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Preface

Our meeting at the Warsaw Agricultural University, Poland, took place in one of the most modern set of buildings that ESNA has ever had the pleasure to visit. The new lecture hall provided the working group with a perfect setting for a series of thought provoking papers.

In Radioecology, Brambilla / Italy and Oncsik / Hungary started by presenting a nice piece of collaboration using Brambilla's model VENTOMOD for tomatoes grown on soil contaminated with ^{134}Cs in an experiment undertaken in Hungary. Oncsik / Hungary gave a talk on the contamination of Paprika (Capsicum) with ^{134}Cs and ^{85}Sr and the transfer of these radionuclides from soil or plant surface. Scarlou et al. / Athens presented results of their continuing research on classifying soil systems with transfer factors of Cs and Sr from soil using reference plants, e.g. corn, which was followed each year by cabbage in different soils. Sysoeva et al. / Obninsk, Russia gave first results of her Ph.D. work, on the modelling of the uptake of Sr from soil, using data for barley and lupine to test her model and observing that the calcium content in soil was a controlling parameter for these plants. Putyrskaya et al. / Minsk presented results of her Masters thesis on the relevance of preferential flow for uptake of plants in contaminated areas and showed the differences between agricultural soils and forest soil. Zibold et al. / Germany showed for spruce forest soil that most ^{137}Cs is fixed in the top 5 cm in Oh and/or Ah horizons as measured 4, 9, 11, and 16 years after contamination of the soil surface.

In Soil Science and Plant Nutrition Kieliszewska-Rokicka / Poland reported on the examination of microbial communities in soil using signature fatty acids, and she could differentiate the microbial biomass under 14 forest tree species. Gerzabek / Vienna gave 3 interesting examples of the potential of computational chemistry as applied to soil science. Brohi / Turkey reported on the effects of Nitrogen and Phosphorus fertilisation of soil on rice crop. Budoï / Romania discussed transfer functions in soil science which can be used to establish amendment and fertilizer rates. Budoï et al./ Romania went into detail in 6 additional papers to discuss: agrochemical properties of reddish-brown soil and long run fertilisation, Dana explained the susceptibility of maize to Zinc deficiency, Rizea talked on soil resistance to acidification, and Soare presented results on foliar fertilisation of grapevine and apple tree.

The participants of the working group session thank the local organizers Professor Szczawinski and Dr. Szczawinska and their team for their efforts and our warm welcome. Our stay on the campus of Warsaw Agricultural University was a real pleasure, not only because of the interesting city, but also because of the good infrastructure of the campus and the special care of our hosts.

**Nick Mitchell and Gregor Zibold,
Co-Chairman of Working Group 3**

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Gregor Zibold

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EVALUATION OF A MODEL FOR LEAF TO FRUIT TRANSFER OF RADIONUCLIDES IN PROCESSING TOMATO PLANTS USING AN INDEPENDENT SET OF DATA

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Abstract

Because of their many possibilities of consumption, tomato fruits are an important component of the human diet. This paper presents results on the valuation of a dynamic model for the short term behaviour of radionuclides deposited on tomato plants (*Ventomod*) following a direct contamination event.

Being created for practical purposes it can help in assessing the risk of radionuclide contamination of the human diet. For this reason it has been tested with an independent dataset about the leaf to fruit transfer of ¹³⁴Cs in a typical Hungarian tomato variety (Dwarf of Kecskemet). Data obtained from this pot experiment were used to evaluate the model behaviour. Model constants were varied taking into account the differences between the considered scenario and the one used to calibrate it. Results show that the model output well fits the observed activity of fruits if fallout and contamination stage are varied.

The main body of this report summarises the experimental protocol, compares the experimental results with model predictions generated by *Ventomod* and makes recommendations for both updating model parameters and undertaking further experimental work.

1. Introduction

It is well known that agricultural products can be polluted by radionuclides from both acute and continuous atmospheric releases. Edible fruits are an important dietary component; nevertheless, models on this large group of plant products have been given little attention until present. As reviewed by Watkins & Maul (1995) radionuclides, following a release into the atmosphere, can reach fruits in many ways among which direct deposition to exposed plant surfaces (followed by retention, absorption and translocation) and to fruits must be taken into special account.

Of course, the relative significance of each pathway depends on the kind of radionuclide, on the stage of plant development, on the crop and on the season when the contaminating event occurs. As stated by Müller & Pröhl (1993), the processes of radionuclides' deposition on and interception by vegetation and soil are the starting points for their transfer into the food chain. To simulate the transport of radionuclides in soils, plants and domestic animals mathematical models have been developed both for agricultural and natural environments (Antonopoulos-Domis, Clouvas & Gagianas, 1990; Whicker & Kirchner, 1987; Frissel, 1994; Brown & Simmonds, 1995; Müller & Pröhl, 1993; Thorne & Coughtrey, 1983).

The purpose of this work was to evaluate the behaviour of *Ventomod* (Brambilla, Strelb, Carini & Gerzabeck, 2002), comparing the model outputs with data obtained from an independent pot experiment carried out in a different environment (Hungary) using a local tomato crop variety (Dwarf of Kecskemet).

2. Material and Methods

The transfer of ^{134}Cs to tomato fruits was investigated after acute releases in the form of wet depositions. Pot experiment with tomato plants was established on alluvial meadow soil on 9th May 2000. Each pot was provided with 5.5 kg of absolute dry soil previously mixed with fertilizer (150 ppm N, 200 ppm P, 200 ppm K). Leaf to fruit transfer was examined; experimental data were processed by help of the statistic software SPSS 8.0.

2.1. Foliar Contamination Scenario

The foliar contamination was effected sprinkling tomato plants three times during the growing season: 5th June, 4th and 24th July. These dates coincided with three different phenological stages (flowering, green yield and "red ripening").

Table 1: Number of days elapsed between foliar contamination and harvest

Date	Growing Stage	Harvests			
		7 th July	26 th July	2 nd August	10 th August
5 th June	<i>Flowering</i>	32	51	58	66
4 th July	<i>Green Yield</i>	3	22	29	37
24 th July	<i>Red ripening</i>	-	2	9	17

All treatments were carried out by use of an amount of water appropriate to 1 mm "rainfall" and on each treatment plants were sprayed with three different levels of ^{134}Cs activity (50, 100 and 150 kBq/pot) using an aqueous solution of ^{134}Cs in chloride form. For each level of contamination four harvests, picking up full ripe tomato fruits from each plant, were planned. These were carried out on 7th July, 26th July, 2nd and 10th August measuring each time the fresh weight (f.w.) and the activity of ripe fruits. Times elapsed between contaminations and harvests are displayed in Table 1.

Table 2: Fresh weight of ripe fruits (grams f.w.) expressed as arithmetic mean and standard deviation of 9 replicates.

Date of Harvest	Contamination Stages		
	Flowering	Green Yield	Red Ripening
7 th July	137 ± 9.25	170 ± 71.4	-
26 th July	397 ± 60.1	377 ± 52.5	372 ± 31.1
2 nd August	575 ± 78.2	476 ± 29.7	490 ± 33.6
10 th August	695 ± 87.8	623 ± 22.8	590 ± 23.8

According to Ho (1996), as far as tomato plants are concerned, fruits behave as absolute sinks for both potassium and metabolites. Given that radiocesium tends to follow the same pathways of potassium (Ward Wicker et al., 1972; Pendleton et al., 1965), for each contamination level, the red fruits' activities and fresh weight of each harvest were summed up (Table 2 and 3).

Ripe fruit contamination has been expressed as Bq/kg fresh weight too by dividing the total red fruits activity (Bq/pot) by their fresh weight expressed as kg f.w./pot. These activities

allowed us to compare the model output with the experimental results (see Table 3). In both Table 2, and 3, as far as the Red Ripening contamination stage is concerned, fruit samples picked up on 7th July (1st harvest) weren't considered because this harvest was carried out before red ripening.

Table 3: ¹³⁴Cs cumulated activity in ripe fruits (Bq/kg f.w.) in the different harvests and in all the considered contamination levels (1 to 3). Data are expressed as arithmetic mean \pm standard deviation of three replicates.

Foliar Treatment	*	Harvests			
		1 st	2 nd	3 rd	4 th
<i>Flowering</i>	1	1893 \pm 171	3750 \pm 176	5189 \pm 193	6257 \pm 258
	2	4373 \pm 57.4	8770 \pm 125	11896 \pm 179	14614 \pm 397
	3	7950 \pm 285	15777 \pm 208	20490 \pm 364	25300 \pm 345
<i>Green Yield</i>	1	1750 \pm 249	3074 \pm 209	4570 \pm 638	6026 \pm 609
	2	2346 \pm 33.4	4984 \pm 109	6728 \pm 87.5	10006 \pm 55.9
	3	4531 \pm 129	7691 \pm 96.8	12364 \pm 312	16656 \pm 280
<i>Red Ripening</i>	1	-	4091 \pm 155	13915 \pm 2110	17599 \pm 2234
	2	-	10076 \pm 556	20028 \pm 868	25513 \pm 1046
	3	-	13964 \pm 2429	29371 \pm 2375	41923 \pm 2138

* 1: 50 kBq/pot; 2: 100 kBq/pot; 3: 150 kBq/pot

2.2. The Model

2.2.1. Model Description

By help of the simulation software VENSIM[®] PLE Plus 4.2a (Ventana Systems Inc.) a set of equations representing the considered system with a chosen time resolution of one day was developed. The general approach and the compartments required were mapped out using the logic rules implicit in the software (see Fig. 1).

In the simulation the time-integrated behaviour of the plant system, i.e. the development of radionuclide levels in different plant parts and compartments, is reproduced. *Ventomod* is divided into three sub-models:

1. Weathering / Absorption model.
2. Redistribution model: from green biomass to red fruits and root and substrate compartments.
3. Red Fruits growth model.

The 1st and 2nd sub-models reflect the radionuclides' behaviour in each step of their global translocation from leaf surfaces, which are the starting point of plants' contamination, to red

tomatoes. The 3rd sub-model is introduced to simulate the fresh biomass increase of red fruits (fresh weight) to calculate the “Bq/kg f.w. in red fruits” state variable. It is assumed that the driving force of nutrient translocation is the biomass build-up of fruits. Six state variables (levels) are defined: “Activity outside the plant”, “Weathering loss”, “Activity inside the green biomass”, “Activity in root and peat”, “Activity in red fruits” and “Red fruits fresh weight”.

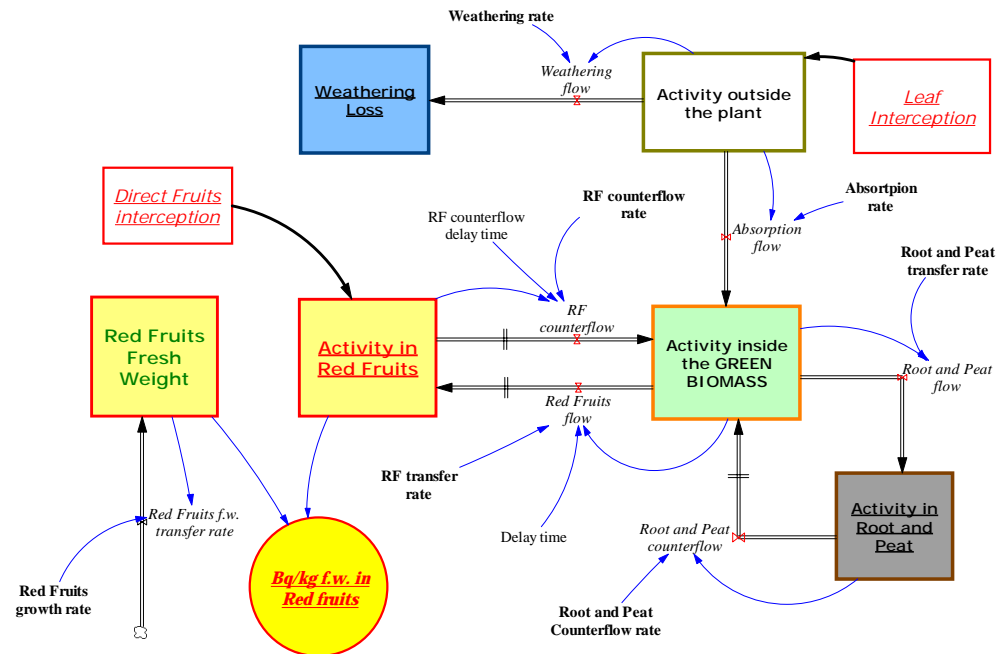


Figure 1: Conceptual diagram of the model. Boxes indicate state variables (pools), double line arrows give flows and feedback mechanisms. Delayed flows are marked by a double line passing through perpendicularly at the arrow handle.

Flows between these variables are represented by the “Weathering flow” (weathering processes) and “Absorption flow” (leaf absorption) for the first sub-model. “Root and Peat flow” and “Red Fruits flow”, together with the corresponding reverse flows (“Root and peat counterflow” and “RF counterflow”), represent fluxes in the redistribution model. Each flow is controlled by the corresponding rate (expressed as day⁻¹) that had been previously calculated on the basis of one experimental data set carried out in Piacenza (Italy) using the processing tomato cultivar *PSI296* (Brambilla, Fortunati, Carini 2002; Brambilla, Strebli, Carini, Gerzabeck 2002).

The model was set up assuming that at time zero (t_0) all the intercepted activity is completely outside the plant while at the endpoint of the simulation only 1 Bq of each radionuclide is left on the plant surface. Every day a certain amount of radioactivity enters the plant but at the same time weathering processes cause a loss of activity. The higher the radionuclide concentration outside the plant, the higher are both the absorption and the weathering flows (Watkins & Maul 1995).

2.2.2. Model valuation

The model has been valuated running it formerly using defaults values (see Table 4) and latterly adjusting parameters to see the changes in the model outputs. Given that simulations concerned the ¹³⁴Cs only, the “RF Counterflow” (fig. 1) was not considered therefore the related rate was set to zero.

When adjusting parameters, the prime objective was to achieve a reasonable estimate based on all available data. The aim of any adjustment was intended to provide a conservative prediction for dose assessment (ripe fruits).

Table 4: Ventomod rates used to perform the model valuation

Constants (day ⁻¹)	Default Value	Adjusted Value
Weathering Rate	0.071	0.108
Absorption Rate	0.012	0.039
Red Fruits Transfer Rate	0.015	-
R&P Transfer Rate	0.013	-
R&P Counterflow Rate	0.075	-
Red Fruits Growth Rate	0.099	0.0494

The adjusted values were those that can be defined as "*scenario-dependent*", their values are reported in Table 4 and 5:

- *Leaf Interception* (Bq): is the amount of radioactivity effectively intercepted by leaves. It has been estimated as % of the whole administered activity.
- *Weathering Rate* (day⁻¹): this constant describes the loss of activity due to weathering factors.
- *Absorption Rate* (day⁻¹): it describes the absorption process according to which radioactivity enters the plant.
- *Direct Fruit Interception* (Bq): it is the total amount of radioactivity intercepted by red fruits during the final stages of the growing cycle. It has been estimated as % of the whole administered activity.
- *Red Fruit Growth Rate* (day⁻¹): it determines the red fruits fresh weight increment during the growing cycle which is assumed to be single exponential.

The model outputs for the considered dates (7th July, 26th July, 2nd and 10th August) were then plotted against the respective experimental result of each replicate. The mentioned model parameters were adjusted to check the model behaviour at their varying: first of all the model was run using the default rates and considering as standard the red fruits growth rate even though it had been obtained from a different cultivar. A second set of runs was then carried out to obtain a specific red fruit's growth rate by analysing the fresh weight of the red fruits belonging to the set of plants contaminated at flowering. Latterly even the weathering and the absorption rates were adjusted: as a matter of fact the defaults values were obtained from plants which were grown with a drop irrigation system while in this case sprinkler irrigation was used. For this reason the absorption and the weathering rates needed to be recalculated on the base of the set of plants contaminated at flowering by applying the equations derived from its basic assumptions (Brambilla, Strebl; Carini, Gerzabeck 2002).

The setting combinations used were marked with numbers from 1 to 3 as follows:

1. *Ventomod* standard rates.
2. Default values for absorption and weathering rate but adjusted value for the red fruit growth rate.
3. Adjusted weathering-, absorption-, and red fruits growth rate.

The ratio between predicted and observed values was studied considering all available paired data for each foliar contamination with reference to all the administered activities.

Table 5: Values of leaf interception and direct fruit interception estimated from literature

Stage of Contamination	Administered Activity	Leaf Interception (Bq/pot)	Direct Fruit's Interception (Bq/pot)
Flowering	50kBq/pot	35150	-
	100 kBq/pot	70300	-
	150 kBq/pot	105450	-
Green Yield	50kBq/pot	27350	-
	100 kBq/pot	54700	-
	150 kBq/pot	82050	-
Red Ripening	50kBq/pot	19550	1900
	100 kBq/pot	39100	3800
	150 kBq/pot	58600	5700

3. Results and discussion

The results for ^{134}Cs foliar uptake presented below (Table 6) show the ratio of predicted plant content to that obtained from the field experiments using all the available paired data varying the combination of the model settings. On these data the analysis of variance has been carried out and with determination of the less significant difference ($P < 0.05$).

It can be noticed that *Ventomod*, in short term assessment, tends to be in good agreement with the experimental data. Most part of our results are consistent with Rombke & Moltmann (1996) who suggested that, in case of good closeness between data from the field and model forecasts, the ratio between the assessed and the measured value should not be greater than a factor of ten. Differences due to the varying of parameter combinations are always significant with exception for the contamination carried out at Red Ripening administering 50 kBq/pot of ^{134}Cs .

Running *Ventomod* with the default parameters tends to underestimate the ^{134}Cs content in ripe fruits ranging from a factor of 0.068 for the Red Ripening contamination at 50 kBq/pot of administered activity to 0.80 for plants contaminated at Flowering with the same level of activity. It appears evident that the shorter the length of the simulation the worse the agreement between the predicted and the observed activities.

Running the model with parameter combination n° 2 means keeping weathering and absorption rate unchanged and adjusting the red fruits growth rate (Table 4). This significantly affects the model output: as a matter of fact, running the model with this set of values overestimates the activity of tomato fruits. Model predictions range from 1.0 to 8.8 but in this case, because of the overprediction, at the shortening of the simulation the agreement between predicted and observed values tends to improve. This proves the fact that the red fruit growth rate, in tomato plants, is very important because it comes out from the cultivar and the environmental conditions in which plants were grown.

Table 6: Ratio of Predicted to Observed ^{134}Cs activity (Bq/kg f.w.) in tomato ripe fruits (mean \pm standard deviation).

Contamination Level	Set of parameters	Flowering		Green Yield		Red Ripening	
50 kBq/pot	1	0.80 \pm 0.40	a	0.33 \pm 0.23	a	0.068 \pm 0.036	a
	2	8.8 \pm 1.6	c	4.9 \pm 3.0	c	1.0 \pm 0.40	b
	3	3.5 \pm 0.73	b	1.9 \pm 1.2	b	0.90 \pm 0.38	b
100 kBq/pot	1	0.69 \pm 0.35	a	0.39 \pm 0.26	a	0.077 \pm 0.013	a
	2	7.5 \pm 1.3	c	5.7 \pm 3.8	c	1.3 \pm 0.38	c
	3	3.0 \pm 0.58	b	2.2 \pm 1.5	b	0.79 \pm 0.50	b
150 kBq/pot	1	0.59 \pm 0.28	a	0.32 \pm 0.30	a	0.071 \pm 0.025	a
	2	6.6 \pm 1.5	c	5.1 \pm 3.3	c	1.1 \pm 0.15	c
	3	2.6 \pm 0.66	b	2.0 \pm 1.3	b	0.70 \pm 0.46	b

Parameter combination n° 3 is the one that gives the best model performance for the set of data analysed. It has been obtained adjusting both absorption, weathering and red fruits growth rate to the considered scenario by applying the assumptions at the base of this dynamic model. With reference to the contaminations carried out at Green Yield and Red Ripening the Predicted/Observed ratio ranges from 0.70 to 2.2 providing good agreement at varying of the contamination stage independently of the radioactivity supplied with the sprinkling.

Even though these predictions can be considered acceptable, the fact that in the Red Ripening contamination the activity of ripe fruits is under predicted suggests that a need of some adjustment in the plant short term internal distribution is required. In particular it appears that a better estimation of the direct interception of fruits could consistently improve the output's reliability.

4. Conclusions

The results of this study show how Ventomod's behaviour is sensitive to the changes in scenario-dependent parameters, namely: absorption, weathering and red fruits growth rate. In particular the role played by the red fruits growth rate has been given particular prominence because of the improvement in the agreement with the experimental data followed to its adjustment.

Confidence in the leaf to fruit transfer of caesium in Ventomod has greatly increased as result of this study: the further improvement of the model outputs following the application of basic assumptions confirms that the most important factors involved in the leaf to fruit contamination of processing tomato fruits have been identified. Nevertheless, to achieve a more general use of this model, further testing with independent data sets obtained in various environmental conditions should be carried out not only with reference to radio caesium but considering radio strontium too.

Further development with data from other horticulturally important species is also required to expand the possibility of model application.

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RATIO ^{134}Cs TRANSFER FACTOR CABBAGE / ^{134}Cs TRANSFER FACTOR CORN FOR PLANTS GROWN ON DIFFERENT SOILS: TWO YEARS RESULTS

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ABSTRACT

A coordinated research project with the participation of 16 countries was initiated in 2000 by FAO/IAEA/IUR to classify soil systems according to TFs of radiocaesium and radiostrontium from soil to reference plants. The objective of the Greek contribution is to produce data on TF of ^{134}Cs in Greek soils (two "representative" and two volcanic). The experiments are carried out in pots which contain soil artificially contaminated with ^{134}Cs . Corn was selected as a reference crop followed each year by cabbage, in order to check the constant ratio supposed to exist between the TFs of the two plants in the different soils. The results of the second year of experimentation showed the same tendency as those of the 1st year although TFs were significantly lower by an average factor of 6. This reduction may be attributed to the effect of time and/or to the addition of potassium fertilizer. Despite the differences in growth of the plant species, this year also TFs were significantly higher in the two volcanic soils than in the other soils by a factor ranging from 3 to 6. The calcareous - clay soil continued to show the lowest TF value. The ratio ^{134}Cs TF cabbage / ^{134}Cs TF corn (seeds) in the four soils was reduced and ranged from 2 to 8 (5 to 13 the 1st year) with a mean value of 4 (7 previous year). The second year of experimentation two new varieties of corn and cabbage were used for comparison reasons and significant differences in the TF values between the varieties of the same plant were observed. Considering the ratios TF cabbage / TF corn for all studied varieties and in all possible combinations gave mean values ranging from 2 to 15.

INTRODUCTION

This study is part of the FAO/IAEA/IUR Research Co-ordinated Project “The Classification of Soil Systems on the basis of Transfer Factors of Radionuclides to Reference Plants” which was initiated in 2000 with the participation of 16 countries.

Our contribution will be to produce data on transfer factors of ^{134}Cs from soil to reference plants in a range of Greek soil systems in order to characterize systems in which TFs might differ substantially from what would be regarded as normal; it will also help to replace generic data of TFs with those more relevant to local conditions. The purpose of the present work was to study ^{134}Cs uptake by corn and cabbage grown on “representative” and volcanic Greek soils. Conversion factors for cabbage using corn as reference plant were also calculated. Based on corn’s TFs in the different studied soils, reference TFs for corn are presented.

MATERIALS AND METHODS

Experimental set up

Four soils with contrasting properties were selected; two volcanic from Santorini island and two from South Eastern Greece (Peloponese) representative of big agricultural areas. The main characteristics of the selected soils are presented in Table 1.

Table 1: Main soil characteristics

SOIL	Clay (%)	Silt (%)	Sand (%)	Texture	PH (1:1)	O.M. (%)	C.E.C cmol _c /kg	Exch. K ⁺ cmol _c /kg
1	8.6	18.0	73.4	SL	5.6	0.46	7.39	0.23
2	29.3	47.0	23.7	CL	7.4	2.11	17.39	0.42
3	8.6	27.2	64.2	SL	5.8	0.56	3.48	0.39
4	7.0	18.0	75.0	LS-SL	6.9	2.71	9.44	1.06

Soil 1 is classified as Alfisol, suborder xeralf¹; it is an acid soil of coarse – medium texture at a high level of development.

Soil 2 is a medium to heavy textured, calcareous Entisol, suborder fluvent, at its early stages of development, representing a high percentage of the Greek agricultural soils.

Soils 3 & 4 are volcanic ash soils, from Santorini island, developed on pumice and volcanic ash and are classified as Andisols, suborder xerand, according to the recent establishment of this soil order in Soil Taxonomy; The soil genesis process of these soils is determined mainly from the age (approximately 1500 years, when a very strong volcanic eruption took place), the climate of the island, the mineral composition and the texture of the volcanic ash.

According to Misopolinos et al. (1995), the soils in Santorini are characterized by their low clay content and most of them are neutral to alkaline. In the surface soil layers heavier particles are present e.g. gravels of aluminum-iron composition or pumice. The presence of gravels can be explained by the intense wind erosion, where the strong winds take away the fine particles of the soil surface. Gravels also prevent the loss of soil moisture by evaporation, which is crucial for plant growth considering the land on the island is not irrigated. It is noticed that the average rainfall in the island is low (ave 350 mm/year)

The two selected soils from Santorini are of low clay content, but differ in other soil properties, as pH, organic matter content, cation exchange capacity and concentration of exchangeable potassium (Table 1).

The plants were grown in pots which contain 14 kg air-dried soil, in four replications. The size of pots is considered sufficient for providing reliable data and preventing water shortage and nutrient deficiency problems.

Soil was contaminated with ¹³⁴Cs (1.9 MBq pot⁻¹) as CsCl on July 28th 1999. The soil was transferred to each pot in seven layers of approximately 2 kg of soil each. On the top of each layer 100 ml of the radioactive solution was added in the form of very small drops. The above technique of soil contamination has been used successfully in previous experimentation with

¹ The soils were classified according to US Soil Taxonomy

annual and tree crops (Skarlou et al., 1996 and 1999). The distribution of the radioactive material throughout the pot is well controlled by this method and loss via cracks or edges is absent.

The soil in pots was moistened to field capacity and left to stand for two months for the ^{134}Cs to reach equilibrium.

Experimental conditions

Corn was selected as a reference crop followed each year by cabbage in order to check the constant ratio supposed to exist between the TFs of the two plants in the different soils.

Plant species

2000-2001: Corn, var. Corduna
Cabbage, var. local-Kozanitiko

2001-2002: Corn, var. Corduna and sweet corn var. Elite*
Cabbage, var. local-Kozanitiko and var. Brunswick*

The second year, in addition to NH_4NO_3 , 5g of K_2SO_4 were added in each pot.

Analytical methods

Cation exchange capacity of the soils was determined by the Na-acetate method (Bower et al., 1952). Organic matter content was determined by the Walkley-Black procedure (Nelson and Sommers, 1982). Mechanical composition was determined by the Bouyoukos hydrometer method (Bouyoukos, 1951) and the pH by glass and calomel electrodes in 1:1 soil-water ratio. Exchangeable bases were extracted by 1M NH_4 -acetate.

