK treatment, averaging 0.69%. In the treatments with FYM application the organic carbon content of the soil was higher than in that involving mineral fertilization only.

Table 1. Concentration of organic carbon in soil for different fertilization management

Treatments	C_{org} concentration (%)		
	Initial	32-year average	Range
1. 0		0,65 a	0,60 – 0,73
2. FYM		0,75 bc	0,66 – 0,80
3. NPK	0,67	0,69 ab	0,65 – 0,76
4. ½ FYM + ½ NPK		0,74 bc	0,66 – 0,80
5. FYM + ½ N		0,77 c	0,66 – 0,85
NIR/ LSD	0,065[*]		

* - value used to test the significance of differences between the initial value and long-term average for individual treatments

** -values followed by the same letter in the column do not differ significantly ($p < 0.05$)

Both, the application of the full FYM-dose and of the half dose together with mineral fertilizers, produced a similar cumulative effect on organic carbon content in the soil. The long-term average content in those treatments was 0.75 and 0.74%, respectively. The greatest amounts of organic carbon accumulated in the soil fertilized with the full FYM dose supplemented with mineral nitrogen. Throughout the study, the average content for that treatment was 0.77%.

The analysis of alterations in organic carbon content of the soil during the test period compared to the initial value showed, that in non-fertilized soil and in the soil fertilized with mineral fertilizers only, organic carbon stayed at the starting level. Contrary, fertilization involving FYM caused a substantially increase of organic carbon content in the soil.

In the study of Adamus et al., (1989), carried out at the same trial site, changes in the content of humic compounds due to the fertilization systems were established. The amount of humic acids increased in the fertilized treatments compared to the unfertilized control. The lowest increase of those compounds was found in the NPK-treatment.

Long-term fertilization without regular liming caused adversely effects, like increasing acidification of the soil, mobilization of aluminum and the decline of basic cations on the sorption complex (Stanislawska-Glubiak and Wrobel, 1999; Wrobel and Stanislawska-Glubiak, 1993; 1995). Two-time application of lime carried out every fourth year improved the physicochemical properties of the soil, however the increase of organic carbon content was slight (Fig. 2).
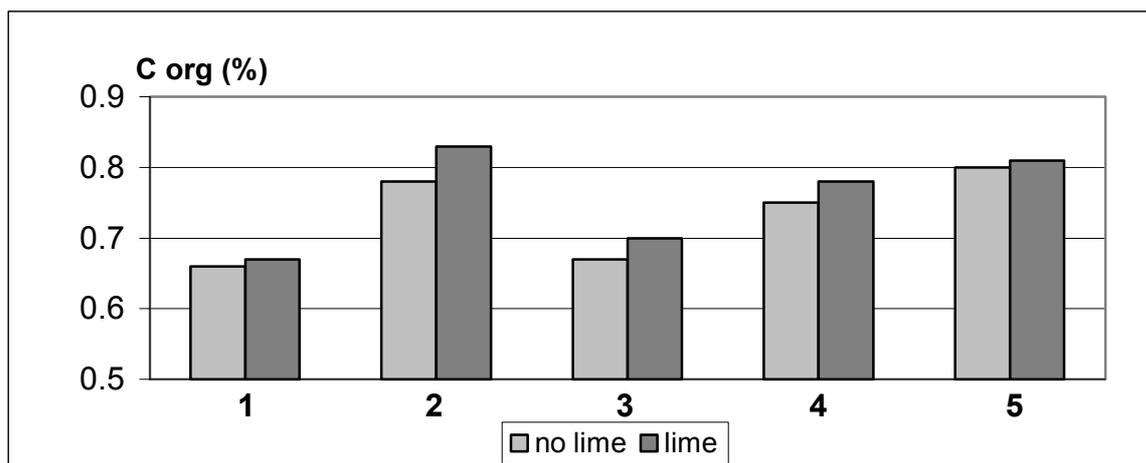
Figure 2. Organic carbon content (averaged over the last two rotation cycles) in limed vs. non-limed soil for different fertilization systems: 1- control, 2 – FYM, 3 – mineral fertilization, 4 – ½ FYM + ½ mineral fertilization 5 – FYM + ½ N

Comparisons were made for organic carbon content in limed vs. non-limed treatments over the last 8 years. For the different fertilization systems the increase of organic carbon content ranged from 4 to 6% on average compared to the non-limed variants.

CONCLUSIONS

1. Long-term cropping under Norfolk-type rotation without any fertilization ensured a sustained level of organic matter in light soil.

2. Long-term mineral NPK fertilization adjusted to crop requirements sustained the organic carbon level at the initial value.

3. Regular application of farmyard manure (FYM) or combined organic and mineral fertilization caused a significant increase in organic carbon content of the soil.

4. Two-time application of lime (4 years interval) increased the organic carbon level negligible, regardless of the fertilization system applied.

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EFFECTS OF DIFFERENT AGRICULTURAL MANAGEMENT STRATEGIES ON SOIL ORGANIC MATTER

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SUMMARY

Data from long term field experiments under different climate and soil conditions were used to evaluate effects of diverse agricultural practices on soil organic carbon (SOC) and potential nitrogen mineralisation (PNM).

After 17 years of different tillage treatments a distinct stratification has occurred. With minimum tillage SOC and PNM were significantly enhanced in 0-10 cm soil depth, however, SOC was lower in 20-30 cm compared to the ploughed plots. Over 0-30 cm SOC and PNM were slightly higher with minimum tillage than with ploughing (SOC: 18.9 vs. 17.4 g kg^{-1}). Reduced tillage using a cultivator showed intermediate results. The incorporation of crop residues increased SOC (+1.53 g kg^{-1}) and PNM in the top soil significantly (P<0.05) as compared to the removal only at the site Marchfeld after 20 years. In the Alpenvorland the crop rotation with the highest portion of sugar beet resulted in the lowest SOC and PNM after 16 years. SOC increased with a reduction of sugar beet and with the introduction of red clover fallow into the crop rotation. Selected crop rotations showed a significant increase of SOC only with high N fertilisation as well as with low and medium N-fertilisation in combination with the incorporation of crop residues. Additional applications of sewage sludge resulted in significantly higher PNM, but not of SOC.

KEY WORDS: soil organic carbon, potential nitrogen mineralisation, field experiment, agricultural practice, soil tillage, crop rotation

INTRODUCTION

Soil organic carbon (SOC) is regarded one of the most important indicators of soil quality and influences soil chemical, physical and biological properties. It is, for instance, well described as a source of nutrients, has impacts on the cation exchange capacity of soils, improves soil

structure and aggregate stability, influences water content, aeration and temperature of the soils. Changes in the quantity and quality of organic matter affect important soil functions such as production-, regulatory- and the habitat-function (Blum, 2002) and are of interest for sequestering or release of CO_2 to the atmosphere. Different land use and soil management systems may change soil organic C, which is reported to be higher in forest and grassland soils than in arable land and vineyards (e.g. Gerzabek et al., 2003). Different management strategies as tillage, crop rotation and various amendments (mineral and organic fertilisation, irrigation,..) have an impact on C input and turnover in arable cropping systems (Antil et al., 2005). An appropriate management of arable soils is necessary to obtain or maintain optimal quantities of soil C (Körschens et al., 1998). Therefore, the evaluation of long term field experiment data is a useful tool to highlight site specific effects of different agricultural practices on soil organic matter in arable soils (Dersch and Böhm, 2001; Körschens et al., 2002). In addition to SOC we analysed potential nitrogen mineralisation (PNM), a microbial parameter, which is assumed to be a more sensitive indicator for management changes than element contents (e.g. Friedel et al., 1996).

MATERIAL AND METHODS

Sites and treatments

Different agricultural practices were investigated in long-term field-experiments. They were carried out on three sites in Lower Austria, Alpenvorland, Waldviertel and Marchfeld under different climate and soil conditions, see Table 1.

Table 1. Characteristics of the experimental sites and investigated soil management measures

Site	ALPENVORLAND	WALDVIERTEL	MARCHFELD
Meter above sea level	290	550	150
Annual rainfall (mm)	836	740	540
Mean annual temperature (deg C)	8.5	6.8	9.1
Soil type (FAO)	Gleyic Luvisol	Dystric Cambisol	Calcaric Phaeozem
pH	6.6	6.5	7.5
Texture	Loamy Clay	Loamy Sand	Sandy Loam

Investigated soil management measures	- crop rotation - N-fertilisation - manuring	- crop residues	- crop residues - tillage - sewage sludge

Soil sampling and pre-treatment

Soil samples were normally collected in autumn, at the tillage experiment in spring. On each plot at least 16 sub-samples were taken with a single-gouge auger (cores of 30 mm diameter), mixed and stored in plastic bags. Prior to the analyses, the soil samples were air-dried and sieved <2mm.

Soil Analyses

Soil organic carbon (SOC) was analysed by dry combustion (LECO CNS-2000). Potential N-mineralisation (PNM) was measured using the anaerobic incubation method (Keeney, 1982), modified according to Kandeler (1993).

Statistical procedure

All analytical results were given as arithmetic means of results from three or four plots. Statistical analyses were carried out with a multiple analysis of variance and subsequent multiple t-tests (LSD 0.05). All calculations were performed using the SPSS package.

Field experiments

The following field experiments were investigated focussing on long term changes in SOC and PNM (the site and the initial year in brackets):

- Tillage (Marchfeld, since 1988), more detailed description in Spiegel et al., (2002)
    - MT (minimum tillage): rotary driller without any primary treatment before seeding, cultivation depth: 5-8 cm
    - RT (reduced tillage): cultivator in autumn and after the harvest; cultivation depth: 15 cm
    - CT (conventional tillage): reversible plough in autumn and cultivator after the harvest; cultivation depth: up to 25-30 cm,
- Management of crop residues (Marchfeld and Waldviertel, since 1982)
    - incorporation
    - removal of crop residues
- Crop rotation (Alpenvorland, 1988 - 2004) including different N-fertilisation levels without and with incorporation of crop residues,), a more detailed description is given in Dachler and Köchl (2003)
    - 67% cereals + 33% sugar beet
    - 67% cereals + 33% sugar beet + manure (6x 30 t ha^{-1})
    - 83% cereals + 17% sugar beet
    - 100% cereals
    - 100% cereals + cover crops
    - Annual red clover fallow, once in a 6 year crop rotation
    - Biennial red clover fallow in a 6 year crop rotation
- Application of sewage sludge (Marchfeld, since 1973)
    - On average every 3 years, per application on average 5 t DM, 2.3t OM, 240 kg N and 180 kg P_2O_5 ha^{-1}

RESULTS AND DISCUSSION

For the interpretation of the results it is important to bear in mind, that SOC content is mainly dependent on site characteristics as climate and texture (Dersch and Böhm, 2001; Körschens, 1998). Long term diverse soil management caused partly significant changes in the investigated parameters.

After 17 years of different tillage treatment a distinct stratification has occurred. With minimum tillage SOC and PNM were significantly enhanced in 0-10 cm soil depth (Fig. 1), however SOC was lower in 20-30 cm compared to the ploughed plots. This may be due to organic matter from crop residues brought with ploughing treatment into deeper soil layers. Over 0-30 cm SOC and PNM were slightly higher with minimum tillage than with ploughing (SOC: 18.9 vs. 17.4 g kg^{-1}). Reduced tillage with the cultivator showed intermediate figures. Higher frequency of tillage measures with reduced and conventional tillage compared to a single treatment per year in the minimum tilled variant probably has lead to a decrease of SOC and PNM.
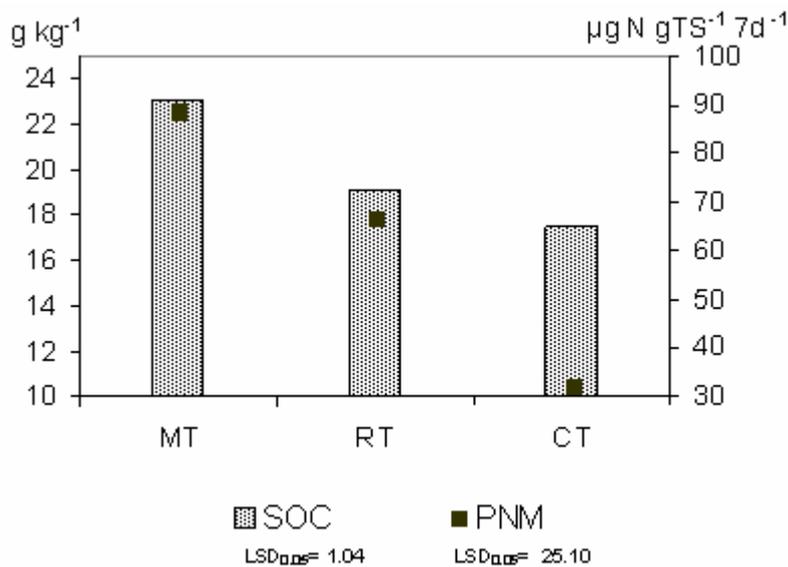
Figure 1. Effects of different tillage treatments on SOC and PNM (in 0-10 cm) after 17 years

The incorporation of crop residues has caused higher PNM in the upper soil layer (0-25 cm, diagram not shown) and enhanced SOC in both layers under investigation at Marchfeld and Waldviertel after 20 years (see Figure 2). However, the differences were significant (P<0.05) only in the upper soil layer at Marchfeld (SOC: +1.53 g kg^{-1}). This is probably due to different site specific crop rotations, such as higher portion of root crops and the cultivation of corn instead of silomaize at Marchfeld, causing higher amounts of crop residues and consequent C input as compared to the site Waldviertel.

Figure 2. Effects of the crop residue management on SOC in two soil layers after 20 years
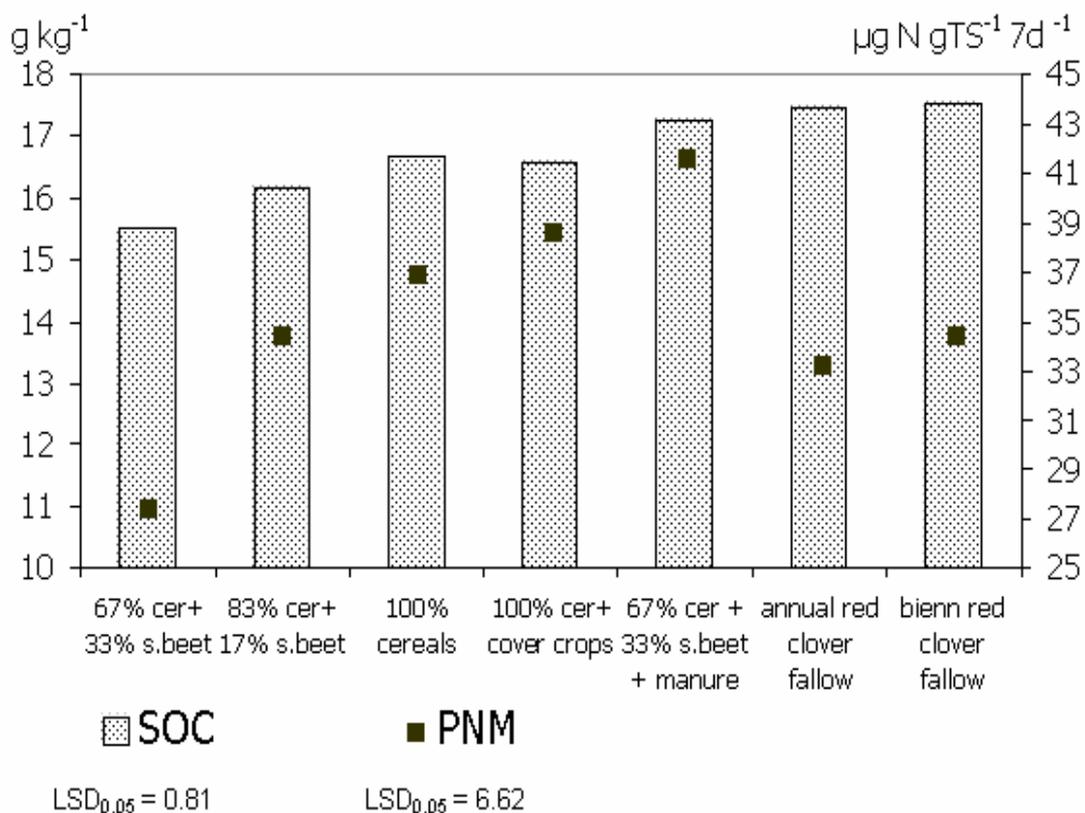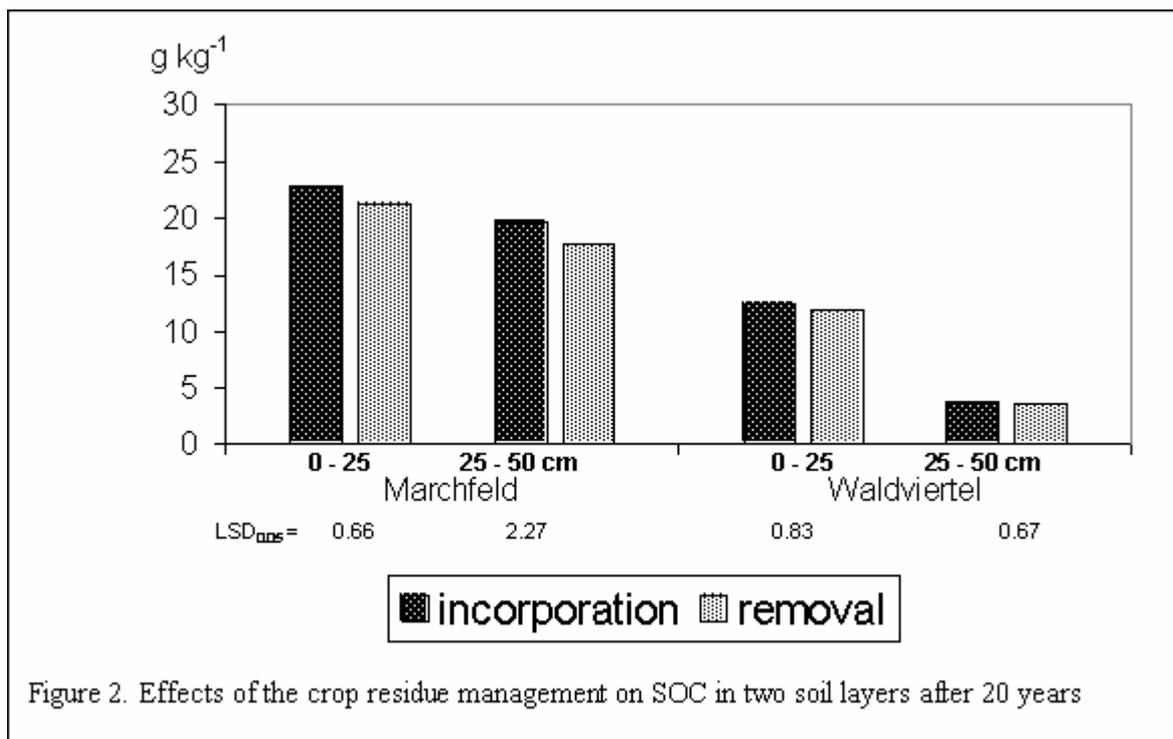
Figure 3. Effects of different crop rotations on SOC and PNM (0-20 cm) after 16 years

As can be seen from Figure 3, the crop rotation with the highest portion of sugar beet resulted in the lowest SOC and PNM after 16 years.

A lower portion of sugar beet (17%) did not change SOC, however, PNM was significantly higher. The omission of sugar beet (=100% cereals) caused significant increase both for SOC and PNM. Overall, SOC increased with a reduced portion of sugar beet and with the introduction of red clover fallow into the crop rotation. PNM did not respond to the red clover fallow. No differences could be stated between annual and biennial red clover fallow.

The application of manure (4 times 30t per ha) to a crop rotation with 67% cereals and 33% sugar beet increased SOC (+ 1.72 g kg^{-1}) and PNM significantly.

