STATIONARY EXPERIMENTS WITH AMENDMENT AND FERTILISATION OF ACIDIC SOILS FROM RESEARCH STATION LIVADA, ROMANIA

The stone block on the outer cover summarizes the effects of the main soil-forming factors on the formation of these particular soils: the parent rock of volcanic origin and the falling raindrop shape suggesting the role of the rainfall regime. At the bottom of the cover one can notice an aerial view of the stationary experience with amendment and fertilisation of acidic soils.

Photos taken by Patrick Ursan.

STATIONARY EXPERIMENTS WITH AMENDMENT AND FERTILIZATION OF ACIDIC SOILS FROM RESEARCH STATION LIVADA, ROMANIA

Authors

Dr. Paul Kurtinecz, agronomist engineer.

Dr. Cecilia Bănăteanu, agronomist engineer.

Biologist Patrick Ursan

Horia Domnariu, ICPA BUCURESTI

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"Assessing the environmental impact of long-term fertilization and liming in the context of global warming to ensure sustainable management of acidic soil fertility„

2022

Foreword

Soil has always been the bedrock of human existence. Most accentuated degradation processes of the luvic soils in the north-west of Transylvania, are acidification and excess humidity. The pedological and agrochemical studies carried out so far in the area have shown that approximately 60% of the agricultural land has an acidic reaction, soil acidity being a natural phenomenon in areas with excess water regime. Changes in land ownership in the last 20 to 30 years have amplified this process, as it had as a consequence a decrease in the percentage of land that received lime amendment.

Practicing a sustainable agriculture requires a certain balance between the degradation and regeneration processes in the soil, which can be influenced mainly by human activity. Due to the adoption of the sustainability theory in agriculture, the issues of sustainable, efficient, quality and non-polluting agriculture that conserves soil resources have become a priority. In this respect, the importance of experiments performed in stationary mode has been re-evaluated worldwide.

The present work aims to present the main results obtained in the stationary experiments with amendment and fertilisation of acidic soils, during the period 1962-2021.

Livada, October 2022 **Authors**

Content

1. Natural conditions

1.1 The soil

The research was carried out on two representative soil types for the North-Western (N-W) area of Transylvania: Haplic Luvisols and Albic Luvisols.

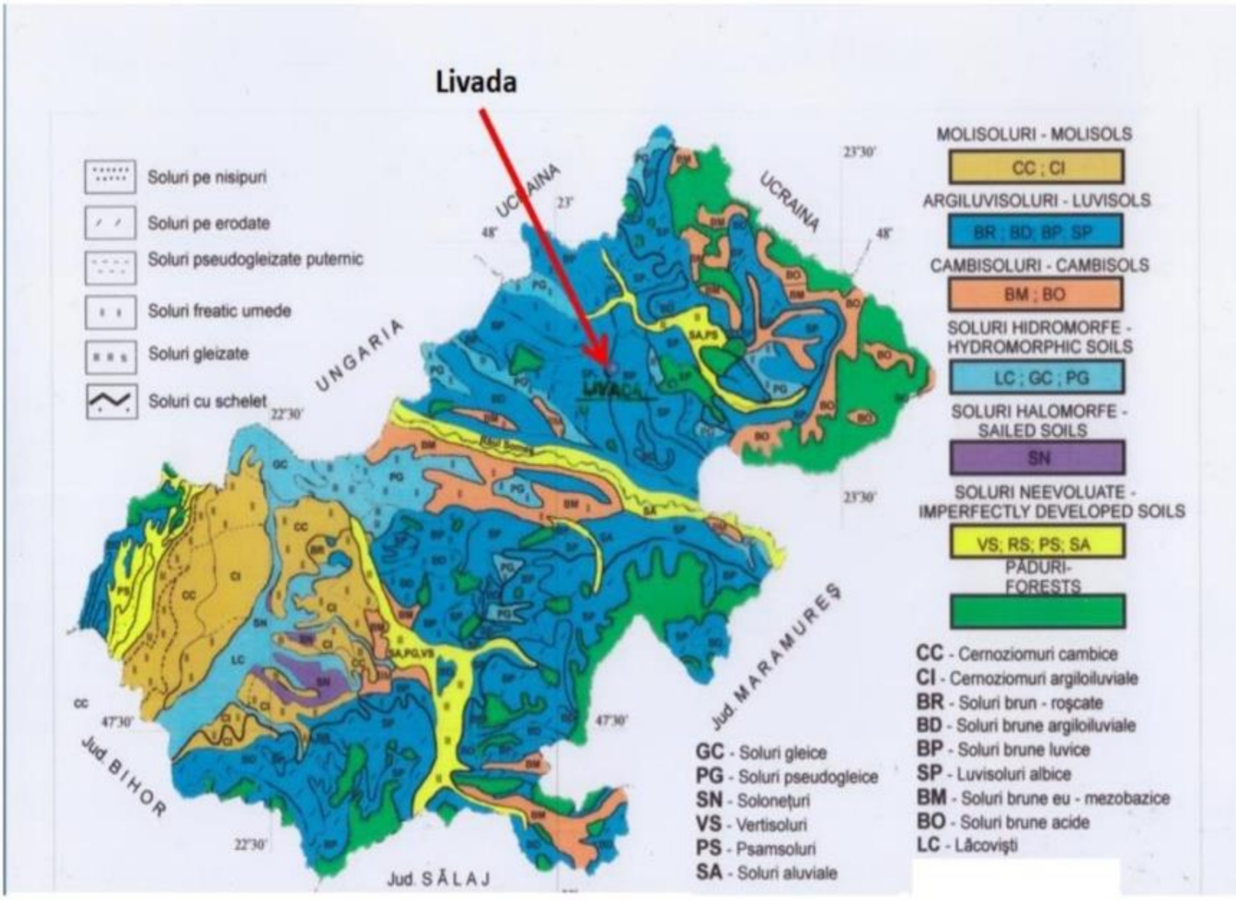


Fig. 1 Soil map of Satu Mare County (Asvadurov and Boeriu, 1982.) Scale 1: 100,000.

The conducted research is located in the middle of the area occupied by Luvic soils, within the experimental fields of the Agricultural Research Station Livada (A.R.S. Livada) (47°52'07.3"N 23°07'10.2"E) in Satu-Mare County (Fig. 1).

The Haplic Luvisol (Fig 2) has the profile of the Ap-E1-EB- Bt1-Bt2-Bt3 type and was formed on fluvial sedimentary deposits, with groundwater at 4-6 meters. From an agrochemical point of view, the Ap horizon has a low humus content, it is poor in mobile phosphorus, it is medium to well supplied with mobile potassium and it has a medium to strong acidic reaction (Tab. 1). The main factors limiting the harvest are the acidity of the soil, and the low supply with nutritional elements.

The Albic Luvisol is characterized by the profile of the type Ap-Ea-BEw-Btw1- Bt2- Bt3. In terms of agrochemical aspects, in the upper horizon, it has a low humus content, it is medium supplied with mobile phosphorus, poor in mobile potassium and it has a strong acidic reaction. Pronounced acidification, low supply of humus and potassium and defective aero-hydric regime, impose serious restrictions on cropping.

The existence of these two typical but very different situations of soil acidity greatly facilitated the elucidation of certain aspects of soil and plant chemistry.

Fig. 2 Profile of Haplic Luvisol

Tab. 1 Haplic Luvisol properties

Properties	Brown forest soil	Luvisol
Clay-%	21,0	19,0
Humus-%	1,41	1,86
pH_{H2O}	5,19	4,80
C.E.C.-me/1000	11,86	11,05
PAL-ppm	11,0	14,0
KAL-ppm	144	64

From the analysis of the profile morphology, it can be noticed that the soil-forming factors exert an influence deep into the soil profile unlike in the case of other types of soil (Fig. 2).

1.2. Climate

The N-W area of Transylvania falls into the climatic province Cfbx (according to Köppen), characterized by a moderate temperate continental climate. The average multiannual temperature recorded at the weather station A.R.D.S. Livada over 60 years is 9.9°C. In the period 1961-2021, at Livada, the multiannual average amount of precipitation was 753.2 mm. (Fig. 3).

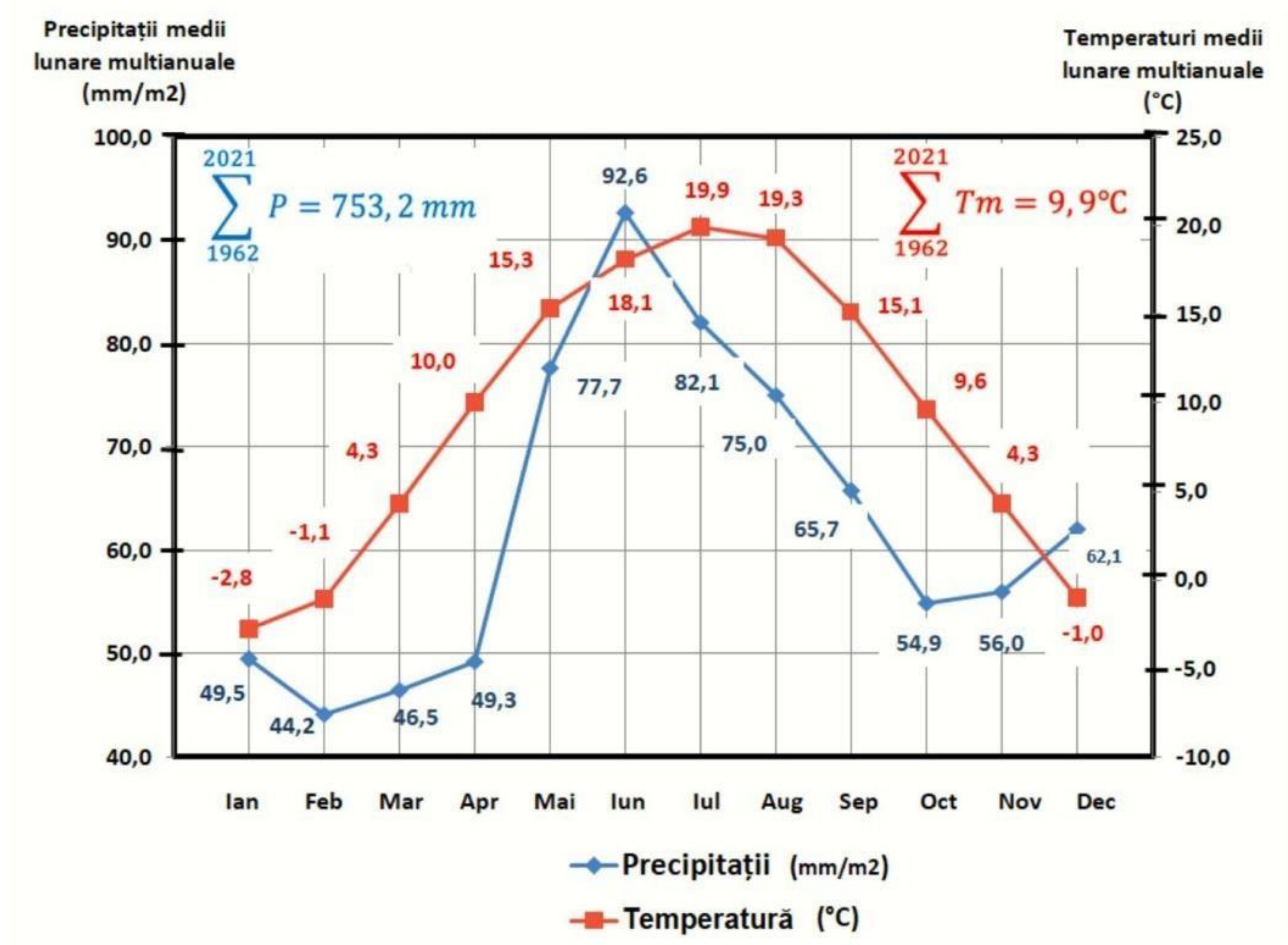


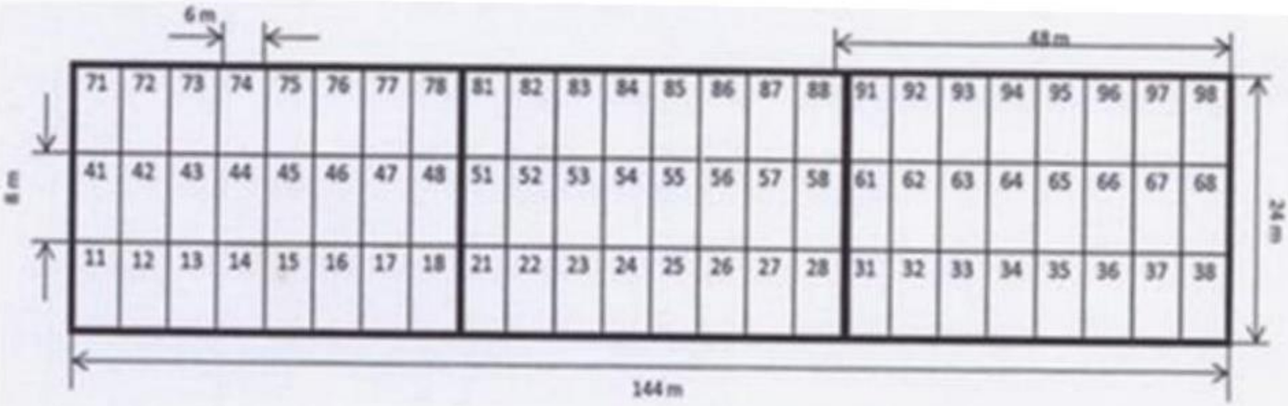
Fig. 3 Evolution of monthly multi-annual average of temperatures and mean precipitation sum recorded in the period 1962-2021 at SCDA Livada.

2. Description of experimental design

The establishment of the experiments was initiated in the autumn of 1961, by Dr Ioan Boeriu, an advocate of agricultural research in North-Western Transylvania and the manager of the Fertilizers and Amendments Laboratory. From September 1, 1974 until the end of 2022, the management of the trial was taken over by Dr. Paul Kurtinecz.

Initially, on two parcels of both the Haplic Luvisol and Albic Luvisol there were created three levels of amendment with 0, 2.5 and 5 t limestone/ha, and 0, 5 and 10 t limestone/ha, respectively.

Table. 2 Stationary experiments with amendment and fertilization of acid soils



A-AMENDAREA (LIMING)
90% $CaCO_3$ (t/ha)

	1961	1966	1971	1977	1986	1998	2012	2022 $\sum$ 1961
1	0	0	0	0	0	0	0	0
2	5	0	0	0	0	5	0	10
3	10	0	0	0	0	10	0	20
4	0	5	0	5	5	5	0	20
5	5	5	0	5	5	5	0	25
6	10	10	0	10	10	10	0	50
7	0	5	5	5	5	5	5	30
8	5	5	5	5	5	5	5	35
9	10	10	10	10	10	10	10	70

B-FERTILIZAREA (FERTILIZATION)

		N Kg/ha	P_2O_5 Kg/ha	K_2O Kg/ha	G t/ha
1	0	0	0	0	0
2	N	100	0	0	0
3	P	0	70	0	0
4	NP	100	70	0	0
5	NPK	100	70	60	0
6	G	0	0	0	20
7	5+6	1oo	70	60	20
8	>NPK	150	100	80	0

N=azotat de amoniu
P=superfosfat
K=sare potasică
G (FYM)=gunoi de grajd

N=ammonium nitrate
P=superphosphate
K=potassium salt
FYM (G)=farmyard manure

The stationary experiments with liming and fertilizers were established according to the method of subdivided plots, in a bifactorial manner. Initially, three levels of the amendment factor were created by applying 0; 2.5 and 5 t of limestone/ha in the case of Haplic Luvisol, and double doses in the case of Albic Luvisol. Consequently, in 1966, by subdividing the length of the replicate into three strips of eight m. each, there were created nine levels of amendment which offer a very wide range of practically testing such ameliorative measurements (Table 2).

In these experiments, the "Fertilization" factor presents 8 levels and is of "Mangelversuch" type, offering the possibility of successively testing the effectiveness of nutritional elements, a concept valid for the period in which the experiences were initiated and in a region where information was completely lacking regarding the effect of fertilization. Regrettably, worldwide, there are relatively few stationary experiments with liming of acidic soils, and for the existent ones the "limestone" factor does not present several gradual levels. Fertilization was carried out with ammonium nitrate, concentrated superphosphate, potassium salt 40%, semi-fermented farmyard manure. Liming used Bucium limestone and precipitated calcium carbonate from "Azomures".

The crop rotation practiced in these experiments involved mostly cereals. At the end of the 70's, the beginning of the 80's, at the country level, the issue of liming acidic soils and fertilization was considered sufficiently elucidated and this led to the abolition of stationary experiments with amendments and fertilizers located in several other research stations (Horodnic, Suceava; Husasaul de Tinca, Bihor; Albota, Arges, etc.).