After harvesting plants were separated into edible and vegetative parts, where necessary (corn and sunflower); representative plant samples were cut into small species, dried at 70°C and counted for ^{134}Cs with the following system: HpGe detector (efficiency 22% and FW 1.8 keV for the 1332 keV ^{60}Co γ -ray) connected to a CANBERRA 35⁺ 4K multichannel analyzer plus a computer with suitable software for gamma-ray spectroscopy analysis. Quantitative determination of ^{134}Cs was made at the photopeaks of 604.7 and 795.8 keV by measuring the activity of the samples and taking into consideration the efficiency calibration of Ge crystal for known ^{134}Cs concentration in quite similar geometry ($d = 7$ cm, $h = 2$ cm). The concentration of ^{134}Cs in plant samples was expressed in Bq kg^{-1} dry material.

RESULTS

Transfer factors for the studied plant species are presented in Tables 2 (corn) and 3 (cabbage). Despite the differences in growth TFs were also this year significantly higher in the two volcanic soils than in the other soils by a factor ranging from 3 to 6. This high caesium absorption may be due to the sandy texture of these soils as well as to the presence of pumice which has a high water capacity. Soil 2 showed always the lowest TF, significant only for Elite variety (corn). It is a calcareous soil with a high clay content and high CEC, factors

* The new varieties were introduced for comparison reasons according to the modifications of the 2nd meeting of the CRP.

resulting in a more effective fixation of caesium compared to other soils (Frissel et al. 1990; Gerzabek et al., 1998; Nisbet, 1993; Skarlou et al., 1996).

Comparing mean TF for all soils and for the two studied varieties (corn-Corduna and cabbage-Kozanitiko), there was a significant decrease ($P < 0.001$) of the mean TF in the 2nd year (Tables 2 and 3). This reduction may be attributed to the effect of time and/or to the addition of potassium fertilizer. TF values of cabbage and corn showed the same trend as in the previous year (higher in soil 3, lower in soil 2). This behaviour supports previous results, that if a crop species has a high or low TF in a soil then all crop species will show the same behaviour in that soil (Skarlou et al., 1996; Massas et al., 2002).

Table 2: Transfer factors of ^{134}Cs (Bq kg^{-1} D.W. plant / Bq kg^{-1} D.W. soil) of corn plants grown on the four soils.

Soil	Corduna 1 st year		Corduna 2 nd year		Elite 2 nd year	
	Seeds	Vegetative	Seeds	Vegetative	Seeds	Vegetative
1	0.036*	0.230 (0.051)	0.015*	0.090 (0.019)	0.029 (0.004)	0.155 (0.019)
2	0.005 (0.001)	0.037 (0.009)	0.004*	0.026 (0.008)	0.007 (0.002)	0.056 (0.017)
3	0.127	0.677 (0.233)	0.072	0.369 (0.046)	0.098 (0.015)	0.655 (0.101)
4	0.070*	0.440 (0.094)	0.061	0.310 (0.072)	0.040 (0.007)	0.184 (0.042)
Mean	0.060 (0.052)	0.346 (0.275)	0.038 (0.034)	0.199 (0.166)	0.044 (0.039)	0.265 (0.272)

* calculated values

Table 3: Transfer factors of ^{134}Cs (Bq kg^{-1} D.W. plant / Bq kg^{-1} D.W. soil) of cabbage plants grown on the four soils.

Soil	Kozanitiko		Brunswick 2 nd year
	1 st year	2 nd year	
1	0.183 (0.020)	0.051 (0.022)	0.137 (0.044)
2	0.071 (0.022)	0.030 (0.008)	0.061 (0.057)
3	1.036 (0.175)	0.237 (0.117)	0.469 (0.138)
4	0.370 (0.090)	0.137 (0.037)	0.420 (0.099)
Mean	0.415 (0.432)	0.114 (0.094)	0.273 (0.203)

For both species the TFs of the two new varieties of corn and cabbage (Elite and Brunswick, respectively) were significantly higher ($P < 0.01$) than the respective values of Corduna (corn) and Kozanitiko (cabbage) (Tables 2 and 3). These differences have to be confirmed by next year's data.

Conversion factors and reference TFs

In a recent publication Frissel et al. (2002), described a method to correlate radiocaesium uptake as a function of the soil type. It is based on two observations. The first is, that most individual species of a crop group show almost the same soil-to-plant uptake factors on the same soil and second is, that between crop groups uptake factors seem to be more or less constant.

A reference transfer factor (reference TF) depending solely on soil properties is derived for a reference crop. A requirement for the reference crop is that this should be widely cultivated and that sufficient data are available. Crops are divided into groups, depending on the characteristics of the group; cereals serve as a reference group. The transfer of the other groups can be calculated by multiplying values for cereals with a conversion factor.

Based on this method conversion factors for cabbage were calculated (Tables 4 and 5).

Table 4: Calculated ratios TF cabbage (Kozanitiko) / TF corn (Corduna)

<i>Soil</i>	<i>1</i>	<i>2</i>	<i>3</i>	<i>4</i>	<i>Mean</i>
<i>Year 2000</i>	6	13	6	5	7
<i>Year 2001</i>	3	8	3	2	4

The calculated ratio ^{134}Cs TF cabbage / ^{134}Cs TF corn (seeds) in the four soils was reduced the 2nd period and ranged from 2 to 8 (7 to 13 in the 1st year) with a mean of 4 (7 in the previous year).

Meanwhile, no significant difference between the ratios of the two years was observed probably due to the wide range of the values.

Table 5: Calculated conversion factors

	<i>Corn</i>	<i>Cabbage</i>
Cs conversion factor	1	4
Range		3 - 8

Considering the ratios TF cabbage / TF corn for all studied varieties and in all possible combinations gave mean values ranging from 2 to 15 with a mean value of 6 (N=16). This value is very close to that of the previous year (mean value 7) and it coincides with the generic values reported by Frissel et al. (2001) for cereals and leafy green vegetables.

A first attempt was also made to classify the studied soils according to reference TFs of corn seeds for the two varieties (Table 6). In general no significant differences were observed either between the two years (var. Kozanitiko) or between the two varieties.

Table 6: Reference ¹³⁴Cs TFs for corn

Soil type	Corduna		Elite
	1 st year	2 nd year	2 nd year
<i>Calcareous-Clay</i>	0.005	0.004	0.007
<i>Acid-Sand</i>	0.015	0.015	0.029
<i>Volcanic</i>	0.100	0.066	0.069
Mean	0.048 (0.048)	0.028 (0.033)	0.035 (0.031)

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RADIOACTIVITY OF PAPRIKA (CAPSICUM) APPLYING ARTIFICIAL CONTAMINATION OF SOIL AND PLANT

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Introduction

The transfer of radiocesium and radiostrontium from contaminated soil to plants has been studied extensively throughout the world since the 1960s. Numerous laboratory and field experiments with artificially contaminated soil, and studies on the transfer of radionuclides from test weapons and radiation accidents fallout have yielded the basic understanding of the processes and factors governing the uptake of strontium and cesium by plants (Kroughev et al. 1997, Papastefanou et al. 2002, Rauret et al. 1995). A special emphasis was given to the long-term trend in plant availability of radionuclides. It is now well established that changes in the radionuclide soil-to-plant transfer depend on the interactions of a large number of factors acting on both plant physiology and soil chemistry levels (Massas et al. 2002, Simon 1996).

In our study the fate of ^{134}Cs and ^{85}Sr in the above ground of paprika plants after wet deposition on soil and leaves was examined under field experiment conditions. The aim of foliar contamination was to determine the ^{134}Cs and ^{85}Sr uptake by paprika depending on the time and level of radioactive contamination.

Materials and methods

The field experiment of paprika was established on alluvial meadow clay soil on 10th May 2001. Some soil characteristics of the experimental field: pH (KCl): 6.55, Viscosity: 52, Organic matter: 2.86%, Available P (AL-method): 140 ppm, Available K (AL method): 180 ppm. Variety of paprika: Feherozon. (Hungarian).

At the same time of the planting of paprika we have contaminated the soil by watery solution of ^{134}Cs and ^{85}Sr isotopes in different amount of solution: 1, 10, 20, 30l/m². We have repeated the same treatments during the vegetation season on 10th July. The soil and plant surface were contaminated by radioactivity 2.3125 MBq/m².

The paprika was harvested at full ripening stage, on 18th July, 13th August, 30th August, 20th September, 3rd October. So, the yield was picked 5 times during the vegetable season, and finally stems, leaves and roots of plants were collected. The radioactivity of each plant part was determined separately. The isotope uptake of plants from the soil was characterised by the transfer factor.

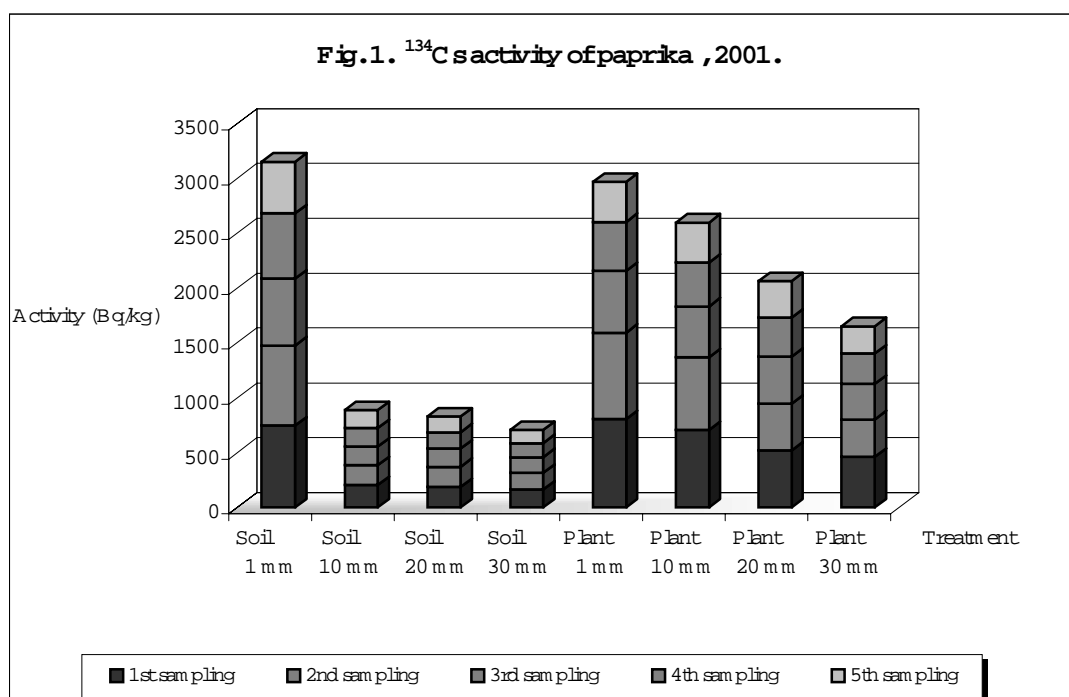
Results and discussion

The radioactivity of paprika plants was measured in the edible part, leaves, stem and root samples after harvest. In Table 1. are shown the data of yield of paprika. The average yield of fresh paprika was 6661g/m² and the yield of by-products was 336 g dry weight/m².

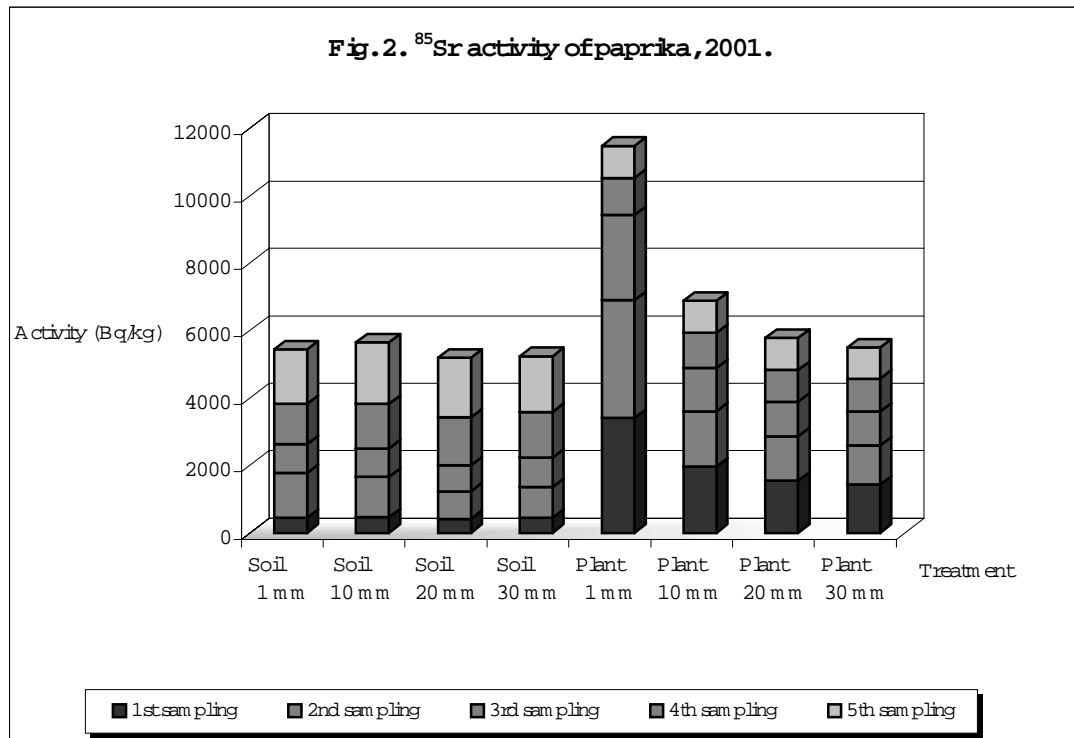
Table 1. Data of yield of paprika experiment, 2001.

Treatment			Yield, g/m ²			
Cod e	Time	l/m ²	Paprika, fresh	Leaves, dry matter	Stem dry matter	Root dry matter
P/1	05. 10.	1	5400	143,80	35,44	106,36
P/2	05. 10.	10	5610	131,40	28,12	120,52
P/3	05. 10.	20	4740	100,80	27,68	86,36
P/4	05. 10.	30	5950	140,28	34,44	138,96
P/5	07. 10.	1	7780	132,68	41,12	111,56
P/6	07. 10.	10	7620	102,40	34,12	87,76
P/7	07. 10.	20	7650	126,76	45,20	107,68
P/8	07. 10.	30	9700	100,24	36,60	57,52
P/9	∅	0	5500	115,20	27,32	80,32
Average			6661	203,75	33,34	99,67

The results of ¹³⁴Cs radioactivity of fresh paprika are shown in Fig. 1. The specific activity of paprika has changed between 600-3000 Bq/kg fresh weight depending on the amount of water solution. The radioactivity of edible part depended on the amount of precipitation.



The ^{85}Sr activity of capsicum varied between 5000-11000Bq/kg fresh weight. (Fig. 2.). The radioactivity of edible part increased during the plant contamination.



The isotope uptake of plants from the soil was characterised by the transfer factor (TF). In Table 2 are summarised TF values of paprika (capsicum)..

Table 2. Soil-plant transfer factors for paprika. 2001.

Code	^{134}Cs : Transfer factor, $\text{m}^2 (\text{kg dry matter})^{-1} * 10^{-3}$					
	1. sampling	2. sampling	3 sampling	Dried paprika	4. sampling	5. sampling
P/1	0,3240	0,3140	0,2640	13,50	0,2580	0,2030
P/2	0,0886	0,0788	0,0729	0,939	0,0735	0,0704
P/3	0,0817	0,0788	0,0715	0,761	0,0652	0,0618
P/4	0,0707	0,0659	0,0620	0,736	0,0551	0,0513
Code	^{85}Sr : Transfer factor, $\text{m}^2 (\text{kg dry matter})^{-1} * 10^{-3}$					
	1. sampling	2. sampling	3. sampling	Dried paprika	4. sampling	5. sampling
P/1	0,196	0,571	0,370	1,99	0,516	0,701
P/2	0,202	0,516	0,366	2,13	0,572	0,786
P/3	0,181	0,353	0,330	2,21	0,621	0,761
P/4	0,191	0,397	0,375	2,25	0,590	0,715

Based on the measurements it was found that the TF value characterising the ^{134}Cs contamination of the yield changed between $0,0513-0,324 \cdot 10^{-3} \text{ m}^2 (\text{kg dry matter})^{-1}$ depending on the amount of precipitation. The ^{134}Cs accumulation was the highest in the leaves after plant contamination.

Table 3. Soil-plant transfer factors for by-products. 2001.

Code	^{134}Cs : Transfer factor, $\text{m}^2 (\text{kg dry matter})^{-1} \cdot 10^{-3}$			
	Seed	Stem	Leaves	Root
P/1	1,570	1,11	1,87	1,36
P/2	0,563	1,46	3,37	3,06
P/3	0,666	1,48	2,12	2,04
P/4	0,612	1,05	3,05	3,07
Code	^{85}Sr : Transfer factor, $\text{m}^2 (\text{kg dry matter})^{-1} \cdot 10^{-3}$			
	Seed	Stem	Leaves	Root
P/1	2,860	13,4	4,96	3,23
P/2	0,337	14,5	9,19	7,50
P/3	0,277	14,0	6,35	4,59
P/4	0,228	7,66	6,63	4,31

In Table 3 are shown TF values of by-products. The stems and leaves of Paprika (capsicum) were highly contaminated in case of soil contamination and the transfer factors were much higher than for fruits. The ^{85}Sr uptake of stems and leaves continuously increased at time of plant contamination. The increase was higher than 300% as compared to the soil contamination.

CONCLUSIONS

- The ^{134}Cs and ^{85}Sr uptake of paprika increased after foliar contamination.
- The activity rate of paprika and stems have changed with all treatments, the ^{134}Cs activity of stems was higher in all cases comparing to the paprika fruit.
- The radioactivity of paprika and by-products samples decreased parallel with increasing amount of precipitation.
- It was found that the TF value characterising the ^{134}Cs contamination of the yield changed between $0,0513-0,324 \cdot 10^{-3} \text{ m}^2 (\text{kg dry matter})^{-1}$ depending on the amount of precipitation. Stems and leaves of capsicum were highly contaminated in case of soil contamination and the transfer factors were much higher than for fruits.

- The TF values of ^{85}Sr fluctuated between $0,181-0,786 \cdot 10^{-3} \text{ m}^2 (\text{kg dry matter})^{-1}$ in the yield. The highest radioactivity was shown by the stem of paprika (capsicum) and the TF values were also the highest in these parts with values of $4,96-9,19 \cdot 10^{-3} \text{ m}^2 (\text{kg dry matter})^{-1}$.
- The TF values for ^{85}Sr uptake of paprika are several times higher than those for the ^{134}Cs uptake of paprika. According to the activity results of the experiments there was significant difference between the contamination of the plant parts.

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BIOAVAILABILITY OF RADIOSTRONTIUM IN SOIL: PARAMETERIZATION USING SOIL CHARACTERISTICS

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Summary

A mechanistic model that predicts the radiostrontium uptake by plants is proposed. The model includes a three-chain system: solid soil- soil solution- plant root. It's shown that the radiostrontium soil-to-plant transfer factor can be parameterized through readily available soil characteristics: the radiostrontium exchangeability and the exchangeable calcium. The model was tested for a wide range of Russian soils using the radiostrontium uptake data for barley and lupine in a pot trial. Barley and lupine were grown for 14 days on ten soils artificially contaminated by ^{90}Sr . Good agreement of the model predictions with the experimental data allows a recommendation of the approach for adaptation in a Geographical Information System predicting food chain contamination for a radiostrontium deposit in agricultural systems.

Introduction

A key component in the estimation of food chain contamination by the radionuclide is the evaluation of soil-to-plant transfer factor (TF), which is the ratio of the activity concentration in the plant to that in the soil. The values of TF determined experimentally in different conditions for a particular plant can differ by a factor hundred or thousand (IAEA, 1994). Therefore, using a plant-average TF leads to a considerable uncertainty in the prediction of food contamination by radionuclide.

For the best evaluation of TFs it's necessary to develop mechanistic models that predict radionuclide uptake by plants taking into account the mechanisms of sorption-desorption and fixation-remobilization of radionuclides in the soil as well as root uptake processes controlled by the plant. An equilibrium model that predicts the radiocaesium transfer to forest plants (Konoplev et al., 1997) from readily available soil parameters has recently been developed. The similar approach could be used for radiostrontium uptake. The objectives of this study were to identify soil properties contributing to variation in ^{90}Sr TF, develop a predictive model and to parameterize TF through soil characteristics.

Model development

The conceptual model of radiostrontium soil-to-plant transfer includes 3 compartments: the solid soil, the soil solution and the plant. The model takes into account ion exchange sorption-desorption processes on the soil and ion exchange at the root exchange complex (REC). It is usually assumed that Sr may be absorbed by the transport systems of its nutrient analogue Ca. Prior to plant uptake, the radionuclide must pass through the cell wall free space, characterised by a specific cation exchange capacity, the bulk fraction of which is associated with carboxylic groups (Haynes, 1980). The most accepted mechanism for Ca uptake is

passive movement through the volume of the cell wall, where ions are in equilibrium between the soil solution and the REC. The effect of the root exchange complex on Sr transfer from soil to plant has been demonstrated by the linearity of strontium uptake by plant and root cation exchange capacity (Mouat, 1960).

The proposed model of radiostrontium soil-to-plant transfer is based on the following assumptions:

- only the exchangeable portion of Sr inventory in the soil is involved in the immediate exchange with the soil solution;
- Sr^{2+} is taken up by the plant from the soil solution, and its concentration in the plant is a linear function of the radionuclide loading in the root exchange complex;

$$[{}^{90}\text{Sr}]_{\text{plant}} \sim Z_{\text{Sr}} \quad (1)$$

- Ca^{2+} is the main competitive cation for Sr^{2+} .

The ionic composition of the root exchange complex is governed by the composition of its equilibrium solution. The selectivity coefficient for the Sr/Ca equilibrium can be written as:

$$K_{(\text{Sr}/\text{Ca})}^{\text{REC}} = \frac{Z_{\text{Sr}} [\text{Ca}]_{\text{ss}}}{Z_{\text{Ca}} [\text{Sr}]_{\text{ss}}} \quad (2)$$

where Z_{Sr} , Z_{Ca} - the fractional loading of Sr and Ca in the REC; $[\text{Sr}]_{\text{ss}}$, $[\text{Ca}]_{\text{ss}}$ - molar concentrations in the soil solution. Equation (2) can be rewritten as:

$$\frac{Z_{\text{Sr}}}{Z_{\text{Ca}} \rightarrow 1} = K_{(\text{Sr}/\text{Ca})}^{\text{REC}} \frac{[\text{Sr}]_{\text{ss}}}{[\text{Ca}]_{\text{ss}}} \quad (3)$$

The solid soil and the solution are in equilibrium. Sr/Ca ratio in the solution is related with the composition of the soil exchange complex as:

$$\frac{[\text{Sr}]_{\text{ss}}}{[\text{Ca}]_{\text{ss}}} = \frac{1}{K_{(\text{Sr}/\text{Ca})}^{\text{SOIL}}} \frac{[\text{Sr}]_{\text{ex}}}{[\text{Ca}]_{\text{ex}}} \quad (4)$$

where $K_{(\text{Sr}/\text{Ca})}^{\text{soil}}$ - the selectivity coefficient for the Sr/Ca equilibrium in the soil; $[\text{Sr}]_{\text{ex}}$, $[\text{Ca}]_{\text{ex}}$ - the content of exchangeable cations in the soil. Since both ion exchange complexes, the soil and the root, are in equilibrium with the same soil solution, we can combine equations (3) and (4) to give the fractional loading of the radionuclide in the REC:

$$Z_{\text{Sr}} = \frac{K_{(\text{Sr}/\text{Ca})}^{\text{REC}}}{K_{(\text{Sr}/\text{Ca})}^{\text{SOIL}}} \frac{[\text{Sr}]_{\text{ex}}}{[\text{Ca}]_{\text{ex}}} \quad (5)$$

$K_{(\text{Sr}/\text{Ca})}^{\text{REC}}$ is governed by the composition of the cell wall matrix that is a plant species dependent. As values of the selectivity coefficient for the Sr/Ca equilibrium for most mineral soils are close to 1 (Khasawneh et al., 1968), we can neglect the differences in values of $K_{(\text{Sr}/\text{Ca})}$ for soils under study. TF is written by substituting equation (5) in equation (1):

$$TF = \frac{[^{90}\text{Sr}]_{\text{plant}}}{[^{90}\text{Sr}]_{\text{soil}}} \sim \frac{Z_{\text{Sr}}}{[^{90}\text{Sr}]_{\text{soil}}} \sim \frac{[^{90}\text{Sr}]_{\text{ex}}}{[^{90}\text{Sr}]_{\text{soil}}[\text{Ca}]_{\text{ex}}} \sim \frac{\alpha_{\text{ex}}}{[\text{Ca}]_{\text{ex}}} \quad (6)$$

where α_{ex} is the portion of the exchangeable ^{90}Sr in the soil. The ratio $\alpha_{\text{ex}}/[\text{Ca}]_{\text{ex}}$ may be accepted as a *bioavailability factor* ^{90}Sr (A). It follows that ^{90}Sr transfer from soil to plant is described by a linear function of the *bioavailability factor* (A):

$$TF(^{90}\text{Sr}) = B \cdot A \quad (7)$$

where B is a plant species dependent characteristic. In fact, equation (6) can be used as a basis for prediction of TF. The bioavailability factor ^{90}Sr is the combination of two soil parameters: 1) portion of exchangeable form of ^{90}Sr (α_{ex}) characterising the fixation ability of the soil; 2) content of the exchangeable calcium.

Materials and methods

The model was tested using the radiostrontium uptake data for barley and lupine in a laboratory pot trial. Barley and lupine were grown for 14 days on ten soils artificially contaminated by ^{90}Sr . Soils were sampled from the arable horizons (0-20 cm) at locations situated in different soil-climatic zones of the European part of Russia. General soil properties were determined as follows: pH in a 1:2,5 soil/1M KCl suspension (for peat S/L 1:25); soil texture using the pipette method, humus content with a wet combustion technique using $\text{K}_2\text{Cr}_2\text{O}_7$ and H_2SO_4 ; the exchangeable cations (Ca, Mg, K) in 1 M NH_4OAc soil extract (S/L 1:10) by atomic absorption spectrophotometry. The CEC was calculated by summing exchangeable cations and potential acidity estimated using 1M CH_3COONa . Physico-chemical soil characteristics are given in table 1.

Soils were sown with 10 (lupine) and 15 (barley) germinated seeds per pot. Soil weight per pot varied between 375 and 500 g. Four replicates were used per type of soil. The ^{90}Sr activity in the soil and plant samples was counted using a beta-counter "Nuclear Chicago". The ^{90}Sr activity in soil was 100 Bq g^{-1} dry weight.

