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Results of Long Term Fertiliser Experiments - Use in Sustainable Soil Fertility Protection Measures

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ABSTRACT

Long-term experimental research is a model for a superior approach to the long-term effects of vegetation and plant production factors, in relation to the modification of soil-plant components, their productivity, environmental protection and food security. In their fairly well-established and evaluated existence of 180 years, one can assess and record the existence of these experiments on almost all continents, with particular and relevant responses to be implemented for the development of sustainable systems in the development of agriculture and the resolution in time of contemporary challenges for both agriculture and the environment. (Recording of the 180th anniversary of the founding of the "long term model" at Rothamsted - "Three - day hybrid event hosted online and at Rothamsted Research, West Common Harpenden" UK, 20th-22nd June 2023).

This paper aims to interpret the changes in the soil-plant system, based on studies and research in experimental and soil analysis field, after long term effects in the experiments at Băcăinți - OSPA Alba and Turda - SCDA, with subsequent proposals for protection and increase of soil fertility and environmental conditions. In the same context, certain interpretations and limits are promoted in the foundation of agrochemical measures for fertility modelling and increased effect of fertilizers.

Keywords: stationary experiments, agrochemical interactions, fertility protection.

INTRODUCTION

Long-term experiments are widespread in over 700-800 conditions (locations) around the globe, after Liebig (1840-1845) makes the enunciation of the "law of the minimum" and the principles of mineral nutrition. Further on, they consequently experience a worldwide development especially at the beginning of the century. The concepts of vegetation factors' interaction were developed thanks to Mitscherlich (1913-1929). The "long term" and stationary experimental model was conceived and initiated at Rothamsted by John Bennet Lawes (1843) and continued by his disciple Gilbert (Liebig's former doctoral student at the University of Leipzig), who initially took an approach to the effect of phosphorus and organic fertilisers (immediately after the discovery of the principle of superphosphate production by acid attack of calcium phosphates in bones). From the point of view of fertilizers and promotion of their long-lasting effects, a favourable similarity can be assumed - the originators took into account and studied the novelty of the effect of the phosphates produced and subsequently, during the development period for these experiments, they also took into account the results of the production of nitrogen fertilizers (after the successful synthesis of NH_3 by Haber-Bosch in 1913) and thus the support of some interactions (including NP) proposed by Mitscherlich (in the law of "action of vegetation factors") was identified.

The identification, inventory and archiving of long-term experiments worldwide (Debreczeni and Korschens, 2003; Donmez et al., 2022) as well as bibliographical material due to the recent agreement between Bonares (www.bonares.de) and Ejpsoil (www.ejpsoil.eu) carried out under the auspices of the European Community, provides information for 616 long-term experiments older than 20 years in 30

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European countries (Körschens, 1997; Debreczeni and Körschens, 2003; Sin and Partal, 2021; Donmez et al., 2022).

The geographical distribution of these experiments shows their predominance mainly in Europe, followed by the USA and countries in Asia, Africa, etc., with a predominant time span between 1950 and 2000, mainly on arable land, less in other uses and with mainly such objectives as tillage, fertilization and last but not least, crop rotation. In the last 2-3 decades, after the re-evaluation of these experiences for sustainable technologies and systems, the objectives are diversifying and converging towards considerations for soil and environmental protection (heavy metals, CO_2 emissions, carbon sequestration, impact of global warming) (Hera, 2008; Johnston and Poulton, 2018; Singh et al., 2021; Mayer et al., 2022).

In most of the long-term sites, it can be mentioned that the scientific and applied value of the results obtained has increased over time, throughout the duration of the experiments, as a multitude of challenges and response alternatives were provided by the data obtained. Thus, the research platforms established in this field were: Broadbalk Wheat Experiment - 1843, Rothamsted; Dehrain Plots - 1875, France; Eternal Rye Experiment - 1878, Germany; Askov - 1894, Denmark; Palace Leas Meadow - 1896, UK; Static Fertilizer Experiment - 1902, Germany; etc. and others like in the USA: Morrow Plots - 1876; Sanborn Field - 1888, Magruder Plots - 1892, USA or the results obtained from experiments set up and completed between 1950 and 2000, all of which are remarkable for the improvement of methods and methodology of field and laboratory study of long-term experimentation but also for the probity of application and usefulness of this research for the protection of fertility and the increase of soil productivity. Essentially, through this research, long-term experimentation can be an applied and applicative method for the comprehensive study of fertility and environmental protection (Houot and Chaussod, 1995; Schmidt et al., 2000; Miles and Brown, 2011; Nafziger and Dunker, 2011; Christensen et al., 2022).