Considering the large prevalence of acidic soils in the northwest, at A.R.S. Livada it was deemed necessary to maintain these experiments, mainly for the continuous follow-up of limestone secondary effects.

Analyses performed

Most of the current analyses were performed according to the standard methods in use in Romania. To identify possible mineralogical changes, X-ray determinations were also conducted. A portable infrared gas analyzer (LCi-ADC Bioscientific Ltd) was used to highlight the influence of the studied factors on soil respiration. The content of microelements was determined according to the Lakanen and Erviö method.

3. The influence of liming and fertilization on yield

Influence of liming and fertilization on dry substance content

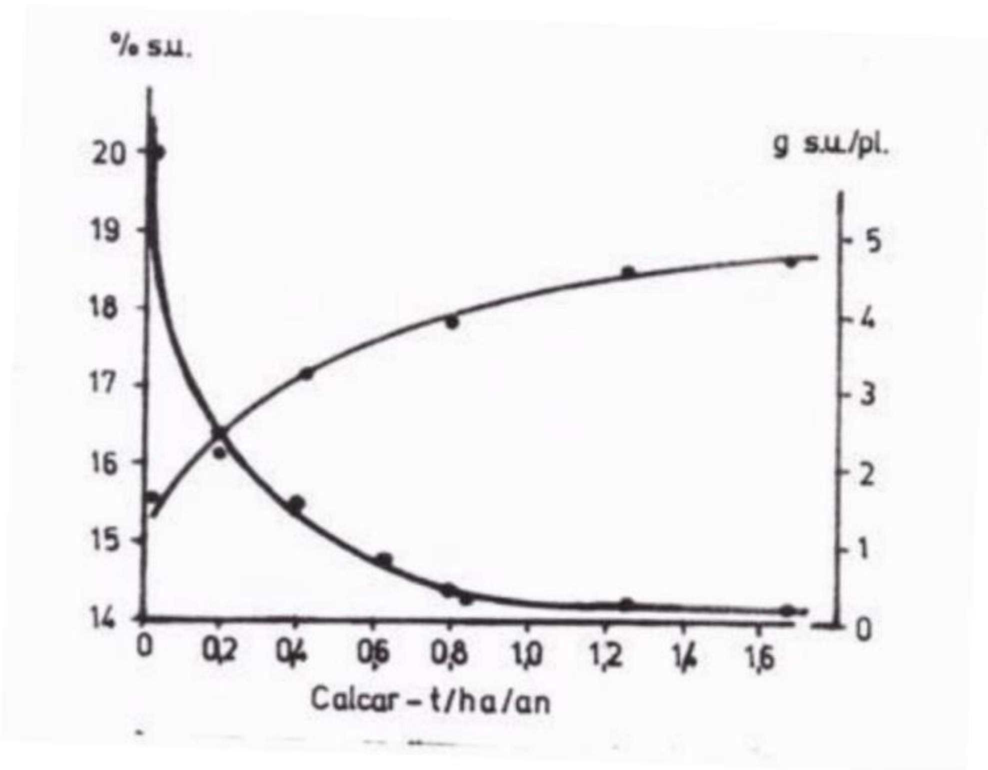


Fig. 4 The influence of liming on the content of dry matter and its accumulation in young corn plants.

In general, tissues that have higher water content are more physiologically active while higher dry matter contents are associated with poor physiological activities. The limestone amendment has a decreasing effect of the dry matter % content depending on the dose applied and this suggests that the physiological activity of the plants is more intense. Young corn plants, in the unamended plots, have a dry matter content of around 20% while in the appropriately limed plots, the percentage of dry matter is maintained at a value of 14-15%. Thus, application of limestone has an effect of clearly increasing the weight of young corn plants (g. dry matter /plant). The weight of young maize plants is strongly influenced by the amount of limestone applied (Fig. 4)

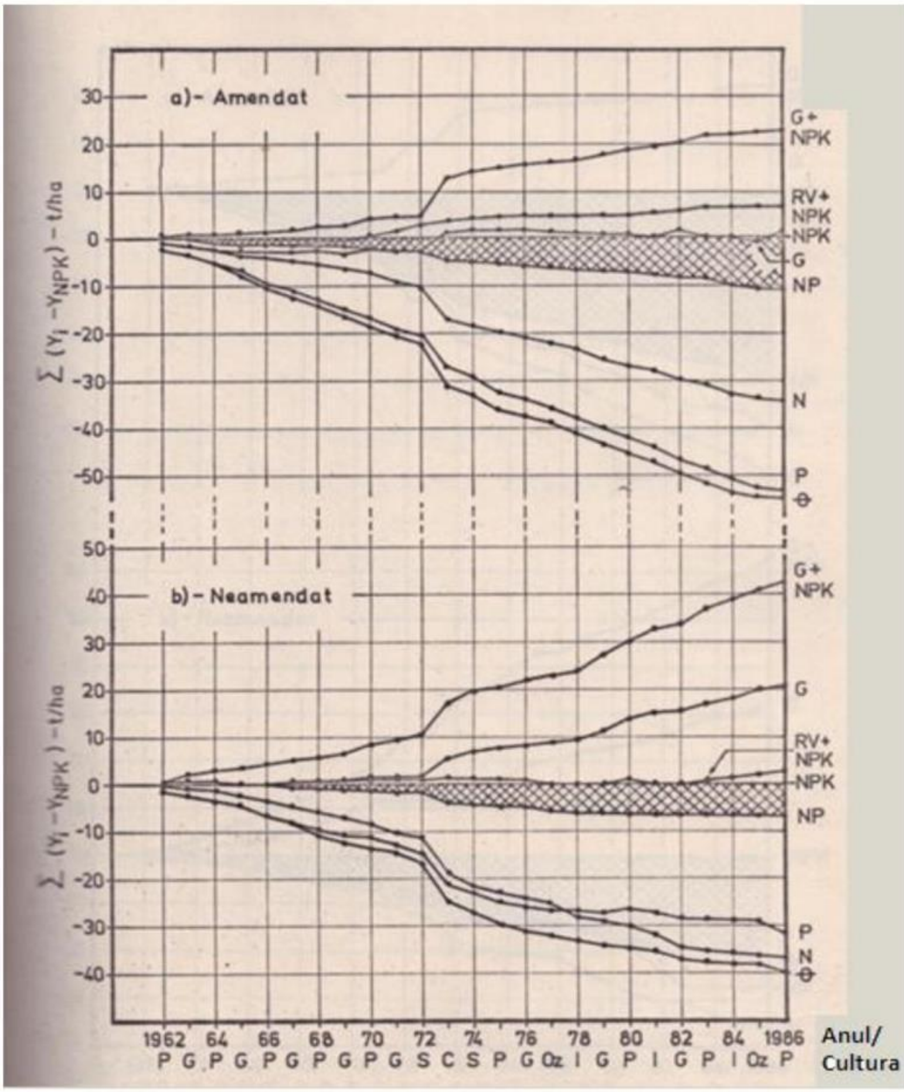


Fig. 5 The dynamics of the cumulative effect of long-term fertilization on limed and not limed soil, in a succession of crops gown on Haplic Luvisols 1962-1986.

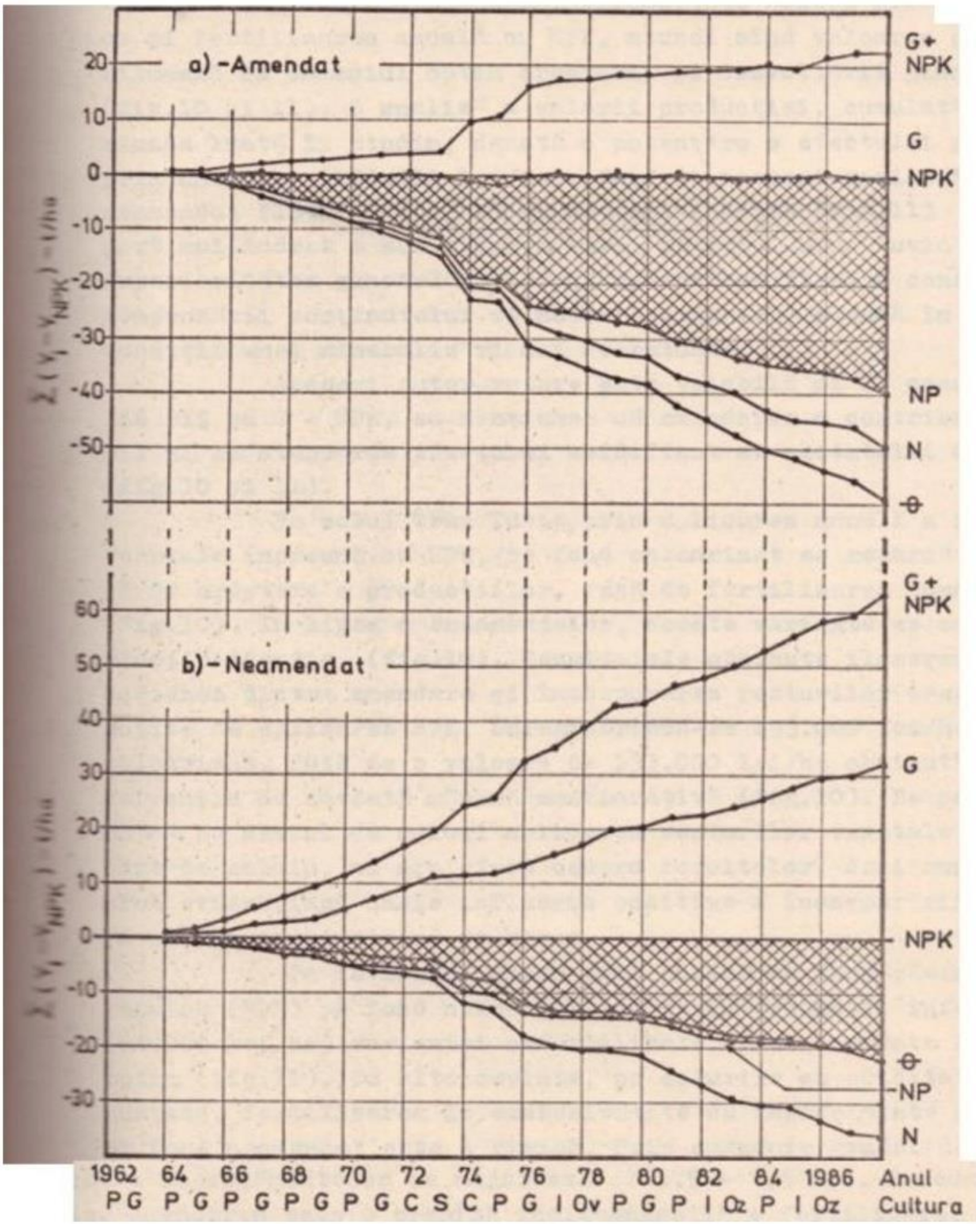


Fig. 6 The dynamics of the cumulative effect of long-term fertilization on limed and not limed soil, in a succession of crops grown on Albic Luvisol between 1962-1986.

The existing research literature contains relatively little information about the processing and interpretation of data from experiments conducted in stationary mode. A satisfactory approach to this problem is difficult to find because most of the data obtained are observations recorded at a certain moment of the trial implementation, but these values also represent cumulative effects. Therefore, in such experiments, the biological cycles that follow each other are not independent of each other, unlike the experiments executed in non-stationary mode.

Considering the characteristics of experimental data (time succession of different crops in the same field), finding a common denominator to express the effects of the studied factors (amendment and fertilization), was a difficult problem to solve from a methodological point of view. The idea that this can be solved by transforming yields into grain units or protein units would mean to make equivalent the crop biological quality.

For at least a partial elimination of the inconveniences arising from the expression of yields in grain or protein units, it was considered appropriate to interpret the yield results through the graphic method proposed by SVAB (1981). Thus the cumulative effect of the treatment factor is given by the positive or negative distances (Y - YNPK) from the abscissa (Fig. 5 and Fig. 6). In the figures, the abscissa axis overlaps with the line generated by the values of the control treatment (annual application of 100 kg N/ha, 70 kg $P_2 0_5$ /ha and 60 kg $K_2 0$/ha). The yields of this treatment were chosen as a basis for comparison, because they presented the lowest susceptibility to the annual fluctuations of the environmental factors and because they faithfully reflect the receptivity to the treatments applied in most of the analyzed situations

The evolution of yield under the influence of prolonged fertilization was analyzed in two distinct situations, i.e. not limed and limed at optimal level, using in interpretations the physical criteria, imposed by the non-systematic succession of crops in the studied time sequence. Comparing the line of the cumulative yield differences in the case of the NP treatment, with the one obtained by the simultaneous application of NP and K, one can say that while the lines are parallel or approximately equally spaced, we do not witness significant differences in yield, that is, the differences created in previous years are maintained. Or in other words, if the line resembles a straight one on certain regions of the graph then the differences between the control and the compared treatment are approximately constant, regardless of the direction. The case of Haplic Luvisol is soil is conclusive in this respect during the period 1962-1972 (Fig. 5). On the other hand, in the case of the Albic Luvisol, the differences between the NP and NPK treatments have increased over the years (Fig. 6). For this type of soil, a low sensitivity to the application of potassium salt is recorded only in the first 2-3 years after the initiation of the experiment and this can be explained by the remarkable ability of clay minerals, predominantly of the Illite type, to preferentially fix between lamellae the potassium ions. There would be arguments for explaining this behavior by the depletion of the mobile potassium pool and the delay in restoring it on account of the non-exchangeable one, compared to the dynamics of consumption in plants. Therefore, the systematic application of potassium on the Albic Luvisol ensures substantial increases in yield, while on the Haplic Luvisol there is only a vague response to the fertilization with this nutrient, a fact that can be mainly the consequence of the different potassium supply of the two types of soil (Fig. 5 and Fig. 6).

The annual application of 20 t/ha of semi-fermented farm-yard manure has practically the same effectiveness on yield as annual fertilization with NPK when the pH value is in the optimum range for plant growth and development. Superiority of farm-yard manure (G) would also be a consequence of compensating the content of organic matter, subjected in these conditions to a more pronounced mineralization. The same interpretation is valid in the case of fertilization with G+NPK, with the mention that the limestone also contributed significantly to the mitigation of the acidifying effect of ammonium nitrate. (Fig. 5 and Fig. 6)

In the case of Haplic Luvisol, through the annual application of plant residues along with NPK and together with liming, one can notice a trend of increasing yield compared to fertilization with NPK. In the case of Albic Luvisol, by applying chemical fertilizers (NPK) on unamended plots, yields are lower than the unfertilized plots that were simultaneously limed at an optimal level. In other words, on soils with pronounced acidity, applying chemical fertilizers without amendment is a waste. By liming, the degree of use of fertilizers is increased by 1.5-2.5 times. In conclusion, liming is a prerequisite for the fertilization of acid soils.

The value of cumulative yield for the period 1962-1985 in the case of the control treatments is relatively the same which demonstrates that similar yields can be obtained on the two soils, but with a double financial effort given the amendment cost of the Albic Luvisol (Fig. 6). Based on these data, it is possible to formulate the recommendation that it is more economically efficient to lime the Haplic Luvisol which is less acid.

4. Changes induced by long-term amendment and fertilization on soil properties

The influence of amendment and fertilization on acidity indicators.