Table 1. Physico-chemical characteristics of soils

№	Soil	pH _{KCl}	Humus, %	Clay, % (<0,001 mm)	Exchangeable cations			CEC
					K ⁺	Ca ²⁺	Mg ²⁺	
					cmol _c kg ⁻¹			
1	typical chernozem	6,2	2,8	35,9	0,76	28,4	4,7	36,8
2	ordinary chernozem	6,1	2,8	29,6	0,66	26,6	5,4	36,2
3	podzolized chernozem	6,9	1,6	21,2	0,46	28,7	2,0	31,8
4	meadow chernozem	7,0	1,4	28,2	1,07	23,7	4,2	29,8
5	leached chernozem	5,6	1,6	18,9	0,37	22,5	4,2	30,0
6	soddy podzolic	5,8	1,8	3,6	0,37	4,8	1,3	9,4
7	peat	5,5	25,2	-	0,59	40,5	2,4	116,8
8	leached chernozem	5,8	2,1	18,5	0,51	23,3	3,7	32,4
9	grey forest soil	5,4	0,6	14,0	0,45	5,2	1,2	9,2
10	chestnut soil	7,4	1,8	30,7	1,04	24,9	6,2	32,4

Results and discussion

For both plants, the highest TFs were observed for soddy podzolic soil (6), a soil with the lowest clay content. The lowest TFs were found for peat (7), a soil with the highest humus content, and for chernozem (1 and 2), soils with high humus and clay content (Table 2). ^{90}Sr exchangeability in soils under study varied slightly and ranged from 0,6 to 0,9. The bioavailability factors were calculated for soils using eqn (6). The dependence of the ^{90}Sr TF on the bioavailability factor is plotted in Fig.1. It can be seen that this dependence is quite well described by a linear function. The slope of the straight line is a plant species constant B from equation (7). It is defined empirically. The good agreement in the theoretical and the experimental dependencies indicates that the proposed model can be used for obtaining site-specific TF of radiostrontium to plants.

Table 2. Dry weight of shoots (mean±standard deviation), portion of the exchangeable ^{90}Sr (α_{ex}), calculated parameter of the biological availability (A) and ^{90}Sr soil-to-plant transfer factor (mean±standard deviation)

№	Shoot dry weight, g		α_{ex} (^{90}Sr)	A·10 ⁻² , kg /cmol _c	TF(Bq·kg ⁻¹)/ (Bq·kg ⁻¹)	
	barley	lupine			barley	lupine
1	0,49 ± 0,02	0,35 ± 0,04	0,70	2,2	0,67± 0,02	0,60 ± 0,06
2	0,46 ± 0,03	0,48 ± 0,13	0,68	2,6	0,50 ± 0,01	0,52 ± 0,04
3	0,35 ± 0,07	0,74 ± 0,01	0,90	3,1	1,06± 0,09	0,74 ± 0,06
4	0,70 ± 0,10	0,42 ± 0,06	0,66	2,8	0,88 ± 0,04	0,84 ± 0,04
5	0,61 ± 0,07	0,57 ± 0,15	0,80	3,6	1,14 ± 0,50	0,78 ± 0,16
6	0,61 ± 0,15	0,56 ± 0,18	0,88	18,3	4,81 ± 0,49	3,43 ± 0,84
7	0,63 ± 0,02	0,37 ± 0,01	0,73	1,8	0,99 ± 0,04	0,53 ± 0,12
8	0,53 ± 0,05	0,61 ± 0,12	0,61	2,6	1,08 ± 0,09	0,77 ± 0,15
9	0,52 ± 0,18	0,46 ± 0,17	0,70	13,4	4,05 ± 0,39	2,73 ± 0,67
10	0,55 ± 0,19	0,69 ± 0,07	0,79	3,2	0,83 ± 0,07	0,73 ± 0,02

Based on early reports that legumes preferentially uptake Sr as compared to cereal (Aleksakhin, 1991), lupine was expected to show relatively high TF values, but that was not confirmed by the results. One of the possible explanations for these findings might be the difference in stock of cationic nutrients in seeds that is important for seedling growth stage. In previous studies, an increase in radiostrontium root uptake from seedling to mature samples has been reported for pea (Roca et al., 1997). It follows that plant species constant B should be defined for mature plant.

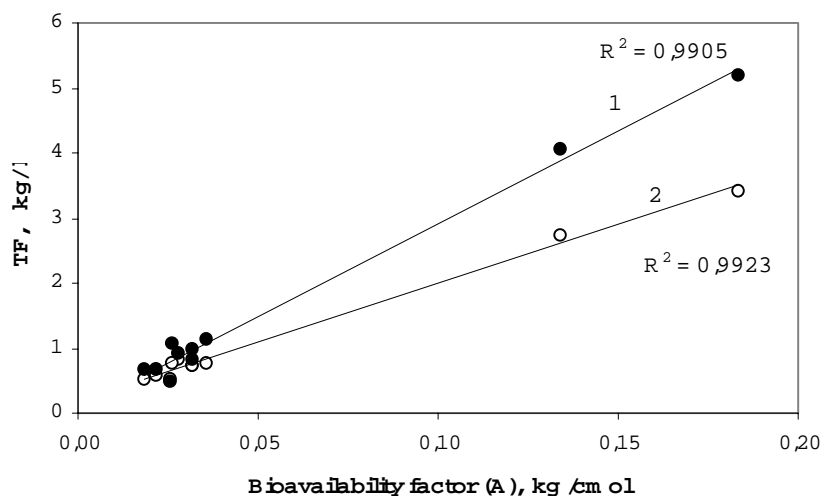


Fig.1 Dependence of ^{90}Sr TF for barley (1) and lupine (2) on the bioavailability factor

Conclusions

- A mechanistic model of radiostrontium soil-to-plant-transfer is proposed.
- It is shown that the transfer factor (TF) should be a linear function of the bioavailability factor A which is the combination of radiostrontium exchangeability and exchangeable calcium.
- The parameterization was tested against the pot trial data on soil-to-plant transfer for a wide range of Russian agricultural soils. A satisfactory agreement has been achieved.
- The approach can be used in radioecological GIS (Geographic Information Systems) to map radiostrontium soil-to-plant transfer factor.

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IS PREFERENTIAL FLOW RELEVANT FOR PLANT UPTAKE IN AREAS CONTAMINATED WITH RADIONUCLIDES

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Summary

The vertical distribution of ^{137}Cs and its chemical forms in soil after the Chernobyl accident depends on its mobility and chemical characteristics, soil structure (grain-size composition and mechanic content) and hydrological features, soil hydromorphity, etc. We are developing a model which can combine fluxes of the radionuclides between the different compartments of the soil and considering it for the following processes: root uptake; transfer into plants; leaf fall; grazing and forest production. The interaction between ^{137}Cs , soil matrix and root distribution have to be taken into account in radionuclide transfer processes assessment. Migration of ^{137}Cs and its chemical forms is delineated by flow patterns in the soil. It was carried out a field experiment on tilled agricultural and forest soils in the South of Belarus affected by the Chernobyl accident. The distinction in accumulation of ^{137}Cs in preferential flow and matrix zones was determined. *Brilliant Blue FCF* was used to dye flow lines and to determine the activity of Chernobyl ^{137}Cs as a function of dye presence and absence. The experiment was carried out on the soddy-podzolic (Podzoluvisols) soils of forest and agroecosystem of South Belarus. Transfer factors of ^{137}Cs were calculated.

1. Introduction

The more recent literature is mostly concerned with measurements and modeling of ^{137}Cs behaviour in soils and plants; this isotope was of principal significance in most of countries affected by contamination from the Chernobyl accident and its 30 year physical half life has ensured that its effects are still being felt in many agricultural communities (Shaw G. and Bell J.N.B., 2001).

After the Chernobyl accident (April, 1986) contamination of the territory of Belarus with ^{137}Cs above 37 kBq/m^2 constituted 23 % of the total area of the republic (Konoplya E.F. and Rolevich I.V., 1996). The total Cs^{137} deposition in Southern Belarus exceeded the level of 1480 kBq/m^2 (Atlas, 1998). Nowadays the main part of total activity is concentrated in soil. It is also known and already calculated that the vertical migration of ^{137}Cs in Podsoluvisol (FAO, 1988) soils estimated to be $0.25 - 0.5 \text{ cm/year}$ (Arapis G. et al., 1997).

However, as recent observations made in forest soils showed that ^{137}Cs content was high in the vicinity of preferential (water) flow paths (Bundt et al., 2000, Flury et al., 1994), we can expect that locally the vertical migration of ^{137}Cs could be faster as previously estimated (Arapis et al., 1997).

The aim of our experiment was then to compare vertical distribution of Chernobyl ^{137}Cs in two different ecosystems in Gomel region, and to determine the activity of ^{137}Cs as a function of presence or absence of *Brilliant Blue FCF* dye as a marker of preferential water flow paths.

2. Materials and methods

Brilliant Blue FCF method (30-km zone, South Belarus)

Field description. The studied area is situated on the Polesye lowland, Sudkovo farm, v. Novosiolki, Khoyniki district, Belarus. It is a monotonous waterlogged flat plain.

For our experiment we took 2 plots (100 × 100 cm) with similar characteristics. Soil type is classified as Podsoluvisol on sandy loam underlying moraine. The difference between plots was in tillage. One plot was situated on the repeated tillage field while another was in the forest where the soil was supposed to be untouched since April 1986. In the field the soil was tilled and harvested two times per year but during our experiment (October, 2001) it was under motley grass.

Plot preparation. All the plants were cut at 5 cm level above the ground from each plot area for γ -analysis; in the forest the litter was removed.

The dye application to the plot area. Brilliant Blue FCF dye was diluted in water in the concentration of 1g/L and was applied to the surface of each plot on 17 October 2001. For this purpose we used a watering can with a flat wide nozzle (volume 10 L). The application of 5 liters of dye was 6 times with the interval in 15 minutes on each plot area (Fig. 1).



Figure 1. Prepared plot after dye application.

Vertical profile observation and soil sampling. The dye distribution was studied by vertical profile observation on 18 October, 2001. Soil samples were taken as described in Fig. 2 and as a function of stained and non-stained zones (Fig. 3). We cut the soil every 20 cm to the 25 cm depth. Every slice was indicated by Latin letters. First slice – A₁, second – B₁, next 20 cm – slice C₁, then – D₁ and E₁. Thus, we received 5 vertical slices: A₁, B₁, C₁, D₁, E₁.

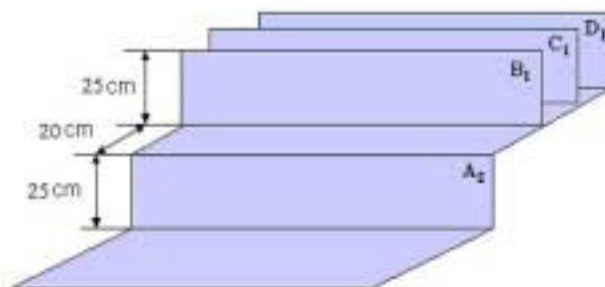


Figure 2. Scheme of vertical profile observation.

Another 5 vertical slices were received by deeping on 20 cm: A₂, B₂, C₂, D₂, E₂.

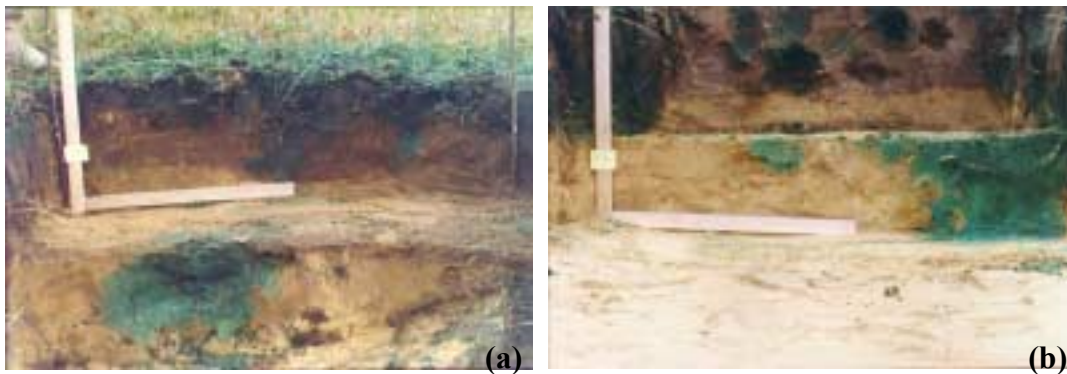


Figure 3. *Brilliant Blue* distribution over the vertical profile. Vertical profile observation in the field (a), forest (b).

Observation of root distribution and sampling. Observation of root distribution consists in signing the root presence on a plastic overlay in a horizontal plane. Root samples were taken from two volumes of soil (20x20x15cm) in the central part of each plot and were washed out of the soil. Once washed out, they were collected in plastic bags and freeze dried for 24h. Afterwards they were weighed and grinded for the γ -spectrometry.

Soil-plant samples preparation for γ -spectrometry. All plant and soil samples were first weighed as fresh, cut into small pieces and afterwards dried for 24 hours for air-dry weight. The ^{137}Cs content of the samples was assayed by γ -spectrometry and *Brilliant Blue* concentration was determined on UV-visible spectrophotometer UV-1601.

3. Results

In agricultural soil ^{137}Cs was evenly distributed throughout the tilled layer (0-20 cm) (Fig.4a). In forest most of ^{137}Cs was in the 0-5 cm horizon (Fig. 4b). In 0-20 cm forest soil and 5-15 cm field soil ^{137}Cs concentration was higher in the matrix (unstained area) than in the flow paths (stained area) (Fig. 4a,b).

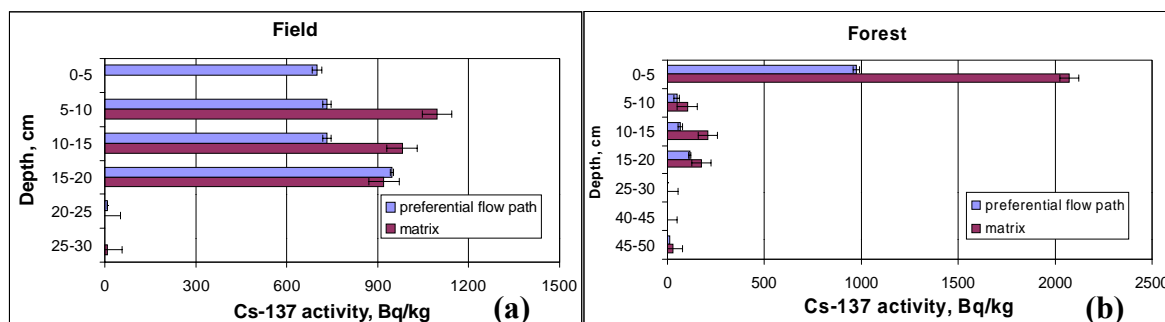


Figure 4. Differences in activities of ^{137}Cs in preferential flow paths and matrix in an agricultural soil (a) and forest soil (b) with depth.

Plants grown on the forest soil had higher activity than the plants grown in the tilled agricultural soil. ^{137}Cs concentration in roots grown in the field was lower than in roots grown in the forest (Table 1).

Table 1. Concentration of ^{137}Cs in different plants grown in the field and in the forest.

Plant type	Field		Forest	
	Dry matter, g/m ²	^{137}Cs activity, Bq/m ²	Dry matter, g/m ²	^{137}Cs activity, Bq/m ²
Motley grass (Compositae, Ranunculaceae, Poacea) and forest graminiae	172	16.9±2.1	117	81.3±3.1
Litter	-	-	375	583.3±7.5
Roots (0-20 cm)	8	0.9±0.1	12.3	38.7±0.4

^{137}Cs activity in the stained area of the forest soil is proportional to *Brilliant Blue* dye concentration only in the deepest 40-50 cm level, while in the field no relationship was found.

As a result of analyses of soil and plant samples, physical and chemical soil characteristics of studied area were defined (Tables 2 and 3).

Table 2. Soil characteristics of experimental plots

Plot	Depth, cm	Soil type	Hygroscopic moisture, %	pH _{H2O}	Soil density, g/cm ³
Field	0 – 20	Soddy-podzolic	0,64	6,86	2,52
	20 – 40	(Podzoluvisols)	0,43	6,85	2,55
Forest	0 – 20	Soddy-podzolic	0,93	5,75	2,29
	20 – 40	(Podzoluvisols)	0,77	6,65	2,66

Table 3. Cation exchange capacity of Podzoluvisol soil of Sudkovo farm

Plot	Depth, cm	Exchangeable cations, mEq/100g soil				
		K ⁺	Na ⁺	Mn ²⁺	Co ²⁺	Fe ³⁺
Field	0 – 20	18,7	2,2	3,7	2,7	2,9
	20 – 40	16,9	1,6	2,5	2,5	2,7
Forest	0 – 20	5,6	1,9	3,4	2,4	3,1
	20 – 40	4,1	1,9	1,5	2,3	2,6

The soil-to-plant transfer factor (TF) is often used to predict radiocaesium accumulation by crops. The quantitative characteristic of ^{137}Cs accumulation by plants is described by the transfer factor, which allows to compare the rate of ^{137}Cs entry into the plants of different ecosystems. We calculated the transfer factor as the following ratio (FAO / IAEA / IUR, 1998):

$$\text{TF} = \frac{C_{\text{plant}}}{C_{\text{soil}}} \quad (1)$$

where C_{plant} is ^{137}Cs activity concentration (Bq/kg) of dry weight of plants and C_{soil} is ^{137}Cs activity concentration (Bq/kg) of dry 20 cm depth soil.

In table 4 calculated transfer factors are presented. They allow to conclude about peculiarities of ^{137}Cs accumulation by plants of two different ecosystems. Thus, for agricultural field the values of TF are not so high as for the forest.

Table 4. Transfer factors for plants of two different ecosystems

Plant	Transfer factor (TF)	
	Field	Forest
Motley grass	0,11	-
Forest graminae	-	0,51
Litter	-	1,14
Roots	0,14	2,32

These values depend on radionuclides concentrations in the soil. Total amount of $^{137}\text{Cs}/\text{m}^2$ in the 0-20 cm horizon was higher in the forest soil (79,3 kBq/m²) than in the agricultural soil (49,7 kBq/m²).

Table 5. The quantitative characteristic of ^{137}Cs accumulation by roots and vegetative mass of plants grown in the field and in the forest of Sudkovo farm

Part of the plant	^{137}Cs activity concentration, Bq/kg	
	Field	Forest
Vegetative mass	98,8 ± 12,3	503,8 ± 23,6
Roots	121,2 ± 17,3	3149,9 ± 35,6

In table 5 the results of measurements of ^{137}Cs activity in root system and plant vegetative mass of two studied areas are presented. These data show that in the forest 86% of ^{137}Cs activity concentration is concentrated in roots, at the same time in the agroecosystem – 59,9% from total activity.

4. Discussion and conclusions

Field experiments have shown significant difference in activity of preferential flow zone and matrix on the depth 20-40 cm. Agricultural soils have equal distribution of radionuclides in the ploughed zone (about 20 cm), while forest soils have distinction in vertical distribution. First 5 cm layer have no any differences between preferential flow and matrix zone because of high ^{137}Cs activity concentration in the litter and silt. In deep layers we could find active preferential flow paths. For automorphic soils the main way of radiocaesium distribution is mechanic transportation on colloidal particles. Also the greatest activity of radiocaesium could be found on the silt fractions of the soil.

Lower activity in the field than in the forest is due to export of ^{137}Cs by crops. It can also be explained by additional contamination from trees and plants in the forest. Besides, agricultural lands are often exposed to soil erosion. Soil ploughing induced a homogeneous mixing of ^{137}Cs in the ploughed layer in the agroecosystem (but there is no ^{137}Cs below 20 cm).

In forest most of activity remained in the upper 5 cm layer (sorbed to humus) and what has leached below 5 cm partly transferred with preferential (water) flow paths. ^{137}Cs concentration in plants grown in the forest is higher than in the field because of higher ^{137}Cs activity in the upper layer and shallow root system.

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MEASUREMENT AND MODELING OF ^{137}Cs IN SOIL AND BIOMASS OF A PREALPINE SPRUCE FOREST

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Summary

The study area is located north of Lake Constance in the south of Germany. Soil samples of podzolic Luvisol type silty loam on a bedrock of young moraine were taken in 1987 and in 1991, 1995, 1997, and 2002. The variation of the ^{137}Cs inventory in the soil ranged from 7 kBq/m² to 17 kBq/m². Compartment model fits for the measured distributions of ^{137}Cs in soil are compared to existing models like RIFE and good agreement is obtained. Residence half-lives of ^{137}Cs in horizon O_h of about 2 years in non-fertilised soil and 3.5 years in fertilised soil are observed for 15 soil profiles from the sampling site and 15 soil profiles from a neighbouring site, treated in 1984 with a fertilizer, 2.5 t/ha. consisting mainly of CaCO₃.

Ecological half-lives of green plants showed values between 2 and 6 years for the first 8 years, however since 1995 aggregated transfer factors soil-plant for fern, blackberry, bilberry, raspberry, and wood sorrel are more or less constant in time.

1. Introduction

We have measured different components of the spruce forest ecosystem with respect to ^{137}Cs : soil, under-storey vegetation, fruit bodies of mushrooms, trees, and wild animals. The distribution of ^{137}Cs inventories of these components measured in the year 2000 is about 91 % in soil, and 6 % in spruce trees if we assume about 3 % in the other components, Zibold et al 2001. To interpret earlier data, Lindner et al. 1994, and Bürmann et al. 1994, and new data on soil profiles from the same sites we used a compartment model similar to RIFE1 to calculate the ^{137}Cs fluxes between components.

2. Materials and methods

Objects of research were samples of plants and soils (number of soil samples: 20, 4, 4, and 2 collected in 29.04.91, 20.09.95, 24.09.97, and 26.04.02 respectively) from neighbouring sites of an 80 to 100 years old spruce stand (*Picea abies* 80 %, *Abies alba* 15%, *Larix spec.* 5%), located in Altdorfer-Wald in the pre-alpine region in south-west Germany (GPS coordinates 9° 41' 26'' E and 47° 44' 45'' N, altitude 650 m).

The soil under study is classified as brown forest soil, podzolic Luvisol, soil family silty loam, with a grain size distribution in (%): clay 17-30; silt 50-70, and sand 0-30 as taken from maps of forest authorities. In 1984 one of the neighbouring sites was treated with a fertiliser consisting mainly of CaCO₃ (83% CaCO₃, 8% MgO, 6% K₂O, 3% P₂O₅) with an amount 2.5 t/ha. Soil samples were taken at each site, each within a frame of 40 cm x 40 cm. and separated during sampling according to the different soil horizons, which were identified in situ by their colour, texture, mean grain size and smell. The thickness of the different horizons was measured and after removal of stones and tree roots, the material of the horizons was air-dried for two weeks. After sieving (2 mm), the ^{137}Cs inventories of the different horizons were measured by gamma spectrometry using HPGe detectors.

Activity concentrations of plant species growing within the sampling frame and within a radius of about 5 m of the sampling site were determined after drying at 105 °C . The sampled species were mainly fern (*Dryopteris carthusiana*), bilberry (*Vaccinium myrtillus*), raspberry (*Rubus idaeus*), blackberry (*Rubus fruticosus*), and wood sorrel (*Oxalis acetosella*). The relative uncertainty of the measured activities is <5% for ^{137}Cs . All activities are decay-corrected to May 1st 1986.

3. Results and discussion

In Figure 1 a survey of the averaged soil depth profiles is given with respect to ^{137}Cs activity concentration. We calculated the activity concentration for the date of sampling, as defined by “inventory divided by thickness of horizon”. Geometric means for each sampling date and plot with respect to thickness of horizon and inventory were calculated. The inventories were normalised with respect to the geometric mean of the total ^{137}Cs inventory of 30 samples at 1.05.86. Maxima of the ^{137}Cs activity concentration were found to be in almost all samples within the O_h or A_h horizons, which means that the migration rates of ^{137}Cs are small.

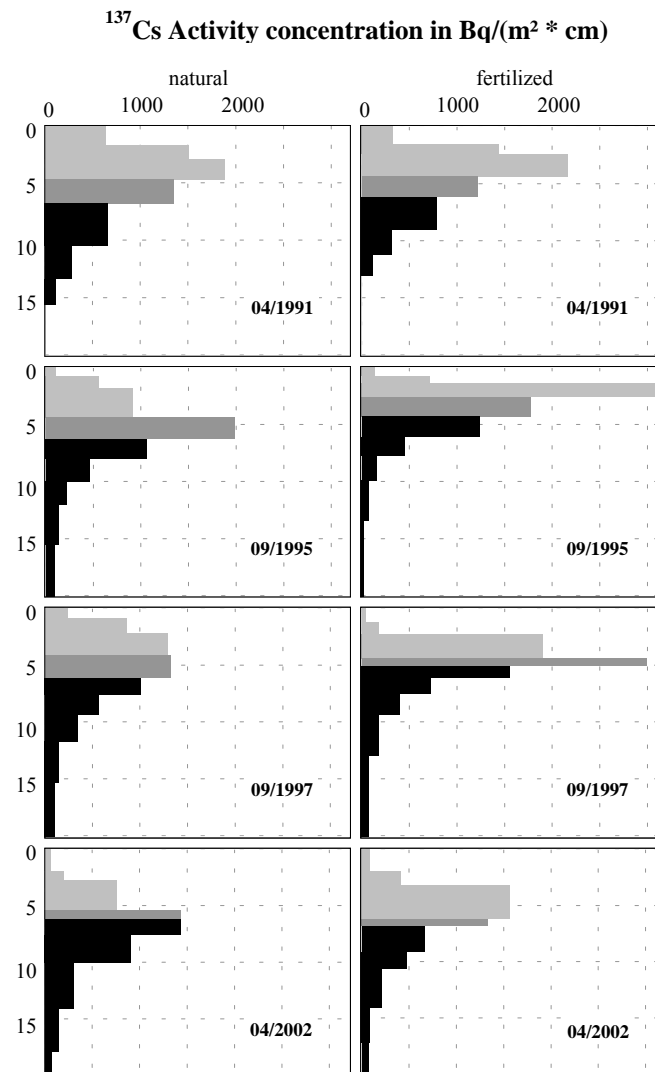


Figure 1: ^{137}Cs activity concentration of natural spruce forest soil horizons (left), and fertilized spruce forest soil (right). Organic horizons (humus layer) are light grey, mineral horizons are black, and A_h is in between.

Values are given in Table 1. The depth of the ^{137}Cs peak (lower bound) increased only in recent years. The thickness of the humus layer (L , O_f , and O_h) stays more or less constant over the years as well as the fraction of ^{137}Cs in organic horizons.

Table 1: Properties of soil profiles in spruce forest

Podzolic Luvisol, nonfertilized				
Sampling date	29.04.91	20.09.95	24.09.97	26.04.02
T_{ag} (fern) [m^2/kg]	0.46	0.37	0.205	0.3548
Total ^{137}Cs inventory [Bq/m^2]	13280	8711	11981	8339
Inv. of org. horizons ($L/O_f/O_h$)	6649	2370	4143	1987
Fraction of ^{137}Cs in org. horizons	0.501	0.272	0.346	0.238
Thickness of humus layer (cm)	4.7	4.4	4.0	5.4
Peak of ^{137}Cs activity conc.	O_h	A_h	A_h	B_1
Depth of peak lower bound (cm)	4.7	6.3	6.1	9.1
pH value (CaCl_2)	3.9 / O_f 3.6 / O_h 3.7 / A_h	3.7 / O_f 3.2 / O_h 3.2 / A_h	3.1 / O_f 2.9 / O_h 3 / A_h	6 / O_f 4 / O_h 3.9 / A_h

All activities are decay corrected to 1.5.86.

pH values are small and due to this fact, aggregated transfer factors T_{ag} as defined by the ^{137}Cs activity concentration in (Bq/kg) of the dry mass of the plant, divided by the total ^{137}Cs inventory (Bq/m^2) of the soil, are high for fern, Drissner et al. 1998 and 1995, and since 1995 T_{ag} of fern is about constant with respect to time.