The effects of different levels of N fertilisation and the incorporation of crop residues (on average of four selected crop rotations without manure, red clover fallow and cover crops) on SOC and PNM are shown in Figure 4. Only the high N-fertilisation and low and medium N-fertilisation combined with crop residue incorporation resulted in a significant increase of SOC compared with zero N fertilisation and removal of crop residues. Significantly higher PNM could only be achieved with medium N-fertilisation combined with crop residue incorporation.
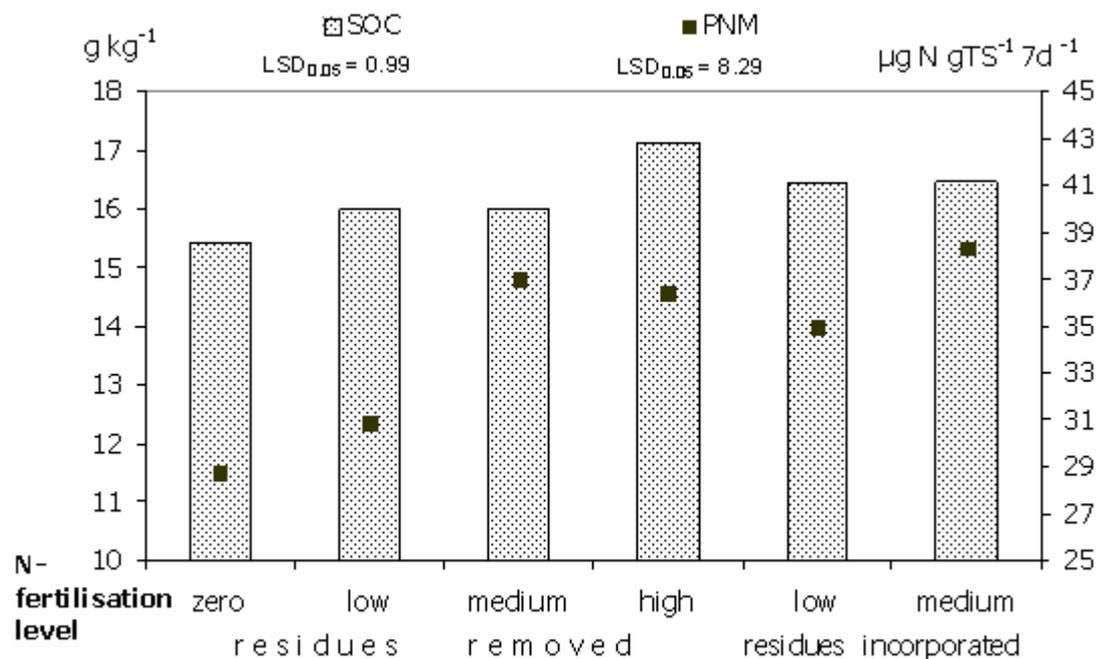
Figure 4. Effects of different crop rotations (average of four selected variants), N-fertilisation levels and the management of crop residues on SOC and PNM (0-20 cm) after 16 years

The application of long-term moderate amounts of sewage sludge (Fig. 5) resulted in significantly (P<0.05) higher PNM, but the increase of SOC was not significant. However, only in this field experiment PNM proved to be a more sensitive indicator for management

changes than SOC. In all the other experiments both parameters responded in an equivalent way.
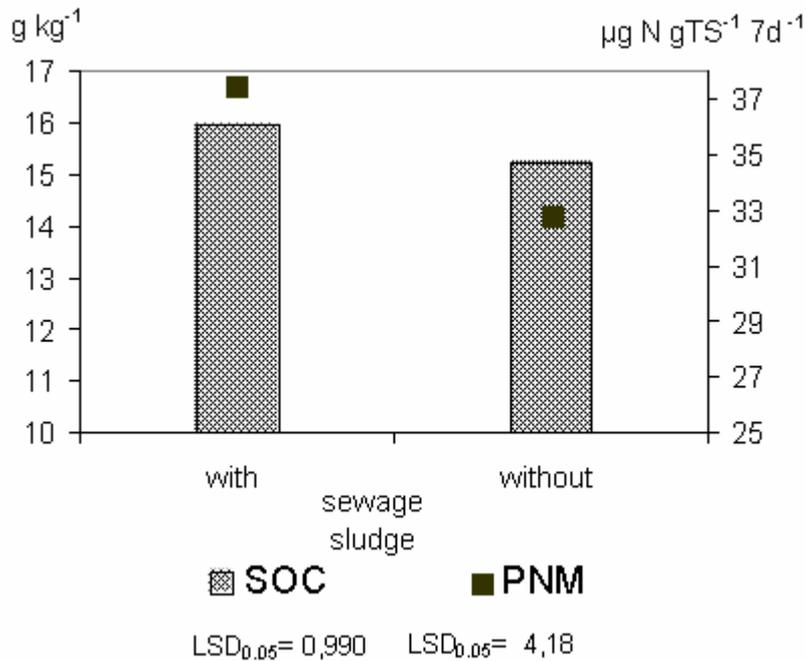
Figure 5. Effects of the application of sewage sludge on SOC and PNM (0-20 cm)

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TRACEABILITY OF MICROBIAL COMPOST COMMUNITIES IN A LONG-TERM FIELD EXPERIMENT

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SUMMARY

The effects of long term application (>10y) of different compost (urban organic wastes, green wastes, manure wastes and sewage sludge) and mineral fertilizer amendments (corresponding to 40 kg N ha^{-1}; 80 kg N ha^{-1} and 120 kg N ha^{-1}) on soil parameters, microbial diversity and community composition were studied. The organic amendments increased the total organic C and total N and had a weak influence on microbial activity and microbial biomass C. Community level physiological profiles (on Biolog GN plates) were significantly affected by the different composts. A structural analysis by polymerase chain reaction (PCR) using universal primers followed by denaturing gradient gel electrophoresis (DGGE) was able to differentiate between the three major groups of treatments, namely organic amendments, organic amendments+mineral fertilizer and mineral fertilizer only. Similar results were obtained with primers targeted at *Streptomycetes* and ammonia-oxidizing bacteria (AOB). The data thus suggest that long-term application of composts leaves microbial fingerprints in the soil; functional traits are more strongly affected by the different composts than the structural composition of the soil microflora.

KEYWORDS: Compost, basal respiration, microbial biomass, Polymerase chain reaction-denaturing gradient gel electrophoresis, DGGE, Community level physiological profiles, CLPP, *Streptomycetes*, Ammonia-oxidizing bacteria, AOB

INTRODUCTION

Microorganisms rapidly adapt to changing environmental conditions, and therefore, microbial biomass and activity are excellent indicators of changes in soil health (Kennedy et al., 1995), and are among the classical parameters for characterizing soils. In order to improve the understanding of soil functions, however, these methods should be supplemented by

microbial community related parameters like Community Level Physiological Profiles (CLPPs) (Garland and Mills, 1991) or DNA fingerprinting techniques (Muyzer et al., 1993). Composts are increasingly used in many European countries to improve agricultural production without adverse environmental effects (Garcia et al., 1994). While it is known that the application of compost to soils increases microbial activities and biomass (Ros et al., 2003), little is known on the effects of compost amendments on microbial diversity and community composition. The present investigation addresses two major questions (1) does the long-term (>10 y) application of composts affect microbial soil properties, and (2) does the application of different composts result in different functional and structural fingerprints in the soil?

MATERIAL AND METHODS

Experimental design

A crop rotation (maize, summer-wheat and winter-barley) field experiment (randomized block of 12 treatments with 4 replicates) was started in 1991 near Linz, Austria. The plot size was 10m x 3m, and the treatments were as follows: (1) mineral fertilisation corresponding to: 0 kg N ha^{-1} (Control); 40 kg N ha^{-1} (40); 80 kg N ha^{-1} (80), and 120 kg N ha^{-1} (120); (2) the organic amendments treatments corresponding to: 175 kg N ha^{-1} were either urban organic waste compost (from source-separate collection) (UWC), green waste compost (GC), manure compost (MC) and sewage sludge compost (SSC); (3) the organic amendment+nitrogen corresponding to 175 kg N ha^{-1} from compost plus 80 kg mineral N ha^{-1} (UWC+80; GC+80; MC+80, SSC+80). Soils from the field experiment were sampled in May 2003 prior to cropping (winter barley) and prior to the incorporation of the annual amendments. Ten random soil cores (20cm depth) were taken from each plot, bulked and sieved (<2mm).

Chemical analysis

The pH was measured in an aqueous extract (1/5 w/v). Total organic C was measured by dry combustion (Insam, 1996). For total nitrogen measurement the Kjeldahl method was used. Total P, total K and heavy metals were determined with Atomic Absorption Spectroscopy after wet acid digestion of samples (ÖNORM L 1085).

Microbial activity

Basal respiration was measured as CO_2 evolution from moist (60% WHC) soil samples at 22°C, at using a continuous flow infrared gas analysis system (Heinemeyer et al., 1989).

Microbial biomass C was determined by substrate-induced respiration (SIR) (Anderson and Domsch, 1978) after the addition of 1% glucose.

Community level physiological profiles (CLPPs)

Community level physiological profiles were determined by the use of Biolog GN plates (Bochner, 1989) containing 95 different C sources and a water well. To obtain the bacterial suspension, the extraction method of Insam and Goberna (2004) was followed. Each well of the GN plate was inoculated with 130µl of suspension and incubated at 28°C in the dark. Optical density (OD_{592}) was measured every 12h for 7d using an automated plate reader (SLT SPECTRA, Grödig, Austria).

Structural analysis

After DNA extraction (performed with the Fast DNA Spin Kit for soil, BIO 101, QBiogene, USA) PCR-DGGE analysis with the universal 16S rDNA primer set 338f (GC-clamp)+907r were performed according to Ros et al., (in press). To specifically amplify *Streptomycetes,* primers sm6f+sm5r (Monciardini et al., 2002) were used. A specific PCR reaction for ammonia-oxidizing bacteria was performed using primer pair CTO189f+CTO654r (Kowalchuk et al., 1997).

Data analysis

All analyses were made in quadruplicate. One-way analysis of variance (ANOVA) followed by Tukey as a post hoc test was used to determine significant differences between treatments and group of treatments. CLPP data (absorbance in each BIOLOG plate well) were subjected to discriminate analysis (SPSS program package). DGGE banding patterns were analysed using the GelCompar 4.0 software (Applied Maths, Ghent, Belgium).

RESULTS AND DISCUSSION

The long-term application of organic and inorganic amendments caused significant changes in soil chemical properties. The amount of organic carbon (TOC) was significantly higher ($p \leq 0.05$) after organic than after mineral fertiliser amendment (Tab.1). This suggests positive effects on the soil C status, inextricably associated with sustainability (Ros et al, in press). Apart from C, N is often a key limiting factor for soil organisms and the addition of N can alter microbial biomass, activity and species composition (Sarathchandra et al., 2001). In the present study organic amendments significantly increased ($p \leq 0.05$) total N concentration compared to mineral fertilizer treatments (Tab.1), which confirms earlier findings (Crecchio et al., 2001).

Table 1. Total organic C (TOC), total N and the C/N ratio of the soils treated with mineral fertilisers or composts. (Standard errors of the mean are given in parenthesis, n=4, similar letters indicate non-significant differences).

	TOC (g kg^{-1})	Total N (g kg^{-1})	C/N
Control	11.8 (0.5)a	1.45 (0.10)ab	8.14 (0.71)
40	11.7 (0.6)a	1.43 (0.13)ab	8.26 (0.65)
80	11.1 (0.5)ab	1.38 (0.13)a	8.12 (0.76)
120	11.4 (0.3)abc	1.50 (0.14)ab	7.68 (0.84)
UWC	13.7 (0.6)abc	1.68 (0.05)b	8.17 (0.47)
GC	13.4 (1.4)abc	1.53 (0.15)ab	8.51 (0.64)
MC	12.6 (0.6)ab	1.48 (0.10)ab	8.27 (0.30)
SSC	14.1 (1.2)abc	1.58 (0.10)ab	9.23 (0.42)
UWC + 80	12.8 (1.1)c	1.65 (0.06)b	8.04 (0.42)
GC + 80	12.9 (0.8)bc	1.63 (0.05)ab	7.95 (0.31)
MC + 80	12.7 (0.6)abc	1.58 (0.10)ab	8.11 (0.80)
SSC + 80	14.0 (0.9)bc	1.60 (0.08)ab	8.74 (0.74)

Several authors have reported positive effects of composts on soil microbial biomass and basal respiration as a result of increased availability of readily decomposable organic matter and nutrients (Perucci, 1993; Garcia et al., 1998). However, in the present investigation the effects on biomass C and basal respiration were less than expected for organic amendment soils. This may be attributed to the fact that the samples were taken nearly one year after the last application.

Based on the intensity of the utilization of the 95 substrates present in Biolog GN plates a discriminant analysis (DA) was calculated, which showed a consistent separation of samples coming from mineral fertilizer treatments, organic amendments treatments and organic amendment+nitrogen treatments (Fig. 1). Furthermore the different composts (except green waste) could be found in separate groups.
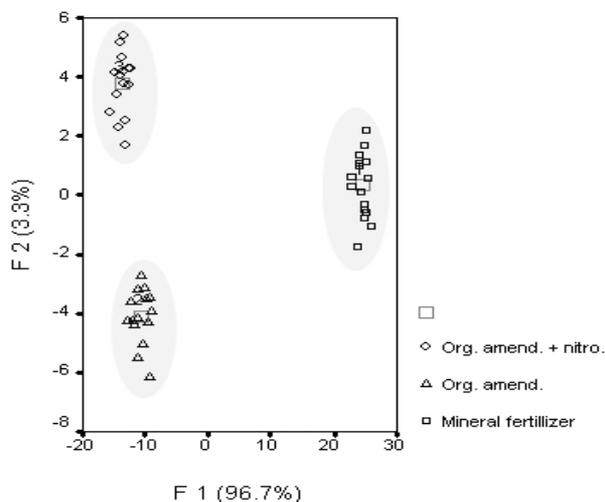
Figure 1. Plot showing first and second canonical discriminant factors of community level physiological profiles (CLPPs) for all three groups (mineral fertilizer, organic amendments and organic amendments +nitrogen) (from Ros et al., in press).
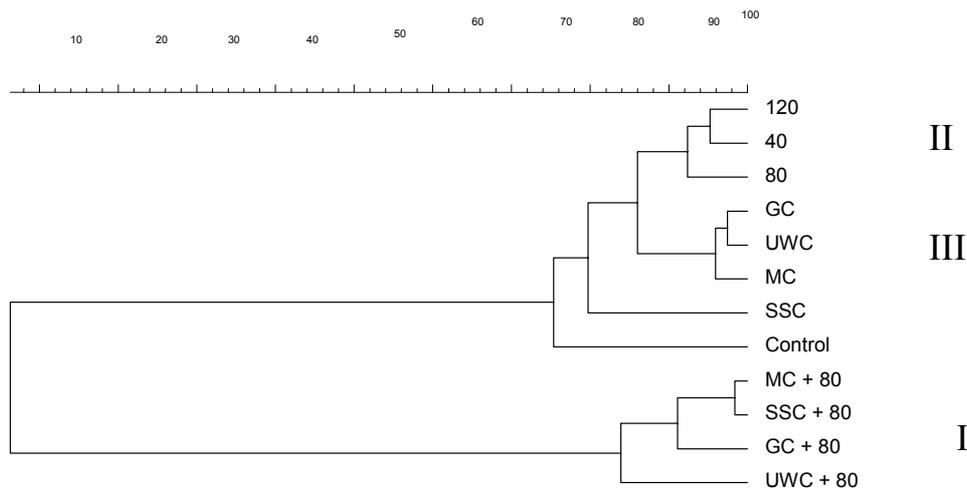
Figure 2. Cluster analysis of the DGGE patterns for the universal 16S rDNA primer set 338fGC+907r (Pearson correlation coefficient and Ward clustering) (from Ros et al., in press)

DGGE analysis performed with universal 16S rDNA primers displayed numerous bands, with about 20 bands shared among all samples. This indicates, at least concerning the dominant groups, a rather stable bacterial community structure, largely determined by inherent properties of the soil and little affected by the amendments. Cluster analysis of the DGGE patterns that also included weaker bands, showed three main clusters (Fig.2): organic amendments+nitrogen treatments (cluster I), mineral fertilized samples (cluster II) and a cluster III (GC, UWC and MC).

PCR-DGGE analysis using specific 16S rDNA primer sets for *Streptomycetes* and AOBs revealed two main clusters, on the one hand soils treated with mineral fertilizer only, on the other hand soils treated with organic amendments and organic amendments+N (Fig.3+4).

The separation into the two major groups by using eubacterial primers is hard to explain. It may be seen in the context of an optimal C and N supply in the case of compost plus additional mineral N, versus suboptimal conditions in the case of only mineral or compost application. In contrast, the separation into three groups using *Streptomycetes* and AOB targeted primers corresponds to the results obtained by CLPP. However, it is unlikely that the bacteria contributing to the CLPP results are *Streptomycetes*, or even less so, AOBs (which are hardly cultivable).
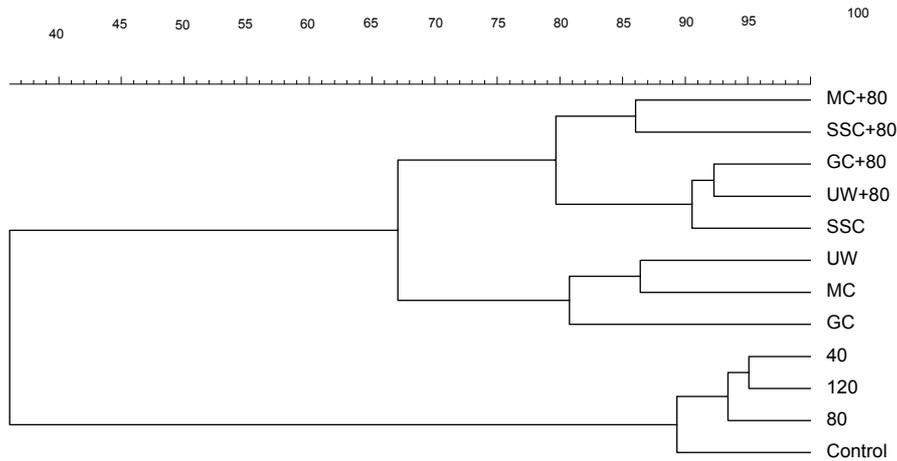
Figure 3. Clustering analysis of the DGGE patterns for the *Streptomycetes* specific primers (Dice correlation and Ward clustering)
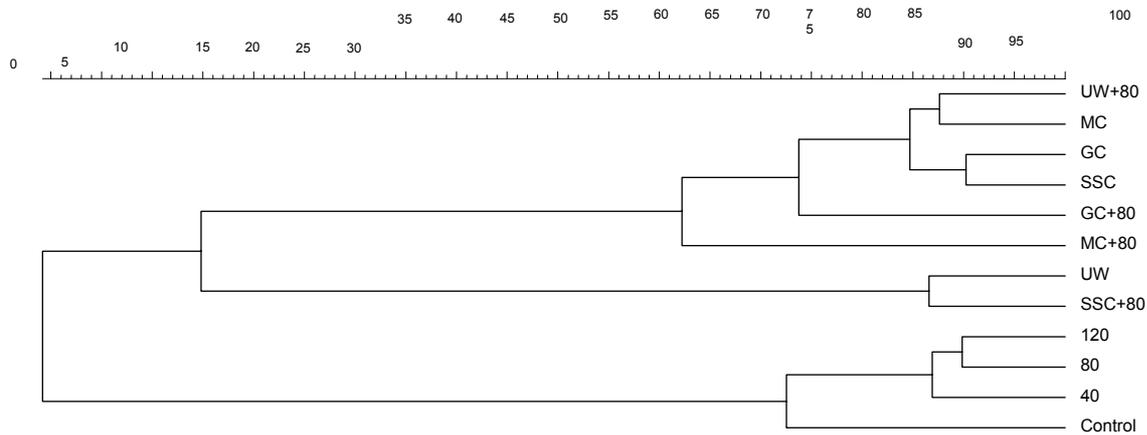
Figure 4. Clustering analysis of DGGE patterns performed with specific primers for ammonia-oxidizing bacteria (Pearson correlation coefficient and Ward clustering) (from Innerebner, 2005)

In conclusion, the long-term application of composts in a crop-rotation did positively affect soil organic C and N, but only weakly affected microbial biomass and basal respiration. Community level physiological profiles were significantly different among major treatment groups, and even among specific composts. PCR-DGGE analysis showed that also structural parameters were affected by the different composts.

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THE EFFECT OF AFFORESTATION OF FORMER CULTIVATED LAND ON THE QUALITY AND QUANTITY OF SOIL ORGANIC CARBON

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SUMMARY

The paper presents preliminary results on changes in quantity and quality of soil organic carbon following afforestation of former light textured arable soils (Haplic Arenosols) with Scots pine *(Pinus silvestris)*. In the study, two soils under 14, and two under 32 & 35 years stand were compared with adjacent cultivated and native forest soils. The soil samples were taken from the whole thickness of humus horizon of the cultivated soils and from three layers (0-5, 5-10, 10-20 cm) in the afforested soils. The following fractions of C were determined: total organic carbon (C_{org}), fraction soluble in 0.1mol NaOH dm^{-3} (humus acids -CH), fraction soluble in 0.5 mol H_2SO_4 dm^{-3} (C hydrolysing - Ch) and residue (Cr). The content of C_{org} in the afforested soils was higher in the top 5 cm but lower in the 5-10, 10-20 cm soil layers in comparison with related horizons of the arable soils. The results suggest that after more than three decades, a net accumulation of C_{org} in mineral humus horizon of former arable soils due to afforestation may occur. Afforestation affected the quality of soil C, i.e. a decrease in the proportion (%) of C of humus acids fraction in C_{org} by several to ten percent and an increase in residue fraction as against their value in related horizons of the arable soils. No clear effect of the stand age on organic carbon quality was observed.

KEY WORDS: organic carbon fractions, afforestation, former arable soils, sandy soils

INTRODUCTION

In Europe today millions of hectares of agricultural land is set-aside and subjected to alternative land use for example afforestation (Vesterdal et al., 2002; Wall & Heiskanen, 2003). In Poland, in the year 2002, the area of abounded land was of 2.3 mio ha (GUS, 2003). "The National Programme of Forestation Increase" in the country predicts afforestation of about 700 thousands of ha until the year 2020 and later, up to 2050, about the same area (MŚ, 2003).