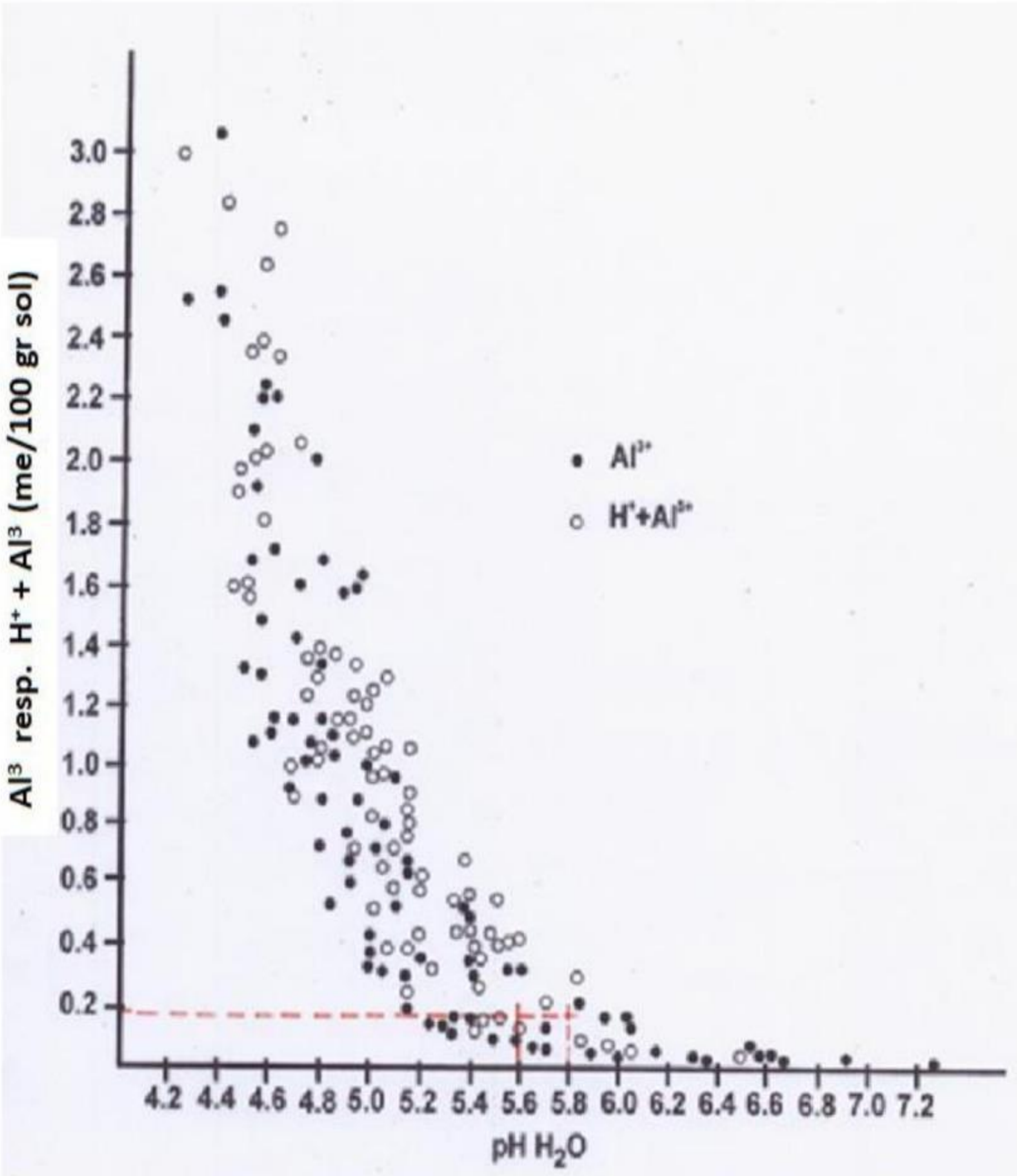


Fig. 7 The influence of H^+ and Al^{3+} ions on the easilyexchangeable acidity recorded on Albic Luvisol and Haplic Luvisol (Livada 1981)

The contribution of H^+ ions to achieving easily exchangeable acidity compared to Al^{3+} ions is insignificant (Fig. 7). In general, lowering the pH value (H_2O) below the value of 5.6-5.8 generates toxic amounts of mobile Al (>0.2-0.3 me/100 g soil).

Tab. 3 Influence of liming and long-term fertilization (58 years) on the pH values of Haplic Luvisols, Livada 2020.

AMENDAREA (Calcar-t/ha/an)	0	0,129	0,345	0,776	0,948	Media fertilizare	+-d
Martor (0)	5,17	5,39	5,62	6,89	7,70	6,16	0
N	4,64	4,70	5,02	6,23	7,97	5,71	-0,44
NP	4,90	5,03	5,43	6,32	7,82	5,90	-0,26
NPK	4,80	5,03	5,35	6,10	7,82	5,82	-0,34
Media amendare	4,88	5,04	5,36	6,38	7,83	x	
+-d	0	0,16	0,48	1,51	2,95		

DL	A	B	AXB
5%	0,31	0,15	0,41

The effect of prolonged fertilization on the pH value was analyzed 58 years from the setup. The unilateral and prolonged application of ammonium nitrate in doses close to the regular ones, determined the acidification of the soil by 0.44 pH units, compared to the unamended version. Due to the intake of calcium, the long-term use of superphosphate significantly reduced soil acidification. The potassium salt had no clear influence on the soil reaction (Table 3). Within these experiments, it was possible to achieve a very wide gradient of the pH value, a particularly useful aspect for prospective researches.

Tab. 4 Influence of liming and long term fertilization on pH (Albic Luvisol, 2001)

AMENDAREA (Calcar t/ha/an)	0	0,25	0,5	0,75	1,5	Media fertilizare	+-d
0	4,61	5,60	6,52	6,99	7,44	6,23	0
N	4,18	5,39	6,37	6,52	7,44	5,98	-0,25
NP	4,35	5,60	6,44	6,76	7,35	6,10	-0,13
NPK	4,40	5,60	6,45	6,85	7,36	6,13	-0,10
Media amendare	4,39	5,55	6,45	6,78	7,40	x	
+-d	0	1,10	2,00	2,40	3,00		

	A	B	AxB
DL 5%	0,28	0,14	0,32

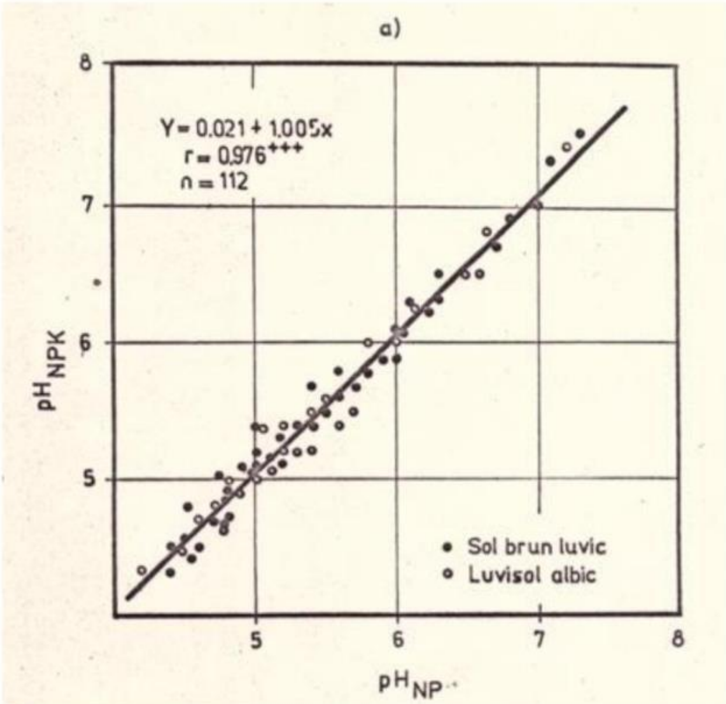
Tab. 5 Soil acidification in the unamended and unfertilized variants after 40 years of experiment. (Albic Luvisol, Livada)

Years	pH_{KCl}	n	±d	s^2
1961	4,21	6	--	0,013
2001	3,67	3	--0,54	0,010

t_{calc}=6,98> t_{tab}(7,5%)=2,37
LSD $_{5\%}$ =0.18

When comparing the pH values after a period of 40 years, a decrease in the pH value by 0.54 units was detected, when pH was measured in saline solutions, less sensitive to seasonal variations. The comparison was made between the years 1961 and 2001 of the unamended and unfertilized variants. A possible explanation for this trend may be related to the effect of acid rains as well as depositions with an acid reaction, given the atmospheric circulation from west to east.

Fig. 8 The influence of long potassium fertilization (1962-1986) on pH (a) and the content of exchangeable cations (b).



b me/100g sol

Fertilizarea	Ca^{2+}	Mg^{2+}	K^{+}	Na^{+}
Luvisol albic				
NP	5.37	0.22	0.16	0.15
NPK	5.28	0.23	0.26	0.16
Sol brun luvic				
NP	5.75	0.53	0.30	0.15
NPK	5.54	0.52	0.41	0.15

There is a linear and direct proportional relationship between the pH values recorded for the NP, respectively NPK variants, both in the case of Haplic Luvisol and in the case of Albic Luvisol (Fig. 8). Long-term fertilization with potassium generates certain changes in the composition of exchange cations, implying the possibility that, by virtue of the laws of cation exchange, a part of the calcium ions are replaced by potassium ions from the fertilizer (Fig. 8b). Potassium thus contributes to the intensification of calcium losses from the soil profile. Since the mentioned ion exchange reactions take place in equivalent amounts, systematic fertilization with potassium has no noticeable influence on the pH value. The intensification of alkaline-earth bases losses from the upper horizons of the soil fertilized with potassium in a steady state is also explained by the increased consumption of cations in the plant mass of the crop, as well as by the migration down the profile, in the form of chlorides ($CaCl_2$ and $MgCl_2$) together with percolating water.

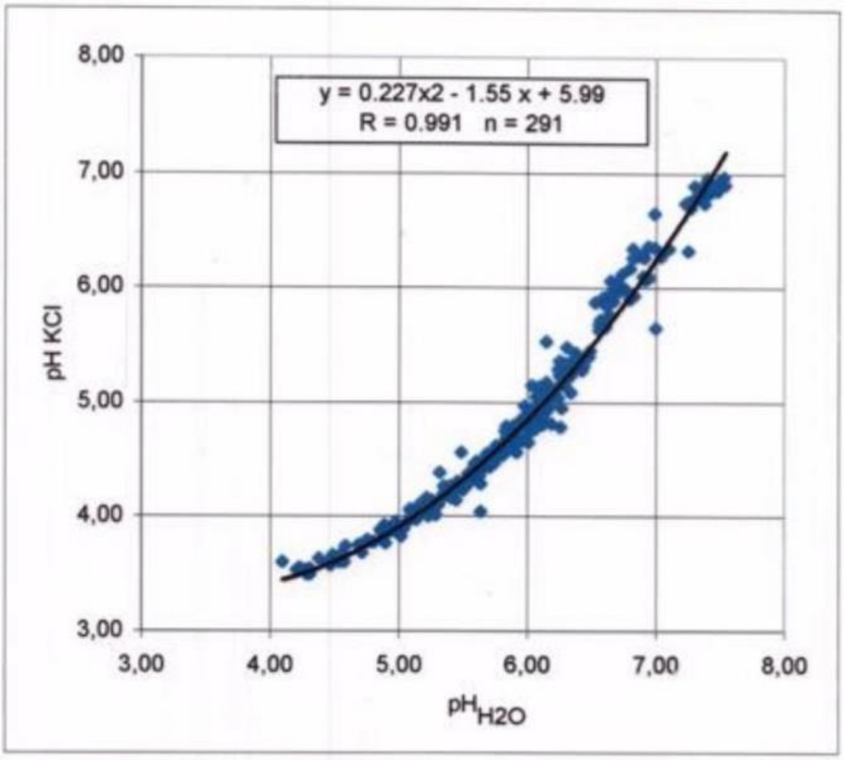


Fig. 9 The correspondent relationship between the pH value determined in water and saline extract based on data from stationary experiments (Albic Luvisol, Livada 2001)

There is a close, positive correlation between the pH value in the aqueous extract and the pH value in the saline extract. For the pH range 4-6 in the aqueous extract, the increase is non-linear, while for the range 6-8, the increase becomes linear (Fig. 9)

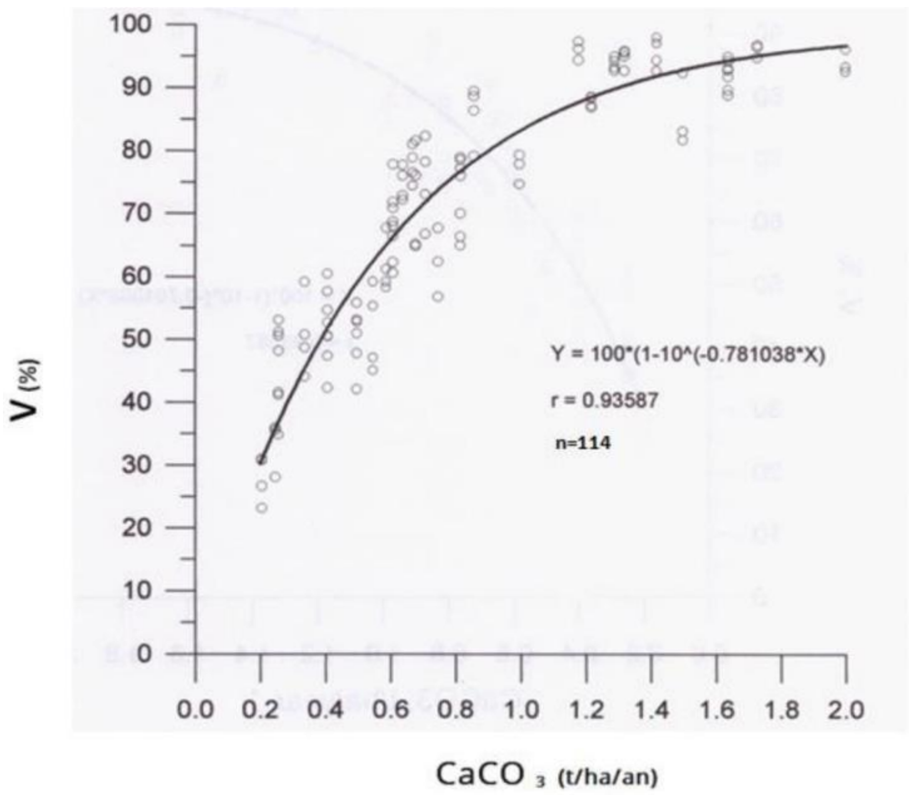


Fig. 10 The relationship between the lime dose and the degree of base saturation registered in the plowed layer of the Albic Luvisol in the mineral fertilized variants, in the period 1965-1999.

The degree of base saturation clearly changed due to the amendment, in a wide range, from 20% to almost 100% of this indicator. (Fig. 10) The value of 70-80% is achieved by applying doses of 800 kg/ha of **CaCo3** in the case of Albic Luvisol. The amendment doses established in this way are recommended to be applied annually or cumulatively once every 4-6 years.

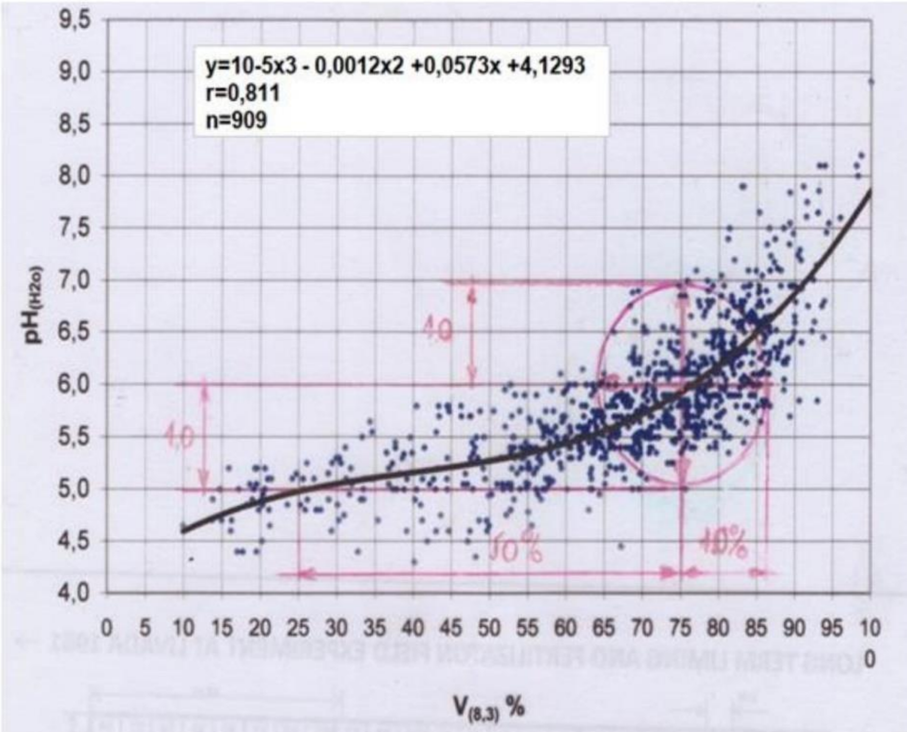


Fig. 11 The relationship between the degree of base saturation V (8.3)-% and pH - of the aqueous extract (1: 2.5) in the upper layers of the luvic soils.

Fig. 11 shows the correlation between pH and the degree of saturation in bases, in the case of more than 900 pedological profiles from the Luvic soils of North-Western Romania. Increasing the soil reaction by one unit in the range between 5 and 6 pH values, causes the increase of the degree of saturation in bases by approximately 50%.