Data of fertilised soil are collected in Table 2 and results can be summarised as follows.

- maxima of the ^{137}Cs concentration were found to be in almost all samples within the O_h or A_h horizons.
- The depth of the ^{137}Cs peak increased only in recent years.
- The thickness of the humus layer (L , O_f and O_h) stayed more or less constant over the years.
- After liming the fraction of ^{137}Cs in the organic horizon O_h increased.

Conclusion: The above described fertilisation has only a small influence on the spatial distribution of the ^{137}Cs in spruce forest soil.

However, pH values are larger in the fertilised reference plot and due to this fact, aggregated transfer factors T_{ag} for ^{137}Cs are smaller for fern by a factor up to 5, Drissner et al. 1996. For fern a minimum of T_{ag} as a function of time is observed around 1997 indicating the effect of fertilization to become smaller in recent years. This effect is probably caused by an increase of the concentration of competing ions for ^{137}Cs .

Table 2: Properties of soil profiles in spruce forest, fertilised in 1984 with 2.5 t/ha of 83% CaCO₃, 8% MgO, 6% K₂O, and 3% P₂O₅.

Podzolic Luvisol. fertilized				
Sampling date	29.04.91	20.09.95	24.09.97	26.04.02
T _{ag} (fern) [m ² /kg]	0.10	0.07	0.046	0.163
Total ¹³⁷ Cs inventory [Bq/m ²]	16753	16705	17002	10323
Inv. of org. horizons (L/ O _f / O _h)	7937	6205	6689	5724
Fraction of ¹³⁷ Cs in org. horizons	0.474	0.371	0.393	0.554
Thickness of humus layer (cm)	4.3	2.5	4.4	6.1
Peak of ¹³⁷ Cs activity conc.	O _h	O _h	A _h	O _h
Depth of peak lower bound (cm)	4.3	2.5	5.1	6.1
pH value (CaCl ₂)	4.9 / O _f	3.8 / O _f	3.3 / O _f	4.6 / O _f
	4.9 / O _h	3.7 / O _h	3.1 / O _h	4.1 / O _h
	4.8 / A _h	3.5 / A _h	3.2 / A _h	4.2 / A _h

All activities are decay corrected to 1.5.86.

Looking more carefully on the distribution of ¹³⁷Cs in the different horizons an accumulation of ¹³⁷Cs activity concentration is found in the O_h horizon of the fertilised soil as can be seen in Figure 2.

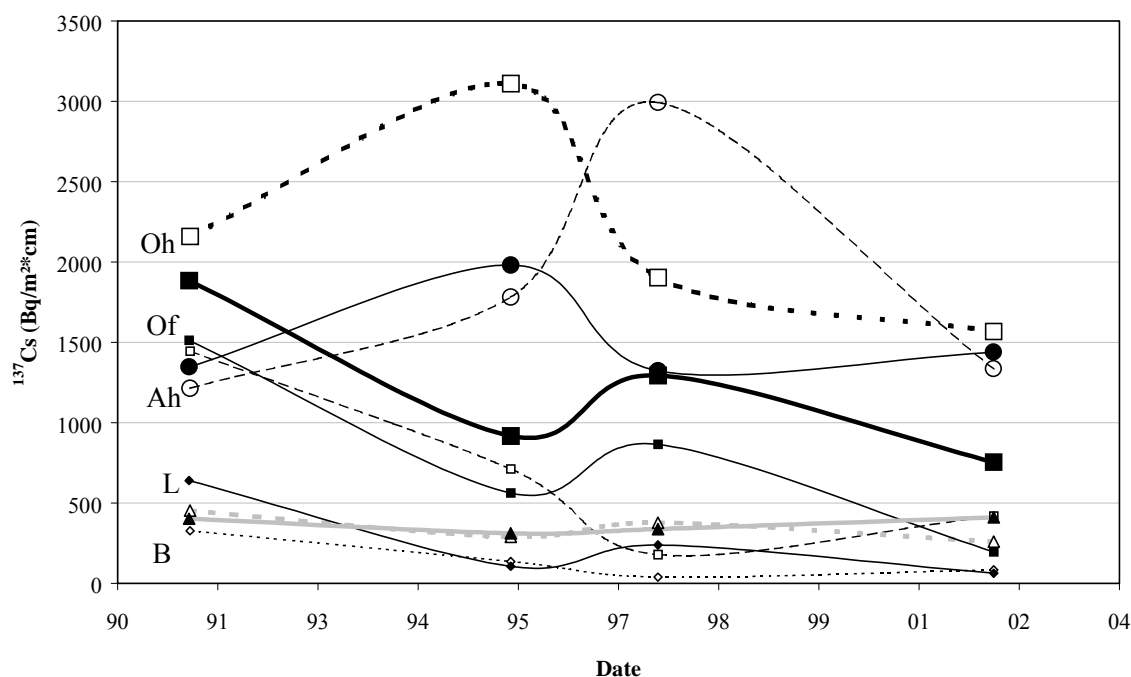


Figure 2: ¹³⁷Cs activity concentration of the different horizons at sampling date. Fertilised plot (dashed) and reference plot (full). Dots are measured values (normalised geometric means), lines are guides for the eye.

We conclude that the fertiliser enhances the production of bio-mass (which has been verified in early summer by looking at the under-storey of the plots) and thus the production of litter contaminated by ^{137}Cs .

To fit the measured ^{137}Cs profiles in soil we used the model RIFE 1, Shaw et al. 1998. Initial inventories of ^{137}Cs at 1.05.1986 are chosen as $I_1 = 68\%$ of the total inventory on the canopy and $I_3 = 32\%$ on the litter surface according to Bachhuber et al. 1982. In addition to the rate coefficients k_1 to k_7 which are calculated in the model, we take into account radioactive decay and get the result listed in Table 3.

Table 3: Effective half-lives obtained with RIFE 1 for Eggwald (EW) and other forests. Belli 2000.

Flow	Half-life	RIFE1 Min (years)	RIFE1 Max (years)	EW (years)	EW Fert. (years)
Tree external - Biomass	T_1	100000	100000	18977	18977
Biomass - Litter	T_2	2.27	5.06	2	1.9
Organic - Biomass	T_3	5.78	69.31	5.9	8.3
Tree external - Litter	T_4	0.45	0.45	0.45	0.45
Litter - Organic	T_5	0.28	2.95	0.17	0.1
Organic - Mineral	T_6	3.47	23.1	5.7	9.5
Mineral-Subsoil	T_7	133	1386	1091	940000

Good agreement is obtained with half-lives of RIFE1, Belli 2000, concerning T_2 to T_6 which are fitted and optimised values. Values for T_1 are assumed values which have not been optimised. Differences between effective half-lives for ^{137}Cs in non-fertilised and fertilised forest soil are very small. although an accumulation in organic horizons due to fertilization is supported by the model as indicated by the increase of T_6 .

To improve our understanding of the liming effect we tried a more detailed model with additional compartments for O_f , O_h , A_h , B_1 , and B_2 soil horizons instead of only organic and mineral horizons. This improved model describes the observed accumulation of ^{137}Cs in the O_h horizon of fertilized soil better than RIFE 1 as shall be demonstrated with the result for residence half-times in the O_h horizon T_{eff} : about 2 y for non-fertilised soil and about 3.5 y for fertilised soil, and the migration rate (thickness of horizon divided by T_{eff}) of ^{137}Cs from O_h to A_h horizon $v_1 = 1.1$ cm/y in the non-fertilised soil and $v_2 = 0.6$ in the fertilised soil. So the accumulation in O_h horizon of fertilized soil can be explained by the model with a smaller migration rate from O_h into A_h horizon.

4. Conclusion

The spatial distribution of ^{137}Cs in spruce forest soil shows little influence of time and liming: During 11 years maxima of the ^{137}Cs activity concentration were found to stay in almost all samples within the O_h or A_h horizons. The depth of the ^{137}Cs peak increased only in recent years. The thickness of the humus layer (L , O_f , and O_h) stays more or less constant over the years. Only the fraction of ^{137}Cs in organic horizon O_h is enhanced after liming. pH increases after liming and as a consequence of this and the increase of the number of competitive ions, the transfer of ^{137}Cs from soil to plant decreases.

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MICROBIAL BIOMASS IN SOIL UNDER CANOPIES OF DIFFERENT FOREST TREE SPECIES EXAMINED USING SIGNATURE FATTY ACIDS

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Abstract

The biomass of microbial community in the humus layer of monocultures of 14 forest tree species were determined by phospholipid fatty acid (PLFA) analyses. The highest mean microbial biomass, measured as concentration of the total PLFAs, was found under canopy of *Betula pendula*, followed by *Carpinus betulus*, *Quercus rubra* and *Pinus sylvestris*. In average there was also more fungal specific fatty acid 18:2 ω 6,9 in soils under *Q. rubra*, *B. pendula* and *C. betulus* than in the rhizosphere of other tree species. Mean concentrations of both, total PLFAs and the fungal specific PLFA 18:2 ω 6,9 under canopies of deciduous species were slightly higher than under coniferous species, however high variability between particular species and plots was found.

Key words: bacteria, fungi, mycorrhiza, phospholipid fatty acid

Introduction

Soil consists of chemical, physical and biological components, and the biological portion is most difficult to quantify. Living component of soil (fungi, bacteria, algae, viruses, microfauna) comprises less than 5% of organic matter in soil. Microbial biomass, however, performs critical functions in soil and the environment. It is responsible for decomposition processes and soil formation, it is a labile source and an immediate sink of C, N, P, S and an agent of nutrient transformation. Soil fungi and bacteria form symbiotic associations with roots and may act as biological agents against plant pathogens. Microbial community includes a wide range of species characterised by various sensitivity to environmental changes (reviewed by Garbaye 1991, Kennedy and Smith 1995).

Different tree species affect the physical, chemical and biological properties of soil under the tree cover a) directly - by their above- and below-ground litter, the root activity and the light and temperature conditions they create in the stand, b) indirectly - by the understorey vegetation established in a stand and by influence of trees on soil microbial population. Microbial growth is stimulated by root exudates, especially sugars and amino acids released by root system. It is known that trees allocate about 40-70% of carbon assimilated by the aerial part below ground and 2-10% of this amount may be exuded by the root system (reviewed by Grayston et al. 1996). Higher concentrations of carbohydrates in the rhizosphere can stimulate the number of microorganisms per gram of soil to be two or three orders of magnitude higher than in the surrounding soil (Garbaye 1991). A high portion of the microbial biomass in forest soils originates from the mycorrhizal fungi, because under natural conditions plant roots are colonized by mycorrhizal fungi (Smith and Read 1997). Most of the tree species in temperate forests are obligatory ectomycorrhizal (ECM) and some of them develop arbuscular mycorrhiza (AM).

The microbial community structure in soil can be detected by analysing of the ester-linked phospholipid fatty acids (PLFA) composition in soil, since some specific PLFAs may have a taxonomic significance (Lechevalier and Lechevalier 1988, Tunlid and White 1992). For instance, the PLFA 18:2 ω 6,9 (linolic acid) is specific for saprophytic and ectomycorrhizal fungi but is not present in arbuscular mycorrhizal fungi (Tunlid and White 1992). PLFAs are constituents of biological membranes of living cells and are degraded rapidly after cell death by the enzymatic release of the phosphate group from the diglyceride and are not used as a storage material (White et al. 1979). The total amount of PLFAs can be used as an indicator of microbial biomass, since it is equivalent to the biomass estimated by ATP and direct microscopic counting of microorganisms (Balkwill et al. 1988) and the total lipid phosphate correlates with the ATP content and substrate-induced respiration of the soil (Frostegård et al. 1991). In addition this method of qualification and quantification of soil microorganisms is less labour-consuming than the traditional methods, like isolation and microscopic counting.

PLFA analysis was first applied to study the microbial communities in terrestrial environments by Frostegård et al. (1991, 1993). There are not many studies, however, comparing the effects of different tree species on soil microbial biomass, activity and community structure. The comparisons reported in the literature were relating to no more than several tree species. The influence of green ash, white pine and Norway spruce on the chemical characteristics of soil was studied by Binkley and Valentine (1991). Priha and Smolander (1999) studied the effect of *Pinus sylvestris*, *Picea abies* and *Betula pendula* on nutrient content and nitrogen transformations in soil and Priha et al. (1999) determined microbial community structure in soils under the three above mentioned species at two forest sites in Finland.

The aim of this work was to compare the living biomass of microbial communities in soils under canopies of 14 tree species with a particular regard to the fungal portion. An experimental plantation in Poland of monocultures, with repeated blocks and plots established in uniform site conditions offers a unique opportunity for such investigations.

Material and Methods

Study sites and sampling

The experimental site is located in west-central Poland (50°14.87' N, 18°06.35' E, 150 m a.s.l.). It is a 30-year-old plantation of monocultures of 14 tree species, planted on a relatively uniform, sandy and nutrient limited soil in replicated plots (20x20 m). The species include six conifers (*Abies alba*, *Larix decidua*, *Pseudotsuga menziessi*, *Pinus nigra*, *Pinus sylvestris*, *Picea abies*) and eight deciduous species (*Acer platanoides*, *Acer pseudoplatanus*, *Betula pendula*, *Carpinus betulus*, *Fagus sylvatica*, *Quercus robur*, *Quercus rubra*, *Tilia cordata*). Eleven of the tree species were planted in three blocks and three species in six blocks. The tree species differ in root and leaf traits, like the structure and longevity, chemical composition, physiological activity. The experiment had completely randomised design.

In October 2001 at each plot one sample, consisting of 20 separate soil cores (core diameter 5.0 cm) was taken from the humus layer (5 cm depth). The samples were sieved (mesh size 4 mm) and stored at -18°C until used.

Soil analysis

The lipid extraction and analysis of PLFA was performed as described by Frostegård et al. (1993). Three g fresh weight soil samples were extracted with a chloroform:methanol:citrate buffer – mixture (1:2:0.8) and the lipids were separated into neutral lipids, glycolipids and

phospholipids on silic acid columns by successively eluting with chloroform, acetone and methanol. The methanol fractions of neutral lipids and phospholipids were subjected to mild alkaline methanolysis and the fatty acid methyl esters were separated by gas chromatography (Hewlett Packard 5890) equipped with a flame ionization detector and phenylmethyl silicone column, 50 m in length, using He as carrier gas. Methyl nonadecanoate fatty acid (19:0) was used as an internal standard. Sum of all PLFAs determined were considered as the total amount of microbial biomass. The quantity of 18:2 ω 6,9 was used as an indicator of fungal biomass.

Results

Thirty two PLFAs were identified in soil samples on the basis of standards determined using GS/MS. High variability in the total PLFAs between soil samples taken under canopies of different tree species was found (Fig. 1).

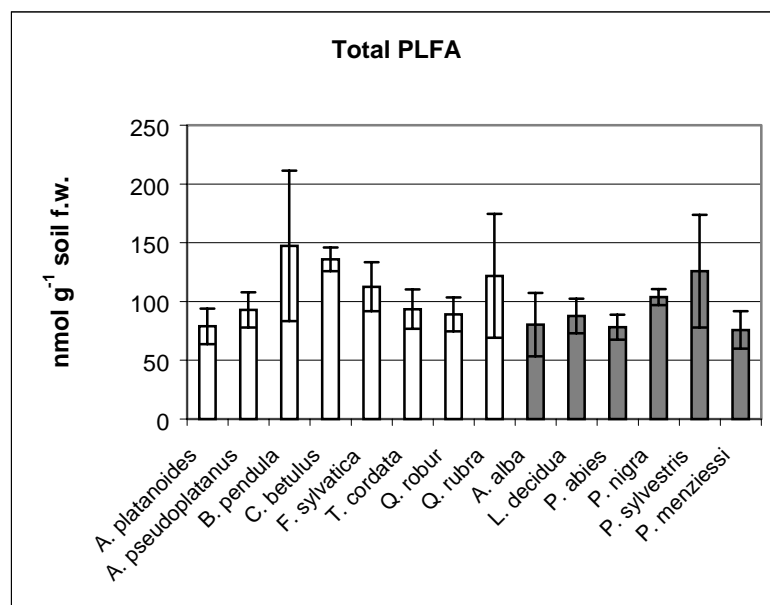


Fig. 1. Average concentration of the total phospholipid fatty acids (PLFAs) in soil (0-5 cm depth) under canopies of different forest tree species in the forest experimental site. Bars indicate standard deviation (n=3-6).

The highest concentrations of total microbial PLFAs was found in soil of *Betula pendula*, *Carpinus betulus*, *Quercus rubra* and *Pinus sylvestris*. Relatively low concentration of the total PLFAs was recorded under canopies of *Acer platanoides*, *A. pseudoplatanus*, *Abies alba*, *Picea abies* and *Pseudotsuga menziessi*. The average concentration of the total PLFAs under canopies of deciduous trees was slightly higher than under coniferous trees (Fig. 2).

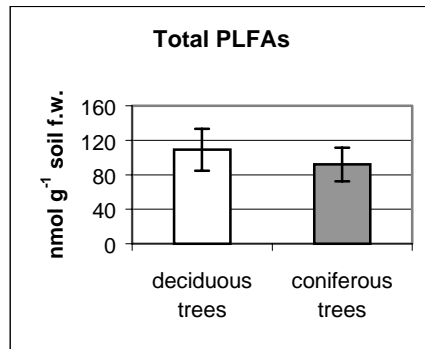


Fig. 2. A comparison of the concentration of the total PLFAs in soil (0-5 cm depth) under canopies of deciduous and coniferous tree species in the forest experimental site. Bars indicate standard deviation (n=23-27).

Priha et al. (1999) comparing the influence of three forest tree species on the microbial community in soil, has shown that the total amount of microbial PLFAs was highest in *Betula pendula* soil in the humus layer and lowest under *Picea abies*. In a pot study where the three tree species were grown from seeds for one growing season, soil microbial biomass and the rate of C mineralization were increased by roots of pine and birch but not by spruce roots (Priha et al. 1998).

In the present paper a high variability was found in concentration of the fungal specific PLFA 18:2 ω 6,9 in soil under different tree species (Fig.3).

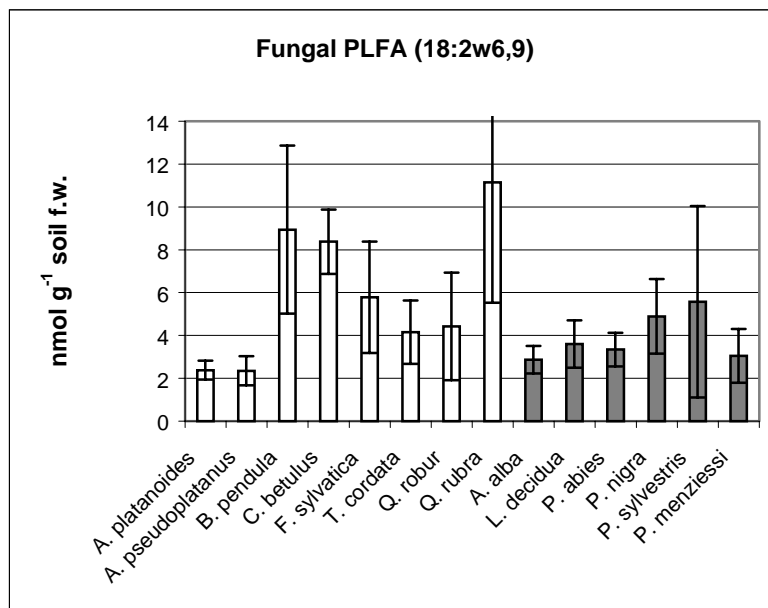


Fig. 3. Average concentration of the fungal specific PLFA 18:2 ω 6,9 in soil (0-5 cm depth) under canopies of different forest tree species in the forest experimental site. Bars indicate standard deviation (n=3-6).

The highest concentration was determined in soil under canopy of *Quercus rubra*, followed by *Betula pendula* and *Carpinus betulus*. The low statistical significance of the differences (high values of standard deviation) was a result of high variability between particular plots. This was probably caused by interaction of the neighbours plots in this completely

randomised experiment. The average concentration of the 18:2 ω 6,9 under deciduous species was slightly higher than under coniferous species (Fig. 4).

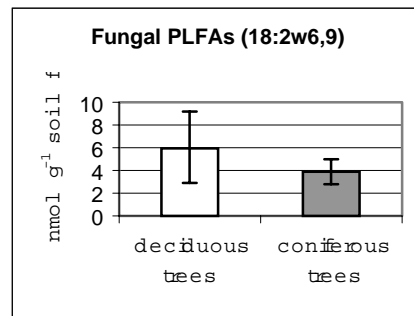


Fig. 4. A comparison of the concentration of the fungal specific PLFA 18:2 ω 6,9 in soil (0-5 cm depth) under canopies of deciduous and coniferous tree species in the forest experimental site. Bars indicate standard deviation (n=23-27).

The lowest concentration, however was found in soil under *Acer platanoides* and *A. pseudoplatanus* (Fig. 3) – the only two species in this experiment which develop arbuscular mycorrhiza, whereas the other species are obligatory ectomycorrhizal. Priha et al. (1999) did not find any differences in concentrations of the fungal specific PLFA in soil under *Betula pendula*, *Pinus sylvestris* and *Picea abies*, however they found in the birch soil increased concentrations of PLFAs specific for Gram-negative bacteria.

The preliminary results show high variability in microbial biomass between species and between plots in the soil humus layer. The further study should give detailed information on the influence of particular tree species on the soil microbial community and the effects of interactions between different neighbour trees.

Acknowledgements

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APPLICATIONS OF COMPUTATIONAL CHEMISTRY IN SOIL RESEARCH

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Summary

Although at present seldom used, numerous applications in soil science, especially in pollution research, can be envisaged for computational chemistry. In this paper we exemplify quite different applications of CC in soil research: (i) the interaction of organic acids with aluminium, (ii) the use of the ONIOM technique to study adsorption sites on clay minerals and (iii) the possible interactions of organic compounds with functional groups of humic substances.

1. Introduction

Soil in many cases is the only effective filter and buffer against pollutants entering the food chain. The use of agrochemicals, the application of organic residues containing different organic and inorganic pollutants to agricultural land and immissions of substances originating from combustion processes and regular or accidental releases from nuclear facilities led to a large variety of pollutants already being immobilised in the soil matrix. Especially the number of relevant organic compounds is increasing rapidly and data on the behaviour and fate of these substances are urgently needed. Laboratory and lysimeter studies are the most important methods in this connection. Anyhow, these studies are quite time consuming and may not be readily available for a first quick risk assessment of a new compound being just in development or recently discovered in the environment.

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Theoretical studies, thus, could be useful to assist the risk assessment and to help understanding the processes of interactions with the soil matrix on a molecular level (GERZABEK et al, 2000).

2. Developments of computational chemistry

Computational Chemistry is a rapidly growing section of Theoretical Chemistry with emphasis on application-oriented molecular problems being solved on the computer. The fundamental equation determining the properties of atomic and molecular systems is the Schrödinger equation. Its analytic solution is only possible for a few simple model cases. Based on the rapid progress in computer technology, very powerful numerical methods and respective computer programs have been developed for the quantum chemical computation of atoms and molecules. These methods have been applied very successfully in practically all fields of chemistry. Several classes of computational procedures are available ranging from ab initio and DFT (density functional theory) level via semi-empirical methods to simple force-fields and interatomic potentials. In these series of methods the first two ones are computational most expensive. However, they give on the average the most reliable results. Semi-empirical methods are computationally less expensive, but require well-tuned parameter sets for successful application. In the present contribution we concentrate on DFT methods. They belong - as has been stated above - to the most "expensive" ones, but combine the required flexibility and reliability with computational efficiency. Most of the calculations described in this work have been set up as benchmark investigations which shall guide future investigations on even larger and more complex systems. Many of these calculations can be carried out even on standard PCs under Linux, which provides a very cost-effective alternative to high-end workstations or central computers.

3. Examples

3.1. Aluminium - organic acids

The aluminium cation plays an important role in soil chemistry. Free forms (e.g. as hexaaquo complex) present toxicological risks for organisms and especially agricultural crops and affect the quality of natural sources of water. Organic acids occurring in the soil have strong influence on the chemical activity of aluminium. Formation of various stable complexes can decrease negative factors of the occurrence of aluminium in soil. Thus, it is important to understand the related chemical processes in more detail in order to develop better strategies for the deactivation of free aluminium. The aluminium cation has an amphoteric character.

This means that the pH of the solution will have a strong influence on the question which complexes will be formed. We focused on complexes where aluminium is sixfold coordinated which is characteristic for a pH below 7. At such conditions organic acids exist in aqueous solution in dissociated form. Thus, aluminium can form complexes in aqueous solution with fully or partially deprotonated organic acids, hydroxyl anions and with water molecules. A typical complex structure can be characterised by the formula $\text{Al}(\text{H}_2\text{O})_p(\text{OH})_q\text{L}_r$ where L_r stands for a deprotonated acid as ligand. In our theoretical investigations (TUNEGA et al., 2000, AQUINO et al., 2000, AQUINO et al., 2001) we restricted ourselves to complexes without OH^- group in the Al^{3+} coordination sphere. The studied species were complexes with the acetate, oxalate and citrate anions as ligands. Figure 1 shows as example the possible interactions for Al and acetate.

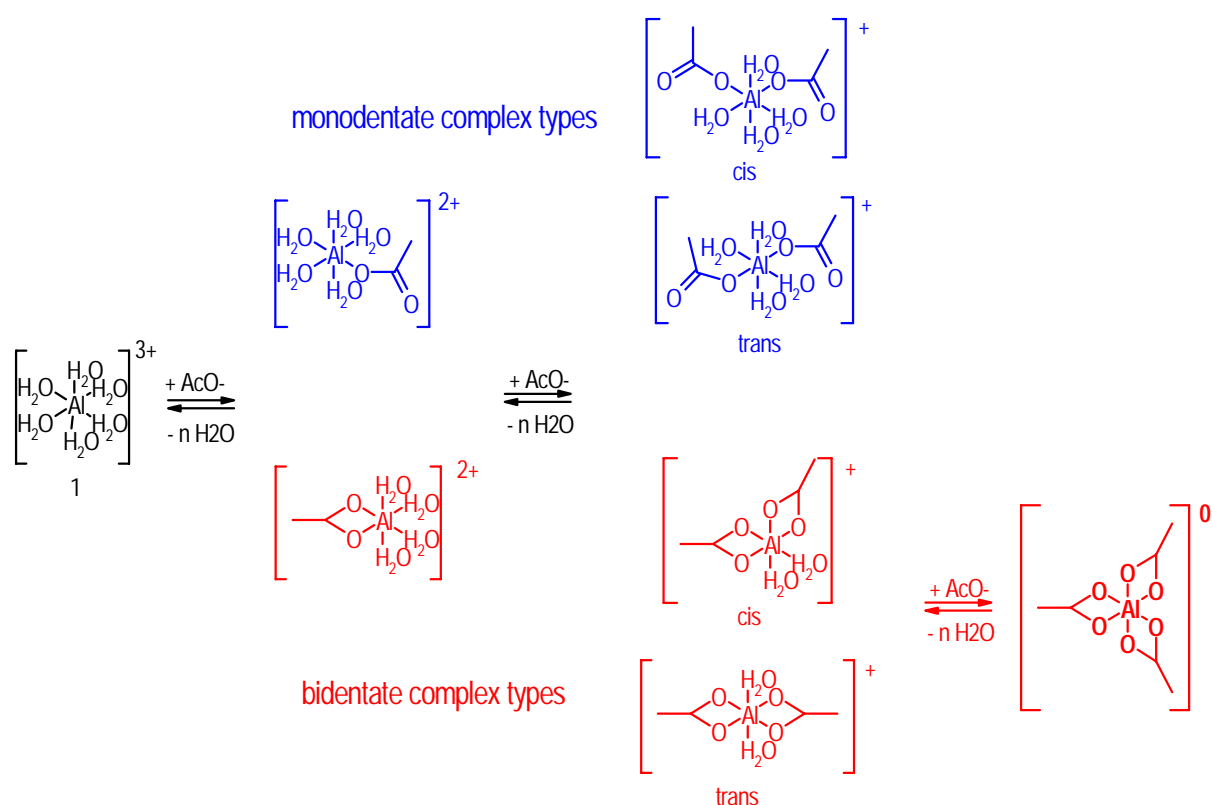


Figure 1. Possible interactions between the Al-hexaquo complex and acetate ligands

The investigation of complexes between aluminium-hexaquo complexes with organic acids (acetate, oxalate, citrate) showed a distinct influence of the specific organic acid and the complex species itself (monodentate, bidentate) on the interaction energies. Generally, it was found that the most stable complexes in the water solution are complexes with citrate ligands, followed by oxalate and acetate. Comparisons with literature values were partly successful,

partly not, because in most cases the specific form of interaction is not known from the experiments.