The afforestation causes radical changes in the land use - partly due to the lack of cultivation (terminating of mineral and organic fertilisation, liming, ploughing) and also due to the effect of trees. Tree vegetation differs from crops mainly in quantity and quality of litter and the root system. The conversion of arable land into forest influences the soil properties, such as: pH, quantity and quality of organic matter, sorptive capacity, content of nitrogen and other elements, bulk density, porosity, biological activity (Brożek, 1993; Post & Kown, 2000; Allen & Chapman, 2001; Smal et al., 2003).

Changes in soil organic carbon due to afforestation are very important for the environment. It is a suggested option (Kyoto Protocol) for mitigation of increased atmospheric CO_2, as forest ecosystems can store the substantial amounts of carbon in both, biomass and soil. However, afforestation by changing soil organic matter content and pH, may also affect heavy metals behaviour (solubility) in the soil (Strobel et al., 2001; Andersen et. al., 2004).

In the review paper, Paul et al., (2002) showed that global data on quantitative changes in soil organic carbon caused by afforestation are highly variable, with soil C content either increasing or decreasing. The authors summarised that among many factors affecting the organic matter the most important proved to be previous land use, climate and the type of forest established. There are very few studies available on the changes in quality of organic carbon due to afforestation.

The aim of the paper is to present our preliminary results concerning the change in quantity and quality of soil organic carbon following afforestation of former arable soils with Scots pine *(Pinus silvestris)*.

MATERIAL AND METHODS

Study site

Four paired sites of the afforested former arable soils with adjacent cultivated fields and two locations of the native forest (fresh coniferous forest) were selected for the study. They were situated in the Lublin region (SE Poland), where the mean multi-annual temperature is equal to about 7.50C and precipitation 550 mm. The area gives an opportunity to study the effect of afforestation within the same soil type. The chosen soils are developed on water-glacial sands and classified as Haplic Arenosols in WRB classification (FAO, 1998). They commonly occur in the region. At two locations the age of stand was 14 years, at two other 32 and 35 years, respectively. The native forests (~ 150 years old stands) were included for comparison to give information on the possible long term changes in soil C. They are situated ca. 500 m

from the afforested sites. The soils are light textured (in majority loose sand and slightly loam sand), poor in nutrients and acid. The cropping system in each location in the past was typical of the light textured soils in the region i.e. potatoes, rye, oats, cereals. In the year of soil sampling in all the sites cereals were grown. Agriculture in the region is of low intensity with a very low fertilisation rate. It was assumed that each pair of plots had similar soil characteristics prior to afforestation and can be considered as control. It was verified for each stand that arable land use had been for centuries prior to afforestation. The forests had not received any fertilisation or weed control, the trees were not thinned.

The soil samples were taken in the late summer after harvesting. At each site a representative profile was excavated. The soil samples were taken from the humus horizons, i.e. from their whole thickness (0-20 cm) of the ploughed soils and from three layers (0-5, 5-10, 10-20 cm) in the afforested soils. The mineral humus horizons in native forest soils were very thin and sampled as one 5cm layer. The samples were air dried and passed through a 2 mm sieve. Part of the sample designated for organic carbon analyses was ground in an agate mortar.

Analyses of soil carbon

The following fractions of C were determined with sequential extraction: total organic carbon (C_{org}), fraction soluble in 0.1mol NaOH (humus acids - CH), fraction soluble in 0.5 mol H_2SO_4 (C hydrolysing - Ch) and fraction not extractable, i.e. residue - Cr. The content of C in particular fractions was determined by wet oxidation method according to the modified Tiurin's procedure (Arinuskina, 1961). The C content of residue was calculated as C_{org} - CH - Ch.

RESULTS AND DISCUSSION

The quantity and quality of soil organic carbon differed between the compared soils (Tab. 1, 2, 3).

The content of C_{org} in the top 5 cm layer in A horizon of the afforested former arable soils was mostly (not at Trójnia) substantially higher (on average 1.15 and 1.46 times, for soils of 14 and older stand, respectively) than in the Ap horizon of the related ploughed soils. In the deeper layers, for the both stand ages, the content of C_{org} was lower than in the respective horizons of the arable soils.

Table 1. Total organic carbon and carbon content of fractions in g C kg^{-1} and in % of C$_{org}$ in humus horizon of arable soils and adjacent afforested soils (14 years old stands – young stands)

Loca-tion/use	Horizon/ layer (cm)	C$_{org}$	Humus acids CH			C hydrolizing Ch		C of residue Cr	
		[g kg^{-1}]	[g kg^{-1}]	% C$_{org}$		[g kg^{-1}]	% C$_{org}$	[g kg^{-1}]	% C$_{org}$
Trójnia									
Field	Ap(0-20)	10.50	4.95	47.14		0.51	4.86	5.04	48.00
Forest	A(0-5)	10.30	3.66	35.53		0.42	4.08	6.22	60.39
	A(5-10)	6.78	2.48	36.58		0.24	3.54	4.06	59.88
	A(10-20)	6.20	2.04	32.90		0.18	2.90	3.98	64.19
Firlej									
Field	Ap(0-20)	8.28	4.09	49.40		0.30	3.62	3.89	46.98
Forest	A(0-5)	11.33	5.58	49.25		0.45	3.97	5.30	46.78
	A(5-10)	6.84	3.27	47.81		0.27	3.95	3.30	48.25
	A(10-20)	5.90	2.58	43.73		0.24	4.07	3.08	52.20
Mean	Ap	9.39	4.52	48.27		0.41	4.24	4.47	47.49
„	A(0-5)	10.82	4.62	42.39		0.44	4.02	5.76	53.58
„	A(5-10)	6.81	2.88	42.19		0.26	3.74	3.68	54.06
„	A(10-20)	6.05	2.31	38.32		0.21	3.49	3.53	58.20
„	A(0-20)	7.89	3.27	40.97		0.30	3.75	4.32	55.28

Changes (ratio of mean values)					
A$_{(0-5)}$/Ap	1.15		0.88	0.95	1.13
A$_{(5-10)}$/Ap	0.73		0.87	0.88	1.14
A$_{(10-20)}$/Ap	0.64		0.79	0.82	1.23
A/Ap	0.84		0.85	0.88	1.16

The mean content of C$_{org}$ in the soils of natural forests (5cm top mineral soil) was the highest among the studied soils and was about 2.4 times higher in comparison with the cultivated soil (Tab. 3). It was also 2.11 and 1.61 times higher than in afforested soils (under young and older forest, respectively). The results suggest that after afforestation of the former cultivated soils, the accumulation of organic matter was very slow and occurred mainly in the upper part of the humus horizon. In the deeper layers, the decomposition of C$_{org}$ prevailed over accumulation. These trends are in agreement with the literature data for comparable soils, trees and climate conditions (Paul et al., 2002; Vesterdal et al., 2002; Dowydenko 2004).

The mean content of C$_{org}$ in the whole former plough layer (0-20 cm) was about 16% lower in the soils under 14 years stand (Tab. 1), whereas it was about the same in soils under older stand in comparison with the related Ap horizons of the cultivated soils (Tab. 2).

Table 2. Total organic carbon and carbon content of fractions in g C kg^{-1} and in % of C_{org} in humus horizon of arable soils and adjacent afforested soils (32 & 35 years old stands)

Location/use	Horizon/ layer (cm)	C_{org}	Humus acids CH		C hydrolizing Ch		C of residue Cr	
		[g kg^{-1}]	[g kg^{-1}]	[% C_{org}]	[g kg^{-1}]	[% C_{org}]	[g kg^{-1}]	[% C_{org}]
Kol. Żurawiniec								
field	Ap(0-20)	10.80	5.60	51.85	0.21	1.94	4.99	46.20
forest	A(0-5)	15.30	5.64	36.86	0.36	2.35	9.30	60.78
	A(5-10)	9.30	3.36	36.13	0.24	2.58	5.70	61.29
	A(10-20)	7.60	2.88	37.89	0.15	1.97	4.57	60.13
Żurawiniec								
field	Ap(0-20)	8.70	4.26	48.97	0.27	3.10	4.17	47.93
forest	A(0-5)	13.10	5.37	40.99	0.16	1.22	7.57	57.79
	A(5-10)	6.80	3.60	45.00	0.15	2.21	3.59	52.79
	A(10-20)	5.90	2.78	47.12	0.18	3.05	2.94	49.83
Mean	Ap	9.75	4.93	50.41	0.24	2.52	4.58	47.07
„	A(0-5)	14.20	5.51	38.93	0.26	1.79	8.44	59.29
„	A(5-10)	8.05	3.21	40.56	0.20	2.39	4.65	57.04
„	A(10-20)	6.75	2.83	42.51	0.17	2.51	3.76	54.98
„	A(0-20)	9.67	3.85	40.67	0.21	2.23	5.62	57.10
Changes (ratio of mean values)								
	A$_{(0-5)}$/Ap	1.46	0.77		0.71		1.26	
	A$_{(5-10)}$/Ap	0.83	0.80		0.95		1.21	
	A$_{(10-20)}$/Ap	0.69	0.84		1.00		1.17	
	A/Ap	0.99	0.81		0.88		1.21	

This would indicate that during more than three decades following pine planting, a substantial increase in C_{org} contents of the top 5 cm was offset by its decrease in the lower part of the mineral humus horizon. Similar findings were presented by Paul et al., 2002, Vesterdal et al., 2002, Paul et al., 2003 in the studies on soil C dynamics in mineral surface layer in temperate climates following afforestation. This observation would also imply that afforestation of arable light textured sandy soils with pine in the studied climate conditions does not lead to net accumulation in 0-20 cm of organic carbon in soils until 35-40 years. This period may be transient and then a slow increase of C_{org} in the former plough layer will occur. However, more research should be undertaken to confirm this suggestion as well as to get more information on time frame needed for increase in C content close to the values in the soils of natural old forests.

The quality of organic carbon varied between the studied soils (Tab. 1, 2, 3). In the arable soils the pool of C_{org} consisted of humus acids fraction in about 49%. Generally, in all the

humus layers of the afforested and natural forest soils, the proportion (%) of this fraction was lower by several to ten percent in comparison to that value.

Table 3. Total organic carbon and carbon content of fractions in g C kg $^{-1}$ and in % of C_{org} in top 5 cm layer of humus horizon of native forest soils and their comparison with related horizons of arable and afforested soils

Location	Horizon	C_{org}	Humus acids CH		C hydrolizing Ch		C of residue Cr	
		[g kg^{-1}]	[g kg^{-1}]	[% C_{org}]	[g kg^{-1}]	[% C_{org}]	[g kg^{-1}]	[% C_{org}]
Firlej								
	Ah	26.20	11.04	42.14	0.39	1.49	14.77	56.37
Kol. Żurawiniec								
	Ah	16.90	8.52	43.92	0.18	0.93	10.70	55.15
Mean	Ah	22.80	9.78	43.03	0.29	1.21	12.74	55.76
Changes (ratio of mean values)								
	Ah/Ap[a]	2.38		0.87		0.36		1.18
	Ah/A(I)[b]	2.11		1.02		0.30		1.04
	AhA(II)[c]	1.61		1.11		0.66		0.94

[a] Ap as mean from four sites, [b] A(I)- 14 years old stands, [c] A(II)-32 & 35 years old stands

In the 5 cm top layer of the afforested soils, this lower percentage share of humus acids fraction in relation to C_{org} compared to the arable soils, indicates that the rate of organic carbon accumulation there was higher than its humification. In the deeper layers it may show that the decrease in C_{org} occurred mainly due to the decomposition of the humus acids fraction.

Generally, no clear relationships were found between the proportion (%) of C of humus acids fraction in C_{org} and the age of trees. On average, in 0-20 cm layer of the afforested soils it was equal to about 41%, for soils of both age stands. This value was similar to that stated for Ah horizon of natural forest soils (43%).

In the afforested soils the content of C in residue fraction contributed to the total C_{org} in the highest percentage and it was comparable to the proportion of this fraction in the natural forest soils.

Among the analysed fractions of organic carbon the lowest part of its total content (<5%) was extracted by H_2SO_4 solution. In most cases the percentage share of C hydrolysing was lower in the afforested soils in comparison with the arable ones, but higher than in the natural forest soils.

CONCLUSIONS

1. The content of C_{org} in the afforested soils was substantially higher in the top 5 cm but lower in the 5-10, 10-20 cm soil layers in comparison with related horizons of the arable soils. This shows that within the studied time frame the increase in C_{org} content following the afforestation of former arable soils was related only to the upper part of the mineral humus horizon.

2. Fourteen years after pine trees planting, the average content of C_{org} in the whole former plough layer (0-20 cm) was lower than in the respective Ap horizons, while in soils under older stands (32 & 35 years) it was about the same. Thus, one may expect that after more than three decades a net accumulation of C_{org} in mineral humus horizon due to followimg afforestation of post-arable soils may occur.

3. In the afforested soils the proportion (%) of C of humus acids fraction in relation to C_{org} was by several to ten percent lower and of residue fraction higher, in comparison with their value in related horizons of the arable soils. No clear effect of the stand age on organic carbon quality was observed.

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THE INFLUENCE OF DIFFERENT FORMS OF SULFUR FERTILIZATION ON THE CONTENT OF SULFATE IN SOIL AFTER SPRING BARLEY AND ORCHARD GRASS HARVEST

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SUMMARY

The aim of present study was to evaluate the influence of a fertilization with different sulfur forms on changes of sulfate sulfur content in the soil.

The study was performed on a base of a strict three-year pot experiment on soil material taken from the ploughing layer of lessive soil with silty dust granulometric composition. The soil was characterized with low sulfate sulfur content. The experiment was set by means of complete randomization. Sulfur form at 8 levels was the variable factor. Sulfur fertilization was applied annually in accordance to plant's nutrition requirements. Following were tested plants: spring wheat and white mustard in the first, spring rape seed and spring barley in the second, as well as spring barley and orchard grass in the third experimental year. Present paper is a fragment of those studies and it includes the influence of experimental factors on sulfate sulfur content in the soil analyzed after the third year of studies.

Applied experimental factors and tested plant species clearly differentiated the amount of S-SO_4 in the soil. The lowest sulfate concentration was found in the soil of object with no sulfur fertilized and where UAN with sulfur was applied. Introduction of elemental sulfur and gypsum in a case of barley as well as potassium or sodium sulfate or sulfuric acid in a case of orchard grass appeared to be the most advantageous. Obviously higher sulfate levels were recorded in soil samples analyzed after orchard grass harvest.

KEYWORDS: sulfate sulfur, soil, fertilization

INTRODUCTION

Sulfur content in mineral soils of Poland most often amounts to 0.05-0.4 $g \cdot kg^{-1}$, and in organic ones it may be even 10 times higher up to 4.5 $g \cdot kg^{-1}$. About 90-95% of that sulfur

quantities occurs in different-type organic combinations, and only 5-10% form mineral compounds, i.e. forms directly available for plants (Terelak et al., 1988, 1995). In a case of mineral soils, these dependencies are as follows:

- total sulfur – 70-1070 mg $\cdot$ kg^{-1} of soil;
- organic sulfur – 60-688 mg $\cdot$ kg^{-1} of soil;
- sulfate sulfur – 1-63 mg $\cdot$ kg^{-1} of soil (Terelak et al., 1988, 1995).

Soil minerals and organic compounds such as amino acids (methionin, cystein), peptides, proteins, sulfolipids, vitamins (thiamin, biotin) are general sources of the element in the soil (Kalembasa et al., 1995). Mineral and organic fertilizers are sulfur source as well. Among mineral fertilizers, ammonium sulfate (240 kg $\cdot$ t^{-1}), potassium sulfate (180 kg $\cdot$ t^{-1}), single superphosphate (120 kg $\cdot$ t^{-1}), gypsum or phosphogypsum (180-190 kg $\cdot$ t^{-1}), magnesium sulfate (130 kg $\cdot$ t^{-1}), kizeryte (220 kg $\cdot$ t^{-1}) and elemental sulfur, are the most important (Chapman, 1997; Fotyma and Boreczek, 1998; McGrath et al., 1996). Some sulfur amounts may introduce into the soil from the atmosphere in a form of dust or acidic rainfalls. However, it is worth underlining that as compared to 1980, when the annual SO_2 emission was 4132 thousand tons, sulfur deposit from the atmosphere has significantly decreased recently (GUS, 1981; Report, 1998).

The decrease of sulfur deposit from the atmosphere as well as the decrease of sulfur amounts introduced along with mineral fertilizers led to the occurrence of that component deficiencies in plant production (Bloem, 1998; McGrath et al., 1996). The sulfur lack can be expected mainly on lighter and usually acidified mineral soils localized far from industrial centers (Report, 1998; Terelak et al., 1995). Therefore, studies aimed to evaluate the influence of fertilization with different sulfur types on sulfate sulfur content in the soil, were undertaken.

MATERIAL AND METHODS

Studies were carried out on a base of a strict, three-year pot experiment using the soil material taken from upper layer of lessive soil with granulometric composition of silty dust. The soil was characterized with low sulfate sulfur level (12 mg $\cdot$ kg^{-1}).

The experiment was set by means of complete randomization. Sulfur form applied in 8 rates was the variable. Sulfur fertilization was applied annually at the rate of 0.025 g S $\cdot$ kg^{-1} for barley and orchard grass according to the scheme: 1 – no sulfur, 2 – UAN with sulfur in a form of $Na_2S_2O_3 \cdot 5H_2O$, 3 – $(NH_4)_2SO_4$, 4 – K_2SO_4, 5 – Na_2SO_4, 6 – elemental sulfur, 7 – $CaSO_4 \cdot 2H_2O$, 8 – H_2SO_4.

Spring wheat of Ismena cv. and white mustard of Borowska cv. were the testing plants in the first experimental year. In the second year, spring rape-seed of Sponsor cv. and spring barley of Rataj cv., and in the third – spring barley of Rataj cv. and orchard grass of Bepro cv. were cultivated. Present paper is a fragment of those studies and it includes the influence of experimental factors on sulfate sulfur content in the soil analyzed after the three years of experiment performance.

In addition, fertilization with N, P, K, and Mg was applied in all experimental objects in rates according to nutrition requirements of tested plants. In a case of barley, nitrogen, phosphorus, potassium and magnesium amounts were as follows: 0.14 g N $\cdot$ kg^{-1}, 0.075 g K $\cdot$ kg^{-1}, 0.038 g P $\cdot$ kg^{-1}, 0.015 g Mg $\cdot$ kg^{-1}. For orchard grass, they were: 0.21 g N $\cdot$ kg^{-1}, 0.11 g K $\cdot$ kg^{-1}, 0.057 g P $\cdot$ kg^{-1}, 0.023 g Mg $\cdot$ kg^{-1}. The nitrogen dose was divided into two parts: one half was introduced at the experiment setting, the other was added after thinning and adjusting the nutrients to optimum quantities. For orchard grass, the nitrogen dose was divided into three parts: 30% was applied at the beginning of the experiment, 30% after plant thinning and the rest 40% after the first cut. Phosphorus, potassium and magnesium were completely applied before sowing. Particular nutrients were introduced in a form of: N – NH_4NO_3, UAN with sulfur, $(NH_4)_2SO_4$, P – $Ca(H_2PO_4)_2 \cdot H_2O$, K – KCl, K_2SO_4, Mg – $MgCl_2 \cdot 6H_2O$.

Content of sulfate sulfur in the soil was determined by means of nephelometric technique according to Bardsley and Lancaster (Boratyński et al., 1975).

RESULTS AND DISCUSSION

Sulfate sulfur content in soil material before experiment was low at the level of 12 mg $\cdot$ kg^{-1} (Terelak et al., 1988, 1995). Applied forms of sulfur fertilization and the species of cultivated plant significantly differentiated the amount of S-SO$_4$ in the soil analyzed after the third year of experiment (Tab. 1).

After the harvest of spring barley, the quantity of sulfates in the soil ranged from 4.3 up to 17.4 mg $\cdot$ kg^{-1}. Although it is accepted that cereals belong to the plant group with relatively low requirements for sulfur (Bona et al., 1996; McGrath and Zhao, 1995), it follows from studies of Withers et al., (1997), that supplying a proper amount of the nutrient affects the increase of grain and straw yields. Those authors suggested that sulfur dose for barley should amount to about 10 kg S $\cdot$ ha^{-1}. The lowest S-SO$_4$ concentration was found in control object soil (with no sulfur) and it was about 3 times lower as compared to the amount recorded before experiment setting and 1.4-3-fold lower in relation to other objects. A clear decrease of

sulfate level in object without sulfur fertilization was probably associated with its intake by barley at its low level in the soil (McGrath et al., 1996). Objects fertilized with UAN with sulfur, sulfuric acid and sodium sulfate were also characterized with low $S-SO_4$ concentration. In contrary to above discussed objects, samples fertilized with sulfur in a form of elemental S and $CaSO_4 \cdot 2H_2O$, the sulfate sulfur level was 1.5-fold higher than that recorded in the soil before experiment and almost 1.3-4-fold higher as compared to other objects.