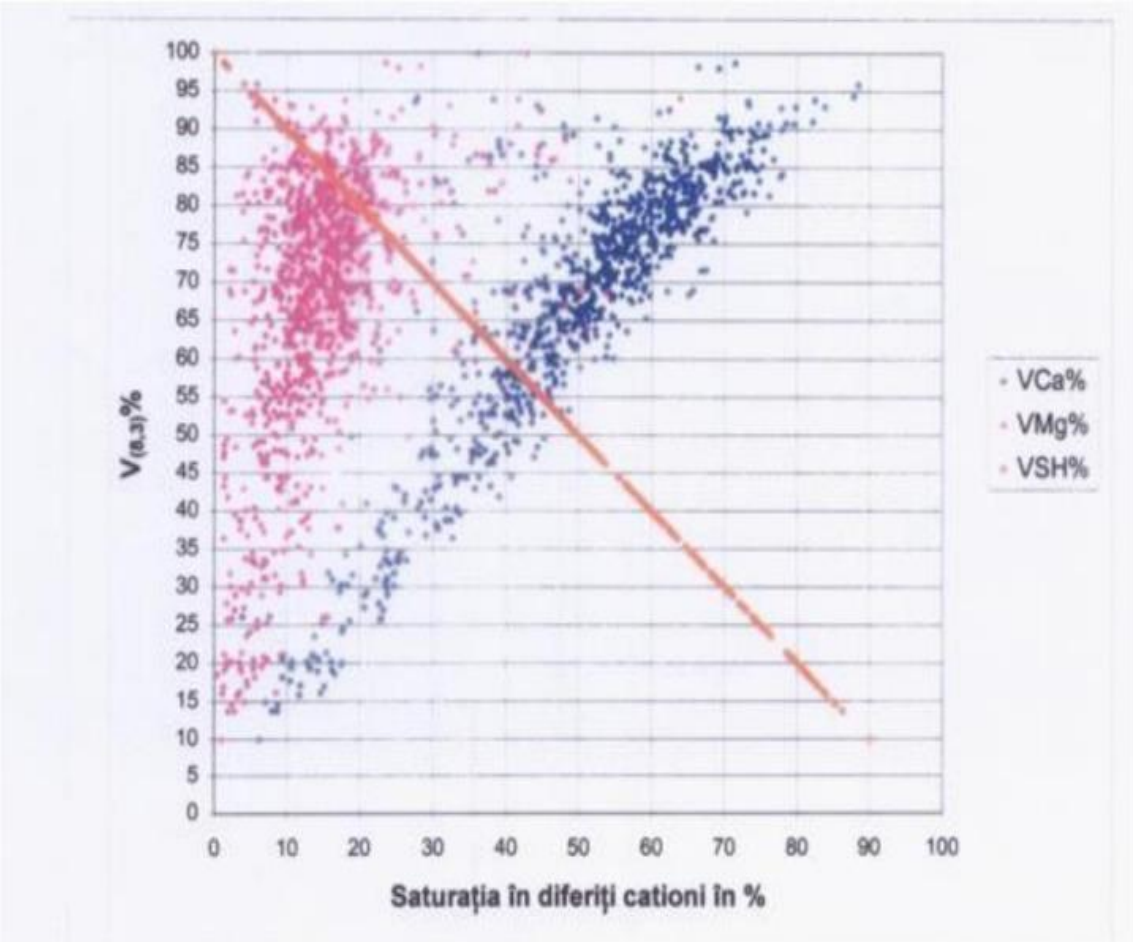


Fig. 12 The variation of Ca (BS Ca%), Mg (BS Mg%), and H saturation depending on the degree of base saturation (V 8,3)% of Luvic soils.

The degree of saturation in calcium shows the greatest variability, mainly due to the amendment of Luvic soils, while the degree of saturation in magnesium shows a lower variability. In the case of the correlation shown in Fig. 12, the variability is mainly generated by the different calcium input through amendment, which increases the weight held by calcium ions in the adsorptive complex.

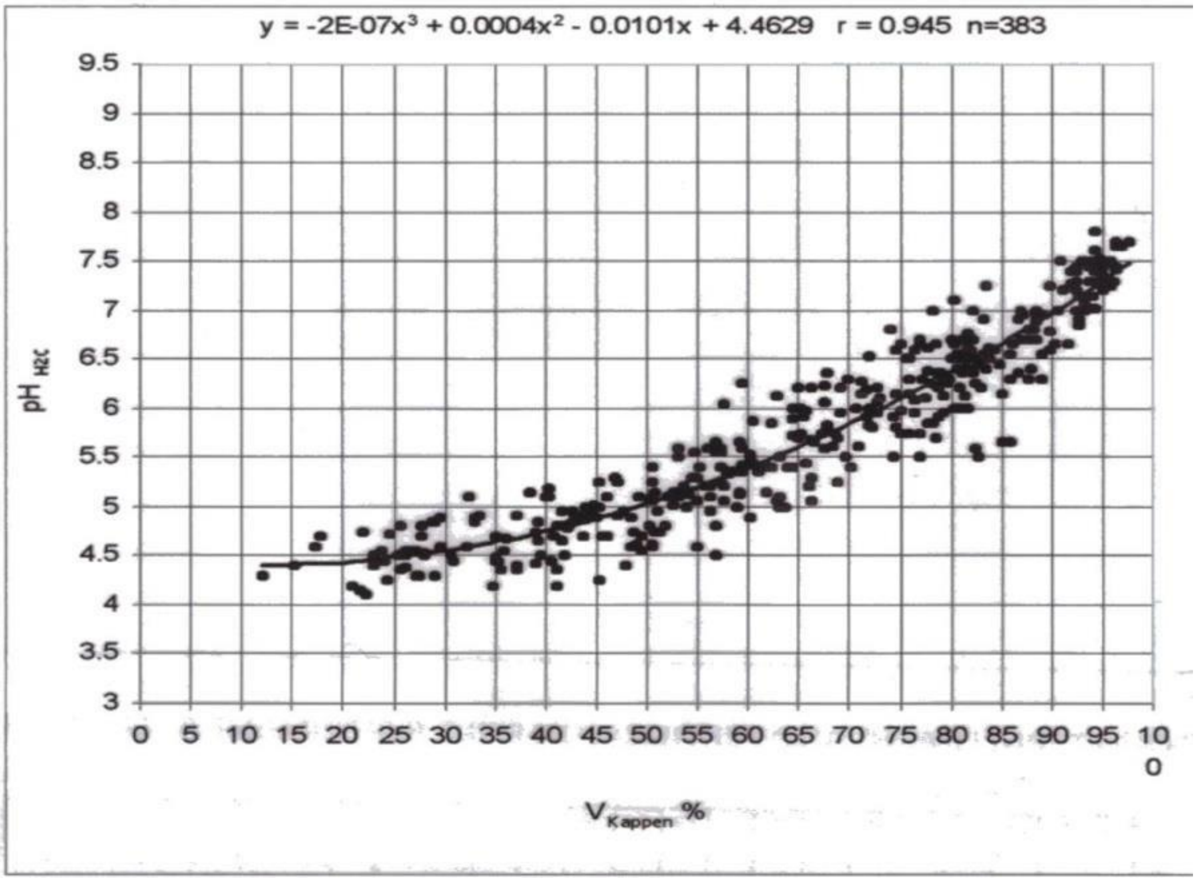


Fig. 13 The relationship between the degree of base saturation V (8.3)-% and the pH (H20) value of the aqueous suspension (1: 2.5) successfully calculated with data of stationary experiments.

Fig. 13 shows the relationship between base saturation and pH, in the case of the long term amendment and fertilization trial. Comparing Fig. 11 and Fig 13, one can notice a close similarity.

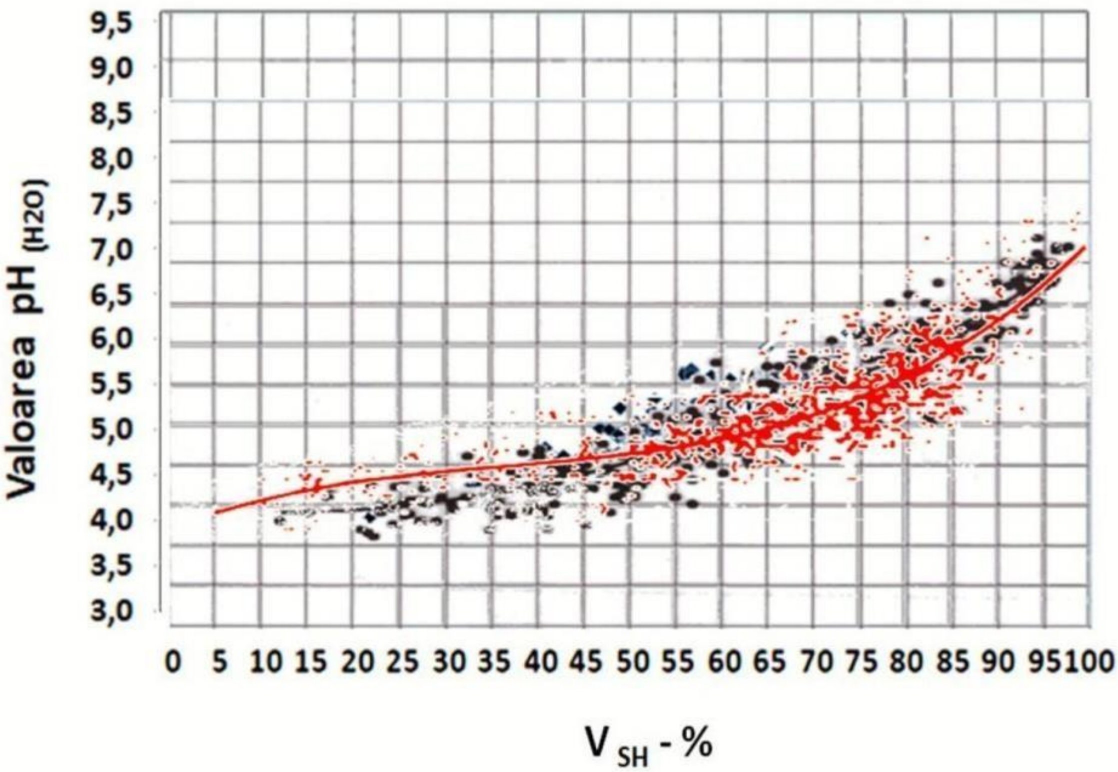


Fig. 14 Overlap of dispersions regarding the correlation between the degree of saturation in bases (%) and the pH value from stationary experiments of Livada and from the north-west soils of Romania.

Analyzing the correlation between the degree of saturation in bases and the pH value (Fig. 14), an almost perfect overlap of the dispersion of values derived from the stationary experiences and those derived from the agrochemical and paedological maps carried out in the area is found. The overlap of the two dispersions highlights that the stationary experiences with the amendment of acidic soils very faithfully reflect the reality in the field, and can be the basis of prospective research on the collateral effects of the amendment of acidic soils and its environmental implicationsAnalyzing the correlation between the degree of saturation in bases and pH, the same relationship was noticed for the results of the stationary experiments and the results of agrochemicals studies made for other luvic soils in the region.

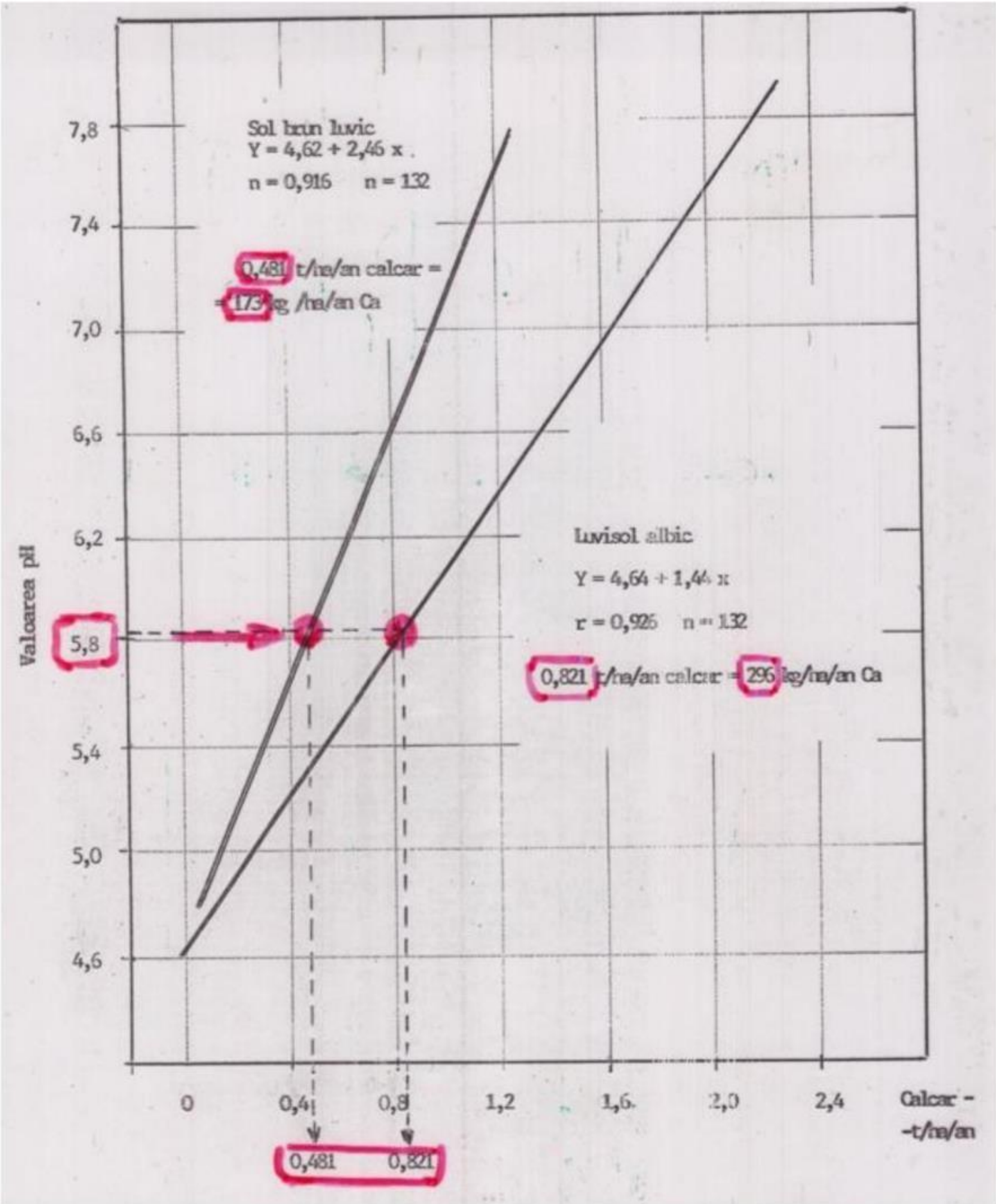


Fig. 15 Change in the pH value according to the amendment in the period 1962-1991

Based on the results obtained over a long period of time (30 years), the conclusion can be formulated that: the sustainable maintenance of the pH value around 5.8 is achieved by applying around 500 kg of limestone in the case of Haplic Luvic soil and 800 kg of limestone in the case of Albic Luvic soil, respectively, in annual or cumulative doses every 4-6 years (Fig. 15). In the case of Albic Luvisol, the amount of calcium applied is equivalent to 296 kg calcium/ha/year, while in the case of Haplic Luvisol it is equivalent to 173 kg calcium/ha/year. The maintenance dose was transformed into elemental calcium, so that it can be compared with data obtained in the literature regarding calcium losses taking place in lysimeters under similar soil conditions. The quantities determined in lysimeters confirm the quantities established in the stationary experiences of Livada.