3.2. Dickite - organic compounds

Clay minerals represent an important inorganic component of soils and significantly affect physicochemical processes therein. Clays are usually small particles ($< 2 \mu\text{m}$) with a high specific surface area and a high chemical surface activity. Adsorption of mobile chemical species from soil solution on mineral surfaces is a very important process occurring in soil. The aim of the present work was the study of the interaction of water, acetic acid and acetate with different adsorption sites of the 001 surface of minerals of kaolinite-type applying the cluster model approach together with the ONIOM layer technique (DAPPRICH et al., 1999). These model systems represent the basis for future investigations of pesticide-clay interactions. The cluster model of the single kaolinite layer was derived from the structure of the mineral dickite (JOSWIG and DRITS, 1986). It consists of 78 atoms and contains one ditrigonal tetrahedral ring and one octahedral ring. Dangling bonds were saturated with hydrogen atoms. The structure of the layers can be seen in Figure 2. The adsorbants were placed above holes on both sides of the layer – water and acetic acid (HAc) and 2,4-D above the tetrahedral side and water, acetate anion (Ac^-) or 2,4-D above the octahedral side. It could be shown that water and acetic acid interact only weakly with the tetrahedral side of the clay mineral, whereas the adsorption and interaction with hydrogen bonds on the octahedral side was significant. E.g. the interaction energy between dickite and water was $-4.14 \text{ kcal mol}^{-1}$ on the tetrahedral side, but $-8.29 \text{ kcal mol}^{-1}$ on the octahedral side of the clay mineral. For acetate the values were even more different: $-2.79 \text{ kcal mol}^{-1}$ on the tetrahedral side and $-67.13 \text{ kcal mol}^{-1}$ on the octahedral side. This study was repeated with the pesticide 2,4-D. Similar results were obtained as for the acetate ion (TUNEGA et al., 2002). The ONIOM approach turned out to be a powerful and effective method for investigations of the interactions of relatively large molecular systems interacting with clay mineral surfaces.

D(O)-HAc

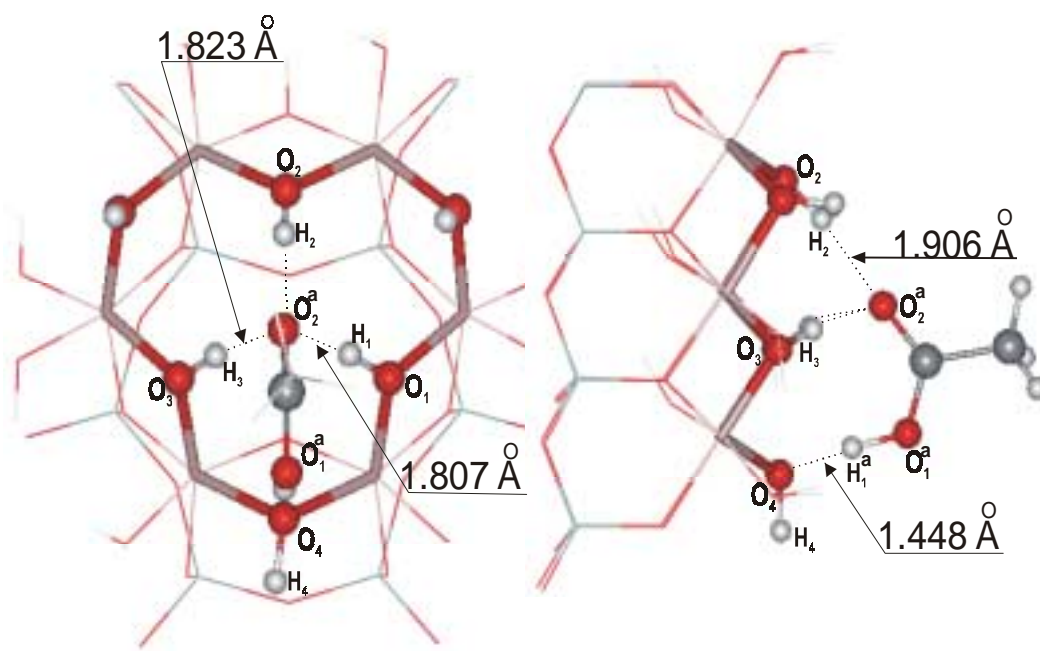


Figure 2. Example for the interaction of acetic acid with the octahedral side of the dickite mineral (TUNEGA et al., 2002)

3.3 Modelling of humic acid interactions with organic compounds

The most complicated task is the development of models for interaction of pesticides with humic acids, which is - from the practical point of view - one of the most important processes determining the behaviour of pesticides in soil. As humics are a highly complex group of substances and not a single molecular structure can be defined, we did not attempt to define a single humic model, but concentrated on the investigation of specific interactions of a model pesticide (2,4-D) with functional groups, which are known to be present in humic substances. These investigations were performed under varying chemical environments (from polar to unpolar). Basic results were obtained on the influence of the polarity of the environment on different. As it can be seen from Figure 3, differences between charged and polar interactions decrease with increasing polarity of the chemical environment in which the interaction takes place and the strength of all interactions generally decreases at the same time. This could have a practical consequence. A pesticide present in the soil solution might be less strongly adsorbed at certain functional groups of humics as compared to the same compound, which

has previously diffused into a humic micell, where unpolar conditions are more likely. This phenomenon might add to the well known effect of "bound residues" of pesticides in soil.

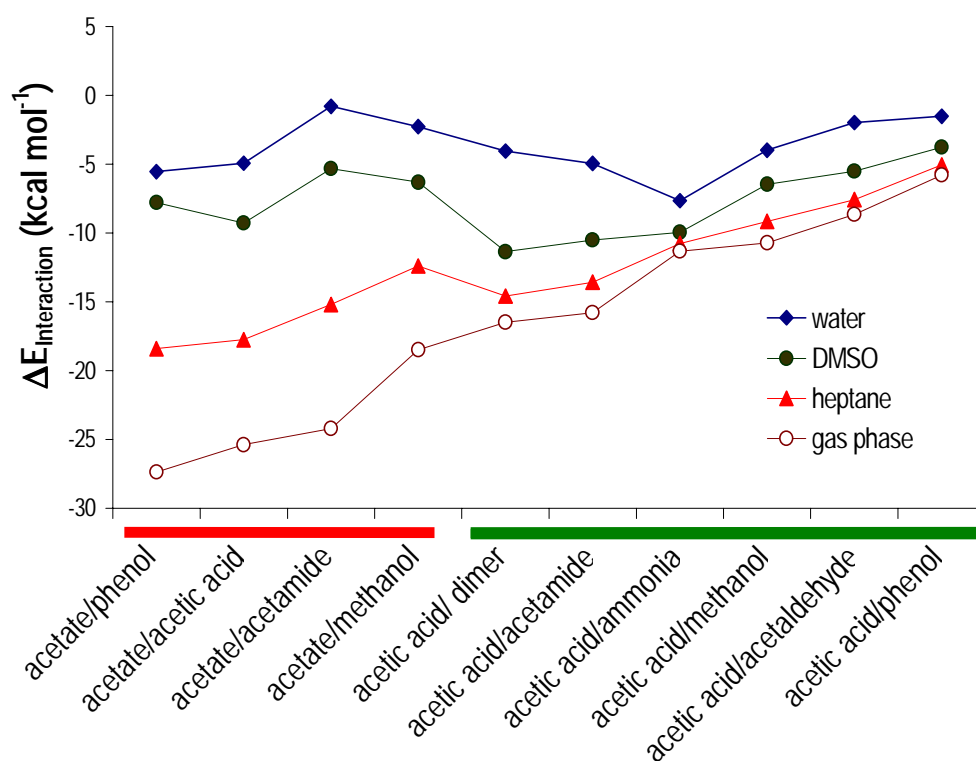


Figure 3. Interaction energies of selected charged (left) and polar (right) interactions with increasing dielectric constant (gas phase, heptane, DMSO, water) (HABERHAUER et al., 2001)

4. Conclusions

We may conclude that computational chemistry is likely to become a useful tool in soil science, especially for:

- elucidating principle processes of adsorption, desorption, diffusion, modelling of molecular structures and their interactions
- the investigation of the impact of environmental changes on the above processes.

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TRANSFER FUNCTIONS IN SOIL SCIENCE

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Summary

The paper presents researches that have been done on a series of over 700 analytical data sets from soil survey studies and field and laboratory experiments carried out by authors or by the county offices for pedological and agrochemical studies (OJSPA) on soils from all over the country – among the most different ones from pedogenetical point of view and their properties, from very acid to alkaline soils

Based on the analytical data, numerous significant correlations between different agrochemical indexes of the soil have been established, as well as a series of transfer functions which can be used for evaluating some agrochemical indexes on the basis of another. Their utility is important especially when indexes more difficult to obtain are estimated on the basis of others, easily to be obtained analytically.

The data obtained based on the transfer functions are extremely useful for practical purposes, for establishing the liming materials and and fertilizer rates, for example. Also, such functions are very useful in modelling processes and in realizing softwares in the field of soil science and plant nutrition.

1. Introduction

The transfer functions in soil science are those functions that can be used in order to obtain some soil indexes (agrochemical indexes, for example) on the basis of other indexes. Their utility is important especially when indexes more difficult to be obtained are estimated on the basis of others easier obtained analitically. The data obtained based on the transfer functions are extremely useful for practical purposes, such establishing the liming material rates, fertilizer rates, prognosing the evolution of soil indexes. Also, such functions are very useful in modelling processes and in realizing softwares.

2. Materials and methods

The researches have been done on a series of over 700 analitical data sets from soil survey studies carried out by authors or by the county offices for pedological and agrochemical studies (OJSPA) on soils from all over the country – among the most different ones from pedogenetically point of view and their properties, from very acid to alkaline soils (samples from 0-20 cm on arable soils, and on 0-10 cm on pasture soils). Data from numerous field experiments with lime and fertilizers have also been used, as well as data obtained by treating with lime, in laboratory conditions, the acid soils from such fields. The pH_{H_2O} has

been determined in a suspension of distilled water on the ratio soil/water 1/2.5, and pH_{KCl} in a suspension of KCl 0.1M on the same ratio soil/solution. The *sum of exchangeable bases*, SB , and the *hydrolytic acidity*, Ah , have been determined by the Kappen method, and the *degree of the base saturation* of the soil was calculated, $V_{Ah}, \% = [SB/(SB + Ah)] \cdot 100$. The soil *humus content* ($H, \%$) was determined by Walkley-Black method (wet oxidization) modified by Gogoasă, and the index of the oxidizable soil organic substances – *IOSOS*, was determined by Borlan method (1982). The analytical data have been processed by correlation and regression methods, which allowed establishing a series of transfer functions. Some relations have been mathematically deduced from other known relations.

3. Results and discussion

The transfer functions for evaluating pH_{H_2O} based on $pH_{KCl\ 0.1M}$ or $pH_{CaCl_2\ 0.01M}$ and conversely. The pH_{H_2O} is higher than the pH_{KCl} , on an average, by 0.75 units on acide soils as well as on alkaline soils; but the individual values differ by 0.5–1.5 pH units, the most frequent being 0.5–1. The equations for evaluating pH_{H_2O} based on pH_{KCl} are:

$$pH_{H_2O} = 0.996 \cdot pH_{KCl} + 0.77 \quad pH_{KCl} = 0.903 \cdot pH_{H_2O} - 0.261$$

Examples: if $pH_{KCl} = 5$, $pH_{H_2O} = 0.996 \cdot 5 + 0.77 = 5.75$; if $pH_{H_2O} = 5.5$, $pH_{KCl} = 0.903 \cdot 5.5 - 0.261 = 4.7$.

In order to convert values of pH_{CaCl_2} (soil/solution ratio: 1/2.5) into pH_{H_2O} values, and conversely, the Sillanpää (1982) equations can be used:

$$pH_{H_2O} = 0.934 pH_{CaCl_2} + 0.937 \quad pH_{CaCl_2} = 1.044 pH_{H_2O} - 0.808$$

Examples: if $pH_{CaCl_2} = 5$, $pH_{H_2O} = 0.934 \cdot 5 + 0.937 = 5.6$; if $pH_{H_2O} = 5.6$, $pH_{CaCl_2} = 1.044 \cdot 5.6 - 0.808 = 5.04$.

According to Sillanpää equations, the pH_{H_2O} is higher by 0.34–0.7 units than the pH_{CaCl_2} , the differences being higher to acide soils than to alkaline soils: 0.7 to pH_{CaCl_2} 3.5 and 0.34 to pH_{CaCl_2} 8.5.

These equations allow unitary comparisons of the pH determined in different suspensions, especially for the optimal area of the pH to different plant species.

The transfer function $pH = f(V_{Ah})$ for evaluating pH_{H_2O} based on the degree of the base saturation of the soil, V_{Ah} (%). The very straight positive correlation (fig. 1) between soil pH and V_{Ah} ($r^2 = 0.99997$, $r = 0.99998^{***}$) shows that pH_{H_2O} can be established as a function of V_{Ah} either graphically (fig. 1) or by calculation with the transfer function:

$$\text{pH} = 8.752 - 0.485036865 \cdot V_{\text{Ah}} + 0.0160175065 \cdot V_{\text{Ah}}^2 - 0.0002018826 \cdot V_{\text{Ah}}^3 + 0.0000008933224 \cdot V_{\text{Ah}}^4$$

This polynomial function of 4th degree can be used for V_{Ah} between 35 % and 100 % which correspond to pH above 4; the extrapolations under 35 % are not allowed.

Examples: if $V_{\text{Ah}} = 35$ %, $\text{pH} = 8.752 - 0.485036865 \cdot 35 + 0.0160175065 \cdot 35^2 - 0.0002018826 \cdot 35^3 + 0.0000008933224 \cdot 35^4 = 4.08$; if $V_{\text{Ah}} = 65$ %, $\text{pH} = 5.4$; if $V_{\text{Ah}} = 80$ %, $\text{pH} = 5.69$.

The transfer function $V_{\text{Ah}} = f(\text{pH})$ for evaluating the degree of the base saturation of the soil, V_{Ah} , based on the $\text{pH}_{\text{H}_2\text{O}}$. V_{Ah} is an extremely useful index for soil characterization and enters in the equations used for calculation of the liming material rates for acid soils and of the acidifying material rates used to decrease the soil pH. The very straight positive correlation between V_{Ah} and soil pH ($r^2 = 0.8755$, $r = 0.935^{***}$) shows that V_{Ah} can be established as related to $\text{pH}_{\text{H}_2\text{O}}$ either graphically (fig. 2) or by calculation with a specific transfer function. The higher number of available data allowed to establish the following transfer function, a more accurate one than that published by Budoi et al, 2000:

$$V_{\text{Ah}}, \% = 0.3291 \cdot \text{pH}^3 - 11.228 \cdot \text{pH}^2 + 116.31 \cdot \text{pH} - 280.53$$

This equation makes it possible for the V_{Ah} to be established more rigorously as a function of the optimum soil pH of the cultivated species (see Budoi, 2000), in this way the accuracy in the establishment of the rates of liming materials for acid soils, as well as of the acidifying materials being increased.

Examples: if $\text{pH} = 4.08$, $V_{\text{Ah}} = 0.3291 \cdot 4.08^3 - 11.228 \cdot 4.08^2 + 116.31 \cdot 4.08 - 280.53 = 29.06$ %; if $\text{pH} = 5.4$, $V_{\text{Ah}} = 71.96$ %; if $\text{pH} = 5.69$, $V_{\text{Ah}} = 78.4$ %;

Theoretically, when using the transfer function $\text{pH} = f(V_{\text{Ah}})$ to convert the V_{Ah} values calculated with the transfer function $V_{\text{Ah}} = f(\text{pH})$, we expect to obtain the same values for pH, and conversely, for V_{Ah} . This can happen only if the two transfer functions are of the same type and have symmetrical graphs one to another, as in the case of linear type. But, as these two transfer functions are of different types, with a little different graphs, some small differences appear. For example, if using the transfer function $V_{\text{Ah}} = f(\text{pH})$, for $\text{pH} = 4.08$ results a $V_{\text{Ah}} = 29$ %, while using the transfer function $\text{pH} = f(V_{\text{Ah}})$, the $\text{pH} = 4.08$ results for a $V_{\text{Ah}} = 35$ %, that means 6 % more; if using $V_{\text{Ah}} = f(\text{pH})$, for $\text{pH} = 5.4$ results a $V_{\text{Ah}} = 72$ %, while using $\text{pH} = f(V_{\text{Ah}})$, the $\text{pH} = 5.4$ results for a $V_{\text{Ah}} = 65$ %, that means 7 % less; if using $V_{\text{Ah}} = f(\text{pH})$, for $\text{pH} = 5.69$ results a $V_{\text{Ah}} = 78$ %, while using $\text{pH} = f(V_{\text{Ah}})$, the $\text{pH} = 5.69$ results for a $V_{\text{Ah}} = 80$ %, that means only 2 % more. These differences can be considered acceptable. Improvements of these two important transfer functions are to be expected in the future.

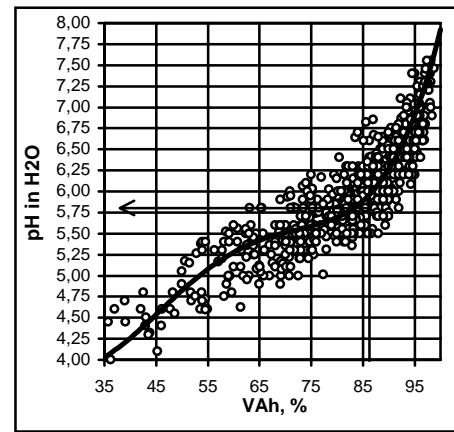


Fig. 1 – Correlation between soil $\text{pH}_{\text{H}_2\text{O}}$ and degree of the base saturation, V_{Ah} , and the corresponding transfer function (708 pairs of data from all Romania and a very large scale of types of soils)

$$\text{pH} = 8.752 - 0.485036865 \cdot V_{\text{Ah}} + 0.0160175065 \cdot V_{\text{Ah}}^2 - 0.0002018826 \cdot V_{\text{Ah}}^3 + 0.0000008933224 \cdot V_{\text{Ah}}^4$$

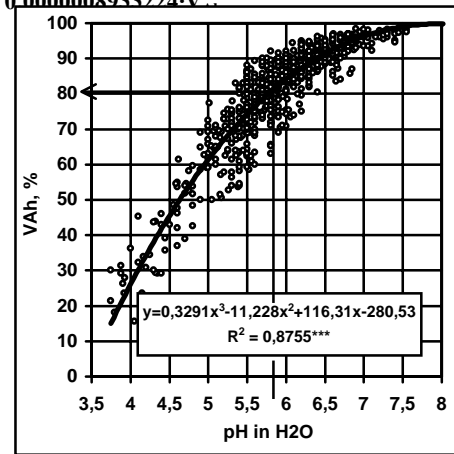


Fig. 2 – Correlation between soil degree of the base saturation, V_{Ah} , and $\text{pH}_{\text{H}_2\text{O}}$, and the corresponding transfer function (708 pairs of data from all Romania and a very large scale of types of soils)

$$V_{\text{Ah}}, \% = 0.3291 \cdot \text{pH}^3 - 11.228 \cdot \text{pH}^2 + 116.31 \cdot \text{pH} - 280.53$$

The transfer function $A_h = f(\text{pH})$ for the estimation of the hydrolitic acidity, A_h (Kappen method), on the basis of $\text{pH}_{\text{H}_2\text{O}}$:

$$A_h, \text{ meq/100 g sol} = 931.34 \cdot e^{-0.9712 \cdot \text{pH}}$$

Example: if $\text{pH} = 5$, $A_h = 931.34 \cdot e^{-0.9712 \cdot 5} = 7.355$ meq/100 g soil.

The transfer function $\text{SB} = f(\text{pH})$ for the estimation of the sum of exchangeable bases, SB (Kappen method), on the basis of $\text{pH}_{\text{H}_2\text{O}}$:

$$\text{SB}, \text{ meq/100 g sol} = 0.0074 \cdot \text{pH}^{4.2949}$$

Example: if $\text{pH} = 7$, $\text{SB} = 0.0074 \cdot 7^{4.2949} = 31.54$ meq/100 g soil.

The transfer function $A_h = f(\text{SB}, V_{\text{Ah}})$ for the calculation of the A_h on the basis of SB and V_{Ah} :

$$A_h, \text{ meq/100 g sol} = \text{SB} \cdot \frac{(100 - V_{\text{Ah}})}{V_{\text{Ah}}}$$

Example: if $\text{SB} = 20$ meq/100 g sol and $V_{\text{Ah}} = 70\%$, $A_h = 20 \cdot (100 - 70) / 70 = 8.57$ me/100 g soil.

Equation for the prognosis of the degree of the base saturation of the soil, V_{Ah} , that will be realized by the application of an amount of liming material on an acid soil:

$$V_{\text{Ah}}, \% = V_{\text{Ahi}} + V_{\text{Ahi}} \cdot \frac{\text{DAC} \cdot \text{PNA}}{5 \cdot \text{SB}_i \cdot h \cdot G_v}$$

where: DAC = rate of liming material applied, t/ha;

SB_i = initial sum of exchangeable bases of the soil, meq/100 g soil;

V_{Ahi} = initial degree of the base saturation of the soil, %;

h = liming depth, cm;

G_v = soil bulk density, g/cm³;

PNA = neutralization power of the liming material or calcium carbonate equivalent of the liming material, as % of pure CaCO_3 . $\text{PNA} = 100$ for CaCO_3 , 178 for CaO , 132 for $\text{Ca}(\text{OH})_2$, 109 for $\text{CaCO}_3 \cdot \text{MgCO}_3$, 119 for MgCO_3 , 86 for CaSiO_3 , 248 for MgO , 166 for $\text{Mg}(\text{OH})_2$ (PNA computed on the basis of chemical equivalent, Budoi, 2000);

$\text{DAC} \cdot \text{PNA} / 5 \cdot \text{SB}_i \cdot h \cdot G_v$ practically represents the fraction of V_{Ahi} with which V_{Ahi} will increase by the application of the liming material in DAC rate.

Example: if $V_{\text{Ahi}} = 60\%$, $\text{SB}_i = 10$ me/100 g sol, $\text{DAC} = 7.5$ t/ha, $\text{PNA} = 100$, $h = 25$ cm, $G_v = 1.2$ g/cm³, then $V_{\text{Ah}} = 60 + 60 \cdot ((7.5 \cdot 100) / (5 \cdot 10 \cdot 25 \cdot 1.2)) = 60 + 60 \cdot 0.5 = 90\%$.

Prognosis equations are not typical transfer equations, but they are very important from practical point of view, and they use agrochemical indexes obtained by using transfer functions or they can evaluate agrochemical indexes necessary in transfer functions.

Equations for the prognosis of the degree of the base saturation of the soil, V_{Ah} , that will be realized by the application of an amount of acidifying material in order to decrease the soil pH to the optimum level for the cultivated plant species.

a) For species cultivated on noncarbonatic soils (unsaturated with bases), where the rate of acidifying material is computed and expressed at unit surface (see Budoi 2001), the following equation can be used to prognose V_{Ah} :

$$V_{\text{Ah}}, \% = V_{\text{Ahi}} \cdot \frac{10 \cdot \text{SB}_i \cdot h \cdot G_v}{10 \cdot \text{SB}_i \cdot h \cdot G_v + \text{DMA} \cdot \text{Ah}_{\text{ma}}}$$

where: Ah_{ma} = hydrolytic acidity developed in soil by the acidifying material, meq/100 g material (tab. 1);

DMA = amount of acidifying material, kg/m²;

the other terms have the same meaning as above;

the fraction from the right hand of the equation practically represents a subunitary demultiplication factor of V_{Ahi} .

Example: if $V_{Ahi} = 60\%$, $SB_i = 10$ meq/100 g sol, $h = 40$ cm, $Gv = 1.2$ g/cm³, $DMA = 26.67$ kg *Sphagnum* acid peat (air dried)/m², $Ah_{ma} = 90$ meq/100 g, then $V_{Ah} = 60 \cdot (10 \cdot 10 \cdot 40 \cdot 1.2) / (10 \cdot 10 \cdot 40 \cdot 1.2 + 26.67 \cdot 90) = 60 \cdot 0.667 = 40\%$.

b) For species cultivated on substrates (in pots or containers), where the rate of acidifying material is computed and expressed as mass unit (see Budoi 2001), the equation for evaluating V_{Ah} is:

$$V_{Ah}, \% = V_{Ahi} \cdot \frac{1000 \cdot SB_i}{1000 \cdot SB_i + DMA \cdot Ah_{ma}}$$

where: DMA is the amount of acidifying material, kg/t substrate (other components than the acidifying material); the other terms have the same meaning as above.

Example: if $V_{Ahi} = 80\%$, $SB_i = 10$ meq/100 g sol, $DMA = 30$ kg *Sphagnum* acid peat (air dried)/t substrate (other components than peat), $Ah_{ma} = 90$ meq/100 g, then $V_{Ah} = 80 \cdot (1000 \cdot 10) / (1000 \cdot 10 + 30 \cdot 90) = 80 \cdot 0.787 = 63\%$.

This equation is useful especially when we cannot exceed an amount (weight) of acid peat for a given substrate (mixture of different components) and this amount is not enough to decrease the pH to the optimum level necessary for the cultivated species and another acidifying material has to be applied additionally. In such a case, it has to evaluate the V_{Ah} that can be reached with the peat, and this V_{Ah} enters as V_{Ahi} in the formula (see Budoi, 2001) used to calculate the amount of the acidifying material to be additionally applied (elemental S for example).