A fruitful Romanian tradition due to our forefathers, pioneers in the field, includes Ion Ionescu de la Brad's concept recommending to work the land "without impoverishing its fertility", Haralambie Vasiliu's experiments in Moldavia and Basarabia, with the organized approaches coordinated by Gh. Ionescu-Sișești after the establishment of ICAR (1927) and the achievements of the "School of Soil Science" in Romania (with Teodor Saidel, Gr. Coculescu, David Davidescu, Gh. Pavlovschi, R. Mavrodineanu) and of this field in the Geological Institute (coordinated by Gh. Munteanu-Murgoci), have all created the basic foundation of experimentation and research in the field of rational use of fertilizers, plant nutrition and soil fertility. (Hera, 2016).

The sites with amendments and fertilizers retained today as assets in the field and laboratory include the stationary ones on "Amendment and fertilization of acidic soils at SCDA Livada" (1961/1962, Boeriu I. - 1961-1974; P Kurtinecz - 1974-2023; P. Ursan - 2023-present) and "Long-term experiments" with NP, NPK, and organo-minerals (Hera - Borlan model) from 1966/1967, mentioned and archived at European level (Debreczeni and Korschens, 2003; Donmez et al., 2022).

In Romania, long-term experiments with fertilizers were initiated in 1966:

The long-standing fertilizer experiments in our country (14 archived in 2003 and 2022 at European level) were located according to a uniform concept, under differentiated ecological conditions and representative of the agricultural area where they are located (1966/1967). The new concept was developed by Cristian Hera (then senior researcher at the Fertilizer Laboratory of National Agricultural Reaserch and Development Institute Fundulea) who consulted the Agrochemical Methodology Laboratory and established specialists in the field for the locations in question and the attached set of analyses (Mihăilă and Hera, 1994; Hera, 1996, 2008).

The proposed project focuses on at least three directions of research in the experimental field, with 3-5 year soils and a set of soil-plant analyses as part of the research objectives. The content and experimental factors, are achieved as objectives and gradations, in the three main directions:

- the study of the effect of nitrogen and NP interaction with the optimization of fertilization systems and agrochemical changes determined in soil-plant system;
- effect of potassium application against the background of NP fertilization, with the objectives of rationalization and balance of NPK fertilization;
- effect of organo-mineral fertilisation (manure + NP), fertilisation efficiency and soil quality.

Initially, the sites of these experiments covered 20 locations in the NARDI Fundulea network and Office for Pedological and Agrochemical Studies units (subordinated to Minstry for Agriculture and Rural Development) 14 of these locations were actually archived at European level. It is obvious that the change in land tenure relations in Romania and the high costs of long-term experimentation call for a reformulation of the sites, an updating of the objectives in the conviction that at present the relevant answers to the main problems of nutrition, fertility and fertilisation can only be obtained through experiments carried out on a multiannual and stationary basis (Kurtinecz and Rusu, 2007; Kurtinecz et al., 2023).

MATERIAL AND METHODS

The long term experiments presented here were located in the Băcăinți Experimental Centre (of OSPA Alba), on soils - typical preluvosol (pH 5.8; V%-75-78; mobile-Al-0.2-0.3 m.e/100 g soil) and on an alluvial mollisol (pH 6.8-7.2; V%-92-95%, humus 2.60%), on the vertical leached chernozem at SCDA Turda (pH 7.4; V% 95-98, humus - 3.70%).

The experiments were located in a wheat-corn-soybean rotation system (3-year fallow) with the following experimental designs:

NP experiment: 0, 40, 80, 120, 160 kg a.i. N/ha for wheat and 0, 50, 100, 150, 200 kg a.i./ha for maize;

0, 40, 80, 120, 160, kg s.a. P O$_{25}$ /ha, for wheat and maize;

0, 30, 90, 120, 150 kg s.a. N/ha- soybean.