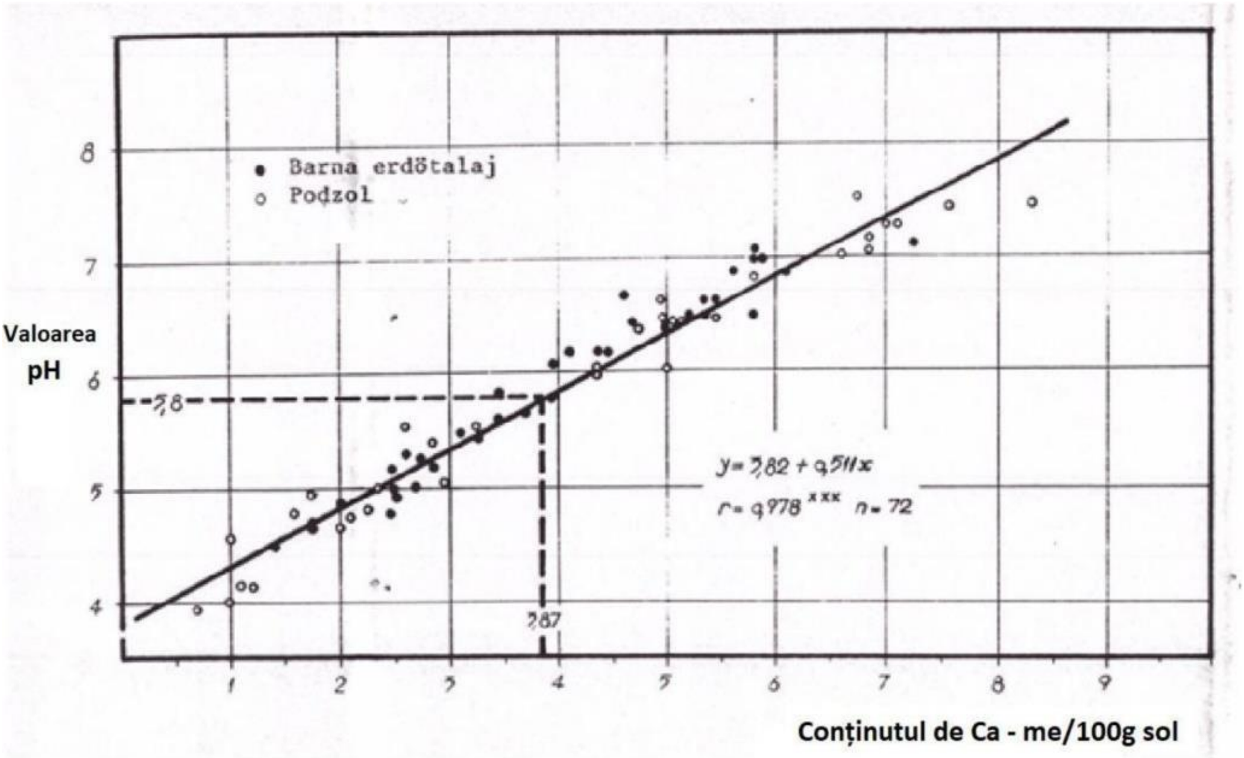


Fig. 16 The influence of Ca^{2+} content on pH of plough horizons

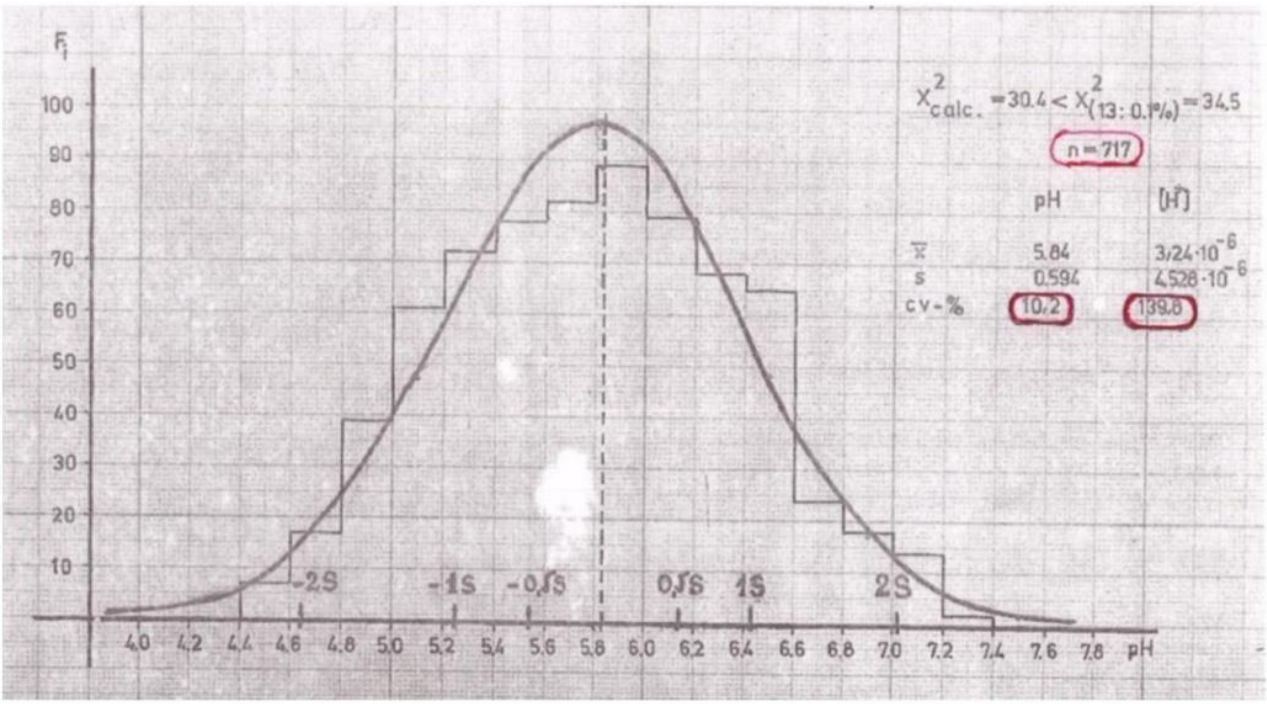
In the figure 16 that shows the correlation between the Ca content (me/100 g soil) and the pH value, between the 2 variables there is a linear and direct proportional relationship. The pH value of 5.8 can be maintained sustainably by ensuring a content of 4 me/100g soil.

Tab. 6 Calcium losses (kg/ha/year) from the Albic Luvisol profile (0-80 cm) after 18 years of experimentation

Limestone (t/ha)	5	10	20	40
NP	98	110	192	354
NPK	170	230	319	508
FYM	190	244	447	681

The losses of calcium from the soil profile increase simultaneously with the progressive doses of limestone applied. Compared to NP, NPK causes increased calcium losses through leaching in the form of calcium chloride. Manure contributes even more to the amplification of this phenomenon, due to the intensification of microbiological activity and the resulting carbon dioxide, causing calcium losses in the form of calcium bicarbonate (Tab 6)

Fig. 17 Histogram and the normal distribution curve of pH values registered at SCDA Livada, 1989



The distribution curve of pH values characterizing an area of approximately 1500 ha confirms the law of normal distribution of the data. 68% of the analyzed values are in the -1 sd. and 1sd. range, 95% of the values are in the -2sd. and 2sd. range and 99% of the values are in the -3 sd. and 3sd. range. The coefficient of variation of soil acidity calculated based on pH values is 10.2%, which indicates a negligible value of data variability, pH being the logarithm with changed sign of the effective concentration of hydrogen ions in the solution. However, expressing the pH value in the form of the effective concentration of H+ ions in the solution, taking into account the definition of pH as a logarithmic scale, it is considered to reflect reality much more objectively than the transformed form of the concentration of hydrogen ions, i.e. the pH value. The value of the coefficient of variability multiplies in such a case for more than 10 times (140 %). So, in evaluating soil pH variability, it is not correct to operate with pH values.

4.2 Changes in total carbon content

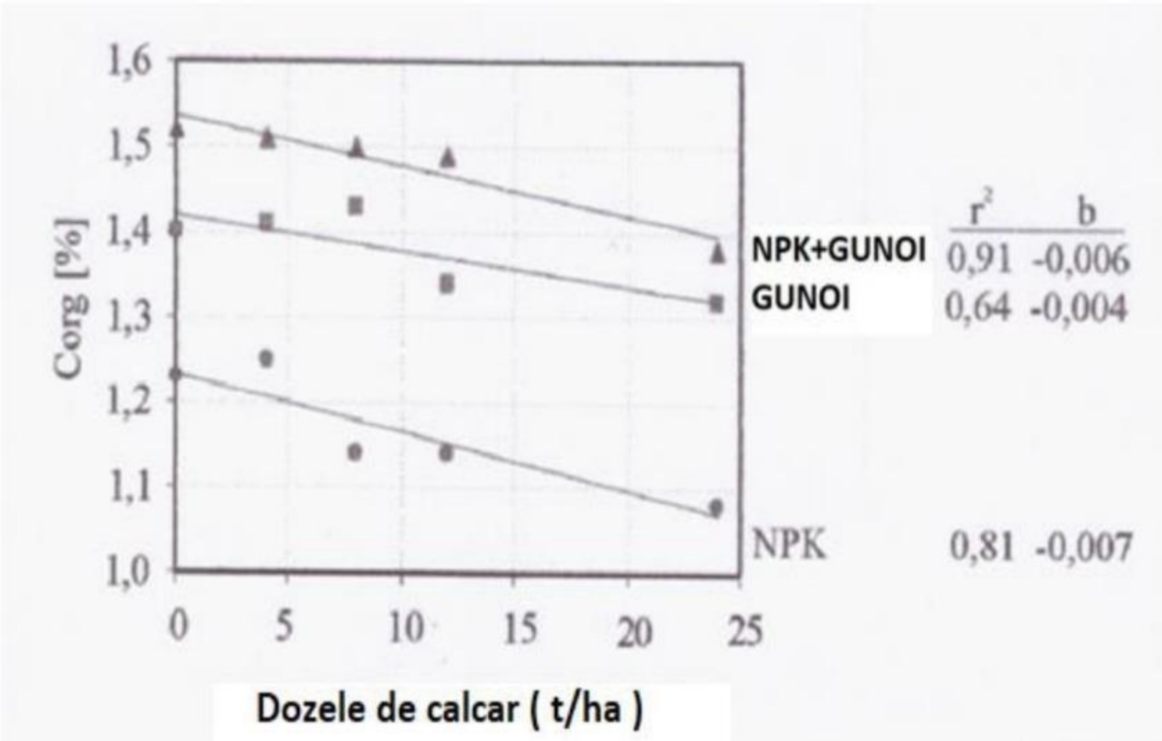


Fig. 18 Influence of long-term amendment and fertilization (1961-2002) on soil organic carbon content of stationary experiments (Livada, 2002)

The organic matter content of the soil is one of the most conservative properties; however, the amendment has an effect of decreasing the carbon content simultaneously with the dose of limestone applied. This tendency is manifested regardless of whether the fertilization was mineral, organo-mineral or organic, given the background of depleted humus content based on fulvic acids (Fig. 18).

Table. 7 The influence of liming and fertilization on carbon content of Albic luvisol (Livada 2001)

Amendare (t/ha)	1961	0	5	10	5	10	$\bar{x}$
	1966	0	0	0	5	10	
	1971	0	0	0	5	10	
	1977	0	0	0	5	10	
	1986	0	0	0	5	10	
	1998	0	5	10	5	10	
Calcar (t/ha)	$\sum_{1961}^{2002}$	**0**	**10**	**20**	**30**	**60**	
Fertilizare							
0 (martor)		1.09	1.06	0.95	0.99	0.92	**1.00**
N		1.11	1.06	1.02	1.01	0.94	**1.03**
P		1.05	1.02	0.96	0.93	0.91	**0.97**
NP		1.07	1.06	1.02	0.99	0.98	**1.02**
NPK		1.13	1.15	1.14	1.14	1.01	**1.12**
G		1.40	1.41	1.43	1.34	1.32	**1.31**
G+NPK		1.52	1.51	1.50	1.49	1.38	**1.48**
1,5 x NPK		1.23	1.25	1.14	1.14	1.08	**1.17**
$\bar{x}$		**1.20**	**1.19**	**1.15**	**1.12**	**1.03**	**1.14**

$N = 100 kgN \cdot ha^{-1} \cdot an^{-1}$
$P = 70\ kgP_2O_5 \cdot ha^{-1} \cdot an^{-1}$
$K = 60\ kgK_2O \cdot ha^{-1} \cdot an^{-1}$
$G = 20\ t \cdot ha^{-1} \cdot an^{-1}$
G (Farm yard manure)=gunoi de grajd

	A	B	AxB
$GD_{5\%}$	0.13	0.07	0.19

The amendment with different doses determined a decrease of carbon content on average by 0.17%. The negative effect of the amendment on the organic carbon content can be explained by the stimulation of microbiological activity, under these conditions, with a more pronounced mineralization of the organic matter and the simultaneous intensification of soil respiration. The long application of potassium had a favorable influence on the carbon content. Also, the same effect is recorded in all cases of organo-mineral fertilization (Tab. 7).

Changes in total sulfur content

Tab. 8 Effect of long term amendment and fertilization on total S in topsoil, after 40 years (Albic luvisol, Livada, 2001)

Lime – t/ha	1961	0	5	10	5	10	Mean
	1966	0	0	0	5	10	
	1971	0	0	0	5	10	
	1977	0	0	0	5	10	
	1986	0	0	0	5	10	
	1998	0	5	10	5	10	
	$\sum_{1961}^{2002}$	**0**	**10**	**20**	**30**	**60**	
O		168	158	147	126	124	**145**
N		182	161	145	134	126	**150**
P		160	153	137	128	124	**140**
NP		174	153	155	143	128	**150**
NPK		183	173	159	153	151	**163**
FYM		212	208	200	216	201	**207**
FYM+NPK		235	222	258	219	228	**232**
1,5+NPK		200	189	183	148	159	**176**
Mean		**189**	**177**	**173**	**158**	**155**	**X**

LSD 5%	A	B	A x B
	19	9	26

N = 100 kg N x ha^{-1} x an^{-1}
P = 70 kg P_2O_5 x ha^{-1} x an^{-1}
K = 60 kg K_2O x ha^{-1} x an^{-1}
FYM = 20 t x ha^{-1} x an^{-1}

The total S content of the soil shows a decreasing trend similar to the carbon content, depending on the increase of the applied amendment doses. An increase in the total sulfur content of the soil was noted in the case of the variants of systematic fertilization with potassium, manure and manure + NPK, respectively (Tab. 8).

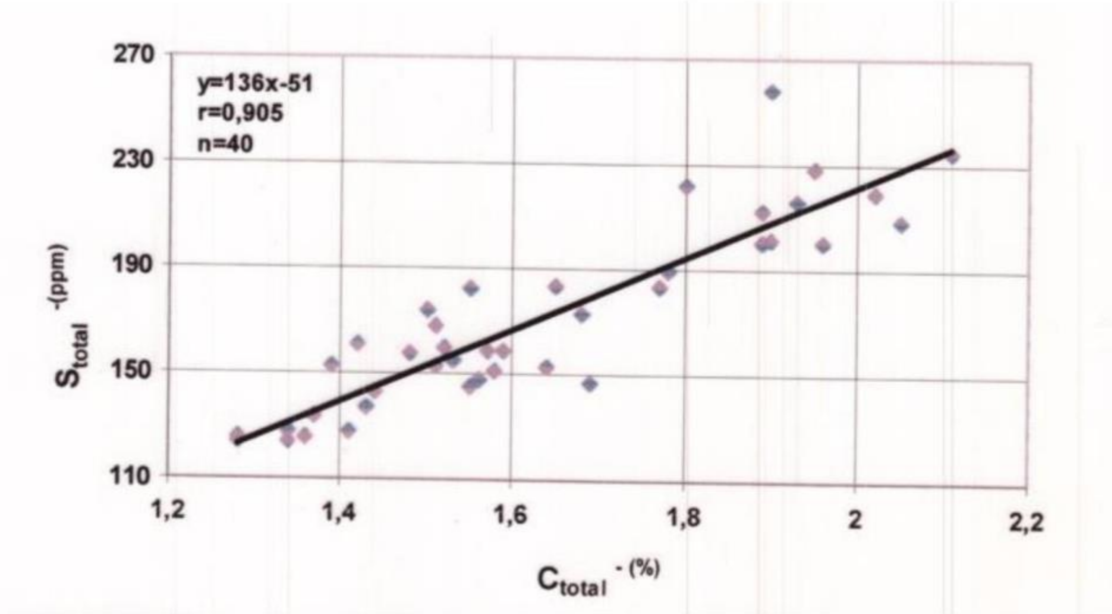


Fig. 19 The relationship between the content of Ctotal and Stotal in topsoil in stationary experiments at Livada, Albic luvisol, 2001.

Between the content of total carbon in the soil and total sulfur, there is a linear and direct proportional relationship. As total carbon content increases total sulfur content also increases (Fig. 19).