The transfer functions for the evaluation of the soil humus content (H) on the bases of the index of the oxidizable soil organic substances (IOSOS). The following relations can be used (Budoi, 1997):

$$H, \% = 4.765 (1 - 10^{-0.06303 \cdot IOSOS})$$

$$H, \% = 0.621 \cdot IOSOS - 0.0262 \cdot IOSOS^2$$

The IOSOS is a soil agrochemical index much easier obtained analytically than H. The evaluations with these two relations are practically not different in the IOSOS area from 2 to 10.

Examples: if $IOSOS = 5$, $H = 4.765 (1 - 10^{-0.06303 \cdot 5}) = 2.46\%$, and $H = 0.621 \cdot 5 - 0.0262 \cdot 5^2 = 2.45\%$.

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Table 1

Hydrolytic acidity developed in soil by some acidifying materials, Ah_{ma}

Acidifying material	Ah_{ma}^* meq H ⁺ /100 g material
<i>Sphagnum</i> acid peat, air dried	(90)
Al ₂ (SO ₄) ₃	1754
Al ₂ (SO ₄) ₃ ·18H ₂ O	901
FeSO ₄	1317
FeSO ₄ ·7H ₂ O	720
H ₂ SO ₄	2040
S	6250
NH ₃	5882 (2960)
NH ₄ Cl	3738 (2560)
(NH ₄) ₂ SO ₄	3027 (2200)
NH ₄ NO ₃ ·(NH ₄) ₂ SO ₄	2828 (1860)
CO(NH ₂) ₂	3333 (1680)
NH ₄ NO ₃	2500 (1200)

* theoretical values (for ammoniacal fertilizers it has been taken in calculation also the acidity resulted by total nitrification); in parenthesis are practical values

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RESEARCHES CONCERNING THE EVOLUTION OF SOME AGROCHEMICAL PROPERTIES OF THE REDDISH-BROWN SOIL UNDER THE INFLUENCE OF LONG RUN FERTILIZATION

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Summary

The paper presents the evolution of the soil pH, humus content (H), index of the oxidizable soil organic substances (IOSOS), mobile P and K content of the arable layer of the forest reddish-brown soil from Moara Domnească under the influence of the long run fertilization with chemical fertilizers and manure in the winter wheat-corn-soja rotation.

Ammonium nitrate determines the significant decrease of the pH, as much as the N rate is higher, from 6.5 reaching 5.9, near the limit of reclamation (5.8). The superphosphate, K salts and manure do not significantly influence the soil reaction.

There is a very significant correlation between IOSOS and H. Although the H and IOSOS changes are not significant, IOSOS has higher values in the experiment fertilized with manure as compared to those fertilized only chemically.

The content of the mobile P continuously increases, in an exponential manner, with the increase of the P rate applied yearly; the slow increases to the small rates become higher and higher with the rate increase, tending to become linear. New items in the area are the average specific rates (ASR) and the marginal rates (MgR) of the increase of the mobile P content, as ppm P/kg P₂O₅ applied on the entire experimental period. ASR – computed dividing the increase of the mobile P versus unfertilized control by the total amount of phosphorous (Q) applied on the entire experimental period –, increases linearly with Q and with phosphorous rate applied yearly (PRY). MgR determined by the ultimate fractions of 40, 80, 120, 160 kg P₂O₅/ha yearly from the total rates applied, increases in an exponential manner with Q and PRY increase. The smaller weight the last fraction from the rate has, the higher the MgR determined by this fraction is.

Fertilization with K salt determines a linear, significant increase of the mobile K from soil with the rate applied. Organic fertilization induces the increase of the mobile P and K.

The average and marginal specific rates of change of the agrochemical indexes are useful for the prognosis models of the soil properties evolution.

1. Introduction

Long run field experiments are a treasure which must be valorized under all aspects. Over the years, many researches have been done concerning the evolution of soil properties: chemical, physical, biological ones etc. But, this subject is so vast, so complex and so important, that practically one can't say that it can be exhausted. Each research paper which deserves its name brought something new in this area. It is the aim of this paper too.

2. Materials and methods

The researches are based on three long run field experiments with mineral fertilizers and with manure, on mollic reddish-brown soil from Moara Domneasă. These have been set up in the autumn of 1982, during the years winter wheat, corn and soja being cultivated, in rotation in this order.

The experiments, codified I, III and VI, are: *exp. I – NP* (combinations between N rates – 0, 50, 100, 150 and 200 kg N/ha-year and P rates – 0, 40, 80, 120 and 160 kg P₂O₅/ha-year); *exp. III – NPK* (K rates – 0, 50, 100 and 150 kg K₂O/ha on different backgrounds of P and N: P₀N₀, P₀N₁₀₀, P₁₀₀N₀ and P₁₀₀N₁₀₀); *exp. VI – G + NP* (semi-fermented manure rates – 0, 20, 40 and 60 t/ha, on different backgrounds of P and N (P₀N₀, P₀N₁₀₀, P₁₀₀N₀ and P₁₀₀N₁₀₀)). Each variant has been set in 4 replicates.

The mineral fertilizers used were ammonium nitrate, concentrated superphosphate and K salt with 40 % K₂O; those with P and K were applied in autumn, all the yearly rate, and the N was fractionated: in autumn and in spring. The manure was applied once in each three years, in autumn, each time on corn, in the period 1983-1991 being three applications.

The soil samples have been taken from the first 20 cm depth, from 3 or 4 replicates of each variants, the analytical data presented in the paper representing their average values. The soil analyses have been done by RISSA Bucharest official methodology (1981). The index of the oxidizable soil organic substances – *IOSOS* was determined by Borlan method (1982).

The results have been processed statistically by analysis of variance and by Tukey and Student tests for establishing the signification of the differences, and by correlation and regression methods.

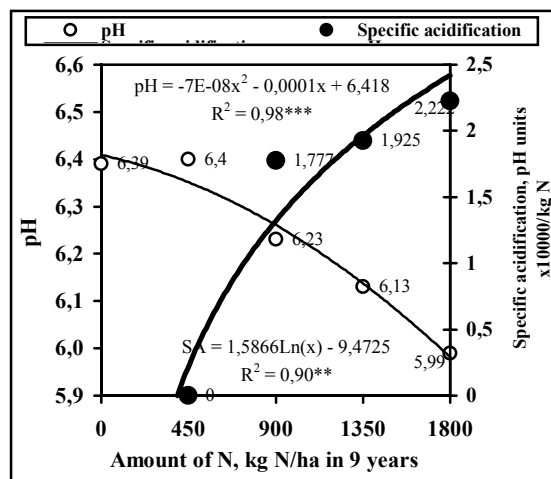
The data used in this paper are from the research reports that can be found in the archive of the Agrochemistry Department of UȘAMV Bucharest (Budoï et al, 1991-1994, Caramete et al, 1984-1990, Țigănaș et al, 1991), PHD theses (Budoï, 1997) and already published papers (Alexandrescu et al, 1994).

3. Results and discussions

Evolution of the soil reaction. The application for 9 years (1983-1991) of NH₄NO₃ lead to the pH decrease into the ploughed layer and, thus, to *soil acidification*, irrespective of the P rate applied. The higher the N amount was, the higher the decreases were (fig. 1), being significant, statistically assured, at the maximum rate of 200 kg N/ha/year (1800 kg/ha in 9 years), that is from 6.39 at control (N₀), to 5.99 at N₂₀₀ (average values of the phosphorous backgrounds).

Fig. 1 – Soil acidification (pH units) under the influence of NH₄NO₃ and specific acidification, SpA (pH units/kg N) related to N amount applied during 1983-1991 (*exp. I*) (for pH: LSD 5% Tukey = 0.35; LSD 5% Student = 0.20)

Specific acidification (SpA) determined by N (average values on P rates), in pH units/kg N applied for 9 experimental years, increases with the N amount applied, reaching values of 2.22·10⁻⁴ pH units/kg N (fig. 1). Neither phosphorous and potassium fertilizers, nor manure determined significant changes of pH.



Evolution of the humus content (H) and of the index of the oxidizable soil organic substances (IOSOS) and the relation between these two indexes. H and IOSOS did not change significantly, statistically assured, neither under the influence of chemical fertilizers, nor even of that of manure. However, both H and IOSOS reached higher values in the experiment with manure as compared to those in the experiment with only mineral fertilizers.

Data from a varied range of soils (white luvisol, brown luvisol, mollic reddish-brown soil, mollic brown clayilluvisol, cambic chernozem), partly from Borlan and Alexandrescu (1994), Alexandrescu, Budoï and Borlan, (1994), show that *H correlates positively and very significantly with IOSOS* (fig. 2).

This shows that the IOSOS, which can be determined much easier than the humus, can be used as agrochemical index instead of humus in order to estimate the soil supplying degree with organic substances and with N potentially mineralizable.

The very close relation between H and IOSOS makes possible the evaluation of the arable soil humus content using one of the following relations (Budoï, 1997):

$$H, \% = 4.765 (1 - 10^{-0.06303 \cdot IOSOS})$$

or

$$H, \% = 0.621 \cdot IOSOS - 0.0262 \cdot IOSOS^2$$

The evaluations with these two relations are practically not different in the IOSOS area from 2 to 10.

Evolution of the soil mobile phosphorous. Influence of mineral phosphorous fertilizers. The soil mobile P (ppm P) continuously increases, in an exponential manner, together with the P fertilizer rate applied yearly (tab. 1 and fig. 3). The increase is slower at the small P rates, on one hand because of the high soil capacity to immobilize phosphate ions, which to these rates is not totally satisfied, on the other hand because, by comparison with high rates, a much higher proportion from the applied P is consumed by plants. When the rates surpass the consumption's with the yields and the losses by immobilization, the mobile P content records increases. The higher the P rate is, the more emphasized this thing is.

Specific rates of mobile P accumulation in soil, ASR and MgR (tab. 1 and fig. 3 and 4). Calculation of the specific rates of mobile P accumulation allows some important findings.

The average specific rate of mobile P increase (ASR, ppm P/kg P₂O₅), calculated by dividing the mobile P increase (ppm P) versus P₀ (unfertilized with P) to the total phosphorous amount applied during 11 years (kg P₂O₅), increases together with yearly applied fertilizer rate, together with the total P₂O₅ amount applied during 11 years of experimentation respectively. So, at 40 kg P₂O₅/ha×year (440 kg/ha in 11 years) the average rate is 0.0032 ppm P/kg P₂O₅; at 80 kg P₂O₅/ha×year (880 kg in 11 years) is 0.0073 ppm, that means almost 3 times higher; at 120 kg P₂O₅/ha×year (1320 kg in 11 years) is 0.01 ppm and at 160 kg P₂O₅/ha×year (1760 kg in 11 years) is 0.0133 ppm P/kg P₂O₅.

The marginal rates of mobile P increase (MgR, ppm P/kg P₂O₅), determined by the last fractions (parts) of 40, 80, 120, 160 kg P₂O₅/ha from the yearly applied fertilizer rates. It is reminded that the yearly P rates have been applied once a year, in autumn, only the calculations being done for increasing fractions (parts) of these yearly fertilizer rates.

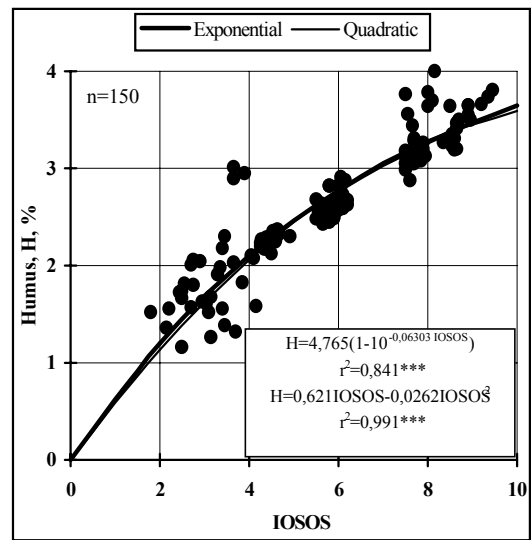


Fig. 2. Correlation between soil humus content, H, and IOSOS (data from different soils: white luvisol, luvic brown soil, mollic reddish-brown soil, mollic brown clayilluvisol, and cambic chernozem)

Table 1: Rates of modification of the mobile P content¹⁾ in the ploughed layer related to the P fertilizer amount applied in 11 years: 1983-1993 (exp. I)

Rate, kg P ₂ O ₅ /ha year	Total P applied, kg P ₂ O ₅ /ha	Average mobile P content	Increases versus P ₀	Increases versus previous level	ASR, average specific rates of increases	MgR, marginal rates of mobile P increase determined by the last fraction of... kg P ₂ O ₅ from yearly rate			
						40	80	120	160
						ppm P		ppm P/kg P ₂ O ₅	
1	2	3	4	5	6	7	8	9	10
0	0	14.8	–	–	–	–	–	–	–
40	440	16.8	1.4	1.4	0.0032	0.0032	–	–	–
80	880	21.2	6.4	5.0	0.0073	0.0114	0.0073	–	–
120	1320	28.0	13.2	6.8	0.0100	0.0155	0.0134	0.01	–
160	1760	38.2	23.4	10.2	0.0133	0.0232	0.0193	0.0167	0.0133

¹⁾ Average values of 4 replicates; soil samples from 1993 to soja

No matter what the measure of the last considered fraction from the total yearly rate is, *MgR* increases together with the increase of yearly rate (tab. 1 and fig. 4); the smaller the weight of the last fraction in total rate is, the higher *MgR* (of positive influence on mobile P, determined by this fraction) is, and conversely. So, when the fraction from the rate is 40 kg/ha, *MgR* is 0.0032 ppm P/kg P₂O₅ when the fraction is even the total rate; 0.0114 ppm/kg P₂O₅ when the fraction of 40 kg P₂O₅ represents 50 % from the yearly rate of 80 kg P₂O₅; 0.0155 ppm/kg P₂O₅ when the fraction represents 33 % from the yearly rate of 120 kg P₂O₅ and 0.0232 when the fraction of 40 kg P₂O₅/ha represents 25 % from the yearly rate of 120 kg P₂O₅/ha-an (tab. 1, column 7).

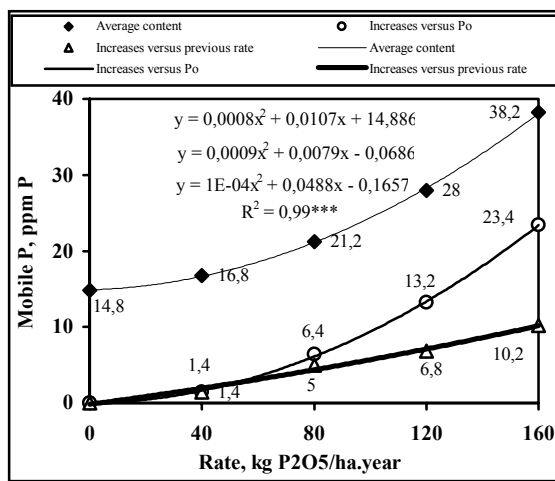


Fig. 3- Variation of the mobile P content, of the increases versus P₀ and of the increases versus previous rate (exp. I)

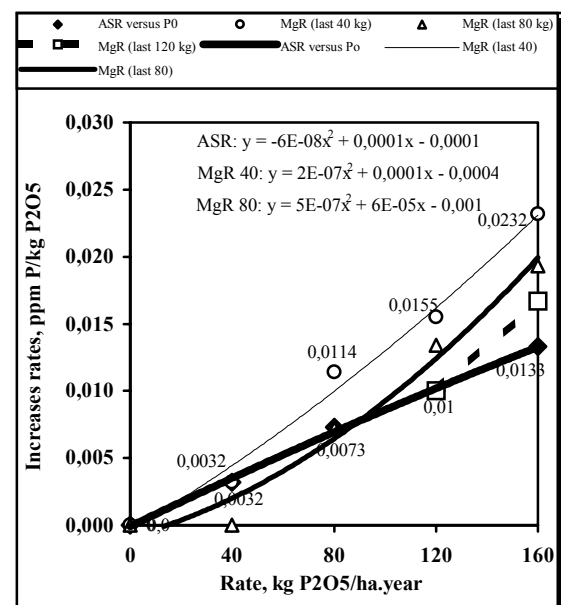


Fig. 4 – Variation of the average specific rates (ASR) of the increase of mobile P content versus P₀, ppm P/kg P₂O₅, and variation of marginal rates (MgR) of the increase determined by the last fraction of 40, 80, 120 kg P₂O₅ from the yearly rate (exp. I)

It can be concluded that *the first fractions from the fertilizer rate serve to satisfy the soil capacity to immobilize the mobile phosphates in hard mobilizable and plant accessible forms, the next fractions serve to satisfy the P needs of plants, and the last fractions of the rates contribute to durable increase of soil mobile P, if the soil capacity of retrogradation and the plants' requirement for nutrition have already been satisfied.*

The above-specified findings are also valuable when we consider the fraction of 80 or 120 kg P₂O₅/ha as the last fraction of the total fertilizer rate (table 1, column 8 and 9). But, the higher the last fraction of the total rate – taken into calculation, is, the smaller the MgR is. This thing can be easily observed if we compare the specific rates from the columns 7, 8, 9 and 10 of table 1 at the same level of the total fertilizer rate.

For example, at a total yearly fertilizer rate of 160 kg P₂O₅/ha, when the last considered fraction is of 40 kg P₂O₅/ha, the specific rate is of 0.0232 ppm P/kg P₂O₅; when it is taken into consideration the action of the last 80 kg from the total rate, the specific rate is 0.0193, when we consider that the last fraction is 120 kg P₂O₅/ha the specific rate is of 0.0167, and when the last fraction is even the total fertilizer rate, MgR is 0.0133 ppm P/kg P₂O₅.

In other words, *the last kg of P₂O₅ from a given rate of P fertilizer determines an increase of soil mobile P higher than the penultimate kg of the rate, this determines an increase higher than the antepenultimate and so on, and the first kg determines the smaller increase of soil mobile P; in exchange, it definitely determines the soil satisfaction to retrograde mobile P.*

The data and the above mentioned aspects concerning the modifications of the specific rates of accumulation of soil mobile phosphates depending on the fraction's size from the P₂O₅ rate applied represent absolute news in agrochemistry.

The average specific rates (ASR) and the marginal specific rates (MgR) of the mobile phosphates increasing can be used in prognosis models of soil agrochemical evolution and in bringing up-to-date relations of soil mobile P, in the interval between two successive soil survey studies, as related to the amounts of applied fertilizers.

Manure's influence. *The soil mobile P content continuously increases, almost linearly, together with the manure rate (fig. 5).*

The average specific rates (ASR) of the mobile P content increasing, as ppm P/t manure applied during the whole experimental period, decreases together with the increase of the manure rate (fig. 5), from 0,157 ppm/t at the rate of 20 t/ha (60 t totally), to 0.113 ppm/t at the rate of 40 t/ha (120 t totally) and to 0.106 ppm P/t at the rate of 60 t/ha (180 t totally).

Evolution of the mobile potassium content of the soil (tab. 2 and fig. 6 and 7). The yearly application of the N and P mineral fertilizers (exp. I), without potassium fertilizers, during 9 years, did not determine significant decreases of the *mobile K content* from the arable layer, the reddish-brown soil showing a sufficient capacity of remaking mobile K from less accessible K types; mobile K maintained around the value of 180 ppm K (tab. 2).

However, it is to be expected that the introduction in rotation of some crops with high K consumptions, such as sugar beet and sun-flower, should determine significant decreases of the mobile K in time.

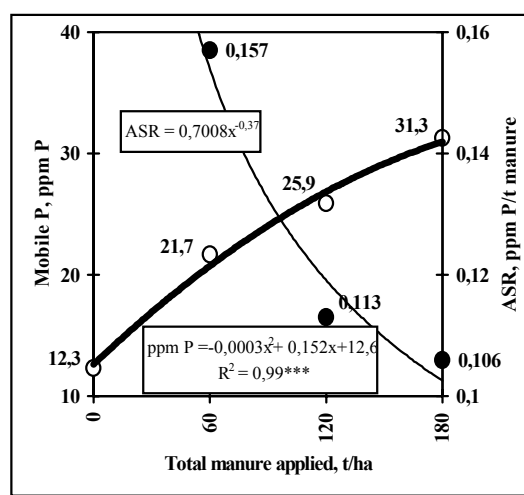


Fig. 5 – Variation of the P mobile content, ppm P, and average specific rate of P accumulation in soil, ppm/t manure, as related to the total amount of manure applied between 1983-1991 (exp. VI)

Table 2: Variation of the soil mobile K content, ppm K, and of the average specific rates of mobile K increasing (ASR), ppm K/kg K₂O, related to yearly rate of K applied 9 years: 1983-1991 (exp. III)

K rate, kg K ₂ O/ha.year	Background							
	P ₀ N ₀		P ₀ N ₁₀₀		P ₁₀₀ N ₀		P ₁₀₀ N ₁₀₀	
	Mobile K, ppm K	ASR, ppm K/kg K ₂ O	Mobile K, ppm K	ASR, ppm K/kg K ₂ O	Mobile K, ppm K	ASR, ppm K/kg K ₂ O	Mobile K, ppm K	ASR, ppm K/kg K ₂ O
0	180	–	181	–	179	–	182	–
50	235	0.1222	209	0.0622	222	0.0955	191	0.0200
100	292	0.1244	245	0.0711	275	0.1066	202	0.0222
150	346	0.1229	287	0.0785	314	0.1000	214	0.0237

In exchange, the application of mineral K fertilizers in yearly rates up to 150 kg K₂O/ha (tab. 2) determined the significant increase of the mobile K, the higher the rate was, the higher the K was, the increases being almost linear (fig. 6). The highest increases have been achieved at single K application or just at K and P application, when the differences versus unfertilized control (P₀N₀K₀) are significant even from the rate of 50 kg K₂O/ha; at maximum K rate, the mobile K surpassed 300 ppm K. On the N background, and especially of N and P, in which the K exports with the higher yields have been higher too, the mobile K accumulation in soil has been more reduced, this reaching only 287 ppm K, and 214 ppm K respectively.

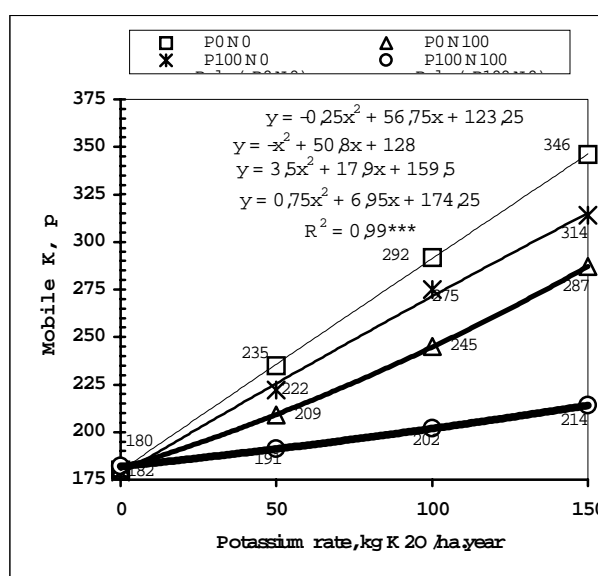
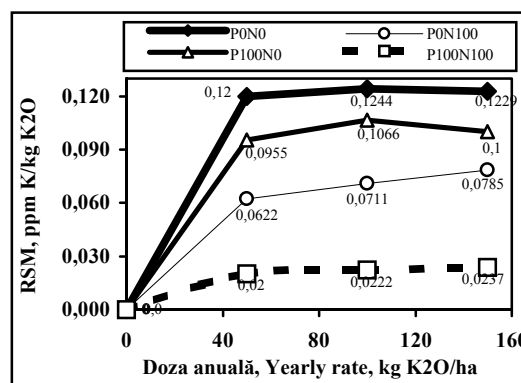


Fig. 6 – Variation of the soil mobile K content related to the yearly rate of K applied 9 years: 1983-1991 (exp. III)

The average specific rate of mobile K increase, ASR, ppm K/kg K₂O applied during 1983-1991, increase together with the fertilizer rate, being 0.020 at the rate of 50 kg, 0.022 at the rate of 100 kg and 0.0237 ppm K/kg K₂O at the maximum rate of 150 kg K₂O/ha year (tab. 2, fig. 7). These data are useful in prognosis models of the evolution of mobile K content.

Fig. 7 – Variation of the average specific rates (ASR) of the increase of mobile K content versus K₀N₀P₀, ppm K/kg K₂O (exp. III)



The manure determined increases of the mobile K content from 152 ppm K to only 172 ppm together with the increase of the rate, increases which were not higher than 20 ppm K, and were not statistically assured by tukey test.

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STUDIES CONCERNING THE SUSCEPTIBILITY OF INBRED MAIZE LINES AND MAIZE HYBRIDS TO Zn DEFICIENCY

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Summary

The paper presents some aspects concerning the absorption and accumulation of P, K and Zn in inbred maize lines (LC 423, LC402) and maize hybrids (F 322, Danubiu). The experiment was carried out to see the effect of the foliar fertilizers on the contents of P, K and Zn in the aerial plant parts at different moments of the vegetation period. Based on the nutrient plant contents calculated the susceptibility index to Zn deficiency was calculated. This index was expressed as the ratio between the numbers of Zn atoms that correspond to 1000 atoms of P and K in the aerial plant parts. According to the results, the susceptibility of the inbred maize lines and maize hybrids to Zn deficiency decreased with the increase of Zn/P and Zn/K ratios.

1. Introduction

Zn deficiency in maize is frequently a nutrition disorder in Romania and has a large extension especially on: acid soils, carbonate soils, overphosphatated soils; psamosoils and erodisoils. Numerous studies concerning the causes and the mechanisms which determine the appearance of the Zn deficiency in maize have been effectuated by Lukas R., 1972, Olsen S. R., 1972, Lăcătușu R., 1980, Borlan Z., 1994, 1995, and they established that:

- Zn deficiency is a complex nutrition disorder that implies other macro and micronutrient disorders in plant and depends on a great number of factors (soil chemical processes; biochemical processes from roots and shoots; technological crop conditions; climatic conditions).
- The symptoms of Zn deficiency appear during 4-6 leaves stage of maize because in this stage the rhythm of Zn absorption in plants is low as compared to the rhythms of N, P, K, Fe and Mn absorption.
- The different susceptibility of the maize hybrids to Zn deficiency is determined by the genetically features of the species.

The paper presents an experiment regarding the effect of special foliar fertilizers on the susceptibility indexes of Zn deficiency for two inbred maize lines and two maize hybrids.

2. Material and Methods

The experiment in pots was conducted in green house on the cambic chernozem from Fundulea with the following properties: humus - 2.5 %; pH (H₂O) - 6.3; mobile P - 40 ppm P; mobile K - 200 ppm K and clay - 29 %. The experiment had 3 factors:

- Factor A (maize cultivar): inbred maize lines - a₁) LC423; a₂) LC402; and hybrids - a₃) F322; a₄) Danubiu.

- Factor B (soil fertilization): b₁) 100 mg N, 150 mg P₂O₅, 50 mg K/kg soil; b₂) 100 mg N, 300 mg P₂O₅, 50 mg K/kg soil.
- Factor C (foliar treatment): c₁) watter; c₂) CFF 622; c₃) CFF 622a. The foliar treatments have been applied 3 times as diluted solutions (1 % concentrations). The chemical composition of the foliar fertilizers are presented in table 1.