Table 1. Influence of fertilization with different sulfur forms on sulfate sulfur content in the soil

Object	After spring barley harvest	After orchard grass harvest
	$mg \cdot kg^{-1}$	
Without S	4.3	1.9
UAN with sulfur	6.0	1.4
$(NH_4)_2SO_4$	13.4	16.9
K_2SO_4	12.9	18.1
Na_2SO_4	10.3	19.6
S elemental	17.4	14.4
$CaSO_4 \cdot 2H_2O$	17.3	17.4
H_2SO_4	8.9	21.4
Before the experiment	12.0	

After orchard grass harvest, the amount of $S-SO_4$ in soil samples taken from majority of objects was higher than in respective levels found after spring barley harvest. Only in control object and UAN with sulfur, the component concentration was very low ranging from 1.4 to 1.9 $mg \cdot kg^{-1}$.

Soil samples from object where sulfuric acid was introduced (i.e. general component of acidic rainfalls), were characterized with the higher content of sulfates. The amount of $S-SO_4$ in analyzed object was 21.4 $mg \cdot kg^{-1}$ and it was 1.8 times higher than the concentration recorded in the soil before the experiment, as well as 1.1-15.3-fold higher as compared to other objects. It may prove the obvious influence of acidic rainfalls on the increase of sulfate concentration in soils (Kaczor, 1994). High levels of the component (about 18.1-19.6 $mg \cdot kg^{-1}$) were also found in soil samples fertilized with sodium or potassium sulfate. The amount of sulfates was within the range of 14.4-17.4 $mg \cdot kg^{-1}$ in other objects.

CONCLUSIONS

1. Content of sulfate sulfur in the soil depended on a form of applied sulfur fertilization as well as cultivated plant species.

2. The lowest $S-SO_4$ concentration was recorded in the soil of control object and that fertilized with UAN with sulfur. Application of elemental S and $CaSO_4 \cdot 2H_2O$ in a case of barley and K_2SO_4, Na_2SO_4 and H_2SO_4 in a case of orchard grass, appeared to be the most advantageous.

3. The level of sulfates found in the soil after orchard grass harvest was in majority of objects higher as compared to values recorded after spring barley harvest.

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ORGANIC MATTER IN ALPINE GRASSLAND SOILS AND ITS IMPORTANCE TO SITE QUALITY

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SUMMARY

The importance of soil organic matter (SOM) to soil fertility and soil quality in alpine regions was investigated. Alpine soils are commonly humus-rich in topsoil primarily because of the slow rate of SOM mineralization and secondarily because of the high below-ground phytomass which is concentrated in the top 10 cm of the soil. Some favourable and unfavourable properties of SOM concerning soil fertility and soil quality will be discussed.

KEY WORDS

Soil organic matter, alpine grassland soils, below-ground phytomass, water-holding capacity, effective cation exchange capacity, aluminum solubility, nitrogen and sulfur content

INTRODUCTION

Soil organic matter (SOM) is an indicator of soil quality as it interacts with other numerous soil components, affecting water retention, aggregate formation, bulk density, pH, buffer capacity, cation exchange properties, mineralization, sorption of pesticides and other agrochemicals, color (facilitate warming), infiltration, aeration, and activity of soil organisms. In addition to the amount of SOM, its quality is also an important indicator of soil quality and soil fertility (Seybold et al., 1998). The quantity and quality of SOM depend on many state factors such as time, parent material, topography, climate, plants, and animals (Jenny, 1980). Generally, it is assumed that SOM increases with elevation (Birch & Friend, 1956; Körner, 2003); this fact enhances its relative importance to site quality at higher altitudes. Furthermore, human influence on alpine soils is commonly negligible compared to soils at lower altitudes, thereby minimizing the effect of management practices on the quantity and quality of SOM. These are the main reasons why these investigations were carried out in alpine soils. The objectives of this study were (1) to provide data on the quantity and quality of SOM in alpine grassland soils, (2) to analyse its dependence on some state factors, (3) to

investigate its interaction with other soil properties, (4) to demonstrate its importance to site quality, and (5) to give some arguments concerning assessment of an optimal humus content in soil.

MATERIAL AND METHODS

This investigation was conducted in the montane, subalpine, and alpine zone of the Austrian Alps in Carinthia. The altitude was ranging from 1340 to 2160 m. Only soils of unfertilized and extensively managed grassland communities were selected for study. Soils were mainly Mollic Leptosols, Rendzic Leptosols, Calcaric Regosols, Mollic Cambisols, Cambic Umbrisols, and alpine forms of Stagnosols. Typical humus forms of the sandy and silty alpine soils were mull, mull-like moder, wet mull, and mull-like wet moder. Soil samples were taken exclusively from the A horizon from 0 to 10 cm depth. Visible roots were removed before the soil samples were air-dried at room temperature and sieved (< 2 mm). Soil analyses have been conducted according to the ÖNORM methods. Because no volumetric soil samples were taken, only concentrations can be mentioned. Relationships between organic carbon content and soil properties were determined by regression analyses.

RESULTS AND DISCUSSION

Table 1 shows the mean organic carbon and total nitrogen content, as well as the organic carbon to total nitrogen ratio in the topsoil (0-10 cm depth) of important grassland communities. Generally, soils under permanent grassland are characterized by a relatively high SOM content in topsoil.

Soils of unfertilized alpine pastures and meadows have on an average the highest concentration of organic carbon and the widest $C_{org}:N_{tot}$ ratio in the A horizon compared to soils of grassland communities at lower altitudes. However, total nitrogen shows no such altitudinal trend. Also, moist grassland communities on hydric soils (*Cirsium oleraceum-Persicaria bistorta*-community, *Iridetum sibiricae*) and plant associations from higher elevations on finer-textured soils (e.g. *Geranio sylvatici-Trisetetum flavescentis*) have a comparatively high SOM content in topsoil. More detailed soil-chemical properties of unfertilized alpine grassland soils are listed in Table 2.

Table 1. Intensity of grassland management, soil water regime, and selected soil-chemical properties (0-10 cm of soil depth) of important grassland communities

Plant community	n	igm	swr	% C_{org}	% N_{tot}	$C_{org}:N_{tot}$
Alpine pastures and meadows**	42	1,egr	b-pm	9.9*	0.7*	14.0
Cirsium oleraceum-Persicaria bistorta-community	19	2	mw-mm	9.8*	1.1*	10.6
Iridetum sibiricae	28	1	mw-mm	9.7*	0.8*	11.8
Geranio sylvatici-Trisetetum flavescentis	46	2-3	b	7.9*	0.8*	9.8
Festuca rubra-Agrostis capillaris-community	45	1-2,egr	b-pm	7.7*	0,6	12.0
Alchemillo monticolae-Arrhenatheretum elatioris	45	3-4	b	6.7*	1.0*	9.5
Alchemillo monticolae-Cynosuretum cristati	24	4-5	pm	5.5*	0.6*	9.0
Narcissus radiiflorus-community	41	1-2,egr	mm-sd	7.1	0.6	11.2
Trifolium repens-Poa trivialis-community	52	4-5	pm	6.5*	0.7	9.3
Mesobrometum erecti	22	1-2,egr	sd	5.8	0.6	10.5
Cardaminopsido halleri-Trisetetum flavescentis	30	2-3	b	5.7	0.7	10.1
Festuco commutatae-Cynosuretum cristati	13	egr	b-pm	4.4	0.5	9.4

** soil samples without roots; n = number of soil analyses; igm = intensity of grassland management (number of cuts/grazings; egr = extensive grazing); swr = soil water regime (mw = moderate wet, mm = moderate moist, pm = periodically moist in topsoil, b = balanced, sd = semi-dry); * = coefficient of variability > 30 %

Table 2. Selected soil-chemical properties (A horizon, 0-10 cm) of alpine grassland soils

n = 42	% C_{org}	N_{tot}	S_{tot}	$C_{org} : N_{tot}$	$C_{org} : S_{tot}$	$N_{tot} : S_{tot}$
Minimum	2,71	0,21	0,02	9,57	63,22	4,19
Maximum	19,67	1,63	0,27	20,36	195,75	12,00
Arithmetic mean	9,93	0,72	0,09	14,03	114,30	8,23
Median	8,50	0,61	0,08	13,32	110,50	7,86

Alpine grassland soils vary greatly in their organic carbon, total nitrogen, and total sulfur content. Mean C:N, C:S, and N:S ratios in the A horizon of unfertilized alpine soils are 14, 114, and 8, respectively. C:N ratios around 14 are typical of less productive alpine soils (Körner, 2003). A high C:N ratio indicates unfavourable conditions for the decomposition of SOM and poor humus quality. The relatively high concentration of organic carbon in the A horizon of many alpine grassland soils is mainly the result of unfavourable climatic and site conditions, such as low mean soil temperatures and long water-saturation of the alpine soils especially during the snowmelt period. These circumstances reduce the microbial activity and hence decrease the rate of SOM mineralization more rapidly than the annual net primary production of alpine plants (Franz, 1979). In addition, the temperature-dependent reduced rooting depth of plants in higher altitudes and the accumulation of a high below-ground phytomass in the top 10 cm of alpine soils are responsible for the high SOM concentration in the A horizon of many alpine grassland soils (Lichtenegger, 1997). At lower altitudes, SOM

is usually diluted over a larger soil profil (Körner, 2003) mainly because of an enhanced rooting depth of plants. In alpine grassland soils, 80 to 93 % of the below-ground phytomass are concentrated in the uppermost 10 cm of the soil (Bohner, 1998). In higher altitudes, the below-ground phytomass is of eminent importance with respect to carbon input into the topsoil (Hitz et al., 2001). The amount of below-ground phytomass in alpine grassland soils ranges from 150 to 360 dt ha^{-1} (Bohner, 1998). Assuming the mean carbon content of roots of 46 %, the carbon storage will be of 6900 to 16560 kg C per ha in the below-ground phytomass. The distribution of carbon and phytomass in an alpine grassland community (*Sieversio-Nardetum strictae*) at an altitude of 1890 m at peak season is given in Table 3.

Table 3. Phytomass and carbon distribution in an alpine grassland community (*Sieversio-Nardetum strictae*) at an altitude of 1890 m at peak season (Bohner, 1998)

	dt ha^{-1}	%	kg ha^{-1}
above-ground phytomass (growing height > 3/5 cm)	21	9	935*
above-ground phytomass (growing height 0-3/5 cm)	40	16	1780*
below-ground phytomass (0-40 cm of soil depth)	185	75	8510**
above- and below-ground phytomass	246	100	11225

* mean carbon content of the above-ground phytomass: 44.5 %; **mean carbon content of the below-ground phytomass: 46.0 % (Bohner, unpublished data)

The majority of stored plant carbon (75 %) is found in the below-ground phytomass. Only a minority (9 %) can be removed due to cutting or cattle grazing. These data also emphasize the importance of below-ground phytomass for SOM accumulation in alpine grassland soils. However, there is no direct relationship between organic carbon content in the A horizon of alpine grassland soils and altitude (not shown).

According to Figure 1 and 2, there is a close relationship between organic carbon content and total nitrogen or total sulfur content in the A horizon of alpine grassland soils. A very strong relationship ($R^2 = 0.9$) also exists between total nitrogen and total sulfur (not shown). In the A horizon of unfertilized alpine soils, almost 100 % of the total nitrogen is present in the form of organic nitrogen (Bohner, 1998). The large organic pools of nitrogen and sulfur in many alpine soils are not directly available to plants. Therefore, many alpine soils have only a high content of potentially mineralizable nitrogen and sulfur in topsoil. The rate of nitrogen and sulfur mineralization and hence nitrogen and sulfur availability to plants are reduced mainly because of the low mean soil temperatures and the temporarily high soil water contents. The clear relationship between organic carbon content and effective cation exchange capacity

(BaCl$_2$-extract) in the A horizon of alpine grassland soils indicates that SOM accounts for a major portion of the cation exchange capacity of alpine soils low in clay (Figure 3).

Figure 1. Relationship between C$_{org}$ (%) and N$_{tot}$ (%)
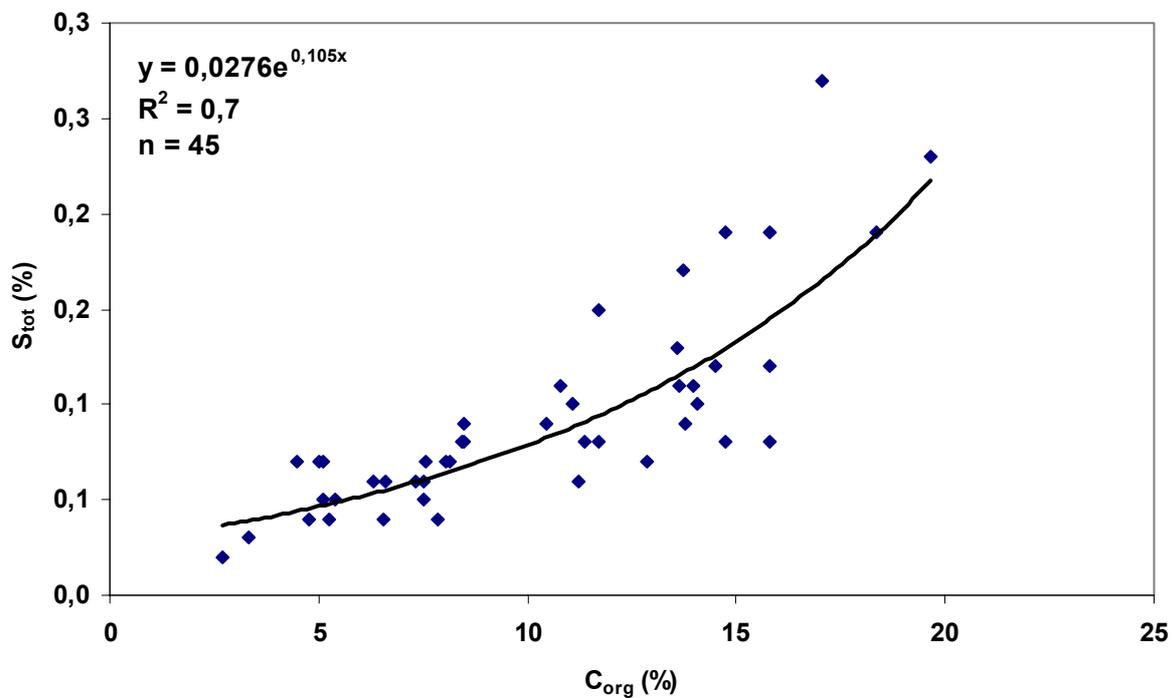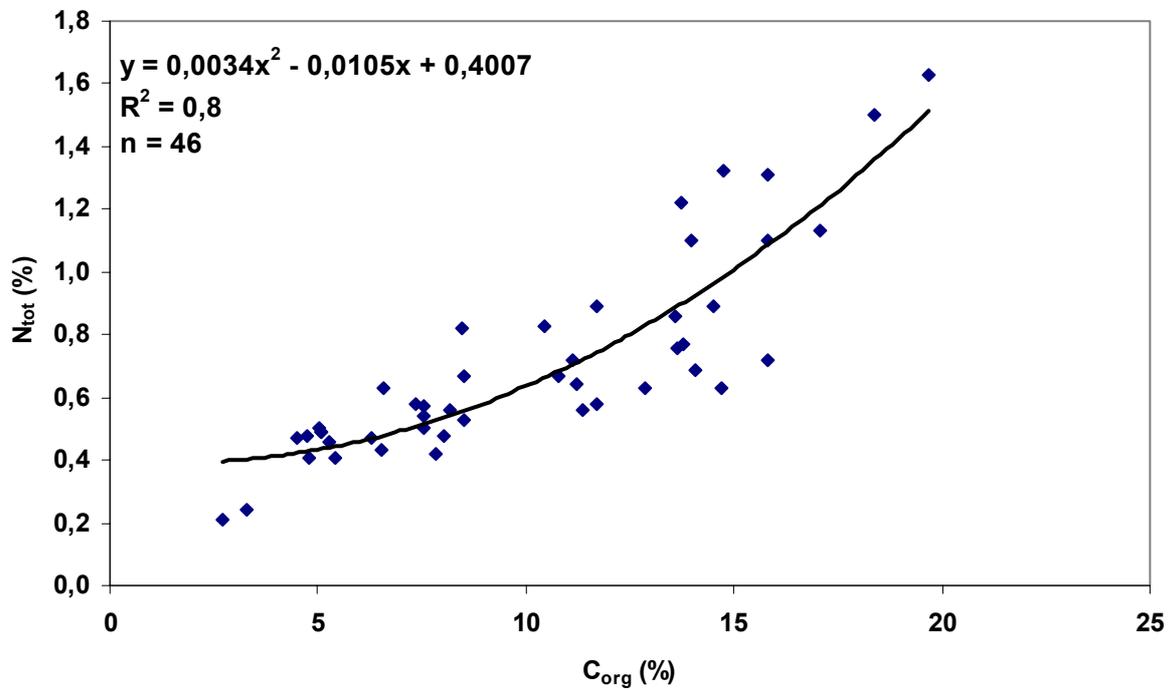
Figure 2. Relationship between C$_{org}$ (%) and S$_{tot}$ (%)
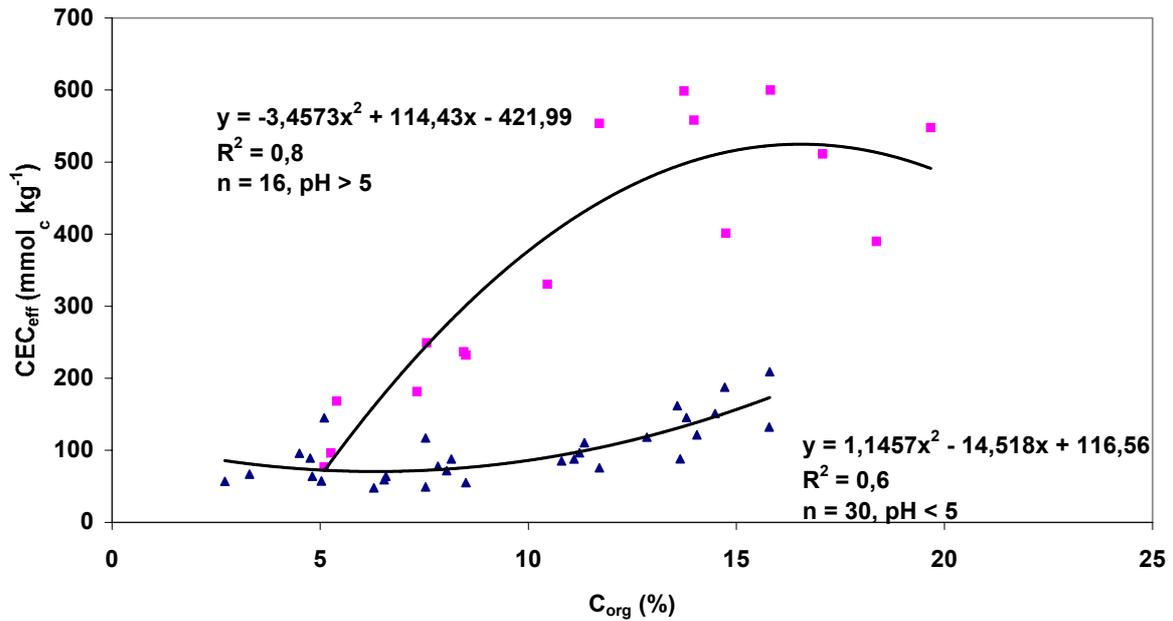
Figure 3. Relationship between C_{org} (%) and effective cation exchange capacity ($BaCl_2$-extract) of alpine soils with pH ($CaCl_2$) > 5.0 and pH ($CaCl_2$) < 5.0
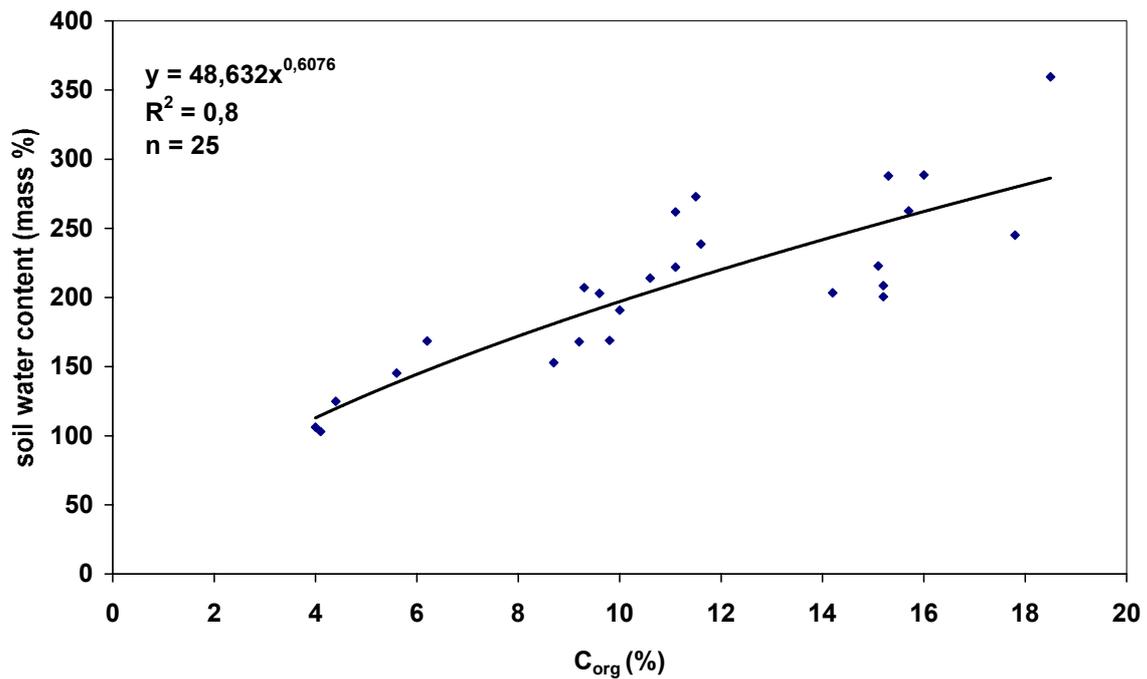
Figure 4. Relationship between C_{org} (%) and soil water content (mass %) at water saturation (liquid limit)