Plant and soil microelements

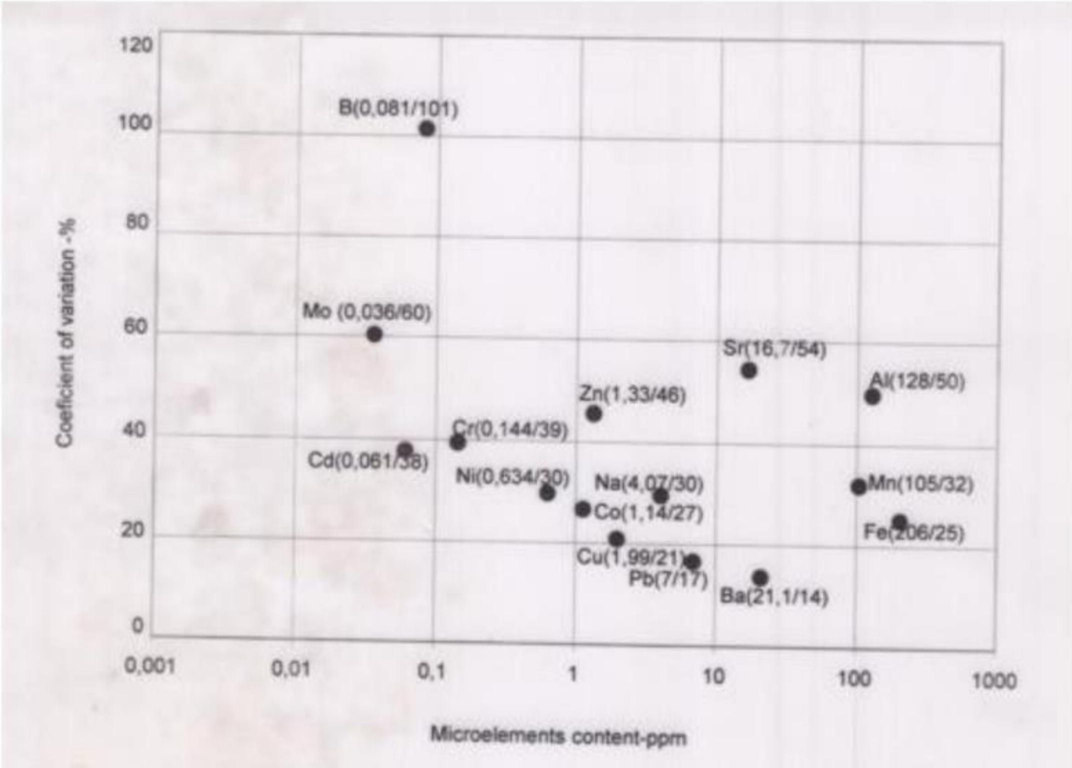


Fig. 20 Variability of microelements content in soil collected from stationary experiences, after 40 years (n=120) (Albic luvisol, Livada)

The highest amounts of trace elements determined in the Albic Luvisol are: Fe (206ppm), Al (128ppm), Mn (105ppm). The variation of B content within the albic luvisol is the highest (101%), followed by Mo (60%), at the opposite end being Ba (14%) and Pb (17%). We chose to present the results as a relationship between a parameter of the central tendency (the average microelement/experience content) and a dispersion parameter (the coefficient of variability) as this offers the possibility of identifying systematic variations under the influence of amendment and fertilization. The results summarizing the influence of amendment and long-term fertilization on the content of trace elements fit perfectly into the concepts of "Chemical Time Bomb" and “Invisible present". In other words, the phenomenon belongs to the category of rare events, several decades being necessary to highlight some effects.

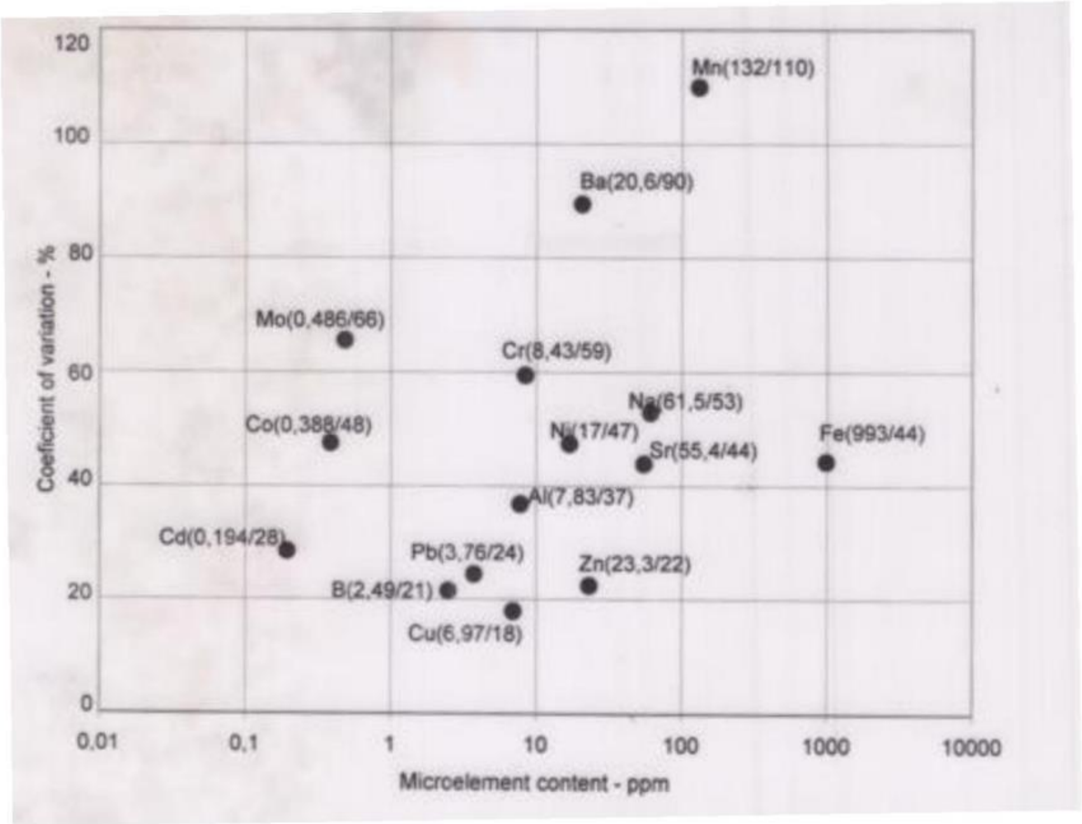


Fig. 21 Variability of microelements content in wheat at tillering stage after 40 years of trial (n=120). Albic luvisol, Livada.

The content of microelements in twinned wheat plants (expressed in ppm) is the highest in the case of iron (993 ppm), followed by manganese (55.4ppm). The lowest values were identified in the case of microelements: Cd (0.194 ppm), Co (0.38 ppm) and Mo (0.486 ppm). The variation in the content of manganese (Mn) and barium (Ba) trace elements in wheat plants was the most pronounced (110% and 90%, respectively). Among the elements with a low content, we noted constant values in the case of copper (18%), boron (21%), lead (24%) and zinc (22%). Within the last years, fertilizing with microelements was frequently advocated, often without robust scientific rationale. The results obtained within this stationary experience with the amendment and fertilization of acidic soils highlight the susceptibility of occurring microelement nutrition disorders.

Changes in the cadmium content of plants

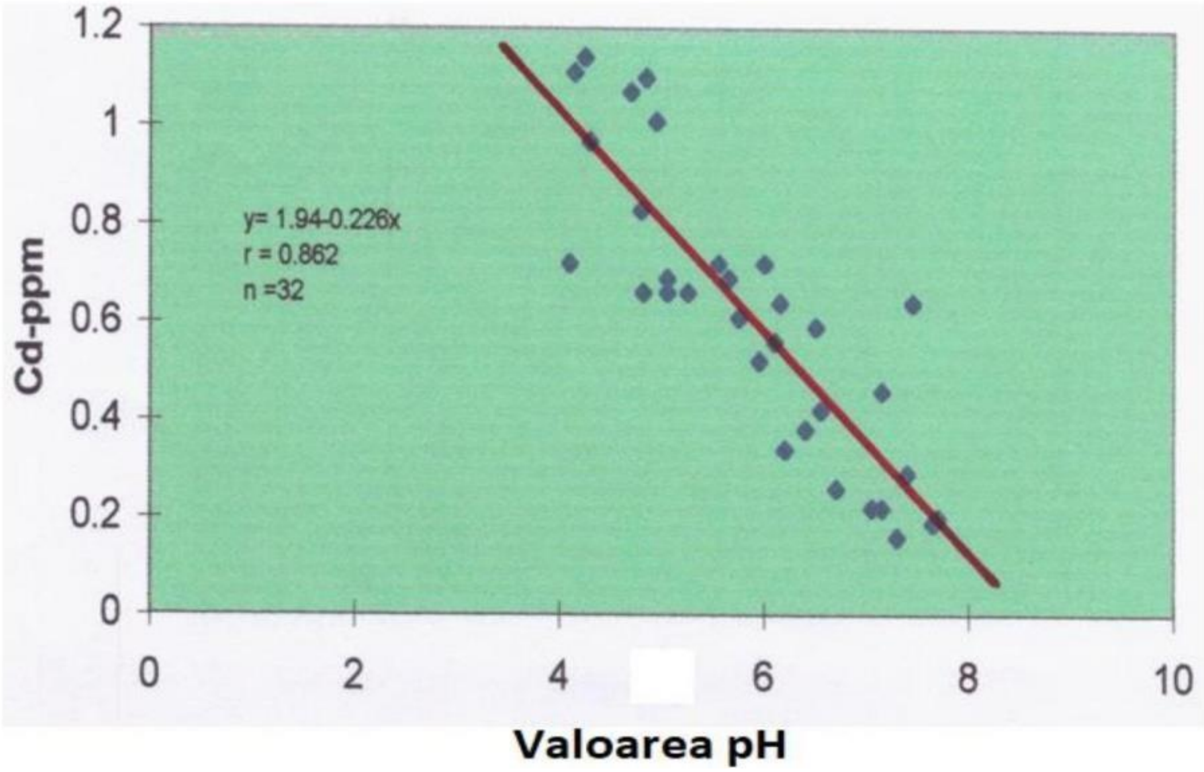


Fig. 23 Relationship between pH value and Cd content (ppm) in young maize plants. Luvisol albic, Livada 2001.

The amendment markedly reduces the absorption of Cd (cadmium) in young corn plants (Fig. 23). Amending can be one of the ways to reduce the toxicity of heavy metals in young corn plants. Numerous researches carried out in Europe have emphasized the danger of Cd and other heavy metal accumulation in these soils, due to the usage of fertilizers with raw phosphatic rocks from North Africa. Thomas' slag also contains appreciable amounts of heavy metals. In Sweden, the use of mercury- based fungicides for 25 years has threatened with extinction some of the bird species. The danger of soil contamination with heavy metals increases when using wastewater and sludge. To the listed sources, there is also the pollution produced by the deposition of dust from atmosphere.

Changes in soil and plant strontium content

Tab. 9 Influence of long term amendment and fertilization on strontium content (ppm) of winter wheat at tillering, 2001.

Lime-	1961	0	5	10	5	10	
(t/ha)	1966	0	0	0	5	10	
	1971	0	0	0	5	10	
	1977	0	0	0	5	10	$\bar{x}$
	1986	0	5	10	5	10	
	1998	0	5	10	5	10	
	Σ	0	10	20	30	60	
O		48,0	72,2	55,5	36,1	29,2	**48,2**
N		55,0	88,5	81,7	46,9	[illegible]	**61,3**
P		100,8	85,8	84,0	54,4	38,4	**72,7**
NP		76,0	104,2	105,6	66,8	45,9	**79,7**
NPK		54,9	77,4	65,4	43,2	32,2	**54,6**
FYM		29,9	41,5	43,8	27,8	21,9	**33,0**
NPK+FYM		38,2	52,1	46,0	34,1	24,1	**38,9**
> NPK		57,1	67,3	55,9	36,7	32,4	**49,9**
$\bar{x}$		**57,5**	**73,6**	**67,2**	**43,3**	**32,3**	**54,8**

	A	B	A x B
LSD 5%	9,0	5,6	14,7 ppm

In the amended variant with cumulative doses of 15 t /limestone/ha, the strontium content increases by 16.1 ppm. compared to the control variant. As progressive doses of amendment are administered, there is a tendency to decrease the content of strontium, reaching the amended version with the highest amounts, namely 60 t amendment/ha, almost half compared to the control version. Fertilization with nitrogen and phosphorus marks an increasing trend, their association with potassium, by virtue of ionic antagonism, decreasing the strontium content. Although strontium is the accompanying ion of calcium in nature, the excess amendment leads to a major decrease in the content of strontium due to the deficient Ca-Sr ratio, thus creating conditions for the manifestation of competition in the absorption of elements (Tab. 9).

Tab. 10 Influence of long term liming and fertilization on strontium content in Albic Luvisol (Livada 2001)

Lime-	1961	0	5	10	5	10	
(t/ha)	1966	0	0	0	5	10	
	1971	0	0	0	5	10	
	1977	0	0	0	5	10	**Mean**
	1986	0	5	10	5	10	
	1998	0	5	10	5	10	
	Σ	0	10	20	30	60	
O		16,2	31,3	39,1	31,8	45,5	**32,8**
N		14,9	28,5	38,9	25,5	50,3	**31,6**
P		17,5	33,8	41,2	34,2	49,2	**35,2**
NP		20,2	33,9	49,2	41,3	47,1	**38,3**
NPK		19,1	30,3	44,9	33,6	49,3	**35,4**
FYM		18,9	29,0	42,8	34,1	50,6	**35,1**
NPK+FYM		21,4	38,1	49,1	32,8	55,8	**38,1**
> NPK		18,8	21,9	51,6	34,1	55,6	**37,8**
Mean		**18,4**	**31,0**	**44,6**	**33,4**	**50,4**	
					A	**B**	**A x B**
				LSD 5%	**4,03**	**3,20**	**7,80 ppm**

In the unamended and unfertilized version, the strontium content is 18,4 ppm. Due to the presence of strontium as an accompanying ion of calcium, simultaneously with the increase in the amendment dose, the content of strontium also increases. Fertilization has no obvious influence. The apatites from the Kola peninsula that served as raw material for the manufacture of superphosphate have a higher content of strontium than the other phosphate rocks.

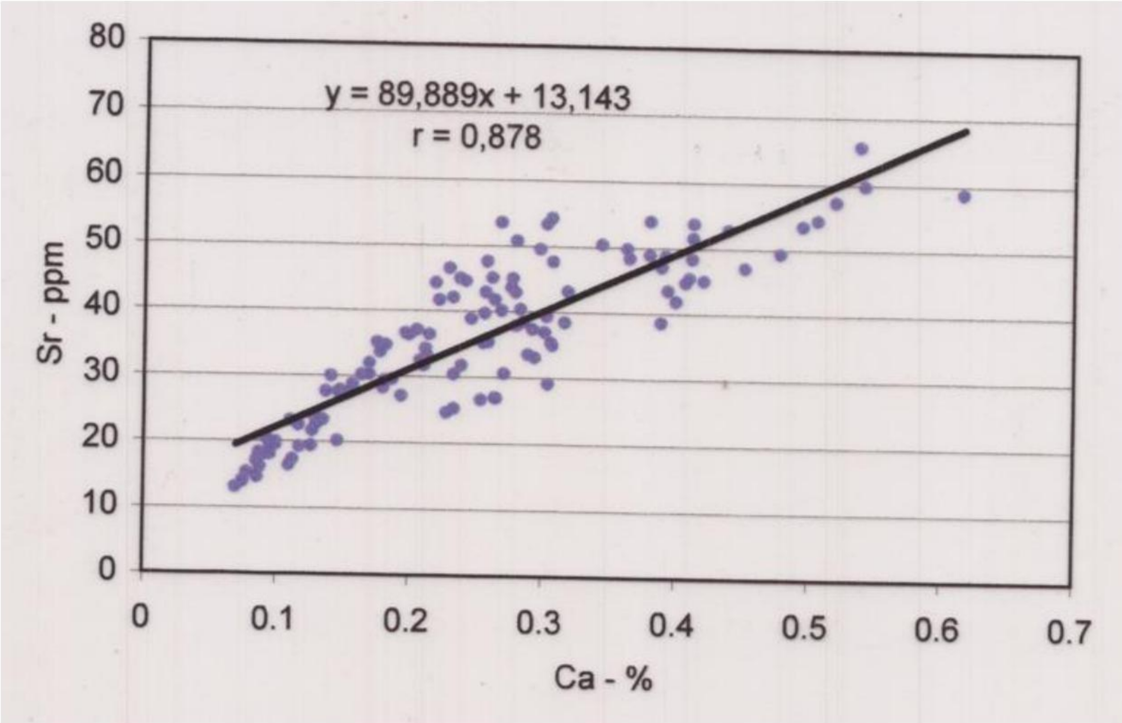


Fig. 24 Relationships between total (HNO3+H2O2) calcium (%) and strontium (ppm) content in the topsoil of stationary amendment and fertilization field experiment after 40 years. (Albic Luvisol Livada, 2001)

There is a linear and direct proportional relationship between the 2 variables. Due to the amendment, the strontium content increases almost seven times (Fig. 24).

Changes in molybdenum content of plants

Molybdenum is the activator ion of nitrate-reductase and has a decisive role in the reduction of nitrates in the plant. Simultaneously with the increase in the doses of amendments, the absorption of molybdenumalso increases, which has a favorable effect on the reduction of nitrates.

Compared to the positive effect of the amendment application on molybdenum content, fertilization has a much more modest influence (Tab. 11).

Tab. 11 The influence of liming and long-term fertilization (1962-2001) on the content of molybdenum (Mo-ppm) in wheat plants (Alex) at tillering stage. (Albic Luvisol, Livada 2001)

-ppm s.u .