Plant sampling:

- 1) 4-6 leaves stage (after a week from the first foliar treatment);
- 2) 9-10 leaves stage (after the next two foliar treatments).

Analyses: total content of Zn, P and K.

Data processing: the experimental data have been processed by the analysis of variance Duncan test for LSD; the susceptibility indexes of Zn deficiency were expressed as ratios between the numbers of Zn atoms to 1000 atoms of P and K in shoots (aerial parts).

Table 1. Chemical composition of the complex foliar fertilizers (CFF) tested on inbred maize lines and hybrids.

Elements and substances	CFF 622	CFF 622a
	g element or substance/kg or litre fertilizer	
N	242	139
P ₂ O ₅	94	164
K ₂ O	125	100
S	28	20
Fe	1	0.6
Zn	0.5	2
Cu	0.2	0.2
Mn	0.3	0.3
Co	-	0.001
Mo	0.1	0.67
B	0.4	1
Mg	-	-
Procaine-HCl ¹	1.20	1.20
Thiamin-HCl ²	0.60	0.60
Aminoacids	27	34
K-naftenates ³	2.4	2.4

¹ Procaine hydrochloride; ² thiamin hydrochloride; ³ potassium naphthenates

3. Results and discussions

The indexes of Zn deficiency susceptibility expressed as Zn/P and Zn/K ratios offer the advantage that reflects the participation of this micronutrient in structure and metabolism of plant. This kind of expression emphasises the changes of rhythms absorption of Zn, P and K in plants.

The data presented in table 2 shows that the stage of vegetation have influenced the values of Zn/P and Zn/K ratios. Thus, in the 4-6 leaves stage, these ratios had values between 0.74-1.62 for Zn/P ratio and between 0.35-0.76 for Zn/K, while in the 9-10 leaves stage, the ratios were high and had values between 1.66-2.75 for Zn/P and between 0.77-1.36 for Zn/K ratio. The change of ratios may be explained by the modification of the intensity of Zn, P, and K absorption during the vegetation period. In the first stage the intensity of P and K absorption exceeds the intensity of Zn absorption. This is reflected by the reduced number of Zn atoms to 1000 of P atoms and K atoms respectively, it inducing an increased susceptibility of plants to Zn deficiency in this stage.

The influence of A factor (inbred maize lines and hybrids) on the indexes of Zn deficiency susceptibility. In the first stage (4-6 leaves stage) there are significantly differences of Zn/P ratio between the inbred maize lines and hybrids and between the inbred maize lines. There are significantly differences of Zn/K ratio between lines, between hybrids

and hybrid F322 and the lines. The smallest values have the lines. In the second stage (9-10 leaves) the Zn/P ratio presents the significantly differences between all cultivars with excepting between LC 402 and F 322, and the Zn/K ratio presents significantly differences for

Table 2: Data regarding the variation of the Zn/P and Zn/K ratios depending on the maize cultivar, soil fertilization and foliar treatments.

A	B	C	4-6 leaves stage		9-10 leaves stage	
			Zn/P	Zn/K	Zn/P	Zn/K
a ₁) LC423	*b ₁) 150 mg P ₂ O ₅ /kg soil	c ₁) Watter	1.07	0.40	1.89	1.00
		c ₂) CFF 622	1.47	0.54	2.31	1.07
		c ₃) CFF 622a	1.62	0.63	2.45	1.33
	*b ₂) 300 mg P ₂ O ₅ /kg soil	c ₁) Watter	1.26	0.56	2.30	0.92
		c ₂) CFF 622	1.52	0.68	2.16	0.86
		c ₃) CFF 622a	1.11	0.54	2.75	1.36
a ₁) LC402	b ₁) 150 mg P ₂ O ₅ /kg soil	c ₁) Watter	1.06	0.41	2.21	1.05
		c ₂) CFF 622	1.26	0.51	2.40	1.10
		c ₃) CFF 622a	1.30	0.51	2.36	1.17
	b ₂) 300 mg P ₂ O ₅ /kg soil	c ₁) Watter	0.75	0.36	1.73	0.99
		c ₂) CFF 622	1.00	0.48	2.44	1.14
		c ₃) CFF 622a	1.09	0.47	1.81	0.83
a ₃) F322	b ₁) 150 mg P ₂ O ₅ /kg soil	c ₁) Watter	1.17	0.63	2.11	0.99
		c ₂) CFF 622	1.29	0.56	2.39	1.10
		c ₃) CFF 622a	1.36	0.60	2.75	1.32
	b ₂) 300 mg P ₂ O ₅ /kg soil	c ₁) Watter	0.85	0.50	1.89	1.27
		c ₂) CFF 622	1.15	0.76	1.71	1.09
		c ₃) CFF 622a	1.20	0.66	1.72	1.13
a ₄) Danubiu	b ₁) 150 mg P ₂ O ₅ /kg soil	c ₁) Watter	1.18	0.58	1.66	0.81
		c ₂) CFF 622	1.27	0.54	2.10	0.92
		c ₃) CFF 622a	1.13	0.47	2.66	1.00
	b ₂) 300 mg P ₂ O ₅ /kg soil	c ₁) Watter	0.74	0.55	1.73	1.13
		c ₂) CFF 622	1.28	0.70	1.89	1.01
		c ₃) CFF 622a	1.22	0.47	1.88	0.77
Averages A factor	a ₁) LC 423		1.34a	0.559b	2.310a	1.094b
	a ₂) LC 402		1.07c	0.458c	2.159b	1.047c
	a ₃) F322		1.17b	0.619a	2.093b	1.148a
	a ₄) Danubiu		1.14b	0.550b	1.921c	0.940d
	LSD 5%		0.055	0.036	0.109	0.046
	LSD 1%		0.074	0.048	0.146	0.062
Averages B factor	b ₁) 150 mg P ₂ O ₅ /kg soil		1.26a	0.533b	2.239a	1.074a
	b ₂) 300 mg P ₂ O ₅ /kg soil		1.10b	0.560a	2.006b	1.041a
	LSD 5%		0.039	0.025	0.077	0.032
	LSD 1%		0.052	0.034	0.103	0.049
Averages C factor	c ₁) Watter		1.01b	0.501c	1.941b	1.019b
	c ₂) CFF 622		1.27a	0.595a	2.175a	1.039b
	c ₃) CFF 622a		1.25a	0.543b	2.251a	1.114a
	LSD 5%		0.048	0.031	0.095	0.040
	LSD 1%		0.064	0.041	0.127	0.053

*) + 100 mg N and 50 mg K/kg soil

all cultivars. The higher values for Zn/P ratio were registered for LC 423 (1.34 in first stage and 2.31 in the second stage). From these it can be concluded that the indexes of Zn deficiency susceptibility are determined by genetically features of the inbred maize lines and hybrids.

The influence of B factor (phosphorus soil fertilization) on the indexes of Zn deficiency susceptibility. The soil fertilization with 300 mg P₂O₅/kg soil assured a significantly decrease of Zn/P ratio in the both stages (1.10 in first stage and 2.006 in the second stage) and determined an increasing of the susceptibility of plants to Zn deficiency.

The influence of C factor (foliar treatments: watter; CFF 622; CFF 622a) on the indexes of Zn deficiency susceptibility. The both CFF had significantly influence on the Zn/P and Zn/K ratios (with excepting Zn/K ratio for second stage and for CFF622) as compared to control with watter and have assured high values of these ratios.

The best results of Zn/P ratio were obtained with CFF 622a (1.25 in first stage and 2.251 in the second stage). In fact, both CFF gave good results concerning Zn/P ratio (good Zn absorption), between these two CFF are not significantly differences. Therefore the foliar fertilizers have an effect of intensification of the Zn absorption in plants. For this reason the foliar fertilizers have to be used in order to diminish of the susceptibility of plants to Zn deficiency.

In figure 1 is presented a positive correlation between the ratio Zn atoms/1000 K atoms and the ratio Zn atoms/1000P atoms. The correlation coefficient is distinctly significant and shows the implication of P and K nutrient in absorption of Zn in plants.

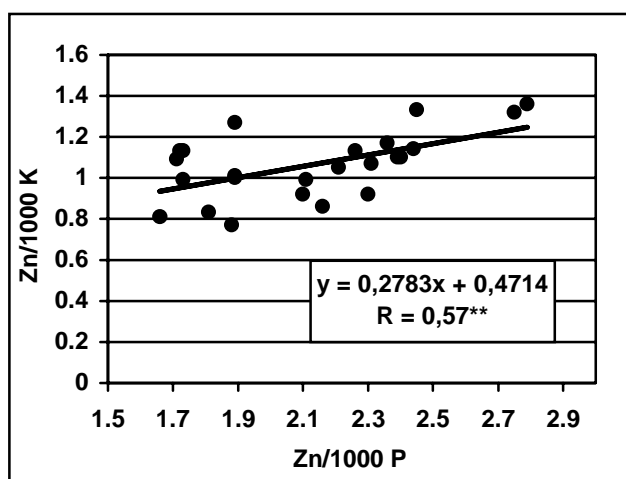


Fig. 1. Correlation between the ratio Zn atoms/1000K atoms and the ratio Zn atoms/1000 P atoms in dry matter (second stage).

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SOIL RESISTANCE TO ACIDIFICATION PROCESS

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Summary

Many actual problems are related to phenomena of acidification of soil reaction, determined by acid rains or some agrochemical practices, like the application of fertilizers with high potential of acidification.

Soil resistance to acidification can be determined using some indices of reaction buffering capacity (I-RBC) expressed as a function of the sum of exchangeable bases (SEB), hydrolitical acidity (Ah), total cation exchange capacity of soil (CEC) and the protons' activity in soil solution.

For this purpose, experiments with controlled acidification on soils that have been different as reaction and cationic exchange properties have been carried out in vegetation house.

As a result of these experiments, high correlation has been found between pH changes versus reference pH (corresponding to a 95 % degree of base saturation) and the above mentioned indices. Also, the soil with the highest buffering capacity for reaction resisted best to the acidification process.

1. Introduction

The reaction buffering capacity of soil provides the ability to resist any tendency to change its reaction in both acid and alkaline senses. Generally, the soil has a significant reaction buffering capacity and for this reason its reaction change is normally insignificant. The researches about reaction buffering capacity are of a present interest and are becoming more important caused by the progressive acidification phenomena of soils (caused by acid rains and the application of fertilizers with high potential of acidification). The paper presents an interesting method of determining the reaction buffering capacity of soils. The objective of this research was to study the influence of the acidification process on the reaction buffering capacity of soils.

2. Materials and methods

For the above mentioned purpose, an experiment with progressive acidification (protonation) was carried out in the green house of the Research Institute for Soil Science and Agrochemistry.

In this experiment soil material from the 0-20 cm layer of three kinds of soil was used: *cambic chernozem* from Fundulea, *albic luvisol* from Albota and *chromic luvisol* from Tâncăbești. Three levels of protonation were set up for each soil type:

- level I, untreated soil;
- level II, soil acidified with 2 me HCl/100 g soil;
- level III, soil acidified with 4 me HCl/100 g soil.

Using progressive acidification (protonation) and four replicates, through these treatments we obtained different values of the cation exchange capacity (CEC), degree of the base saturation (V_{Ah}), sum of exchangeable bases (SEB) and hydrolitical acidity (Ah).

The experiment was carried out in small pots (1.25 kg soil) which have been irrigated with distilled water rised through capillarity from the sand bed.

Using four indices of the reaction buffering capacity of soils (I-RBCS), proposed by Borlan (1995), the studied soils have been characterized and classified from the reaction buffering capacity's point of view. Their formulas and definitions are the following:

$$I - RBCS_1^{IRSA} = \lg \frac{[SEB]}{[Ah]} \quad (1)$$

$$I - RBCS_2^{SEB} = \lg \frac{[SEB]}{(H^+)} \quad (2)$$

$$I - RBCS_3^{Ah} = \lg \frac{[Ah]}{(H^+)} \quad (3)$$

$$I - RBCS_4^{CEC} = \lg \frac{[CEC]}{(H^+)} \quad (4)$$

in which: SEB = sum of exchangeable bases; [SEB] = equivalents \cdot kg $^{-1}\cdot$ 0,4;
 Ah = hydrolitical acidity; [Ah] = moles \cdot kg $^{-1}\cdot$ 0,4;
 CEC = cation exchange capacity; [CEC] = equivalents \cdot kg $^{-1}\cdot$ 0,4;
 H = proton activity in the soil solution; (H $^+$) = moles \cdot liter $^{-1}$.

In order to estimate Δ pH, the pH changes because of the acidification, the folowing formula was used:

$$\Delta pH = pH_t - pH_s \quad (5)$$

in which: pH $_t$ = theoretical pH (pH at 95 % degree of the base saturation);
 pH $_s$ = pH of the soil at a given level of acidification.

The theoretically pH (pH $_t$) was estimated using the formula elaborated by Borlan and Hera (1984) for soils on which fertilizers have been applied:

$$pH_t = \left[\left(a + \frac{b}{[CEC]} \right) + c \cdot V \right] + \lg \frac{[SEB]}{[Ah]} \quad (6)$$

in which: a, b, c = constants (a = 2,55; b = 9,0; c = 0,0255).
 CEC = cation exchange capacity = SEB + Ah; [CEC] = me/100 g soil;
 V $_{Ah}$ = degree of the base saturation, %; V $_{Ah}$ = (SEB/CEC) \cdot 100;
 SEB = sum of exchangeable bases (Kappen method); [SEB] = me/100 g soil;
 Ah = hydrolitical acidity (Kappen method); [Ah] = me/100 g soil.

In order to estimate Δ V $_{Ah}$, the changes of V $_{Ah}$ because of the acidification, the folowing formula was used:

$$\Delta V_{Ah} = V_{Ahr} - V_{Ahs} \quad (7)$$

where: V $_{Ahr}$ = reference V $_{Ah}$ = 95 % to which corresponds the pH $_t$;
 V $_{Ahs}$ = V $_{Ah}$ of the soil at a given level of acidification.

For conventional interpretation of I-RBCS, theirs values have been separated in domains which correspond to certain values of Δ pH (table 1).

Table 1: Border values for conventional interpretation of I-RBCS and significance of separated domains for the reaction buffering capacity of soil acidified by protonation (Borlan et al., 1995)

-ΔpH	Values (domains)				Reaction buffering capacity of soil
	I-RBCS ^{IRSA}	I-RBCS ^{SEB}	I-RBCS ^{Ah}	I-RBCS ^{CEC}	
< 0.0	> 1.00	> 5.6	> 4.6	> 5.6	high
0.0 - 0.5	0.75 - 1.00	5.1 - 5.6	4.3 - 4.6	5.2 - 5.6	very high
0.5 - 1.0	0.50 - 0.75	4.5 - 5.1	4.0 - 4.3	4.7 - 5.2	moderate
1.0 - 1.5	0.25 - 0.50	3.9 - 4.5	3.7 - 4.0	4.1 - 4.7	reduced
1.5 - 2.2	0.0 - 0.25	3.1 - 3.9	3.2 - 3.7	3.5 - 4.1	low
> 2.2	< 0.0	< 3.1	< 3.2	< 3.5	very low

3. Results and discussions

Table 2 presents the pH and cationic exchange properties of the 0-20 cm soil layer for all the three soils used for experiment (*cambic chernozem* from Fundulea, *albic luvisol* from Albota and *chromic luvisol* from Tâncăbești).

Table 2: The pH values and cationic exchange properties of the soils used in experiment (0-20 cm layer)

Location	Soil type	pH (H ₂ O)	Cationic exchange properties			
			SEB	Ah	CEC	V
			me/100g soil			(%)
Fundulea, Călărași	Cambic chernozem	5.83	22.77	1.78	24.55	92.8
Albota, Argeș	Albic luvisol	5.26	11.18	3.04	14.22	78.6
Tâncăbești, Ilfov	Chromic luvisol	5.34	15.65	3.76	19.41	80.6

The modifications of the soil reaction (pH), hydrolytical acidity (Ah), degree of the base saturation (V_{Ah}) and reaction buffering capacity as a result of protonation by HCl application are presented in table 3.

The theoretical pH (pH_t) estimated with formula (5) for a degree of base saturation of 95 % has the following values: pH_t = 6,59 for Fundulea soil; pH_t = 6,81 for Albota soil; pH_t = 6,74 for Tâncăbești soil.

We calculated the values of ΔpH = pH_t – pH_s and we correlated ΔpH with I-RBCS of the three studied soils. There are negative, significant correlations between ΔpH and all the I-RBCS studied indices, but the best correlations, statistically very significant, are those with I-RBCS^{CEC} and I-RBCS^{SEB} (figure 1 and figure 2).

The higher the soil's reaction buffering capacity values are (the I-RBCS^{CEC} respectively I-RBCS^{SEB} values are higher) the lower the ΔpH's values are (the sample's pH approaches the theoretical pH corresponding to a degree of the base saturation of 95 %).

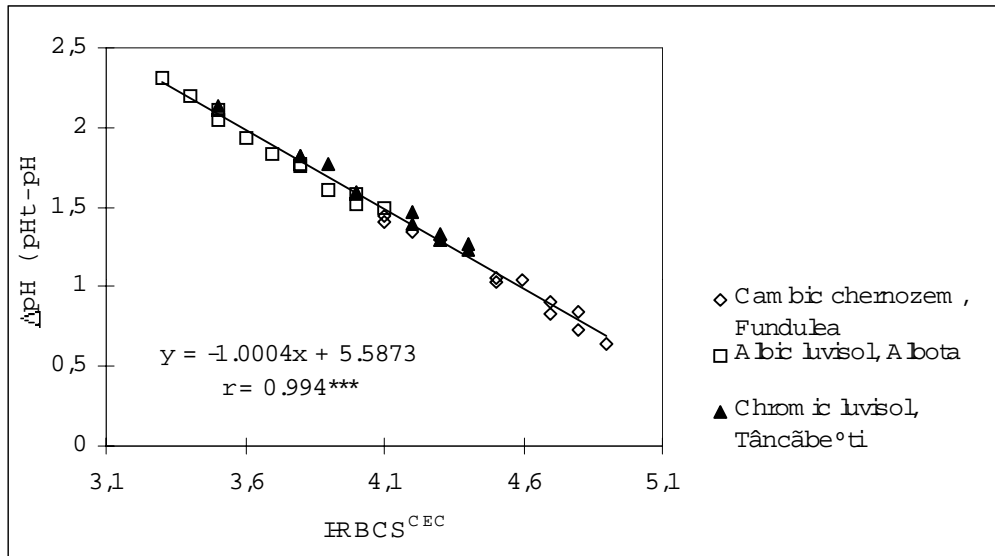


Figure 1. Correlation between ΔpH and I-RBCS^{CEC}

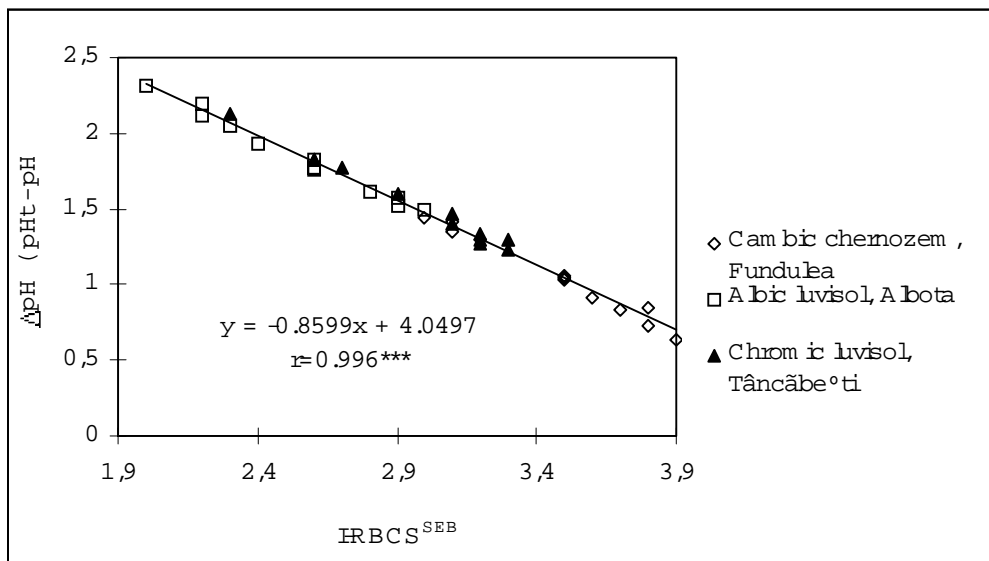


Figure 2. Correlation between ΔpH and I-RBCS^{SEB}

The conventional interpretation of the reaction buffering capacity of the studied soils through the I-RBCS^{CEC} and its change as a consequence of protonation are presented in table 3.

The *cambic chernozem* stands acidification the best and has the highest reaction buffering capacity; in the case of *albic luvisol*, the acidification process is the strongest and this soil shows the lowest reaction buffering capacity. The *chromic luvisol* has an intermediate position from this point of view.

Table 3: Analytical values concerning reaction and cationic exchange properties and soil reaction buffering capacity obtained as consequences of protonation treatments (average values of 4 replicates)

Soil type and treatment*	pH (H ₂ O)	Δ'pH ** (H ₂ O)	SEB	Ah	CEC	V _{Ah}	I-RBCS ^{CEC}	I-RBCS ^{CEC} ***	Reaction buffering capacity of soil
			me/100 g soil			%			
Cambic Chernozem									
Untreated soil	5.83	0	22.77	1.78	24.55	92.8	4.8	0	moderate
2 me HCl/100 g soil	5.58	0.25	20.97	2.72	23.69	88.5	4.6	0.2	reduced
4 me HCl/100 g soil	5.22	0.61	19.71	3.25	22.96	85.8	4.2	0.6	reduced
Albic Luvisol									
Untreated soil	5.26	0	11.18	3.04	14.22	78.6	4.0	0	low
2 me HCl/100 g soil	4.99	0.27	9.30	4.40	13.70	67.9	3.7	0.3	low
4 me HCl/100 g soil	4.64	0.62	8.42	6.01	14.43	58.4	3.4	0.6	very low
Chromic Luvisol									
Untreated soil	5.34	0	15.65	3.76	19.41	80.6	4.2	0	reduced
2 me HCl/100 g soil	5.11	0.23	14.08	4.93	19.01	74.0	4.0	0.2	low
4 me HCl/100 g soil	4.86	0.48	12.76	6.73	19.48	65.4	3.8	0.4	low

* Acidification by HCl; ** Δ'pH = differences between untreated and treated (acidified) soil; *** Δ I-RBCS^{CEC} = differences between untreated and treated (acidified) soil

The differences ΔV_{Ah} between the reference V_{Ahr} (95 %, for which was calculated the theoretical reference pH, pH_t) and the V_{Ahs} of the samples at different levels of acidification correlate negatively and very significantly with the indices of the buffering capacity I-RBCS^{CEC}, which means that the higher the soil buffering capacity is, the smaller the losses of the bases, and the changes of V_{Ah} are, the soil buffering the debasification, and the acidification respectively. From the point of view of the decrease of the buffering capacity and of the V_{Ah} decrease, the three studied soils can be put in the following series: Fundulea cambic chernozem, Tâncăbești chromic luvisol, Albota albic luvisol.

The higher the soil CEC is, the higher the soil reaction (acidification) buffering capacity is. Budoi (2000) showed that to the arable soil, CEC depends in the highest measure on the clay and humus content of the soil and on the nature of the clay minerals and on the humus nature. Only if one or another process, acidification for example, determines changes of the content and the nature of the clays and humus, it also determines changes of CEC, and by this changes of the reaction (acidification) buffering capacity of soil (I-RBCS). Acidification can produce significant changes of the clay nature and of the humus content and nature only if it is high and its action is for long time.

In the case of the three studied soils, the action of protonation with HCl determined decreases of pH with up to 0.6 units, which means not too high, and it was not for a long period of time, so that it did not determine notable changes of CEC (table 3). However, the decrease of I-RBCS^{CEC} with up to 0.6 units as compared to the initial values, which means with up to 15 %, is explained by the decrease of the soil solution pH itself. It is to be noted the parallelism between the decrease of I-RBCS^{CEC} as compared to the initial values and the

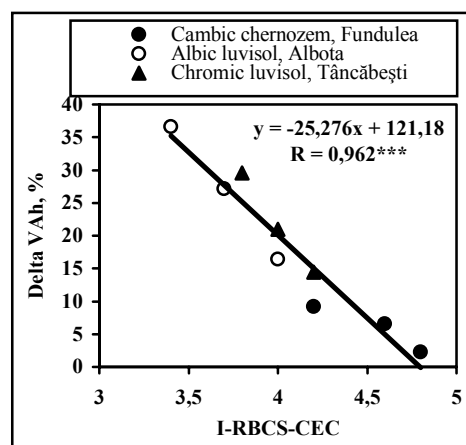


Figure 3. Correlation between ΔV_{Ah} and I-RBCS^{CEC} (average values of 4 replicates)

decrease of pH as compared to the initial values, between them being a linear, very significant correlation (figure 4).

Researches done by Budoï et al. (1988, 2000) showed that the curve of the pH change and the buffering curve (in a large pH area) depending on the amount of acidifying material is of sigmoidal shape, having a linear zone.

The linear correlation between the pH changes versus the initial values and the amount of HCl applied to the three studied soils (figure 5) shows that this experiment has been done in such a zone.

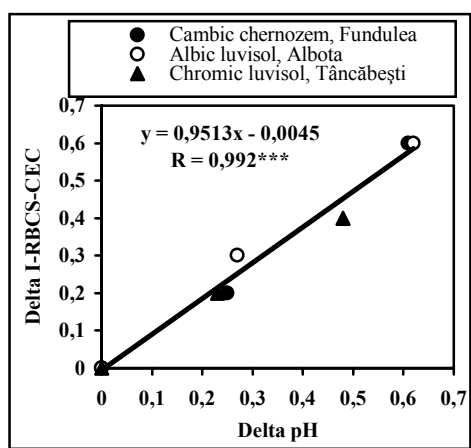


Figure 4. Correlation between $\Delta I-RBCS^{CEC}$ and ΔpH (average values of 4 replicates)

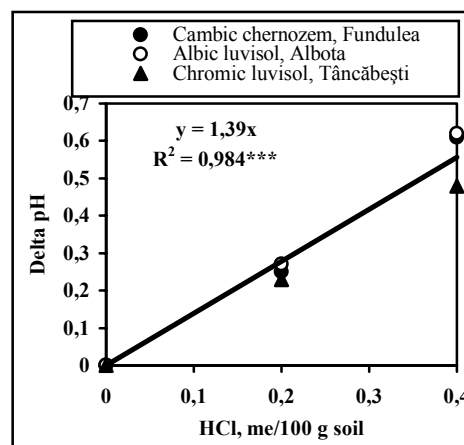


Figure 5. Correlation between ΔpH and the amount of HCl used for acidification (average values of 4 replicates)

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RESEARCHES CONCERNING THE EFFECT OF SOME FOLIFERTFUNGIPROTECT (FFFP) ON FOLIAR DISEASES, YIELD AND QUALITY IN GRAPEVINE

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Summary

The Folifertfungiprotect (FFFP) are special foliar fertilizers from new generation used to stimulate the plant metabolism, to increase the yield and its quality – because of their macro, micronutrients and biostimulative substances – and in the meantime to protect the leaves against foliar diseases, especially mildew, due to the persistent film of dispersed hydroxides and basic salts included in ammonium, potassium and sodium lignosulphonates.