However, the cation exchange capacity of humus-rich alpine soils is markedly pH-dependent, even at low pH. Acid alpine soils (pH $CaCl_2$ < 5.0) have low effective cation exchange capacities compared to alpine soils with pH $CaCl_2$ > 5.0 (Figure 3). Thus, soil acidification considerably decreases the cation holding capacity of alpine soils low in clay. No relationship

was found between organic carbon content and pH ($CaCl_2$) or percentage base saturation in the A horizon of alpine grassland soils. Only a weak relationship was found between C:N ratio and pH ($CaCl_2$) or percentage base saturation; the same is valid for C:S ratio and pH ($CaCl_2$) or percentage base saturation (not shown). These circumstances indicate that both in acid, base-poor alpine soils, and in neutral or alkaline, base-rich alpine soils, an accumulation of SOM is possible with a weak tendency of narrower C:N and C:S ratios at higher pH values.

$$y = 0{,}0213x^2 - 0{,}6734x + 5{,}5574$$
$$R^2 = 0{,}9$$
$$n = 7$$
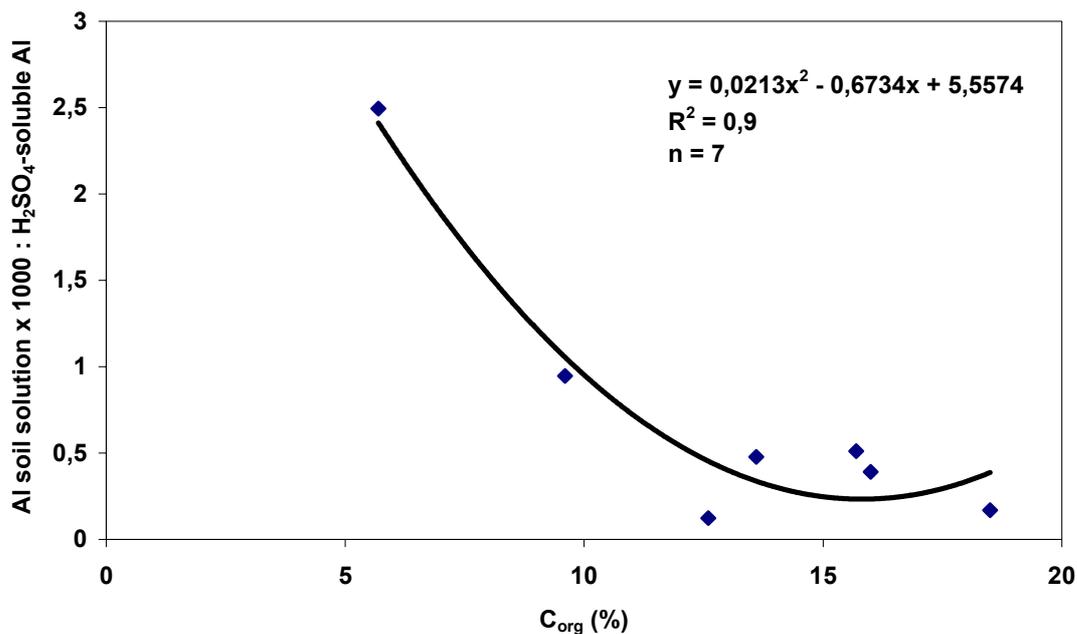
Figure 5. Effect of Soil Organic Matter on aluminum solubility (Al in soil solution x 1000 : H_2SO_4-soluble Al) in acid alpine soils (pH < 4.2)

In coarse-textured alpine soils, the water-holding capacity is determined mainly by SOM (Figure 4). A high SOM content enhances the soil water content, thereby reducing soil temperature (retarded warming) and slowing down the mineralization of SOM. This causes a reduced supply of nitrogen and sulfur to plants and promotes the growth of herbs instead of grasses. In this respect, a high humus content is not a benefit concerning soil fertility and soil quality in cool and humid alpine regions. In humus-rich alpine soils, there is a relatively poor relationship between pH and aluminum concentration in the soil solution of A horizons (not shown) due to the high humus content. This can be concluded from Figure 5. Figure 5 illustrates that with increasing organic carbon content the ratio between Al in soil solution to H_2SO_4-soluble Al is decreasing, indicating lower aluminum solubility at higher humus content. This is beneficial to plants growing on acid alpine soils.

CONCLUSIONS

It is very difficult to assess optimal SOM contents because of the numerous factors influencing it, such as soil reaction (higher in strongly acid soils than in neutral or alkaline soils), soil texture (higher in sandy soils than in clayey soils), and climate (higher in dry regions than in humid regions). Nevertheless, this study contributes to conclude that in cool and humid mountainous regions sandy grassland soils with lower humus content are more favourable than humus-rich, clayey soils, whereas in warm and dry lowland areas, deep and finer-textured, humus-rich grassland soils are characterized by a comparatively higher soil fertility. The amount of SOM can be modified by fertilizing especially with farmyard manure.

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ORGANIC MATTER AND SOME ELEMENT CONTENTS IN SOIL PROFILES OF MEADOWS IN THE MOUNTAIN REGION OF BIESZCZADY – POLAND

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SUMMARY

The protective and buffer role of the surficially accumulated organic matter is clearly visible in the soils of the Bieszczady mountain meadows (acid brown soils – *Dystric Cambisols)*. It prevents erosion, excessive out-washing of base elements (e.g. Ca) in the conditions of serious acidification of these soils.

KEY WORDS: acid brown soils (*Dystric Cambisols),* C-organic, elements (Ca, Mg, K, Fe, Cu, Zn, Pb, Cd), plants, Bieszczady Mountains, Poland

INTRODUCTION

The Bieszczady Mountains constituting a part of a large mountain range of the Carpathians are situated in the south-eastern corner of Poland. The West Bieszczady – the main object of interest for the authors of this paper – are characterised by medium-mountain sculpture and a significant denivelation of the terrain. The slopes of these mountains are steep, often of a concave shape, crossed by numerous torrents (Komornicki et al., 1985).

The utmost part of the soils of the Bieszczady, including the soils of the *poloninas* (mountain pastures), belongs typologically to acid brown soils *Dystric Cambisols* (Dobrzański, 1963; Uziak, 1963; Uziak, 1963a; Uziak, 1992; Dobrzański i Gliński, 1970). And these soils, as well as their plant cover, were the object of the authors' research, mainly because of their dominance and significance. The main factors deciding about their formation and development are the properties of the parent rock – the Carpathian flysch, but also the specific features of the mountain climate and biosphere.

The generally fine grain size of the Carpathian flysch rocks forming the Bieszczady decides about the mechanical composition of the Bieszczady soils.

The thickness of the *polonina* soils is predominantly medium, and according to Uziak (1963a) it amounts to 50 cm, according to Dobrzański (1963) – 25-50 cm, but soils of larger or

smaller depths can also be found.

On the mountain pastures occurring in the Bieszczady at the height of slightly above 1000 m, acid brown soils are overgrown with a natural plant cover, called *poloninas* (Uziak, 1963a). The acid brown soils of the *poloninas* have very acid reaction, in most cases pH_{KCl} is 3-4, although it may also be lower than 3 (Dobrzański, 1963; Uziak, 1963; Uziak, 1963a; Dobrzański and Gliński, 1970). Many authors draw attention to the number of factors deciding about the properties of these soils. They include: the features of the parent rock (Dobrzański, 1963; Uziak, 1963; Uziak, 1963a; Uziak, 1992; Dobrzański and Gliński, 1970), climatic factors (Uziak, 1963; Uziak, 1963a), biosphere (Uziak, 1963; Uziak, 1963a), including also the specific activity of soils microorganisms, erosional (Malicki, 1963; Uziak 1963) and eolian processes (Uziak, 1992).

The climatic factor plays an important role in forming mountain pasture soils. Uziak (1963) calls attention to a high quantity of precipitation, combined with low temperature of the vegetation season. The peaty organic matter is formed in the conditions of high periodic humidity. However, it does not come to complete peat-formation, because the aerobic periods, during which the organic substance undergoes at least partial mineralization and humification, do not allow that (Uziak, 1963). So a specific peat-humus substance is formed with varied share of peat, and thus with undecomposed humus (Uziak, 1963). Thus in the Bieszczady mountains – just like in many mountains all over the world – there occurs the overlapping of organic substance onto mineral horizons, especially of dominating acid brown soils.

The *polonina* soils are rich in organic matter. Uziak (1963a) calls attention to the high content of organic carbon in the entire profile of the acid brown soils of the *poloninas*.

According to Uziak (1963a) the *polonina* soils are characterised by a high absorbing capacity, especially in the accumulation horizons, and the degree of saturation of these soils with cations of alkaline character is generally low, or even very low. The same author also examined the share of particular cations in the sorption complex, stating that hydrogen and aluminium prevail in the *polonina* soils, then there is calcium and magnesium, and potassium and sodium occur in much smaller quantities.

MATERIAL AND METHODS

The research covered the area of the West Bieszczady situated in the territory of Poland. In the years 1991-1992 some soil pits were made in the *poloninas*, in the uppermost parts of the main massifs of the Bieszczady mountains: Tarnica, Halicz, Krzemień, Bukowe Berdo,

Bukowska Polonina, Rozsypaniec, Caryńska Polonina, Wetlińska Polonina, Greater and Lesser Rawka, and passes: Kopa Bukowska – Krzemień and Rozsypaniec – Halicz. The field research, followed by laboratory analyses, was continued in the years 1993-1996, as well as in the years 1999-2001.

Samples of all the genetic horizons of the soils dominating in the *poloninas* were collected for the analyses of the selected elements. The soils were mainly the acid brown soils (*Dystric Cambisols*), but also of other brown soils (*Cambisols*) and rankers (*Leptosols*), occurring insularly and covering small areas. In total, the contents of all the mentioned elements were analysed in 157 samples, coming from 44 selected soil profiles, in the first phase of the research. The near-total content of the presented elements after the mineralization of the soil in $HClO_4$ (on an automatic apparatus for mineralization made by Tecator) was determined in the analysed soils. The organic surface horizons, of decidedly distinguishing properties, were treated like plant material, treating them with the mixture of acids: HNO_3, $HClO_4$ and H_2SO_4 in the proportion of 20:5:1 respectively.

The contents of Ca, Mg, K, Fe, Cu, Zn, Pb and Cd were determined by atomic absorption spectrophotometry method (AAS-3). Cadmium and lead, due to their lower concentration, were determined after their thickening in organic environment (MIBK).

Apart from the content of elements close to the total, the fraction soluble in $1 \, mol \cdot dm^{-3}$ HCl solution was also determined (for the sake of simplicity, this fraction shall be called a soluble fraction hereinafter). A metal fraction soluble in HCl solution was extracted by mixing a soil sample with the solution of the acid for 1 hour, maintaining the soil-solution ratio of 1:10. It should be added that $1 \, mol \cdot dm^{-3}$ HCl solution is used by regional chemical-agricultural stations for assessing the abundance of soil in available forms of microelements.

The basic properties of the examined soils were also determined: soil reaction (pH) was determined in $1 \, mol \, KCl \cdot dm^{-3}$ solution and in redistilled water by potentiometric method, the content of organic carbon (C-org.) was determined by Tiurin method, size distribution – by Bouyoucosa-Casagrande areometric method in Prószyński modification.

The research was continued in the years 1993-1996 and 1999-2001. The aim of this second phase was to define the dependence between the content of the determined elements and other properties of acid brown soils. The material from the dominating plant *Vaccinium myrtillus* (stems, leaves, fruit) and *Calamagrostis arundinacea* from the specially selected places of soil pits (acid brown soil of the thickness of minimum 30-50 cm) was also sampled for analyses in order to determine the chemical composition of meadow overgrowth. The plant samples were

taken exactly from the places of soil pits.

The plant material taken on the *poloninas* was dried, and after having been grinded, it was burnt in Tecator apparatus in the acid mixture of: HNO_3, $HClO_4$ and H_2SO_4 in proportion of 20:5:1, respectively. The content of all the elements in plants was determined by AAS-3 method, and lead and cadmium in plants were determined after thickening in organic phase (MIBK).

RESULTS AND DISCUSSION

The soils of the Bieszczady generated from the waste-mantle of the Carpathian flysch. The acid brown soils, dominating in the Bieszczady, possess their own specific character. The surface, 2-3 cm thick (sometimes 6 cm or more), Ofh layer is formed by organic-humus horizon of litter. Most often it is clearly separated from deeper horizons: Ah, Bbr, C. The acid brown soils of the Bieszczady *poloninas* are characterised by varied depth, but most often it ranges from 30 to 50 cm (occasionally 70 cm and more). On the other hand, in the mineral horizons there is no clear differentiation into genetic horizons, and Br horizon passes gradually into solid bedrock, although it is surficially weathering and cracking. For that reason, BbrC transition horizon is most often the lower genetic horizon of the *polonina* acid brown soils, and C horizon is constituted by large cracked debris of the Carpathian flysch.

The occurrence of surficially-accumulated organic, acid, peat-like substance is specific for the *polonina* soils. Its physical and chemical properties are so different from the deeper mineral horizons that it requires to be treated separately in the process of analysis, and it also requires to be discussed separately.

The examined acid brown soils are characterised by fine graining, the sand content is close to 40% on the average, the content of clay – to 25%, and of colloidal clay – to 9% (geometric means shall be quoted in the text). The reaction of these soils is very acid. The high content of organic matter (of C-organic – from 45 to 50 $g \cdot kg^{-1}$ on the average in the mineral horizons) and the high content of floatable parts decide about high absorbing capacity of acid brown soils.

The basic physical and chemical properties of individual mineral horizons (Ah, Bbr, BbrC) of the *polonina* acid brown soils are presented in Tab. 1.

Ofh and Ah horizons are the most acidified. In acid brown soils, in Ah horizon, pH_{KCl} was sometimes lower than 3 (the minimum stated value was 2.8).

The C-organic content turned out to be decidedly the highest in Ah horizon (ignoring here completely the Ofh surface organic-humus horizon of litter, of low thickness, 2-3 cm in most cases), its variability ranges from 48.5 to 113.5 g · kg^{-1} dm. The carbon content decreases in deeper horizons, but even BbrC horizon is characterised by high C-organic content, ranging from 19 to 45.4 g · kg^{-1} dm (Tab. 1).

The characterisation of the content of the examined elements in mineral horizons of acid brown soils of the *poloninas* of the West Bieszczady was presented in Tab. 2 and 3.

The *polonina* acid brown soils are poor in calcium. The changeability of the overall Ca content (in mineral horizons – alike hereinafter) ranges from 0.13 to 0.43 g · kg^{-1} in d.m. of soil (Tab. 2). The most abundant in both forms of calcium, total and soluble, is Ah horizon. The soluble calcium content, slightly lower from the overall, ranges from 0.06 to 0.38% g · kg^{-1} in d.m. of soil (Tab. 3).

Table 1. Granulometric composition, pH and organic-C content in mineral horizons of mountain pasture (*polonina*) acid brown soils (according to Woźniak, 1996)

Investigationed characteristic		Arithmetic mean	Geometric mean	Range	
				Minimum	Maximum
Granulometric composition % fraction of diameter					
Horizon					
< 0.1 mm	Ah	65.8	64.6	44	82
	Bbr	68.3	67.1	46	83
	BbrC	68.8	67.4	47	87
0.1-0.02 mm	Ah	45.1	44.1	31	62
	Bbr	41.3	40.8	31	53
	BbrC	34.8	33.0	17	62
< 0.02 mm	Ah	19.4	18.6	11	31
	Bbr	27.9	26.2	14	45
	BbrC	38.1	34.2	15	67
< 0.002 mm	Ah	7.8	7.5	4	11
	Bbr	9.3	9.0	6	14
	BbrC	11.0	9.4	4	26
Soil reaction					
pH$_{H_2O}$	Ah	4.1	4.1	3.2	4.4
	Bbr	4.2	4.2	3.2	4.5
	BbrC	4.4	4.4	4.2	4.7
pH$_{KCl}$	Ah	3.3	3.3	2.8	3.6
	Bbr	3.5	3.5	3.0	3.9
	BbrC	3.8	3.8	3.6	3.9

Organic-C content [g · kg⁻¹]					
	Ah	68.5	66.7	48.5	113.5
	Bbr	45.3	44.6	30.9	59.7
	BbrC	31.9	30.9	19.0	45.4

Tab. 2 presents the general content of the determined elements, and Tab. 3 presents the soluble fraction content.

The overall content of magnesium and content of forms soluble in HCl vary in the soil profile. The most abundant in overall magnesium is the deepest BbrC horizon, and the content of soluble magnesium is the highest in Ah horizon.

The analysis of the distribution of the total content of potassium in individual horizons of the examined soils shows the highest concentration of this element in Ah horizon. A similar dependence occurs in case of the forms defined as soluble.

Iron is a dominating element in the examined soils. The total content of this element ranges – on the average for all the horizons – from 15.8 to 41.9 g · kg⁻¹ in d.m. of soil (Tab. 2), and the content of its soluble fraction ranges from 3.6 to 11.1 g · kg⁻¹ in d.m. of soil (Tab. 3). The analysis of particular horizons showed a distinct increase in the concentration in deeper horizons, and the content of both forms is the highest in BbrC horizon.

The total content of copper in acid brown soils ranges from 4.1 to 41.9 mg · kg⁻¹ in d.m. of soil (Tab. 2), and the content of its soluble fraction ranges from 1.2 to 18.1 mg · kg⁻¹ in d.m. of soil (Tab. 3).

Table 2. Total content of elements in mineral horizons of mountain pasture acid brown soils (according to Woźniak, 1996)

Soil characteristic		Arithmetic mean	Geometric mean	Range	
Elements	Horizon			Minimum	Maximum
[g · kg⁻¹ d.m.]					
Ca	Ah	0.28	0.27	0.17	0.43
	Bbr	0.22	0.22	0.13	0.30
	BbrC	0.21	0.20	0.16	0.27
Mg	Ah	4.7	4.4	2.6	7.9
	Bbr	5.0	4.6	2.2	8.3
	BbrC	5.4	5.0	2.4	10.3
K	Ah	11.7	11.1	6.3	18.1
	Bbr	9.7	9.4	6.2	15.1
	BbrC	10.0	9.8	7.1	13.6
Fe	Ah	25.9	24.8	17.1	40.7
	Bbr	27.6	26.3	15.8	40.0
	BbrC	30.3	29.3	17.3	41.9

[mg · kg⁻¹ d.m.]					
Cu	Ah	14.9	12.8	5.5	37.5
	Bbr	16.1	13.6	5.6	37.5
	BbrC	17.2	13.7	4.1	41.9
Zn	Ah	51.0	46.5	20.2	74.5
	Bbr	59.7	56.0	26.9	90.5
	BbrC	61.7	58.1	27.9	91.8
Pb	Ah	52.7	51.5	30.9	69.6
	Bbr	40.2	39.1	20.0	56.0
	BbrC	27.6	26.7	15.0	40.0
Cd	Ah	0.45	0.43	0.26	0.68
	Bbr	0.31	0.30	0.19	0.45
	BbrC	0.22	0.21	0.12	0.35

The total content of zinc is much higher than the content of copper. On the average for all the horizons it ranges from 20.2 to 91.8 mg · kg⁻¹ in d.m. of soil (Tab. 2), and the content of its soluble fraction corresponds to the range from 12.1 to 32.3 mg · kg⁻¹ in d.m. of soil (Tab. 3). The content of forms soluble in 1 mol · dm⁻³ HCl, just like in case of copper, is the highest in Ah horizon.

The distribution of the lead content in mineral genetic horizons of the examined soils definitely departs from the presented for the other elements. With the total content ranging from 15 to 69.6 mg · kg⁻¹ in d.m. of soil (Tab. 2), the highest concentration is always characteristic for the depositional horizon, abundant in organic matter. It should be pointed out, however, that the absolutely highest accumulation of this element occurs in the 2-3 centimetre layer of Ofh organic-humus overlay. The content of forms soluble in 1 mol · dm⁻³ HCl, also high, dominates in the depositional horizons.

The content of cadmium in the *polonina* acid brown soils is high as in case of lead, and the distribution of the content in particular horizons, both for the overall and soluble fractions, is very close to the one presented for Pb. On the average, for the mineral horizons the overall content of cadmium ranges from 0.12 to 0.68 mg · kg⁻¹ in d.m. of soil (Tab. 2).