Calcar - (t/ha)							Media
	1961	0	5	10	5	10	
	1966	0	0	0	5	10	
	1971	0	0	0	5	10	
	1977	0	0	0	5	10	
	1986	0	0	0	5	10	
	1998	0	5	10	5	10	
	$\sum$	0	10	20	30	60	
	$t.ha^{-1} \cdot an^{-1}$	0	0.25	0.50	0.75	1.50	
O		0,13	0,23	0,64	0,76	0,81	0,51
N		0,14	0,22	0,45	0,45	0,88	0,43
P		0,16	0,28	0,83	0,79	0,76	0,56
NP		0,16	0,32	0,47	0,58	0,73	0,45
NPK		0,13	0,23	0,47	0,64	0,76	0,45
#		0,15	0,40	0,83	0,70	0,67	0,55
NPK+#		0,13	0,29	0,65	0,61	0,70	0,48
>NPK		0,14	0,26	0,55	0,54	0,88	0,47
Media		0,14	0,28	0,61	0,63	0,77	

	A	B	AxB
$Dl_{5\%}$	0.24	0.06	0.27

4.4.5 Changes in zinc absorption, deficiency index of zinc and magnesium of plants

There is a non-linear relationship between pH value and zinc absorption in corn and flax for fiber. Increasing the pH value causes a very serious decrease in zinc absorption (Fig. 25). Achieving a pH of 5.8 to neutralize the harmful effect of Al ions, determines at the same time the considerable reduction of Zn content in plants.

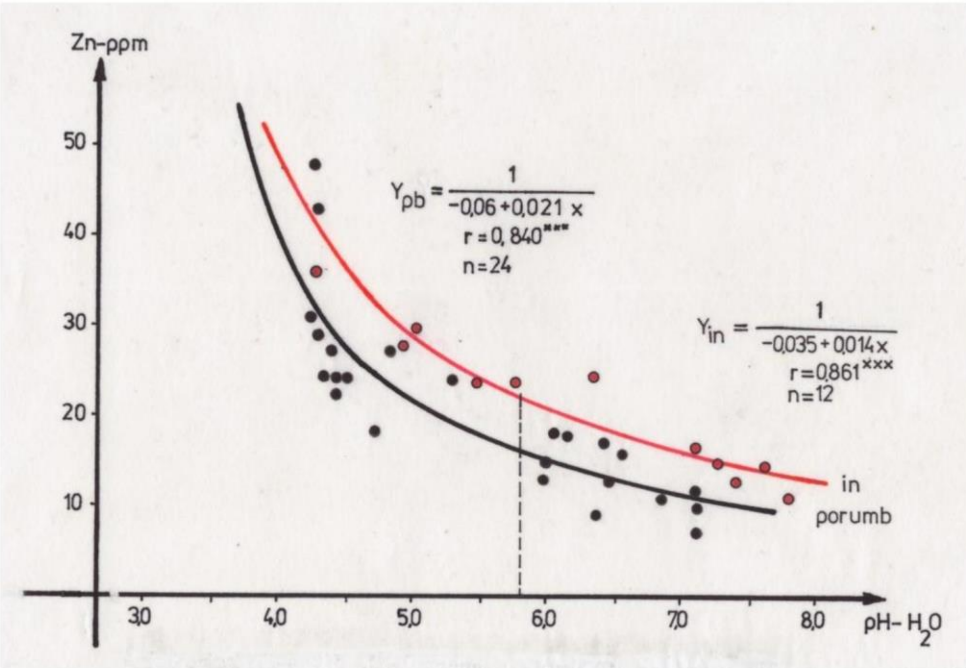


Fig. 25 The influence of pH value on the zinc absorption in maize and flax

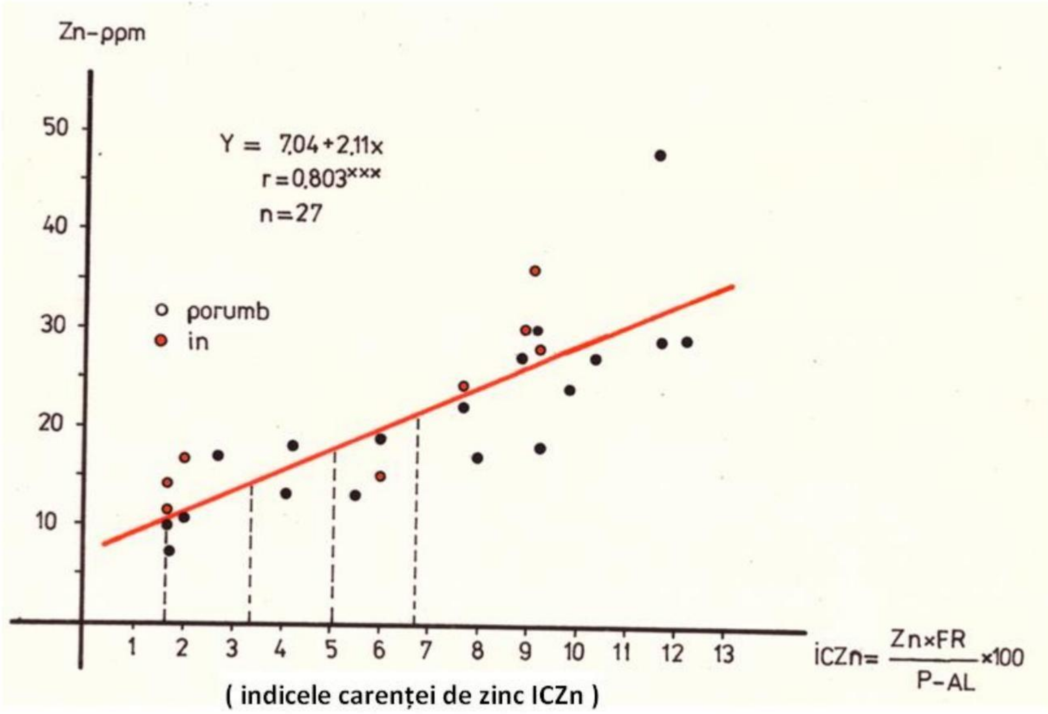


Fig. 26 Relationship between ICZn and Zn content in maize and flax.

The index of zinc deficiency elaborated by Borlan and Hera (ICZn) summarizes the main agrochemical indicators involved in the absorption of zinc: the pH value and the phosphorus content of the soil. Unlike for other types of soil, for the clay-iluvial soils of northwestern Transylvania, the predominant role in triggering zinc deficiency occurs due to the increase in pH through amendment, being well known that these soils are generally poorly supplied with phosphorus and the conditions for the manifestation of antagonism between phosphorus and zinc are not met. Uneven application or excessive doses of amendment are the main responsible for creating the conditions for manifestation of zinc deficiency (Fig. 26).

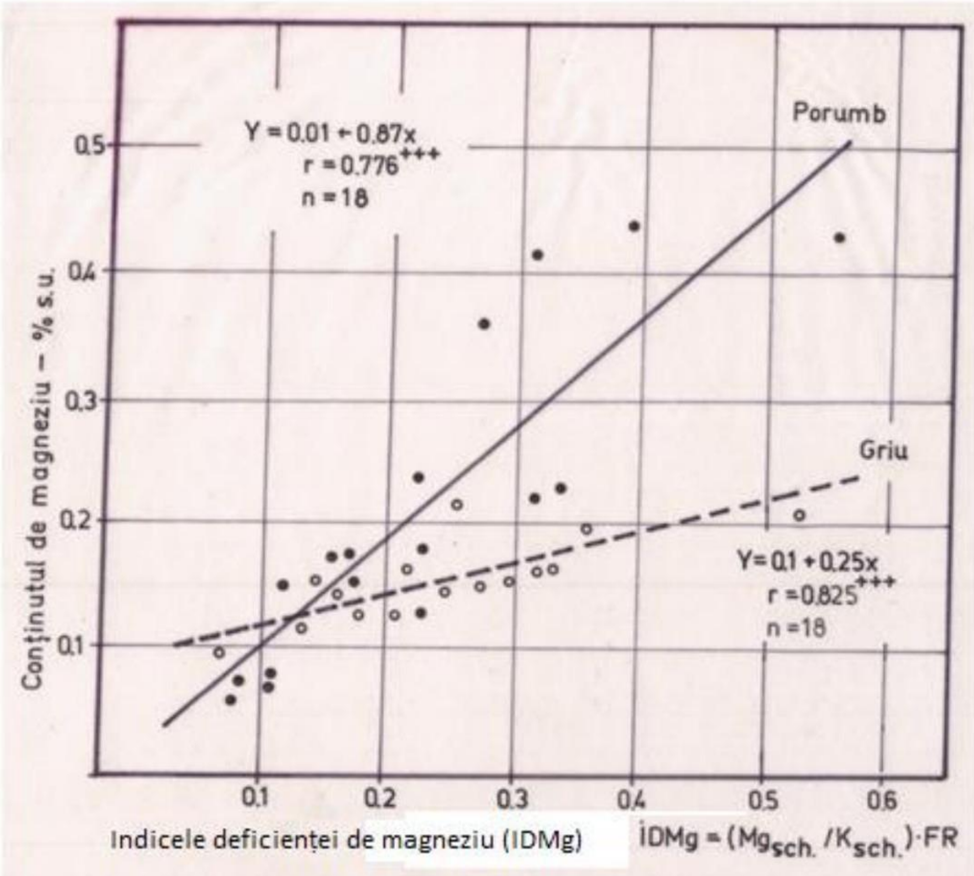


Fig. 27 Relationship between magnesium deficiency index (iDMg) and magnesium content in wheat and maize plants, respectively.

The magnesium deficiency index aggregates the main factors that are incriminated in triggering magnesium deficiency: the exchangeable Mg content ofthe soil, the exchangeable potassium content, and the pH value.

Symptoms of magnesium deficiency from stationary experiences were identifiedin the case of unamended or insufficiently amended variants against the background of applying potassium along with nitrogen and phosphorus.

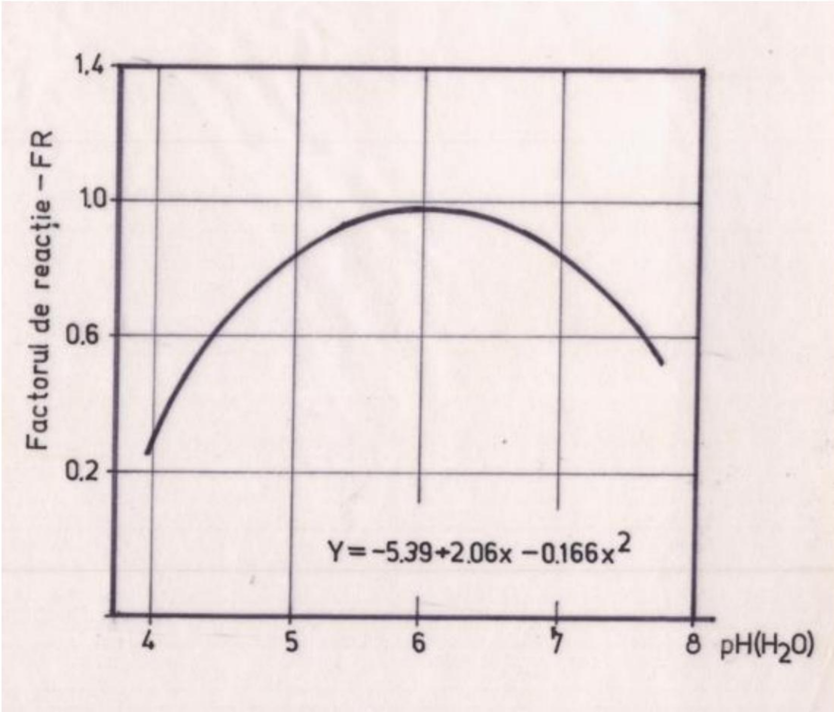


Fig. 28 The change of reaction factor depending on the pH value.

The reaction factor is an index of magnesium absorption at different pH values. The element is best absorbed around the pH value of 6 (Fig. 28). The value of the correlation coefficient highlights the positive or negative interactions, respectively the synergisms/antagonisms between the different nutritional elements contained in the plant. The classic relations of antagonism or synergism between the nutritional elements are confirmed, to which are added the interactions between some microelements, such as strontium which shows a behavior similar to that of calcium (Fig. 22).

4.5 Changes in some physical properties of the soil

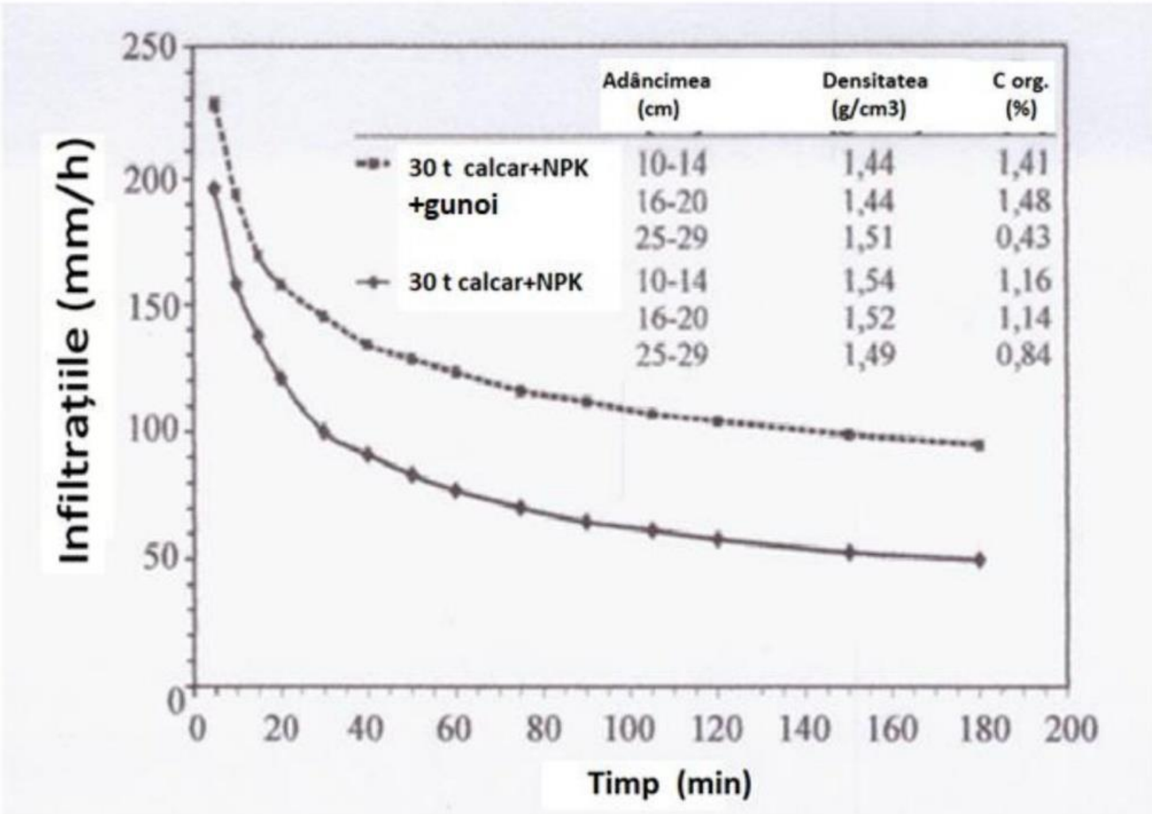


Fig. 29 The influence of long term liming and fertilization on water infiltration (mm/h) in the albic luvisol profile (Livada 2002)

Figure 29 shows the relationship between the time required for water infiltration into the soil (min) and the amount of water (mm/h). The most pronounced infiltrations of water through the soil are in the first 20 minutes. The application of semi-fermented cattle manure has a stronger influence on infiltration compared to the effect of amendment combined only with mineral fertilization.