4 subtypes of FFFP have been tested. They diminished the *Plasmopara viticola* attack in Merlot variety of grapevine from 88 % in control up to 58 %. They also increased the chlorophyll content of the leaves, the photosynthesis intensity, and finally increased significantly the yield.

In this experiment, good positive correlations have been found between total photosynthesis intensity and chlorophyll content, between yield and photosynthesis intensity, as well as between must acidity and its sugar content.

The protective effect of EFFF against foliar diseases is also an environmental protection because the use of pesticides can be reduced.

1. Introduction

The Folifertfungiprotect products, FFFP, are new unconventional means of fertilizers applicable on leaves, with effect of yield increasing and environment protection against pollution with nutrient ions and their associated. FFFP-s resolve the problem of the supplementary fertilization, of plant stimulation by foliar way concomitantly with the efficient protection of these against the diseases produced by pathogen fungi, like is *Plasmopara viticola* in grapevine. They throw aside thus some of the drawbacks that produce the known complex foliar fertilizers (Borlan et al., patent no 96-02279, registered to OSIM).

2. Materials and methods

In order to test the Folifertfungiprotect product, with four subtypes (5, 7, 8, 10), in 1998 an experience was organized to grapevine, var. Merlot/Kober 5 BB, in bearing vineyard from SCPVV Bujoru, that was set up in 1978. Three levels of basic soil fertilization with macronutrients were assured (kg N, P₂O₅, K₂O/ka): N₀P₀K₀; N₅₀P₅₀K₅₀; N₁₀₀P₁₀₀K₁₀₀. On each level, two controls (C.) were used: C.SP – plants were sprayed only with phytosanitary protecting substances (SP); C.water – plants were sprayed only with water. The phytosanitary protecting substances used for each treatment were: I) soaking S + Neoron + Mikal; II) Topas + Ridomil; III) Sandofan + Kumulus; IV) Curzate + Derosal. The four FFFP subtypes (5, 7, 8, 10), which chemical composition is presented in table 1, were applied on leaves as diluted solutions, in concentrations of 0.25 %. Four foliar treatments were applied, corresponding to

the main diagnostic stages: before blossom, at the end of blossom and then at interval of two weeks up to the berries ripening.

Table 1: Chemical composition of the Folifertfungiprotect products – FFFP

Substance	Concentration, g/kg FFFP			
	FFFP 5	FFFP 7	FFFP 8	FFFP 10
Na ₂ B ₄ O ₇ ·10H ₂ O	8,8	0,4	4,4	5,5
CoSO ₄ ·7H ₂ O	5	2,5	2,5	5
CuSO ₄ ·5H ₂ O	225	230	230	235
FeSO ₄ ·7H ₂ O	5	4	4	5
K salt (with 50 % K ₂ O)	30	30	30	-
MgSO ₄ ·7H ₂ O	40	40	40	40
MnSO ₄ ·H ₂ O	28	25	25	30
(NH ₄) ₂ Mo ₇ O ₂₄ ·4H ₂ O	0,4	0,4	0,5	0,5
Urea (N source) with less 1 % biuret	80	75	75	80
S (elemental S)	16	15	12	14
ZnSO ₄ ·7H ₂ O	80	82	84	85
Lignosulphonates*	482	492	493	497

* with 50 % dry substance, neutralized with NH₃ up to a pH of 7

A series of observation and measurements were effectuated: the length of the yearly growings; their degree of maturation; buds viability and shoots fertility et al. From the point of view of climatic condition, the precipitation fall in april – august (210 mm) created favorable conditions for *Plasmopara viticola*. Statistical processing of the results was effectuated by analysis of variance method and Tukey test for the establishment of the significance of differences, and by correlation and regression methods in order to establish the relations between the researched indicators.

3. Results and discussions

The viability of the fruiting buds in 1998 in Merlot variety was between 77 and 97,8 %, being influenced by the basic soil fertilization and by the foliar fertilization, on the best supplied level (N₁₀₀P₁₀₀K₁₀₀) registering the highest percentage of buds viability (92 % as average), as well as a higher fertility of the shoots.

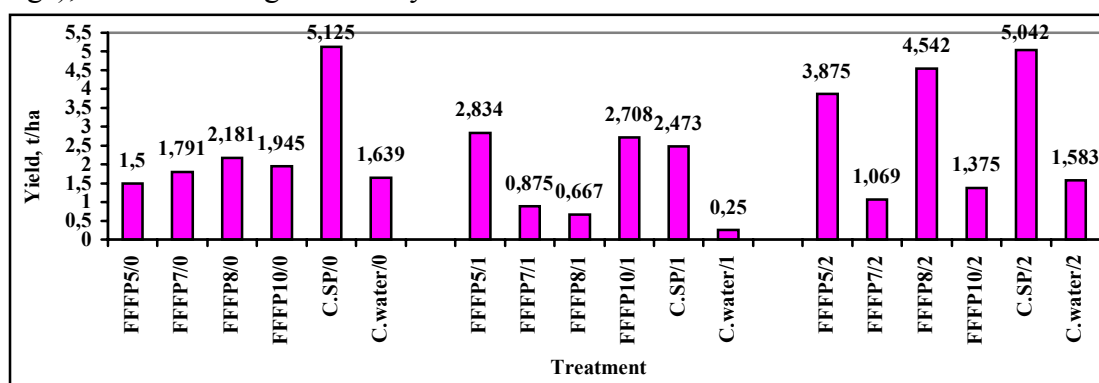


Fig. 1 – Variation of the grape yield related to the type of Folifertfungiprotect (FFFP) and of the basic soil fertilization (0 = N₀P₀K₀, 1 = N₅₀P₅₀K₅₀, 2 = N₁₀₀P₁₀₀K₁₀₀); C signifies control; DL₅ % = 0,44 (averages soil fertilization), 0,52 (averages FFFP), 0,81 (interactions soil fertilization × FFFP)

Grape yield (fig. 1). On the level without soil fertilization ($N_0P_0K_0$), significant yield increases versus control with water brought only the FFFP 8; on the middle level of soil fertilization ($N_{50}P_{50}K_{50}$), FFFP 5 and FFFP 10 determined higher yields versus both controls, but the yield increases were statistically assured only versus the control with water; on the higher level of soil fertilization ($N_{100}P_{100}K_{100}$), the application of the Folifertfungiprotect FFFP 5 and FFFP 8 determined very significant yield increases versus spraying with water, not exceeding that obtained in the control with the phytosanitary treatment.

It is to be noted the fact that the yield increases brought by the foliar treatments with FFFP were as much higher as the soil was better fertilized at basic fertilization. Selection of one FFFP type or another depends on the level of soil fertilization.

The Plasmopara viticola attack. As it concerns the influence of the FFFP on the manna attack we ascertain that, generally, the degree of attack of *Plasmopara viticola* at the clusters level was smaller in the variants with FFFP treatments as compared with the control sprayed with water (fig. 2). Under this aspect, the FFFP 5 and FFFP 7 subtypes detached by that that led to a more substantial reduction of the attack of fungi, with up to 30 % on the middle level of soil fertilization.

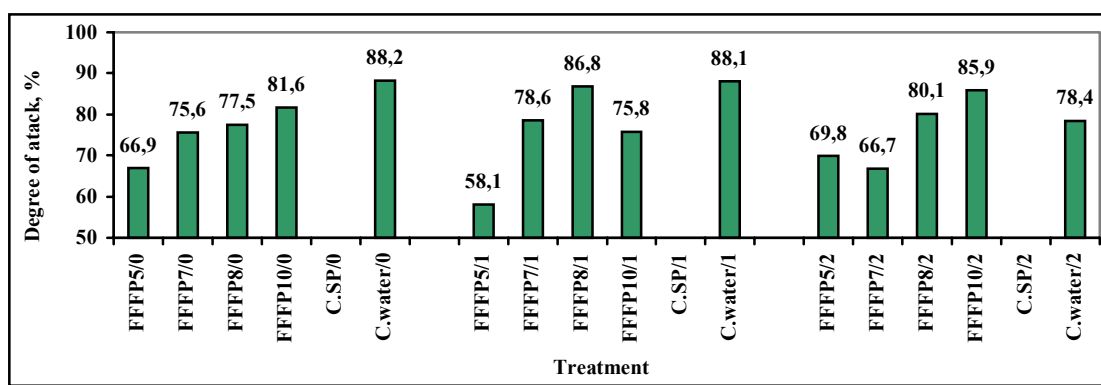


Fig. 2 – Variation of the degree of *Plasmopara viticola* attack, related to the type of Folifertfungiprotect (FFFP) and of the basic soil fertilization (0 = $N_0P_0K_0$, 1 = $N_{50}P_{50}K_{50}$, 2 = $N_{100}P_{100}K_{100}$); C signifies control

Assimilation of the chlorophyll. This was also positively influenced by the foliar application of FFFP, registering an increasing of the total chlorophyll content as compared with the two controls, especially on the medium level of the soil fertilization (fig.3).

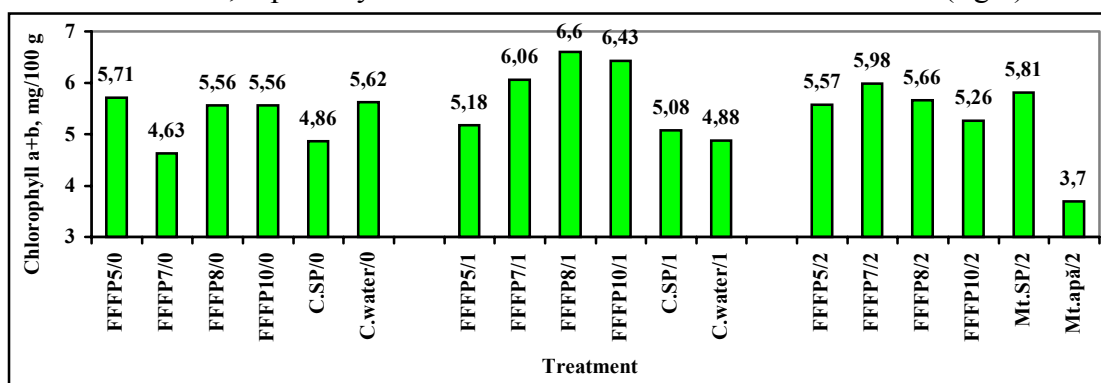


Fig. 3 – Variation of the content of total chlorophyll (a + b) related to the type of Folifertfungiprotect (FFFP) and of the basic soil fertilization (0 = $N_0P_0K_0$, 1 = $N_{50}P_{50}K_{50}$, 2 = $N_{100}P_{100}K_{100}$); C signifies control

Photosynthesis intensity. This was also evidently influenced as effect of FFFP application, the data distinguishing its increasing on the last two levels of soil fertilization (fig.4), standing out the FFFP 8 product.

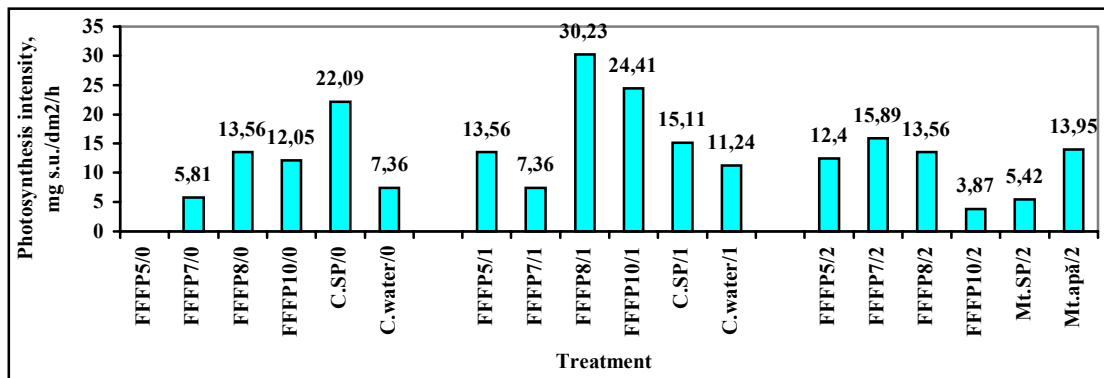


Fig. 4 – Variation of the photosynthesis intensity related to the type of Folifertungiprotect (FFFP) and of the basic soil fertilization (0 = N₀P₀K₀, 1 = N₅₀P₅₀K₅₀, 2 = N₁₀₀P₁₀₀K₁₀₀); C signifies control

Sugar content of the must. Was positively influenced both by the soil and foliar fertilization, this last one determining an increasing of sugar content especially in the variants FFFP 8 and FFFP 10 as compared with the two controls (fig.5).

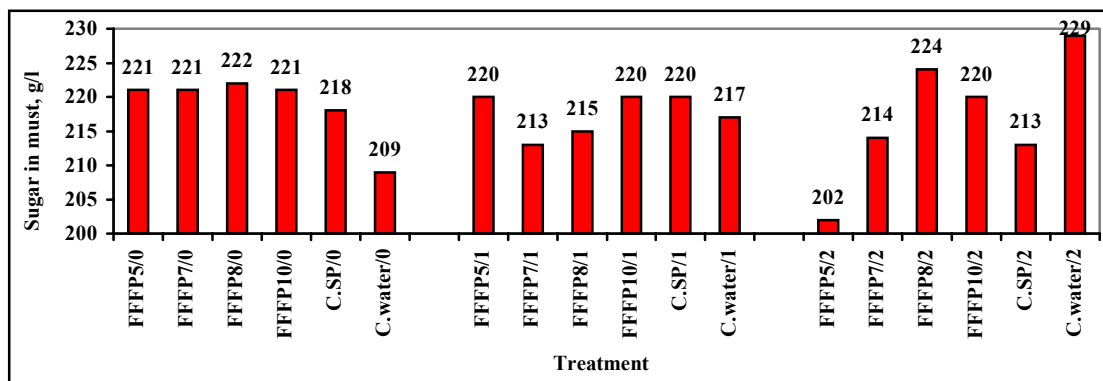


Fig. 5 – Variation of the sugar content of the must related to the type of Folifertungiprotect (FFFP) and of the basic soil fertilization (0 = N₀P₀K₀, 1 = N₅₀P₅₀K₅₀, 2 = N₁₀₀P₁₀₀K₁₀₀); C signifies control

The high sugar content in the control sprayed with water can be explained by the small yield realized; although the FFFP brought yield increases, they maintained also a high sugar concentration, higher yields being not followed by a high dilution effect.

Must acidity. The foliar fertilization with FFFP diminished the level of the must's acidity especially in the variants in which was registered a higher sugar content in must (fig.6).

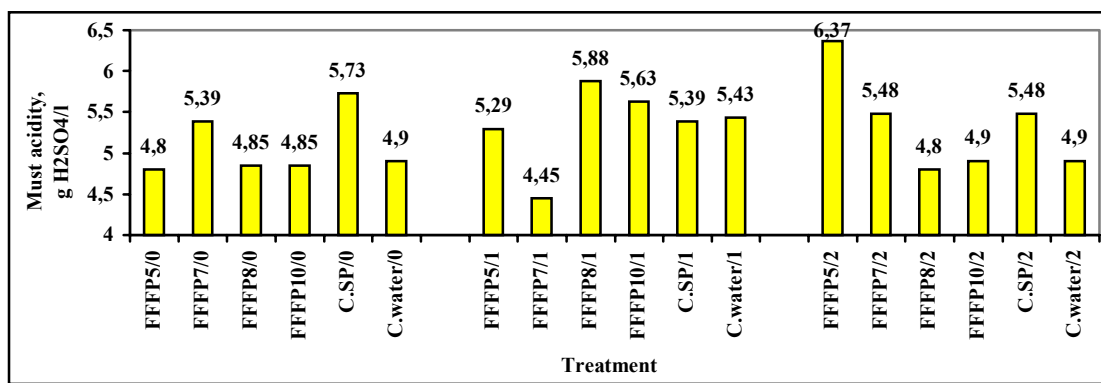


Fig. 6 – Variation of the must acidity related to the type of Folifertfungiprotect (FFFP) and of the basic soil fertilization (0 = N₀P₀K₀, 1 = N₅₀P₅₀K₅₀, 2 = N₁₀₀P₁₀₀K₁₀₀); C signifies control

The data processing by correlation and regression method shows that there is a positive significant correlation (fig. 7) between the intensity of the photosynthesis and the content of total chlorophyll (a + b). And between the yield of grapes and the photosynthesis intensity there is a positive relation (fig. 8), although statistically unassured.

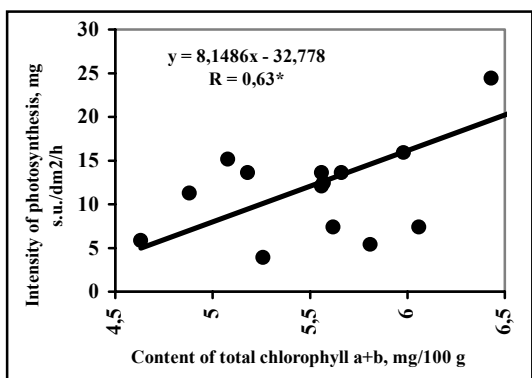


Fig. 7 – Correlation between intensity of photosynthesis and the content of total chlorophyll (a + b)

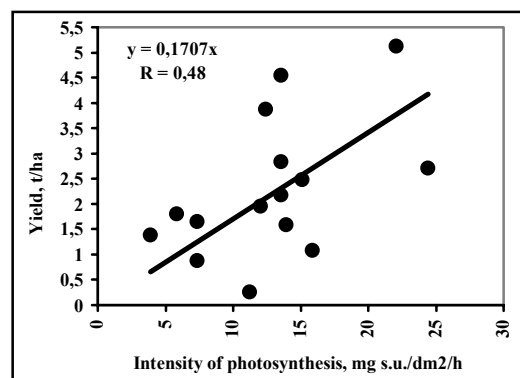
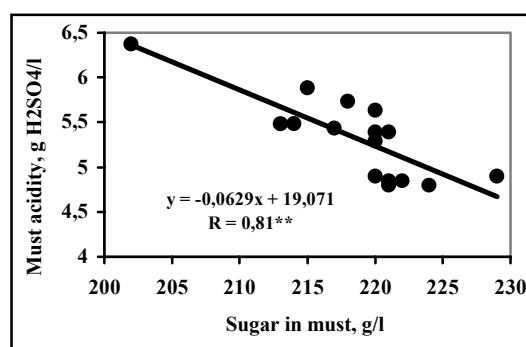


Fig. 8 – Correlation between yield and the intensity of photosynthesis

Fig. 9 – Correlation between must sugar content and must acidity



There is an inverse, distinctly significant correlation between the acidity of the must and the sugar content (fig. 9), the accumulation of the sugar in must determining a decreasing of its acidity.

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THE EFFECT ON FRUIT QUALITY OF SOME NEW COMPLEX FOLIAR FERTILIZERS APPLIED IN APPLE TREE

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Summary

The researches have been carried out in stationary field experiments during 6 years in apple tree, some of the most common fruit trees in Romania. The special complex foliar fertilizers (CFF) tested increased the yields of fruits, and also positively influenced some of the characteristics that assure high quality of fruits. The data obtained in apple trees, Delicious Golden Spur/MM 106, concerning some indexes that reflect the conservation capacity of fruits in storehouse (% of healthy fruits, % of damage produced by diseases, % of damage produced by dehydration), showed the increase of the fruits conserving capacity by almost total reduction of the damage produced by diseases in storehouse and of damages produced by dehydration. Also, the application of some complex foliar fertilizers, such as CFF 6282 and CFF 6288, positively influenced some of the biochemical indexes of the fruits. For example, increases of the sugar content in apple juice with 0.02–0.9 % have been registered.

1. Introduction

All over the world, the application of the nutrients as diluted solutions sprayed on leaves is a current practice, especially in pomiculture. It was demonstrated that foliar fertilization could lead to high yields, with high quality and conservation capacity of fruits in storehouse. The foliar fertilization is also an efficient method because of the reduced consumption of nutrients on unit surface, as well as because of the reduced costs with application, this being done concomitantly with obliged pesticide treatments. The high economically efficiency of the supplementary foliar fertilization is a consequence of high yield increases. Also the foliar fertilization may be considered an efficient measure of protecting the environment against chemical pollution, by a reduced dissipation of the nutrients. This paper presents the positive influence of some new complex foliar fertilizers (CFF) on yield and fruit quality of apple tree.

2. Materials and methods

In the conditions from SCPP Caransebeș area, special researches with complex foliar fertilizers (CFF) have been set up in apple tree, Spur Golden Delicious/MM106, beginning 1987. Besides other numerous aspects, special attention was given in this experiment to the influence of the CFF on the yield level and fruit quality. The different CFF, produced in Romania and other countries, have been tested between 1987-1994. They have been applied as diluted solution on the leaves of plants, in concentration of 0.1–1 %. Generally, four treatments have been applied each year, the consumption of diluted solution being 1000 l/ha for a treatment.

The soil was white luvisol, highly pseudogleized, with medium supply of the main nutrients.

The results obtained have been statistically processed by the analysis of variance method and the Student test.

3. Results and discussions

The effect of the complex foliar fertilizers on the yield

In the area of SCPP Caransebes the unfavourable pedoclimatic conditions for the developments of the apple tree (with long periods of drought, associated with hot summers) negatively influenced the plant growth.

The yield increases, averaged over the five years of experimentation 1987 - 1991 (table 1), are realized as effect of the supplementary foliar fertilization, have been placed between 5.40–9.64 t/ha (32–56 %). Even if they are so high, they are not statistically assured because of the very high variations of the yields due to the variation of the climatic conditions of the years. But, the positive effect of the complex foliar fertilizers (CFF) is emphasized by the yearly yield increases, these being statistically assured. The first three CFF which determined the highest yield increases have been those worded by Borlan et al.: CFF 2954 with 9.64 t/ha (56 %); CFF 2955 with 7.66 t/ha (45 %) and CFF 2953 with 7.57 t/ha yield increase (44 %). The high differences between years concerning the yields are due to the variation of the climatic conditions.

Table 1: Experimental data regarding the effect of the complex foliar fertilizers (CFF) on fruit yield in apple tree, Spur Golden Delicious /MM106 in SCPP Caransebes conditions (1987-1991)

Treatment	1987	1988	1989	1990	1991	Average yields		Av. yield increases, t/ha
	Yields, t/ha					t/ha	%	
Control	12.93	33.33	13.69	11.51	13.96	17.08	100	-
Polimet	15.93	46.66***	17.63**	15.51***	19.36***	23.02	135	5.94
Folifag	17.00	44.07**	17.63**	15.47***	18.22***	22.48	132	5.40
CFF 2951 [#]	20.26**	47.03***	18.64**	15.39***	19.22***	23.99	140	6.91
CFF 2952 [#]	17.70*	42.49*	18.71***	15.42***	19.56***	22.74	133	5.66
CFF 2953 [#]	19.60**	44.44**	23.63***	15.80***	19.78***	24.65	144	7.57
CFF 2954 [#]	20.20**	47.62***	30.26***	16.40***	19.11***	26.72	156	9.64
CFF 2955 [#]	22.70***	45.18**	19.27***	17.24***	19.33***	24.74	145	7.66
CFF 2956 [#]	17.46	46.58***	20.15***	16.97***	19.45***	24.12	141	7.04
DL 5%	4.28	6.65	2.55	0.92	2.22			
DL 1%	5.89	9.16	3.50	1.26	3.06			
DL 0.1%	8.12	12.62	4.77	1.74	4.21			

[#] Worded by Borlan et al.

The low yield levels in 1987 and 1990 are a consequence of the drought in association with high temperature in summer, these being a cause of physiologically falling of the fruits.

1988 has been the most favorable conditions for apple tree, reflected by the high yield levels. Even in control (without CFF), the fruit yield was 33,33 t/ha. In 1994, the CFF from 628 series gave high yield increases: 4.7–7.7 t/ha (18–29 %). The foreign CFF PSP Turbio gave the lowest yield increases when applied alone, but in combination with Romanian CFF the yield levels have been higher even than that of the Romanian CFF applied alone (table 2). All the yield increases were statistically very significant.

Table 2: Experimental data regarding the effect of the foliar fertilizers on fruit yield in apple tree in 1994 (SCPP Caransebes conditions)

Treatment	Yield	Yield increase	
	t/ha	t/ha	%
Control	26.30	-	100
CFF 6282	31.12	4.85***	118
CFF 6287	31.02	4.71***	118
CFF 6288	31.78	5.48***	121
PSP (Turbio)	28.51	2.20***	108
CFF 6282+PSP	33.77	7.46***	128
CFF 6287+PSP	33.03	6.72***	126
CFF 6288+PSP	33.98	7.67***	129
DL 5 %		0.87	
DI 1 %		1.20	
DL 0.1%		1.67	

The effect of the complex foliar fertilizers on fruit quality

The Golden Delicious fruits are very sensible to storehouse diseases, but especially to dehydration. The foliar fertilization positively influenced the conservation potential of the fruits, by reducing almost totally the damages in storehouse produced by diseases and concomitantly the damages produced by dehydration (table 3).

Table 3: Influence of the complex foliar fertilizers on the conservation capacity of apples in storehouse, (Spur Golden Delicious/MM106 apple tree)

Treatment	1987			1988		
	Healthy fruits	Damages by diseases	Damages by dshydration	Healthy fruits	Damages by diseases	Damages by dehydration
	%					
Control	66.9	5.2	27.9	88.2	5.4	6.4
CFF2951	88.4	0.5	11.1	97.1	0.9	2.0
CFF2952	95.4	-	4.6	98.0	0.6	1.4
CFF2953	91.3	0.4	5.3	96.5	1.5	2.0
CFF2954	88.1	0.1	11.8	98.5	1.3	0.2
CFF2955	82.2	-	17.8	96.8	0.4	2.8
ICF2956	85.1	0.7	14.2	97.2	-	2.8
Folifag	91.2	0.1	8.7	97.8	0.2	2.0
Polimet	87.6	0.2	12.2	97.6	0.3	2.1

According to the data from table 4, CFF 6282 and CFF 6288 positively influenced some biochemical indexes of the fruits. Thus, they increased the sugar content with 0.02 % and 0.90 % respectively. Application of CFF 6288 in combination with PSP Turbio determined the highest level of sugar content in apple juice (14,35 %), the increasing versus control (12,5 %) being 1.85 %.

Table 4: Data regarding the effect of the complex foliar fertilizers on some biochemical fruit indexes in apple tree, Spur Golden Delicious/MM106 variety (SCPP Caransebes, 1994)

Treatment	Sugar content of juice (%)	Differences versus control (%)	Acidity (g malic acid/100 g fruits)	Differences versus control
Control	12.50	-	0.2150	-
CFF 6282	12.52	0.02	0.2601	0.0451
CFF 6287	12.40	-0.10	0.2276	0.0126
CFF 6288	13.40	0.90	0.2357	0.0207
PSP (Turbio)	13.50	1.00	0.2438	0.0288
CFF 6282+PSP	12.08	-0.42	0.2276	0.0126
CFF 6287+PSP	12.03	-0.47	0.1869	-0.0280
CFF 6288+PSP	14.35	1.85	0.2601	0.0451

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