NPK experiment: - background NP - 0, 80-60; 160-120 kg s.a./ha

- variants K_2O - 0, 40, 60, 80, 120 kg a.i./ha.

Soil analysis: pH - in aqueous suspension, through potentiometric method;

Organic-C/Schollenberger - through wet oxidation method and dosage titration, according to Walkley-Black;

Mobile and potentially accessible phosphorus according to Egner - Riehm - Domingo spectro-photometric method, in ammonium acetate-lactate extract (P-AL);

Mobile and potentially accessible potassium according to Egner - Riehm - Domingo photometric method, in ammonium acetate-lactate extract (K-AL);

Ah, S_B - Determination of cation exchange capacity and base saturation level using barium chloride solution.

Mobile- Al in KCl extract, using the Sokolov method.

The paper discusses the agrochemical status of the soil during and after the active years of long-term experimentation in relation to production results and recommended measures.

RESULTS AND DISCUSSION

The presented work contains the results of the monitoring and study of the soil properties following the "long term application" (20 - 22 years in the typical preluvosol and alluvial mollisol and 55 years in the vertical leached chernozem) of fertilizers in NP, NPK and organo-mineral compositions and structures, on the basis of which recommendations and assessments were made in relation to soil fertility modelling and protection measures, with conclusions in the design of sustainable soil and environmental protection systems, ensuring the food security of the products.

a. Changes in humus and organic C content through NP and NPK mineral fertilizations.

Considered an essential component of the adsorbent complex, with recognised and analytically determined stability, the humic component of the soil can undergo changes due to technological interventions and the diversity of farming systems practised (Table 1).

Table 1. Changes in humus content through long-term fertilization and amendment (typical preluvosol and alluvial mollisol) (Rotation - wheat, maize, soybean)

Preluvosol							
Wheat	Un-amended			Amended			
N doses	Humus %	P_2O_5 doses	Humus %	N doses	Humus %	P_2O_5 doses	Humus %
0	2.24	0	2.29	0	2.24	0	2.30
80	2.38	80	2.34	80	2.30	80	2.24
160	2.34	160	2.32	160	2.35	160	2.29
Average	2.31		2.31		2.29		2.28
Maize	Un-amended			Amended			
N doses	Humus %	P_2O_5 doses	Humus %	N doses	Humus %	P_2O_5 doses	Humus %
0	2.02	0	2.03	0	2.01	0	2.00
100	2.06	80	2.01	80	2.03	80	1.97
200	2.06	160	2.05	160	2.04	160	1.96
Average	2.05		2.03		2.03		1.98

Our data lead to the conclusion that after 20 years under unamended conditions, in wheat, with soybean as a pre-amended crop, it is possible to maintain the humus content, implicitly organic C- at soil-specific values (biological N input from the pre-amended plant) but the conditions of limestone amendment constantly lead to a reduction of the two humic indicators, caused more by phosphorus and less by nitrogen (Reimer et al., 2023). Differential fertilisation can have positive effects through nitrogen fertilising compounds (as with the legume crop) and apparently negative effects through phosphorus application. It is evident that amendment stimulates microbiological activity by improving the reaction (pH) and cation exchange capacity, conditions under which the phenomenon of humic component reduction by mineralisation advances.

Our results confirm those obtained for 100 years at Morrow Plots - Urbana Illinois, by Nafziger and Dunker (2011) with the observation of the reduction in organic C- content by mineral fertilizer treatments and an alternative reorganization of this component due to the systematic application of plant residues. Also, on the Askov-Denmark platform, in over 125 experimental years (1894-2021), Christensen et al. (2021) describe and comment on the effect of changes in the organic-C regime on soil chemical, physical and biological indicators [as well as Miles and Brown (2011), on the implications of organic-C changes in soil fertility].

Our approaches include the significance of quantitative, percentage and gravimetric representations of organogenic elements in humus, in structures (given by Borlan et al., 1994).

Proportion of elements: C14: N1: P0,1: S0,055: H11,4: O57.

Elemental gravimetric ratios: 168p C: 14p N: 3.1p P: 1.75p S: 11.4p H: 91.2p O.

Percentage weights of elements: 58%C: 4.84%N: 1.07%P: 0.600%S: 3.94%H: 31.55%O.