Table 3. Content of soluble (1 mol · dm⁻³ HCl) forms of elements in mineral horizons of mountain pasture acid brown soils (according to Woźniak 1996)

Soil characteristic		Arithmetic	Geometric	Range	
Elements	Horizon	mean	mean	Minimum	Maximum
[g · kg⁻¹ d.m.]					
Ca	Ah	0.25	0.24	0.16	0.38
	Bbr	0.19	0.18	0.06	0.27
	BbrC	0.17	0.17	0.14	0.26

Mg	Ah	0.099	0.089	0.03	0.17
	Bbr	0.068	0.062	0.03	0.15
	BbrC	0.055	0.051	0.03	0.10
K	Ah	0.20	0.19	0.13	0.28
	Bbr	0.13	0.13	0.10	0.20
	BbrC	0.11	0.11	0.08	0.14
Fe	Ah	6.2	6.0	3.8	8.9
	Bbr	6.4	5.6	3.9	11.0
	BbrC	7.4	7.1	3.6	11.1
$[mg \cdot kg^{-1} d.m.]$					
Cu	Ah	5.98	5.53	3.10	11.20
	Bbr	5.28	4.33	2.00	16.40
	BbrC	5.06	3.64	1.20	18.10
Zn	Ah	22.47	21.72	15.0	32.3
	Bbr	15.57	15.34	12.2	22.0
	BbrC	16.33	15.93	12.1	25.7
Pb	Ah	40.98	40.21	25.5	54.8
	Bbr	26.54	25.79	13.1	33.5
	BbrC	16.44	15.80	8.7	24.7
Cd	Ah	0.30	0.29	0.16	0.52
	Bbr	0.25	0.24	0.13	0.34
	BbrC	0.17	0.16	0.08	0.25

Table 4. Correlation coefficients (r) between total content of elements and some properties in mineral horizons of mountain pasture acid brown soils (selected from Woźniak, 1996)

	Granulometric composition - content of fraction		organic - C
	<0.1mm	<0.002mm	
Ca	-0.29	-0.19	0.63[xxx]
Mg	0.87[xxx]	0.76xxx	-0.27
K	0.59[xxx]	0.29	0.12
Fe	0.81[xxx]	0.56xxx	-0.22
Cu	0.70[xxx]	0.72xxx	-0.20
Zn	0.85[xxx]	0.60xxx	-0.27
Pb	0.07	-0.11	0.68[xxx]
Cd	-0.10	-0.30	0.74[xxx]

r significant at: [x] $a = 0.05$; [xx] $a = 0.01$; [xxx] $a = 0.001$

Tab. 4 and 5 present correlation coefficients between the C-organic content and the content of mineral fraction of a diameter smaller than 0.1 mm and smaller than 0.002 mm, and between the total content of the examined elements (Tab. 4) and the content of their soluble fraction (Tab. 5).

Table 5. Correlation coefficients (r) between soluble (in acid 1 mol·dm^{-3} HCl) form of elements and some properties in mineral horizons of mountain pasture acid brown soils (selected from Woźniak, 1996)

	Granulometric composition - content of fraction		organic - C
	<0.1mm	<0.002mm	
Ca	-0.23	-0.11	0.54^{xxx}
Mg	0.53^{xxx}	0.19	0.49^{xx}
K	0.21	-0.11	0.76^{xxx}
Fe	0.18	0.17	-0.18
Cu	0.58^{xxx}	0.71^{xxx}	-0.12
Zn	-0.04	-0.23	0.48^{xx}
Pb	0.01	-0.21	0.80^{xxx}
Cd	-0.03	-0.29	0.63^{xxx}

r significant at: ^{x} a = 0.05; ^{xx} a = 0.01; ^{xxx} a = 0.001

Table 6. Total content, soluble fraction content and content of Ca and Mg (mg·kg^{-1}) of soil and plants in meadow sward of the same soil profile – some selected profile, typical for the acid brown soils of Bieszczady mountain meadows (*poloninas*)

Location	Soil horizon	Depth [cm]	Organic-C [g·kg^{-1}]	Total content		Soluble fraction content	
				Ca	Mg	Ca	Mg
Połonina Caryńska	Ofh	0-3	387	1824	494	1756	75
	Ah	3-20	53	217	2914	183	63
	Bbr	20-31	18	141	8330	107	61
	BbrC	31-49	11	103	8757	84	42
Połonina Caryńska	*Calamagrostis arundinacea*		*Vaccinium myrtillus* stems		*Vaccinium myrtillus* leaves		*Vaccinium myrtillus* fruits
	Ca	Mg	Ca	Mg	Ca	Mg	Ca	Mg
	1054	701	5519	1001	7123	1599	934	477

Tab. 6 presents (in a profile selected by way of example) the changeability of the contents of Ca and Mg in the soil-plant configuration. The content of calcium, although generally low in acid brown soils, both in case of the total content and the content of the soluble fraction, was definitely the highest in Ofh surface organic horizon. Calcium was clearly accumulated also by the vegetation of the *poloninas*, especially by leaves and stems of perennial *Vaccinium myrtillus*. In case of magnesium, the content of the soluble fraction showed dependences similar to calcium, but it was – in comparison to the total content very low. On the other hand, the total content of magnesium was definitely the highest in mineral, deeper soil horizons (Bbr, BbrC). In comparison to the content of the soluble fraction of Mg the examined vegetation showed a significant accumulation of this element.

CONCLUSIONS

1. The surficially accumulated organic matter in the soils of the Bieszczady mountain meadows plays an important buffer role, and it is also a place of accumulation of biogenic elements, of Ca in particular.

2. The very high, positive and statistically significant correlation coefficient characterised the dependence of the C-organic content in the examined soils and the content of the soluble fraction of K, Ca, Mg, Zn. Apart from the accumulation of the scarce alkali elements, the organic matter of the examined soils also accumulated anthropogenic pollutants - Pb and Cd.

3. Generally, the total content of the examined elements did not show statistically significant correlation with the C-organic content (the exceptions were the contents of Ca, Pb and Cd).

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ORGANIC MATTER AND SOME ELEMENT CONTENTS IN SOIL PROFILES OF ALLUVIAL WATER RACE IN THE MOUNTAIN REGIONS OF BIESZCZADY – POLAND

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SUMMARY

The examined river alluvial soils of the San valley are characterised by many completely different properties than the mountain acid brown soils of the Bieszczady, presented in the analogous publication, formed also from the rocks of the Carpathians flysch. The erosion phenomena and fresh alluvial depositing phenomena lead to the formation of very fertile alluvial soils, rich in most biogenic elements, organic carbon and buffer carbonate. The contemporary censure of aggradation processes should be considered as incorrect.

KEY WORDS: river alluvial soils (*Fluvisols*), fresh alluvial deposits, organic-C, elements (P, K, Ca, Mg, Cu, Zn), San Valley, Poland.

INTRODUCTION

River valleys are the elements of geographical environment, which change its character in time. This results from the fact that they are shaped by one of the most dynamic elements of this environment, which is water (Dembek and Okruszko, 1996). That is why large complexes of valuable grasslands are situated in river valleys.

The agricultural significance of marshy meadows depends on their area, productive potential, accessibility to utilise and treatment (Grzyb, 1993). According to statistical data published by Grzyb (1993), the area of marshy meadows in Poland is about 750 thousand hectare. Marshy meadows have a high productive potential (in natural conditions – crop productivity ranges from 3.5 to 4.5 t hay a hectare, after applying the appropriate pratotechnic – from 7 to 8 t hay ha^{-1}). The quality of fodder obtained on marshy meadows is good or very good (Grzyb, 1993). River overflows and aggradation phenomena are the processes fertilising meadows in spite of their impulsiveness during floods (Kern, 1975). However, most land meliorations of

grasslands and anti-flood investments in river valleys in Poland cut the natural process of aggradation by embankment and canalisation, as a result, the natural fertilising phenomena vanish and the real marshy meadows become dry-ground. Its symptoms are superficial impoverishment and acidification of alluvial soils, which from the subtype of typical alluvial soil or even humic alluvial soil change into the brown alluvial soil. "Free" delivery of biogenes vanishes and as a result, farmers are forced to fertilise these meadows more and more intensively, but it is also a symptom of wasting the natural gifts and an example of destroying the efficient system of interdependences.

The generation of alluvial soil is the result of surface water activities. From the slopes, together with the surface flow, the soil material is transported, but the river waters also transport the washed-out material as a result of side and bottom erosion of main stream (The Systematics of Polish Soils 1989). During overbank flows (sometimes even after a light rain) the waters of most rivers get rich in transported suspended matter, becoming yellowish-brown in colour. The example can be the area of Carpathian flysch, and thus also the region of the Bieszczady and Low Beskid, where you can find springs and headwaters of the San river and its tributaries.

MATERIAL AND METHODS

The area of research covered the durable grasslands of the San valley, beginning from its spring area to the estuary of this river to the Vistula, so it went far beyond the mountain region of the Bieszczady. Large and compact complexes of natural grasslands, situated on alluvial soils near the river, were selected for the research. An important factor of selection was the definition of the meadow utilisation method – only the material from non-fertilised areas was taken for analysis, so of close to natural content of biogenic elements.

Soil and vegetable material samples were taken during the first cut on the durable grasslands. The soil was sampled from two layers of 0-10 and 10-30 centimetres, which corresponds to turfy and subturfy layers.

From these durable meadows, which are under continuous process of aggradation, samples of fresh alluvial deposits were also taken immediately after flood retreat, so that no changes in their properties could take place.

Soils and fresh alluvial deposits were dried to air moisture-free mass and their basic properties were determined by methods generally applied in chemical and agricultural laboratories (Ostrowska et al., 1991): size distribution – by Bouyoucosa-Casagrande areometric method in

Prószyński modification; pH in H$_2$O and in KCl – by potentiometric method, the content of organic carbon – by Tiurin method, the content of calcium carbonate – by Scheibler volumetric method.

In order to determine the content of metallic elements, the soil samples were mineralised in 70% HClO$_4$ acid, in Tecator aluminium block, according to the fixed temperature programme. Next, the contents of forms close to total of K, Ca, Mg, Cu, Zn were determined by atomic absorption spectrophotometry method.

Analogous, in case of metallic elements the content of forms soluble in1 mol HCl dm^{-3} solution was determined by atomic absorption spectrophotometry method. The determination was done in the filtrate obtained after shaking the soil samples for one hour in the appropriate quantity of 1mol HCl solution.

The contents of total phosphorus and of phosphorus soluble in HCl were determined colorimetrically by vanadium-molybdenum method.

RESULTS AND DISCUSSION

The basic results concerning the properties of the examined soils are presented in Tab. 1. Because a lot of results were extremely different from the most common value, apart from arithmetic mean (called average hereinafter) the geometric mean was also calculated.

The examined soils were generally characterised by reaction close to neutral, pH oscillated around the value of 7. Slightly higher pH was determined in deeper layers – the average in the layer of 10-30 centimetres was 6.68 and in 0-10 centimetre layer it was 6.63. The values of pH in KCl were similar.

The examined soils are abundant in calcium carbonate which as a result of weathering of flysch rocks and erosion gets into the rock material transported by the river and is deposited during overbank flows. The range of the content of CaCO$_3$ was very wide, from minimal values of 0.8 g to 72.99 g $\cdot$ kg^{-1} s.m. In the deeper layer (10-30 centimetres) a higher content of CaCO$_3$ was noted (Tab. 1).

The content of organic carbon in the turfy layer ranged from 1.2 to 54.0 g $\cdot$ kg^{-1} s.m. – average 19.7 g (Tab. 1). Slightly lower values of C-organic were determined in the sub-turfy layer, the minimum value was 0.5 g and maximum was 19.6 g $\cdot$ kg^{-1} s.m. of the soils.

Table 1. General characterictic of alluvial soils and fresh alluvial deposits of San Valley.

Investigationed characteristc	Arithmetic mean	Geometric mean	Median	Range	
				Minimum	Maximum
0-10 and 10-30cm layers					
Granulometric composition	% fraction of diameter:				
• 1.0-0.1 mm	26.8	22.5	25.5	4	80
• 0.1-0.02 mm	39.2	37.9	39.0	13	58
• < 0.02 mm	34.0	30.5	32.5	7	73
• < 0.002 mm	9.4	7.5	8.0	1	22
pH_{H_2O}	6.65	7.24	7.42	5.50	8.10
pH_{KCl}	5.27	6.26	6.63	3.88	7.07
$CaCO_3$	21.50	13.54	16.13	0.80	72.99
organic-C	1.55	1.96	1.58	0.05	5.40
Layer 0-10cm					
Granulometric composition	% fraction of diameter:				
• 1.0-0.1 mm	28.9	24.2	26.0	4	80
• 0.1-0.02 mm	38.7	37.1	37.5	13	57
• < 0.02 mm	32.4	28.4	30.5	7	73
• < 0.002 mm	8.3	6.3	7.0	1	21
pH_{H_2O}	6.63	7.14	7.36	5.50	7.91
pH_{KCl}	5.22	6.21	6.55	3.88	7.07
$CaCO_3$	20.86	12.83	13.98	0.80	72.99
organic-C	1.97	1.76	1.94	0.12	5.40
Layer 10-30cm					
Granulometric composition	% fraction of diameter:				
• 1.0-0.1 mm	24.6	20.9	22.0	5	52
• 0.1-0.02 mm	39.8	38.8	40.5	24	58
• < 0.02 mm	35.6	32.8	33.5	13	68
• < 0.002 mm	10.5	9.0	8.5	2	22
pH_{H_2O}	6.68	7.34	7.65	5.54	8.10
pH_{KCl}	5.33	6.30	6.65	4.21	7.07
$CaCO_3$	22.14	14.29	16.92	0.80	57.71
organic-C	1.13	0.93	1.12	0.05	1.96
Fresh alluvial deposits					
Granulometric composition	% fraction of diameter:				
• 1.0-0.1 mm	45.40	36.08	44	2	98
• 0.1-0.02 mm	32.66	27.20	33	1	56
• < 0.02 mm	21.94	16.51	20	1	67
• < 0.002 mm	4.53	3.48	4	1	18
pH_{H_2O}	7.47	7.53	7.51	7.09	8.21
pH_{KCl}	7.17	7.25	7.24	6.66	7.99
$CaCO_3$	49.21	42.03	52.62	9.37	98.24
organic-C	1.84	1.40	1.90	0.042	7.98

The content of C-organic was very variable, both in the examined alluvial soils and fresh alluvial sediments. The variability of content was connected with the place of taking samples and the characteristic feature of alluvial soils − multi-layer construction of their profile and

depositing the aggradate mud at the same place, often of completely different features. The fresh alluvial deposits was very often richer in organic matter than the soil samples taken at the same place, which is another argument for positive evaluation of aggradate mud features. In The Systematics of Polish Soils (1989) the authors pay attention to the possibility of the occurrence of large amounts of organic matter in the alluvia.

The content of the determined elements, both of their general forms and the ones soluble in 1 mol HCl dm⁻³, was presented in Tab. 2-4.

Phosphorus

The content of phosphorus in the examined meadow soils of the San valley was not very high and ranged from 0.32 to 2.33 g $\cdot$ kg⁻¹ s.m. (Tab. 2 and 3). Slightly higher values were noticed in the turfy layer, which is surely connected with the higher content of organic carbon in that layer. The forms of phosphorus soluble in 1 mol HCl dm⁻³ in both layers constituted about 33% of the total content of this element. Just like in case of the general forms, there were more soluble forms in the 0-10 cm layer.

Assuming after Borowiec and Urban (1997) that the content of phosphorus in soils lower than 1 g $\cdot$ kg⁻¹ may indicate clear deficiency of this element, it should be stated that most of the examined soils from the San valley are characterised by lower content of general P. But Fotyma and Mercik (1995) state that the content of general phosphorus in arable layer of most soils is from 0.3 to 1.5 g $\cdot$ kg⁻¹. The highest content of general phosphorus was found in some fresh alluvial deposits samples (Tab. 4), and the maximum is 4.91 g $\cdot$ kg⁻¹. Aggradate mud, rich in organic matter and fine floating molecules may be treated as the source of considerable amounts of phosphorus.

Table 2. Content of investigated elements in layer 0-10cm

Investigated characteristic	Arithmetic mean	Geometric mean	Median	Range	
				Minimum	Maximum
Total content of investigated elements g $\cdot$ kg⁻¹ s.m.					
P	1,01	0,92	0,98	0,36	2,11
K	6,77	6,39	6,26	2,42	13,93
Ca	13,11	9,70	12,77	1,49	34,49
Mg	6,52	6,13	6,37	2,93	15,53
mg $\cdot$ kg⁻¹ s.m.					
Cu	21,08	19,92	21,25	8,00	36,80
Zn	63,71	60,33	60,20	30,30	114,60
Content of forms soluble in acid 1 mol HCl $\cdot$ dm⁻³ g $\cdot$ kg⁻¹ s.m.					
P	0,33	0,31	0,31	0,11	0,66
K	0,17	0,16	0,16	0,08	0,31

Ca	12,77	9,22	12,35	1,00	34,40
Mg	1,93	1,47	1,95	0,20	5,20
mg $\cdot$ kg^{-1} s.m.					
Cu	11,80	10,73	11,85	3,00	26,10
Zn	22,53	20,73	21,75	8,40	67,10

Potassium

In the examined soils the range of the general content of K in both layers was from 2.42 to 13.93 g $\cdot$ kg^{-1} s.m. (Tab. 2 and 4) and there were no significant differences between the shallower and deeper layers.

Table 3. Content of investigated elements in layer 10-30cm

Investigated characteristic	Arithmetic mean	Geometric mean	Median	Range	
				Minimum	Maximum
Total content of investigated elements g $\cdot$ kg^{-1} s.m.					
P	0.90	0.81	0.83	0.32	2.33
K	6.65	6.35	6.46	3.53	11.37
Ca	13.06	9.58	11.89	1.11	29.49
Mg	6.58	6.25	6.67	2.83	12.89
mg $\cdot$ kg^{-1} s.m.					
Cu	24.15	22.35	22.05	12.10	57.80
Zn	58.09	54.91	56.15	26.20	110.10
Content of forms soluble in acid 1 mol HCl $\cdot$ dm^{-3} g $\cdot$ kg^{-1} s.m.					
P	0.29	0.26	0.29	0.03	0.55
K	0.13	0.12	0.11	0.05	0.27
Ca	12.80	9.17	11.85	0.60	29.00
Mg	1.98	1.49	2.05	0.10	4.90
mg $\cdot$ kg^{-1} s.m.					
Cu	14.64	12.77	11.40	5.80	48.50
Zn	19.55	17.69	17.85	3.80	53.40

Table 4. Content of investigated elements in fresh alluvial sediments

Investigated characteristic	Arithmetic mean	Geometric mean	Median	Range	
				Minimum	Maximum
Total content of investigated elements g $\cdot$ kg^{-1} s.m.					
P	1.32	1.09	1.03	0.11	4.91
K	9.37	6.01	5.94	0.73	90.67
Ca	33.19	28.49	30.64	3.97	78.09
Mg	6.80	6.08	6.59	1.02	12.77
mg $\cdot$ kg^{-1} s.m.					
Cu	18.00	15.60	17.60	2.00	44.50
Zn	78.77	68.97	74.30	10.40	282.00

Content of forms soluble in acid 1 mol HCl · dm^{-3}					
g · kg^{-1} s.m.					
P	0.46	0.40	0.36	0.10	1.66
K	0.17	0.15	0.16	0.041	0.389
Ca	29.18	25.93	29.00	3.60	52.30
Mg	2.47	2.26	2.10	0.80	4.30
mg · kg^{-1} s.m.					
Cu	10.01	7.94	10.10	0.10	29.30
Zn	34.56	28.72	30.50	6.40	154.00

Potassium

In the examined soils the range of the general content of K in both layers was from 2.42 to 13.93 g · kg^{-1} s.m. (Tab. 2 and 4) and there were no significant differences between the shallower and deeper layers.

Fotyma and Mercik (1995) state that the general content of potassium in Polish soils is from 8 to 25 g · kg^{-1}. Borowiec and Urban, on the other hand, admitted 1g K · kg^{-1} s.m. of the soil to be a very low content, and the content of 10 g K · kg^{-1} to be very high. In comparison to the ranges mentioned above, the general content of potassium in the examined soils of the San valley can be considered to be rather low: in the 0-10 cm layer of alluvial soils the variability range was from 2.42 to 13.43 g · kg^{-1} (Tab. 2) and in the 10-30 cm layer it was from 3.53 to 11.37 g · kg^{-1} (Tab. 3). The variability range in fresh alluvial deposits was wider – from 0.73 to 90.67 g · kg^{-1} (Tab. 4). The extreme results in plus indicate a possible very high total content of potassium in aggradate mud. Woźniak (1990) indicated the low solubility of potassium compounds in soil deposits connected with the Carpathian flysch.

Calcium

The total content of calcium in the examined soils varied in particular places of taking the samples, but generally it was quite high. The variability range in both examined soil layers was 1.11 – 34.49 g · kg^{-1} s.m. in total (Tab. 2 and 3). The Ca contents in both turfy and subturfy layers were similar.

Both in the examined alluvial soils of the San valley and, especially, in fresh alluvial deposits the content of calcium was high. The results (data) presented and analysed in the chapter indicate that this is mainly calcium carbonate. Fotyma and Mercik (1995) state that the total content of calcium in Polish soils ranges from 3 to 16 g · kg^{-1} s.m. The alluvial soils of the San valley are characterised by the content of Ca exceeding the above-mentioned variability range. Fresh alluvial deposits are much richer, as their total content of calcium ranges from 3.97 to 78.09 g, with a very high geometric mean amounting to 28.49 g · kg^{-1} s.m.