4.6 Changes in mineralogical composition

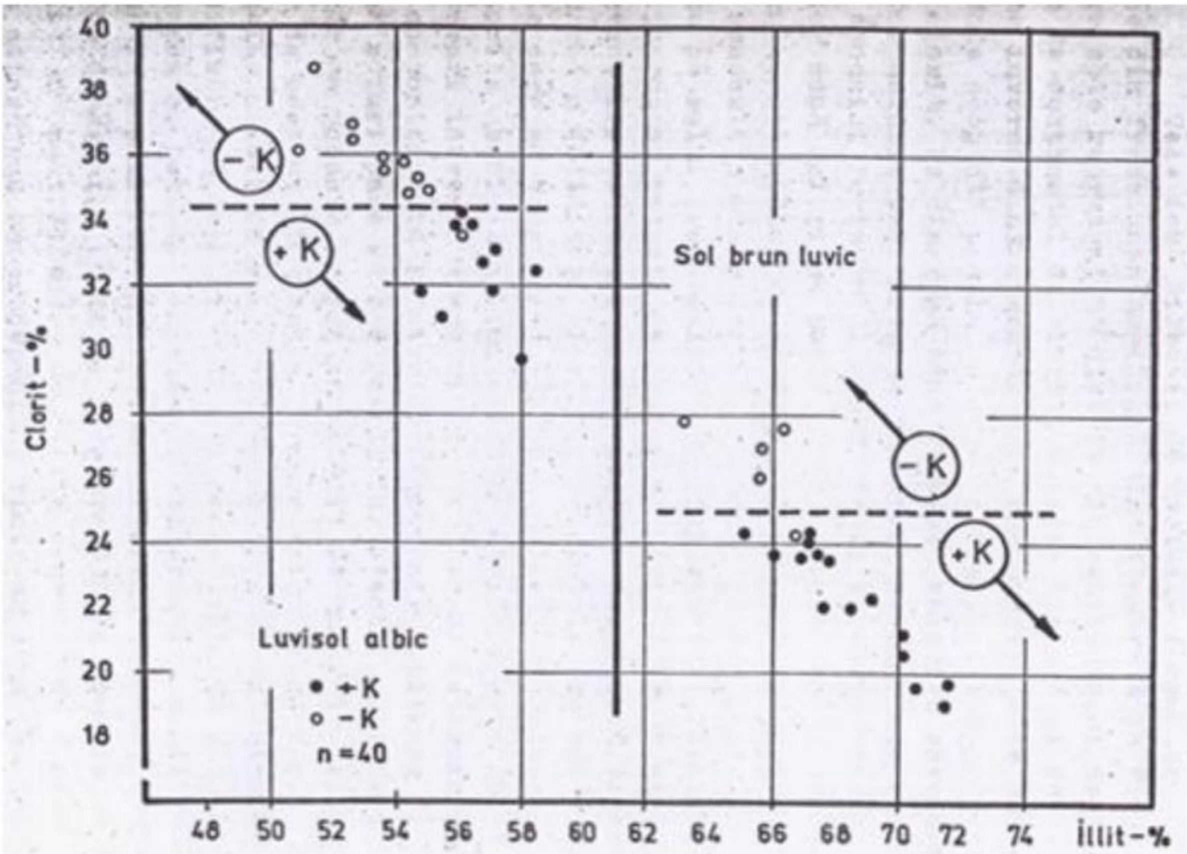


Fig. 30 Reciprocal variation of illite and chlorite content in the clay fraction of the soil from stationary experiments.

The quantitative interpretations of the X-ray diffraction results indicate for the Haplic Luvisol the predominance of illite minerals, whose content varies in the range of 63-73% (Fig. 30). Chloritic minerals have a lower share (19-28%). In the case of the Albic Luvisol, the content of illite minerals marks a decrease, compared to the Haplic luvic soil, the range being between 50-59%, while the chloritic minerals show an increase (29-39%). The two directions of evolution of the mineralogical composition in the clay fraction are illustrated in figure 30, in which the distribution of the chlorite content is represented depending on the content of illite. The linear and inversely proportional relationship between these two components is determined by the method used in calculating the percentage content of illite and chlorite. The values corresponding to both soils are shown on the graph. Although the imaginary line of regression continues in the area of the Albic luvisol, between the representative values of the two soils, a line (zone) of separation can be drawn around the 60-61% illite content, which marks two levels of mineralogical composition. These correspond to the lack of receptivity on the Haplic Luvisol and the favorable reaction to potassium fertilization on the Albic Luvisol, respectively (Fig. 30). Within the sequences of values characteristic of the two types of soil, a clear delimitation can be noted between the samples from the variants that benefited (K) or not (-K) from potassium. Even if the absolute values of the limits drawn in figure 30 are accompanied by inherent errors of the degree of precision of the determination, the compositional difference at the level of the clay fraction between the two soils seems to be real, and the effect of the application of potassium fertilizers on the amount of illite minerals is easy to notice. To the extent that the values corresponding to different levels of mineralogical composition would coincide with some changes regarding the receptivity of the plant to potassium fertilization, they would be of high practical importance. Until the accumulation of a sufficient volume of data, the respective demarcation line can be interpreted as a transitional area, with the possibility that the indicated conventional limit will be reached or even exceeded, in one way or the other, under the influence of systematic technological interventions (potassium fertilization, amendment, etc.). The data obtained for the Haplic Luvisol indicate an evolution in the direction of chloritization due to non-fertilization with potassium. Probably, over time, it is possible to reach in such cases levels of chloritization similar to the Albic Luvisol, with all the unfavorable changes that would accompany such a process (decrease in potassium mobility and supply, increase in aluminum mobility with reaching and exceeding toxicity thresholds, reduction of specific surface area and exchange capacity, etc.).

Even if at present it is difficult to formulate assessments about the time period leading to this evolution, the duration of such a process, determined by anthropic intervention, is much shorter than the duration of the corresponding natural process.

4.7 Changes in soil respiration and emissions of carbon dioxide

The primary and main source of CO_2 emissions in plant production is the respiration of plant roots and soil microorganisms. Previous studies have mainly highlighted the influence of soil moisture and temperature as well as humus content on respiration, but most of them refer to the comparative analysis of different soil types, the various investigations focusing on factors such as moisture, temperature and content of organic matter of the soil; these approaches highlighted the differences that exist naturally and addressed to a lesser extent the anthropic interference on this phenomenon. Separating the factors influencing soil respiration is a methodologically difficult endeavor.

There are relatively few approximations regarding the effect of some factors on soil respiration within the same soil type, especially considering soil reaction and organic matter content. In this context, the conducted research proposes an overall assessment of the phenomenon, and its quantification. In our area, the studies so far have only allowed an indirect assessment of soil respiration, not finding it possible to accurately quantify the phenomenon in the field.

Most of our agrochemical knowledge comes from long-term experiences. The existence of the long-term trial with amendment and fertilization of acidic soils at SCDA Livada provided the opportunity to carry out some investigations regarding soil respiration in the field, thereby proving its usefulness in environmental protection research. These experiences are the oldest in Central Europe and through the complexity of the gradations of the experimental factors they manage to faithfully represent the production conditions within a very wide pH range.

Analyzing the correlation between pH and soil respiration (Fig. 31), it appears that as pH value increases, soil respiration also increases; if at pH values (KCl) below 4 soil respiration is around 1 $\mu mol*m^2*s^{-1}$ this shows a tendency to increase exponentially reaching values of 4-5 $\mu mol*m^2*s^{-1}$ corresponding to the evaluation of 26.04. 2012.

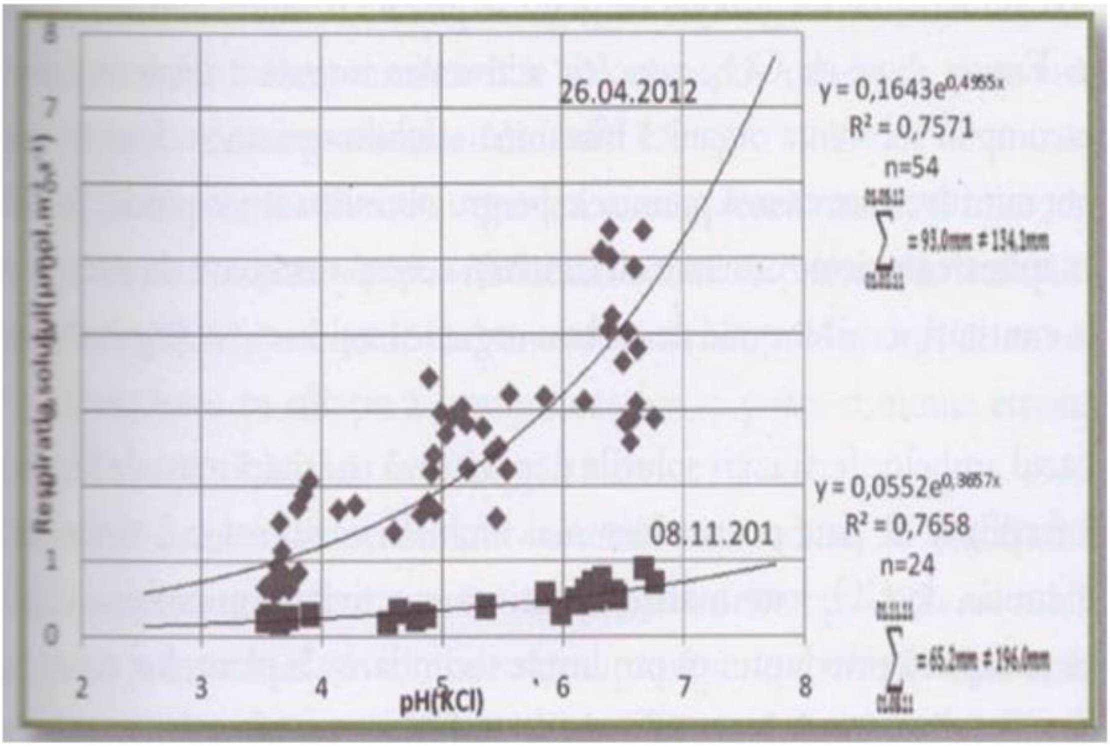


Fig. 31 Correlation between pH value (KCl) and soil respiration.

The determinations regarding soil respiration from 08.11.2011 show only a weak tendency of intensification of this phenomenon, the values of the determinations being between 0 and 1 μmol*m²*s⁻¹. Both moments of field determinations of respiration were made in conditions of severe drought, the pluviometric deficit being 130.8 mm in the case of autumn determinations (between 01.08 - 01.11.2011) and 41.1 mm for spring determinations (02.01.-05.01.2012). The differences in orders of magnitude corresponding to the two moments of determination are largely explainable by the influence of temperature on the activity of soil microorganisms and reveal the seasonal character of this process. The obtained results prove that the increase in CO_2 emissions contributes to the amplification of soil degradation processes.

4.8. Changes in the degree of weeding induced by long-term amendment and fertilization

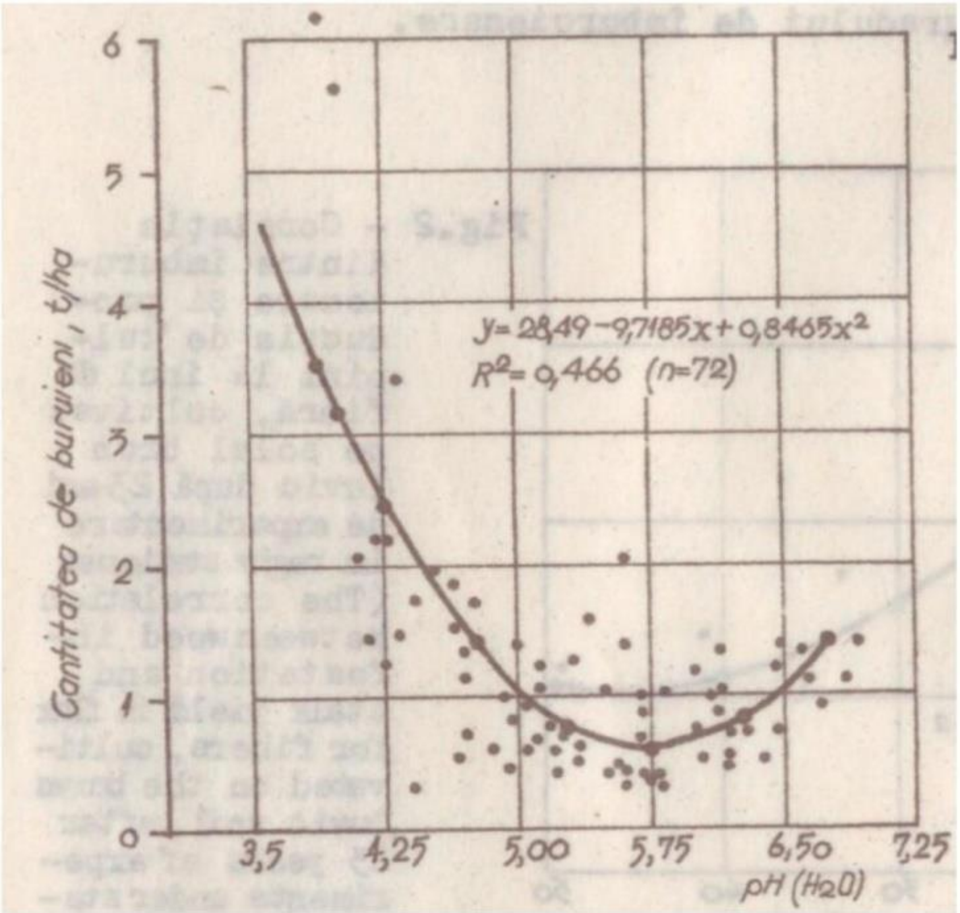


Fig. 32 Influence of pH on weed infestation of a wheat field fertilized for 26 years (Haplic Luvisol, Livada).

On the Haplic Luvisol from Livada, in 1987, after 26 years of amendment and fertilization, within the autumn wheat crop placed in the stationary experiment there was established a clear dependence between weeding and pH (Fig. 32). The decrease in weed biomass was pronounced until around the pH value of 5.75, after which weeding tended to increase due to the presence of dicot species. Over the years, as acidity decreased these species became frequent components of the association of vegetal flora on the soils of Livada. In retrospect it can be said that soil acidification has significantly contributed to the reduction of the number of weed species.

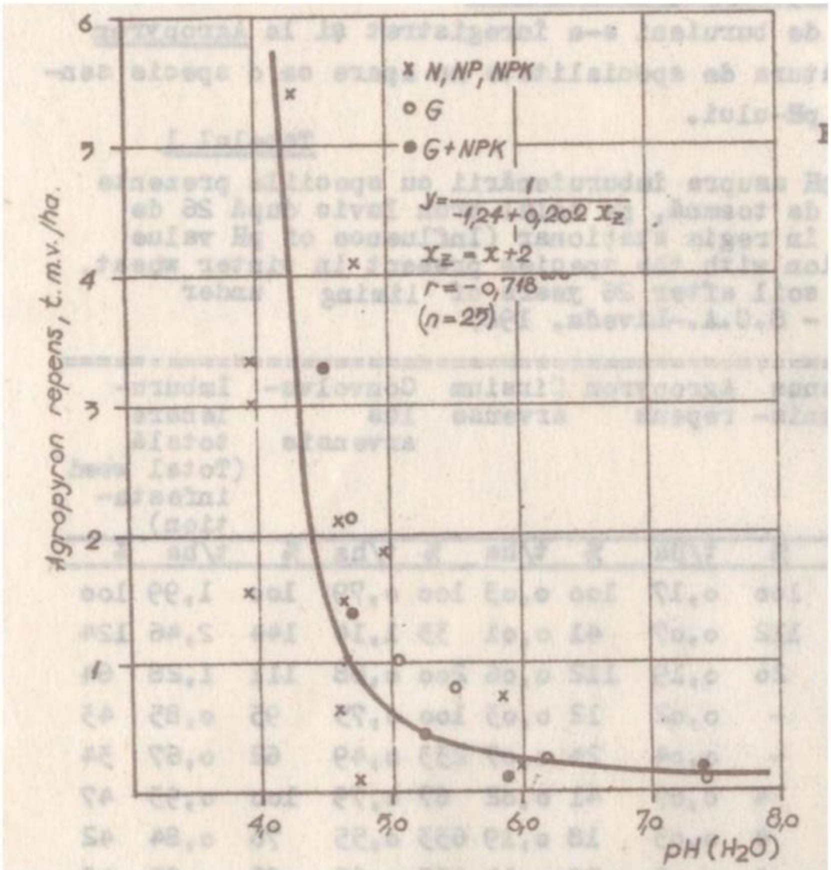


Fig. 33 The influence of pH on weed infestation with *Agropyron repens* in the case of a fertilized wheat field, after 26 years from initiation of stationary experiments. (Haplic Luvisol, Livada).

Weed biomass systematically decreases in all variants of fertilization with the increase in pH, from 4.4 to over 6. The most intense reduction of weeding was recorded for balanced fertilization with nitrogen, phosphorus and nitrogen, the one with phosphorus and potassium, but also in the case of organo-mineral fertilization. At the same time, in the case of single element fertilizations, especially with nitrogen, the reduction is less spectacular and within the limits of experimental errors (Fig. 33).

5. Assessments regarding the execution of the experiences to date

The obtained results demonstrate that the answers to the main dilemmas of plant nutrition and fertilization, even at present, are provided by the experiments performed in the stationary regime, because valid conclusions can only be formulated on the basis of long observations and research. The long-term experiences with amendment and fertilization of acid soils from SCDA Livada are the only experiences in Romania that are bordered by grassy lanes, and have boundary markers at all 4 corners. Recreating the experimental scheme on the ground every year is relatively cheap and convenient.

On another hand, as tilling inevitably leads to moving the soil and thus expending the interference portions between treatments, over the years we end up shrinking more and more the surface of the net plot. There can be found different ways of countering this process: by building concrete walls between the experimental variants (e.g. Ewige Roggenbau - University of Halle) or separating them by boards (e.g. Ultuna Long-term Soil Organic Mater Experiment).

Carrying out field experiments on clayey illuvial soils is more difficult and more expensive than on more balanced soils.

After so many years of experimentation, detailed quantification of the flow of substances from these experiences would be required. It would also be extremely timely to develop studies regarding the microbiological activity of the soil, the emissions of gases relevant for climate change, as well as studies regarding the changes in humus qualities and quantity under the conditions of amendment. The stationary experiences were initiated during a time when we were barely asking questions, and others were already formulating answers.

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