(Tab. 4). When analysing the meadow sites in the Lublin area, Borowiec and Urban (1997) found out that the deficiency of calcium in soils is getting higher and higher every year (similarly in meadow greenness growth). The own research relating to the aggradated alluvial soils of the San valley do not show any occurrence of such phenomenon in systematically aggradated soils.

Magnesium

In the examined alluvial soils of the San valley the total content of magnesium ranged from 2.83 to 15.53 g · kg⁻¹ s.m. (Tab. 2 and 3). When comparing the amount of Mg in the shallow and deep layers (Tab. 2 and 3) no differences were found between the average values, only – as in the case of calcium – a slightly higher variability range was noticed in the deeper layer.

Fotyma and Mercik (1995) state that the total content of magnesium in Polish soils ranges from 0.5 to 6.0 g · kg⁻¹ s.m. The examined alluvial soils of the San valley were very often characterised by a much higher content, with the maximum result of 15.53 g · kg⁻¹ s.m. (Tab. 2).

When writing about the often occurring signals regarding high deficiency of magnesium in the soil-plant environment, Borowiec and Urban (1997) add that not many data can be found about the situation on meadow areas. The examined environment of the aggradated meadow soils of the San valley is characterised by a relatively high content of this element. It can be believed that the aggradation processes help to create and recreate appropriate magnesium resources.

Copper

The total content of Cu ranged from 8.0 to 57.8 mg · kg⁻¹ s.m. (Tab. 2 and 3). The surface horizons of the examined alluvial soils showed a slightly lower content of copper.

The total content of copper in soils can be much differentiated, because, apart from the natural variability, the anthropogenic factors can have a very big influence (Kabata-Pendias and Pendias, 1999). These authors state that the content of soluble copper informs about its occurrence in active forms, which are at the same time easily available for plants.

In both the horizons the total variability of the total content of Cu ranged from 8.0 to 57.8 mg · kg⁻¹ s.m. (Tab. 2 and 3). Kabata-Pendias and Pendias (1999) state that in Polish alluvial soils the variability of the total copper content ranges from 16 to 28 mg · kg⁻¹ s.m., so the examined alluvial soils of the San valley were characterised by a higher variability of the total content of Cu, but in no case did it exceed 100 mg of the content considered by Kabata-Pendias and Pendias (1999) to be allowable in agricultural environment.

Zinc

The range of the content of the general forms of zinc in both soil layers was 26.2 – 114.6 mg $\cdot$ kg^{-1} s.m. (Tab. 2 and 3). A slightly lower content of zinc was found in the deeper layer. The content of soluble forms showed a similar distribution, but the differences were higher. Kabata – Pendias and Pendias (1999) include zinc among the most active metals in soil. The variability of the total content of zinc in Polish alluvial soils range from 55 to 125 mg $\cdot$ kg^{-1} s.m. In the examined alluvial soils of the San valley the total content of copper ranged from 26.2 to 114.6 mg $\cdot$ kg^{-1} s.m. (Tab. 2 and 3), and in aggradate mud the range was from 10.4 to 282.0 mg $\cdot$ kg^{-1} s.m. (Tab. 4). In each case these contents were lower than the ones considered as allowable in agricultural soils, amounting to 250-300 mg $\cdot$ kg^{-1} s.m. (Kabata-Pendias and Pendias, 1999).

Table 5. Some choices profiles of alluvial soils of San Valley

Layer - cm	sand	silt	clay	colloi-dal clay	pH$_{H2O}$	pH$_{KCl}$	CaCO$_3$	organic -C	Ogranic matter
	\% fraction						g $\cdot$ kg^{-1} d.m.		
Humic river alluvial soil									
0-5	22	43	35	8	7.04	6.83	18.47	62.40	107.6
10-15	14	40	46	13	7.30	6.99	15.06	24.38	42.0
40-50	15	36	49	15	7.42	7.22	20.92	9.45	16.3
140-150	1	44	55	15	7.50	7.20	26.87	7.20	12.4
Brown river alluvial soil									
0-10	17	38	45	8	5.50	3.88	5.54	20.10	34.7
10-30	17	33	50	11	5.54	4.21	5.11	11.70	20.2
100-110	17	29	54	22	5.70	4.06	5.11	5.18	8.9
140-150	17	34	49	23	5.72	4.09	5.54	3.08	5.3
Typical river alluvial soil									
0-10	30	41	29	12	7.55	7.21	67.17	14.33	24.7
10-20	40	38	22	9	7.82	7.30	59.87	7.35	12.7
30-40	13	52	35	14	7.78	7.14	59.00	14.10	24.3
90-100	26	39	35	17	7.90	7.20	31.91	8.93	15.4

Some properties of the selected profiles of the examined alluvial soils of the San valley are presented in Tab. 5. One profile of *Mollic Fluvisol, Cambic Fluvisol* and *Eutric Fluvisol* are presented. This table presents the variability of the properties of particular subtypes of the alluvial soils within the San valley area.

Tab. 6 presents the correlation coefficients between the total content of the examined elements and the content of their soluble fractions and the content of organic carbon in the

examined soils.

Table 6. The correlation coefficients between the total content of the examined elements and the content of their soluble fractions and the content of organic carbon in the examined soils

Total content of investigated elements			Content of forms soluble in acid 1 mol HCl · dm⁻³		
	organic C			organic C	
P	0.1328	p=0.197	P	0.1674	p=0.103
K	0.5244*	p=0.000*	K	0.3869*	p=0.000*
Ca	-0.0387	p=0.708	Ca	-0.0415	p=0.688
Mg	0.4088*	p=0.000*	Mg	0.0864	p=0.403
Cu	0.2477*	p=0.015*	Cu	0.1622	p=0.114
Zn	0.5564*	p=0.000*	Zn	0.4073*	p=0.000*

* – statistically essential coefficients (p=0.05)

CONCLUSIONS

1. The examined alluvial soils of the San valley are characterised by a very high variability of the content of organic carbon and examined elements. Those soils contain large amounts of calcium, especially in the form of $CaCO_3$. This is the basic reason of their neutral or even alkaline reaction. The high differentiation in the properties of particular layers does not allow defining precisely the dependence between the content of organic carbon and other elements.

2. Fresh alluvial deposits possess very valuable soil-forming properties. Their abundance in $CaCO_3$, organic carbon and basic biogenic elements demands that flooding on grasslands should be considered as a positive phenomenon (only in clean catchments).

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SPATIAL DISTRIBUTION OF ORGANIC CARBON AND ITS LONG TERM CHANGES IN SEDIMENTS OF EUTROPHIC DAM RESERVOIR "ZALEW ZEMBORZYCKI"[1]

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SUMMARY

The concentration of the organic carbon in the bottom sediments of Zalew Zemborzycki is on the decrease at present in comparison to the period after flooding the reservoir basin. It probably resulted from the contribution of mineral suspensions from the catchment basin susceptible to erosion, covered by loess and loess-like materials, which changed the proportion of the mineral and organic constituents of the sediments. The significant negative correlation was stated between the amount of the mineral particles 1.0-0.1 mm in diameter and the amount of accumulated organic carbon. Within the zones where an elevated level of siltation process occurs, the conditions favourable for Corg. accumulation have not been observed. The zones of accumulation of organic carbon in the sediments were distributed parallel to the reservoir banks, which was evidence of the important role of the terrestrial catchment basin in supplying the reservoir with allochthonous organic matter. The highest content of carbon characterized the sediments formed within the zones neighbouring the afforested areas whereas the lowest was stated within the zones adjoining the agricultural lands.

KEY WORDS: organic carbon, dam reservoirs, sediments

INTRODUCTION

Dam reservoirs are artificial water bodies. Their location and construction are connected with natural conditions of the area where they are built, such as topography, width and shape of a river valley, or local geology and hydrological regime. An anticipated function of a water

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body also makes allowance for its locus. One of the main problems for dam reservoirs around the world is the danger of eutrophication caused by nitrogen and phosphorus compounds (Reynolds, 2003). The most visible manifestation of strong eutrophication is so called "water bloom", that is a mass appearance of planktic algae, and especially cyanobacteria (Wilk-Woźniak, 1998). High concentrations of P and N compounds accelerate the trophy increase and cause an intense expanse of phytoplankton which becomes an autochthonous source of assimilated biological carbon. After the death and sinking into the bottom, cells of planktic microorganisms constitute an integral part of sediments and enrich deposits with organic mater. A presence of autonomously functioning zones in dam reservoirs is also a very important factor influencing differentiation in abundance of organic carbon of sediments. In the majority of such water bodies, three types of zones may be distinguished: those with features typical of rivers (showing characteristics of running water), of lakes (stagnant water) and transitional ones (very slowly running or stagnant water) (Straškraba, 1998). Diversity in quality of sediments in those zones, including content of carbon, is a consequence of that differentiation. In general, an autochthonous, assimilated in situ, organic carbon seems to be predominant within sediments of lacustrine zones, whereas allochthonous forms of carbon, transported with water stream from the catchment basin area, prevail within riverine zones. Afforested or peaty immediate catchment basins are also the source of terrestrial organic carbon and could feed water bodies with this element considerably, for example as dissolved organic carbon (DOC) (Misztal et al., 2003). From ecological point of view, however, aquatic humus seems to be more important for reservoirs than soil humus (Thurman, 1985).

The aim of our study was to determine spatial differentiation of bottom sediments of Zalew Zemborzycki in respect of organic carbon concentration and to find the correlations with other sediment properties. The amount of Corg. can also indicate the level of hazard by eutrophication to the parts of the reservoir.

STUDY AREA

The dam reservoir called Zalew Zemborzycki was established in 1974 to the south of Lublin (SE Poland, N 51°40', E 22°24') in the valley of the Bystrzyca River at the village Zemborzyce. At present, it adjoins the administrative boundary of Lublin. The reservoir is mainly used for recreational purposes such as rest, aquatic sports, and angling. It also regulates water flow by stopping flood-waves and feeding the lower Bystrzyca River with water in a low-flow period. The water table area is about 280 ha on average. Zalew

Zemborzycki belongs to shallow water bodies. Its depth varies between 1 and 4 metres at a normal level of water lifting. Loess and loess-like soils susceptible to erosion cover the catchment basin of the Bystrzyca River and Zalew. The different forms of agricultural land management dominate there. There are also organic soils directly in the valley of the river. The forest overgrows the southern, right-sided bank of Zalew, whereas the arable fields, buildings of farms and leisure centre are located on the left-sided bank.

METHODS

Bottom sediments taken from 20 points of Zalew Zemborzycki have been analysed in this study. Deposits were collected in the autumn of 1999. The Kajak sediment core sampler was used for drawing of material for investigation. The sampling points were located along 4 lengthwise (A-D) and 5 crosswise (I-V) transects (Fig. 1), which regularly divided the area of reservoir, taking into account the diversity of its zones.
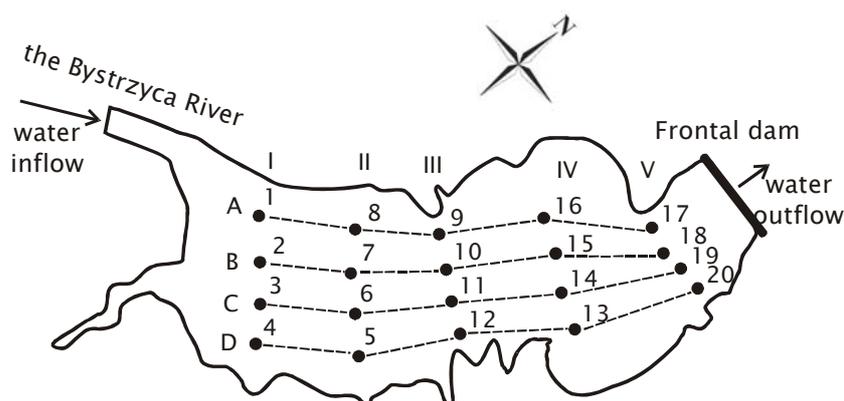

Figure 1. Sampling points of sediments in Zalew Zemborzycki

According to the thickness of sediment strata, several cores of hydrated material in the volume of about 3 dm^3 were drawn from each point. The samples were dried on the air in a laboratory without separation of the pore water because it was assumed that sediments compose a diphasic system (solid and liquid phases). After homogenization of air dry sediments, organic carbon (Corg.) was determined titrimetrically according to the Tiurin's method.

Three categories of the Corg. content in the sediments were established on the ground of central tendency measures – the quartiles. The low concentration was attributed to the samples with organic carbon content from the minimum to the lower quartile value (LQ = 35

g C·kg^{-1}). The high concentration was attributed to the samples abundant with Corg. above the upper quartile value (UQ = 52 g C·kg^{-1}). The mean concentration characterized the samples with the amount of organic carbon which values were located within interquartile range (IQR), i.e. between the LQ and the UQ.

RESULTS AND DISCUSSION

The majority of sediment samples showed the concentration of the organic carbon from 30 to 60 g C·kg^{-1} d.m. (Fig.2) and were contained within the IQR. Thus, on the prevailing area of reservoir, the organic carbon content attained the average and values close to the average assumed for Zalew Zemborzycki on the grounds of the central tendency measures.
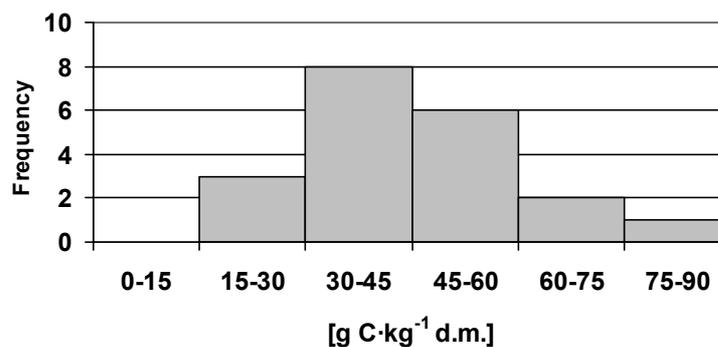

Figure 2. Histogram of Corg. content in the bottom sediments of Zalew Zemborzycki

The current deposits have shown the lower concentration of the Corg. in comparison with the findings obtained by Misztal and Smal (1980) for sediments collected in years 1977-1978, that is from the beginning of this water body existence. Those primary sediments produced during the period of about 2 years after flooding the river valley contained from 40 to 100 g C·kg^{-1} d.m. It is difficult to establish the exact cause of the lower Corg. concentration in the present samples in comparison with the former ones, because regular and complex monitoring observations concerning the dynamics of carbon were not carried out. The study of Misztal et al., (1980) was conducted almost directly after filling the reservoir basin with water. The previous level of Corg. probably reflected the organic matter accumulation typical of terrestrial conditions and an early stage of transformation of submerged soils into the bottom sediments. Before Zalew Zemborzycki came to existence, floodplains of the Bystrzyca valley

were covered by muddy and peaty soils abundant in organic matter. After inundation, the organic soils were enriched in the mineral particles from the easily eroded loess catchment basin, and therefore the quantitative ratios of solid phase constituents (e.g. mineral and organic) were changed. Fine-grained sand and silt fractions are the main element of the mineral phase in the present sediments of Zalew Zemborzycki (Ligęza, Smal, 2002), which is in agreement with results by other authors (Caitcheon, 1998).

We analyzed the dependence between the Corg. content of the sediments and the size of the mineral fraction constituents. The significant correlation between the concentration of Corg. and the percentage share of particles 1.0-0.1 mm in diameter was stated in our study (Fig. 3). The correlation coefficient was r= -0.52 (α=0.05). However, we did not state significant correlations among the Corg. and particles of other dimension sizes, although Fredrickson et al. (2004) reported that the trend of increasing percentages of the Corg. was reflected in the trend in the percentages of bulk silt.
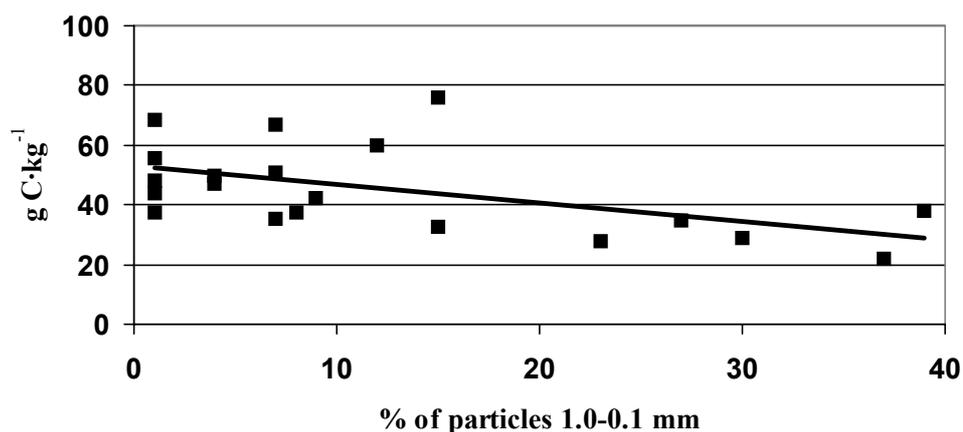

Figure 3. Correlation between Corg. content of sediments and % of particles 1.0-0.1 mm

The relationships between the finest non-organic components in sediments and Corg. may also occur; according to Szpakowska (2003), parts of dissolved humic substances are adsorbed on clay minerals and other mineral particles and undergo sedimentation to the bottom as stable, less dissolved organic matter. Our calculations based on the former results by Misztal and Smal (1980) did not also show dependence between the amount of the Corg. in the sediments of Zalew Zemborzycki and any fractions of the solid phase of the prior sediments.

Spatial differentiation of the Corg. in sediments reflects the influence of many parallel processes and factors acting within reservoirs. For example, they include a rate of water flux that affects transport and sedimentation of seston; depth of water influencing resuspension of

sediments; shape of shoreline. We stated that spatial differentiation of the organic carbon content, expressed by relative standard deviation (RSD) values, was more similar in the lengthwise transects than the crosswise ones. In the arrangement of the transects parallel to the reservoir bank (lengthwise), the lowest minimum and maximum content of Corg. in the sediments was stated at the left-side bank of Zalew Zemborzycki, whereas the highest amount of carbon was stated within the sediments neighbouring to the right-side bank. According to this pattern of the transects, the richest in organic carbon were materials deposited along transects C and D (Fig.1, Tab.1).

Table 1. Corg. content in the bottom sediments of Zalew Zemborzycki within the lengthwise transects

Transect	A[a)]	B	C	D
	g C·kg^{-1}			
Min.	21.7	27.8	42.5	34.6
Max.	37.7	49.5	76.2	68.3
Mean	32.90	40.24	55.62	51.72
SD	6.6	10.9	13.7	15.7
RSD	20%	27%	25%	30%

[a)]description and pattern of transects like in Fig. 1; SD – standard deviation; RSD – relative standard deviation

The amount of Corg. of bottom sediments drawn on the grounds of the quartiles is presented in the Fig.4. This pattern shows that differentiation of sediments in respect of carbon is perpendicular to the frontal dam. This state has not changed since the study of Misztal and Smal (1980). The authors pointed out that this arrangement is different from those observed in water bodies described by other hydrobiologists. It does not also reflect the presence of the zones distinguished by Straškraba (1998) which have the route similar to those in transects I-V

□ low concentration (< 35 g C·kg^{-1})
▨ average concentration (35-52 g C·kg^{-1})
▨ high concentration (> 52 g C·kg^{-1})
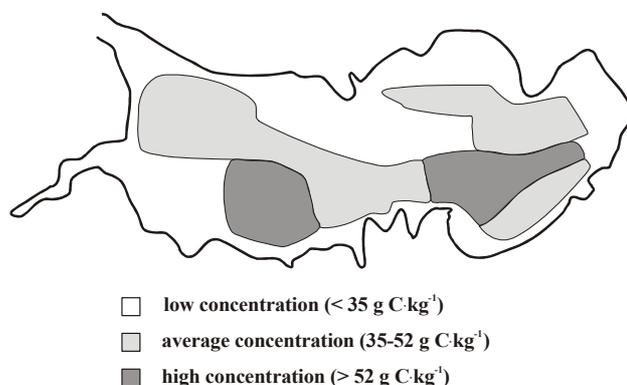
Figure 4. Zones of accumulation of Corg. in the sediments of Zalew Zemborzycki

A size of a reservoir and a way of land use management within a direct catchment basin may be very important for the spatial accumulation of Corg. in sediments. In our study, the highest Corg. concentrations were observed in the zones neighbouring to the forest, and the lowest in the place where agricultural activity predominates. It seems to confirm that the sediments of Zalew Zemborzycki are supplied with allochthonous DOC from the forest catchment basin. The content of Corg. in the sediments of the crosswise transects (I-V) was more variable than in the sediments of the lengthwise transects, which is expressed by considerable dispersion of the RSD values. They ranged from 15% to 45% (Tab.2).

Table 2. Corg. in the bottom sediments of Zalew Zemborzycki within the crosswise transects

Transect	I	II	III	IV	V
	g C·kg^{-1}				
Min.	34.6	32.7	21.7	28.8	37.3
Max.	48.0	68.3	42.5	76.2	59.7
Mean	41.05	50.83	32.50	51.78	48.70
SD	6.0	15.0	9.5	23.3	9.3
RSD	15%	30%	29%	45%	19%

[a])description and pattern of transects like in Fig. 1; SD – standard deviation; RSD – relative standard deviation

The sediments of the central part of the reservoir, that is in transects II, III, and IV, were very variable in respect of the amount of organic carbon (RSD's – Tab.2), although the mean values, except for transect III, were similar and oscillated around 50 g C·kg^{-1}. Crosswise line III clearly differed from the others. Despite the location in the middle part of the reservoir, the average Corg. content was the lowest there. The significant influence on this situation had the large share of sand fraction in those sediments (Ligęza, Smal, 2002). The presence of these particles shows that there is considerable energy of flowing water in this zone. Such conditions are not favourable to accumulation of organic mater in bottom sediments.

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DETERMINATION OF ORGANIC CARBON IN SOILS BY DRY COMBUSTION

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INTRODUCTION (definition of the problem)

At the quantitative determination of organic carbon of carbonate-free soils by dry combustion on the analytical device of the institute (LECO CN 2000) the sample is heated up to at least 1000°C in an oxygen stream and the nascent carbon dioxide developed from carbon is detected infrared-spectrometricaly in the IR-Cell. The measured total carbon is equal the organic carbon.

The determination becomes problematic, as soon as the soil contains carbonates. These are, at least partly, decomposed, driven out (e.g. $CaCO_3 \xrightarrow{t > 900°C} CaO + CO_2 \uparrow$) and detected. A distinction between carbon dioxide which was calcined and the one made by combustion of organic matter is not possible.

There are 3 possibilities to differentiate between the measured organic and inorganic carbon:

1. Destroying the carbonates with acid (preferably phosphoric acid) before measuring, followed by drying the sample and determining the organic carbon in the elementary analyzer.

2. Burning the sample with a temperature so low, that the carbonates are not calcined but the organic carbon is completely combusted.

3. Combustion of the sample at a temperature so high that not only organic carbon is burned, but also the carbonates are calcined (see also OENORM L 1080).

In the second part of this report a comparison between dry and wet combustion is made.

MATERIAL AND METHODS

Destroying the carbonates with phosphoric acid

The destruction of the carbonates was only tested with phosphoric acid. Hydrochloric acid was not used because of the problems caused from the halogens in the Analyzer. In the instrument not only carbon is measured but also nitrogen, therefore nitric acid cannot be used.

Approx. 0.5 g soil is weighed into a steel combustion boat and 2 ml of phosphoric acid (c = 3 mol/l) is added. If no more reaction occurs, the sample is dried at 100°C and measured afterwards in the elementary analyzer. This procedure is very long lasting and not easy to handle. In addition some samples with a higher concentration of carbonate (> 10 %) foam up strongly. In these cases the phosphoric acid has to be added in several steps, whereas the procedure becomes even more complicated.

Phosphoric acid attacks the steel boats and after 20 - 50 measurements the boat cannot be used anymore. Nevertheless there are nickel liners for the boats available, but these can only be used once and therefore were not tested.

The measurements of carbonate-free and carbonate-containing samples at a furnace temperature of 1050°C show that with phosphoric acid treatment losses arise. The recovery rates varied between 65 % and 98 % (mean 83 %). Probably in this acid medium organic matter is lost during the process. For the reasons listed above this method seems to be neither practicable nor supplies correct results.

Combustion of the sample at low temperature

The sample must be analyzed at a temperature which is high enough to combust the organic substance completely, but is low enough not to calcine the carbonates. Lime begins to decompose above 800°C. At this "low" temperature it can happen, that the organic carbon is not completely combusted (due to the construction of the analyzer the retention time of the sample in the furnace is approximately 120 - 240 seconds). It seems also possible that the energy released by the combustion heats up the sample and a portion of the lime delivers carbon dioxide. The results are discussed below.

Combustion of the sample at high temperature

The sample is burned at a temperature higher than 1000°C and the carbonates are thermally destroyed. The total carbon is received. The concentration of carbonates is measured with another method e.g. OENORM L 1084 (Scheibler). The carbonate is subtracted from the total carbon to get the organic carbon. The results are also discussed below.

RESULTS AND DISCUSSION

*Comparison of three different combustion temperatures (700°C, 1050°C, 1150°C)*

Some carbonate-free and carbonate-containing soil samples were measured. The contents of organic carbon were determined in interlaboratory ring tests. Additionally the concentrations of carbonate were determined according OENORM L 1084.

The differences between the 3 temperatures are relatively small. The recovery rate of soils with low concentration of organic matter at a combustion temperature of 700°C is quite low (between 70 % and 90 %). Maybe the combustion for this time where the soil is in the furnace is not complete.

A decomposition of carbonates at this temperature is not noticed. However in the literature a disintegration temperature for magnesiumcarbonate of approximately 350°C is indicated [1]. To use this method, further tests with soils containing magnesite should be made.

Between combustion temperatures of 1050°C and 1150°C no significant differences in % $CaCO_3$ could be found. In the soils carbonate was thermally destroyed quantitatively. Analyses of pure lime were also carried out at a combustion temperature of 1050°C and 1150°C. While at 1050°C starting from a lime quantity which is equivalent to 30 % calcium carbonate in the soil the disintegration of carbonate is not complete, at 1150°C - even with a lime quantity which is equivalent to 75 % calcium carbonate - the decomposition is complete (Fig. 1).

Figure 1: Comparison analyzing lime between 1050°C and 1150°C
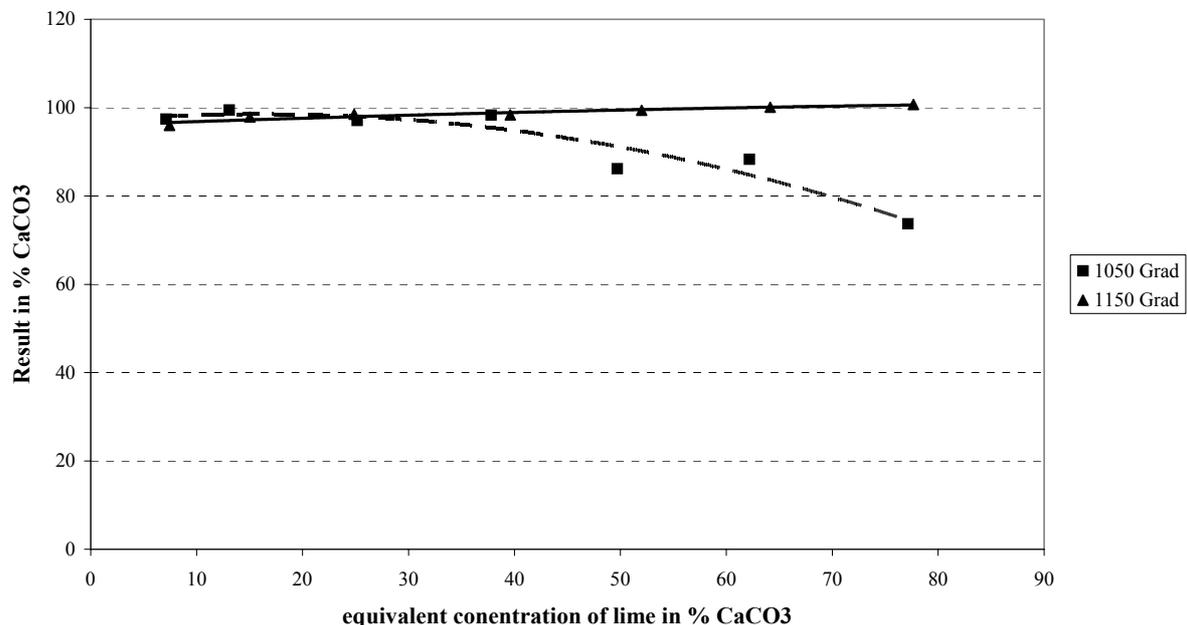
Verification of the method

For the verification of the method two standard-soils and 15 soils from ALVA and VDLUFA interlaboratory ring tests were analyzed at a combustion temperature of 1150°C. Some of them contained carbonate, some not. The recovery rates were throughout between 95 and 105 % (Fig. 2). Therefore it can be assumed that the method supplies correct results.

Figure 2: CaCO₃ recovery rates in standard soils and soils from ringtests
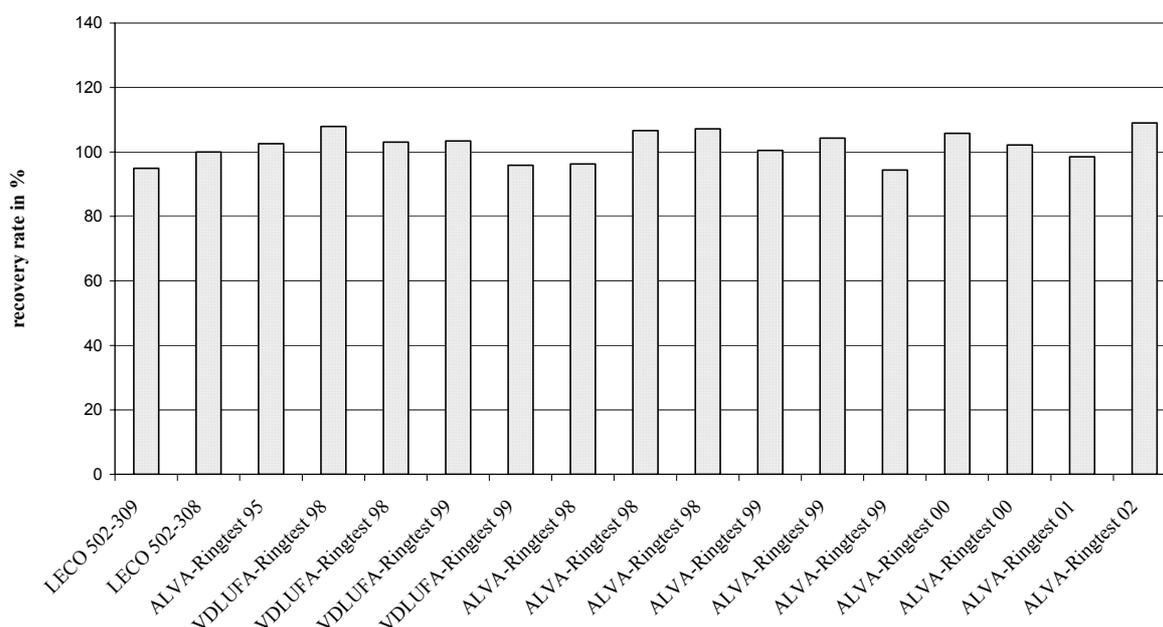
Comparison between dry and wet combustion

Before introducing the elementary analyzer into our division, the organic carbon was determined by wet combustion according to OENORM L 1081. Therefore a comparison between this method and the dry combustion was from highest interest.

For this purpose approximately 350 samples were analyzed with both methods. About 150 of these soils were containing carbonates up to 50 %, the other 200 soils were free of lime. The content of organic matter of the soils was between 0.5 and 15 %.

In Figure 3 it can be seen, that the two methods correlate very well. The correlation coefficient is 0.97.

Comparing the correlation between dry and wet combustion of carbonate containing soils and carbonate free soils it can be seen that there are no differences between this two correlations. The content of carbonate has no influence on the correlation between the two methods.

If the content of organic carbon made by dry combustion is set to 100 %, 87 % of the analyses made with wet combustion have recovery rates between 80 and 120 % and 59 % of the samples have recovery rates between 90 and 110 %. The average is by the way a recovery rate of 98.4 %.

Figure 3: Correlation between dry and wet combustion $y = 1{,}0955x - 0{,}1719$
$R^2 = 0{,}935$
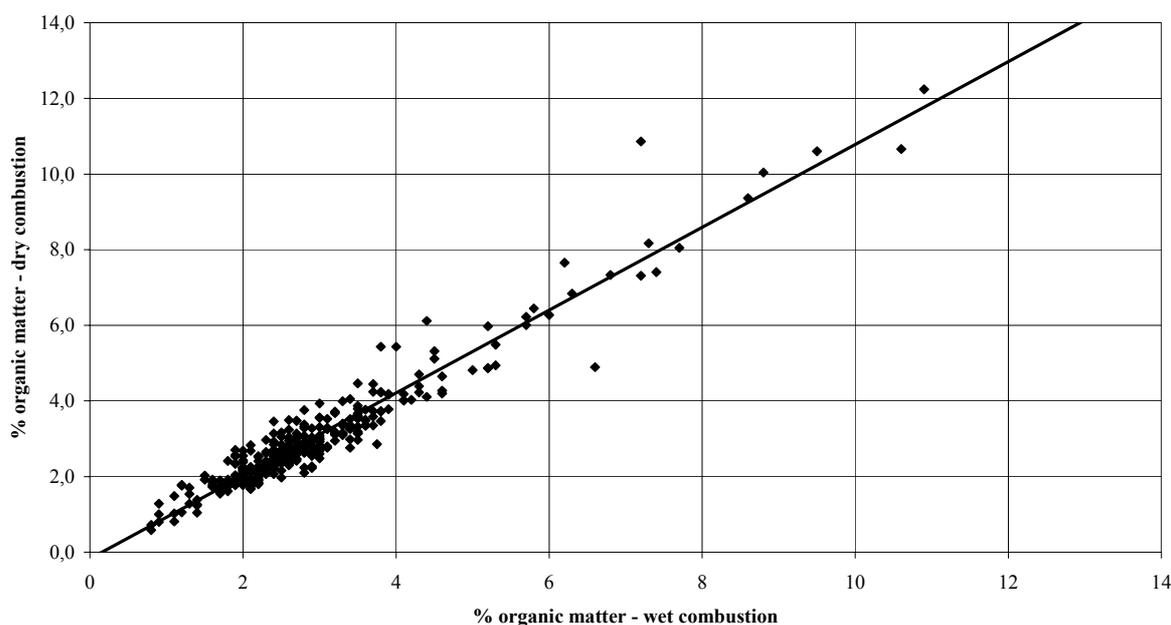
Soils with higher contents of organic carbon have throughout a recovery rate below 100 % but this has probably to do with the method of wet combustion. With this method the oxidation of the organic matter is not complete.

The dry combustion has a higher precision than the wet combustion. Per example the same soil was analyzed 60 times on different days with both methods. The variation coefficient of the dry combustion was 1.9 % and that of the wet combustion 6.6 %.

It can be said, that these two methods correlate very well, but still they are two different methods with completely different measurement principles.

CONCLUSIONS

A method for analyzing the content of organic carbon with a LECO CN 2000 element analyzer was tested. The results are related on the use of this analytical device. Three possible ways of measuring carbonate containing soils were compared. The pre-treatment with phosphoric acid leaded to some problems and consequently to possible wrong results. The combustion at 700°C brought in some cases an incomplete combustion. Between the combustion temperatures of 1050°C and 1150°C no significant differences could be found. However measurements of pure lime showed that only the higher temperature completely destroyed higher contents of $CaCO_3$. For this reasons the following analyses were done at a furnace temperature of 1150°C.

Carbonate containing and carbonate free soils were analyzed by dry and wet combustion and compared. It was found, that the two methods correlate very well. Analyzing soils with higher contents of organic carbon, the wet combustion leads to slightly lower results. Anyway the dry combustion has a better precision than the wet combustion.

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SOM MANAGEMENT & EU SOIL STRATEGY

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ABSTRACT

In the 6th Environment Action Program the European Community took the commitment of addressing soil alongside air and water as an environmental media to be preserved and to develop a Thematic Strategy for Soil Protection. In 2002 the Commission adopted a communication concerning this topic, where eight major soil threats (erosion, decline in organic matter, contamination, sealing, compaction, decline in biodiversity, salinisation, floods and landslides) were identified and actions leading to improvements in soil protection were planned (http://europa.eu.int/comm/environment/soil/index.htm). Stakeholders information and consultation meetings, an advisory forum and five working groups have been established, three of the latter dealing with threats (contamination, erosion, decline in soil organic matter), a horizontal WG for the development of a proposal for a monitoring directive and one for research.
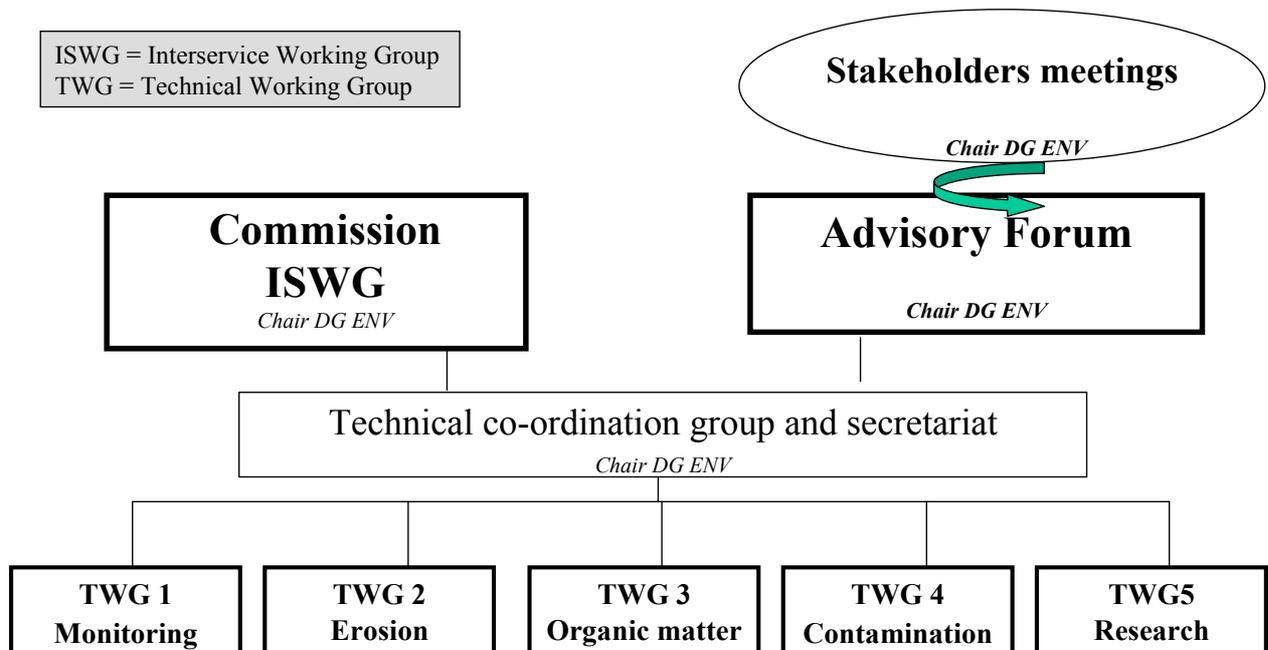
Figure 1. The participatory approach of the EU Soil Thematic Strategy (modified after Van Camp, 2003)

In the WG's, representatives from member states, candidate countries, major stakeholders, EC and experts were involved. The aim of the working groups was to contribute to the deliverables the Commission is committed to: a proposal for soil monitoring legislation related to threats and a knowledge base for action; a communication dealing with the priority areas erosion, decline in organic matter and soil contamination. Within the working groups several tasks were treated in task groups by more than 250 participant s in total. The WG's were active for about one year and presented their final reports including recommendations for further actions in April 2004. Reports concerning the EU soil strategy are available at the soil CIRCA library: http://forum.europa.eu.int/Public/irc/env/soil/library and at the homepage of JRC: http://forum.europa.eu.int/Public/irc/env/soil/home . The working group on soil organic matter (SOM) and biodiversity was organized in seven task groups dealing with 1. Functions, roles and changes in SOM, 2. Status and distribution of SOM across Europe, 3. Soil biodiversity, 4. Exogenous organic matter, 5. Land use practices and SOM, 6. Policy responses in Europe, 7. Impacts on economy society and environment. Research and monitoring concerning SOM were tackled as horizontal tasks. In the final report the importance of SOM and soil biodiversity in maintaining many soil functions including the role as source/sink for greenhouse gases is expressed. Information gaps on SOM status of soils across Europe have been identified. Harmonization of data sets and additional sampling and monitoring programmes, critical examination of land management practices in areas with low SOM contents and the examination of relationships between soil sealing and SOM are recommended. Policies available to improve SOM status are critically discussed (e.g. CAP, Kyoto protocol, Water Framework Directive). Best practices for SOM management include a generalized use of catch crops/green manures, the creation of buffer strips along borders of agricultural fields, maximization of the use of crop residues, conservation tillage and the application of exogenous organic matter in agriculture and avoidance of clear felling and soil preparation in forestry. Of particulate interest is the use of exogenous organic matter if it is of an appropriate quality and application guidelines are followed. The fact that recommendations for optimal SOM management are only valid in a regional context is recognised. The need for monitoring at different scales, allowing inferences on management effects on SOM is expressed. Numerous knowledge gaps in particular on relationships between SOM levels and quality, soil functions and soil properties have been identified.

Based upon the outcome of the EU Thematic Strategy for Soil Protection the new Commission has planned to send a proposal for a Soil Protection Directive to the member states by June 2005 and a consolidated draft to the European Parliament by October 2005.

Workshop – Impressions
(Pictures supp. by PAN, Vienna)