It can be assessed by this reasoning that the changes that have occurred, especially of a negative nature and supporting oxidative humus degradation, affect sufficiently deeply the content and quality of soil organic matter, comprehensive for soil fertility and productivity. A model of this reduction phenomenon for organic-C, humus and total and mobile S content can reveal the complexity of this phenomenon and its potential effects for the soils investigated in this project (Table 2).

Table 2. Evolution of C-organic and sulphur forms in soils fertilized multi-annually (20 years)

Soils amendment/fertilisation	Organic-C %	Humus %	Total-S %	SSI*	$S\text{-}SO_4^*$ ppm
Typical-amended preluvosol					
Wheat:					
P_0N_{0-160}	1.35	2.34	0.021	3.7	4-5
$P_{80}N_{0-160}$	1.31	2.25	0.020	3.6	3-5
Maize: fined					
P_0N_{0-160}	1.20	2.07	0.019	3.3	3-5
$P_{80}N_{0-160}$	1.09	1.88	0.017	3.0	3-5
Alluvial mollisol:					
Wheat:					
P_0N_{0-160}	1.55	2.67	0.027	7.2	5-7-10
$P_{80}N_{0-160}$	1.62	2.79	0.029	8.1	5-7-10
Corn:					
P_0N_{0-160}	1.52	2.62	0.027	7.1	4-6-7
$P_{80}N_{0-160}$	1.55	2.67	0.027	7.2	4-6-7

*) Sulphur Supply Index (SSI) = (% Humus·% S)·100

Vertic clay-silt chernozem		Years / % Humus- / % of original									Different from initial
		1968	1984		1995		1999		2020		
Humus	N_0P_0	3.78	3.90	103	3.21	84	3.18	84	3.12	82	- 0.66%
	$N_{120}P_0$	3.72	3.50	94	3.37	91	3.26	88	3.21	86	-0.51%
	$N_{120}P_{120}$	3.68	3.83	104	3.47	94	3.31	88	3.19	86	-0.49 %
SSI	N_0P_0	13.1	13.7		11.2		11.1		10.9		-2.20
	N_{120} P_{120}	12.9	13.4		12.1		11.5		11.1		-1.18

First and foremost, for the acidic amendable soil (preluvosol) with possibilities of extrapolation to this soil category (pH < 5.8-6.0; V% < 75-78%; Al -mobile > 0.2-0.3 m.e.), the results presented confirm that amendment (with re-amendment after 5-6 years and $CaCO_3$ applied after Ah) leads to a substantial reduction in organic C- content (and humus), more significantly under maize cultivation (as a predator benefiting from conventional tillage). In the alluvial mollisol with pH 7.2; humus -2.60-2.70% saturated soil type, contrary to the effect observed in the acidic soil (due to amendment and tillage), the dynamic process of humus content change leads to the finding that the saturation in bases, better soil buffering capacity lead to stability in the soil-plant system and the water-soluble fractions of humus continuously feed the carbon circuit with controlled dynamics. In the Turda clay-silt chernozem, in more than 55 active experimental years, with a soil having neutral pH, high clay content (50-52% clay) and good humus supply (>3.50%), in the 3-5 year old soils, the humus content was reduced in the unfertilized variety by 0.66% and in the complex fertilized ones by 0.49-0.51%. The S content, characterized by the "S supply index" (SSI) decreased by more than 1 unit in the fertilized variants and by more than 2 units in the unfertilized variants.

Previous and concurrent research carried out over 60 years (1961-2023) at SCDA Livada shows that amendment has a decreasing effect on the organic C- content, concomitant with the applied limestone dose and irrespective of fertilisation (mineral, organic, organo-mineral), against a background of a modified fulvic acid content. The depressive effect of amendment on luvial soils in the north-western part of the country is 0.17% (on average), under conditions of stimulation of microbiological activity and increased mineralization of soil organic matter. The soil total S- content has the same decreasing trend, similar to organic-C and with increasing amendment doses. There is a direct proportionality between total C- and total S- content (Kurtinecz and Rusu, 2007; Gautam et al., 2021; Kurtinecz et al., 2023).

Stationary experiments with organo-mineral fertilizers show that these technologies can prevent the rather correct degressive evolution of some technologies in soil humus amendment (Table 3).

Table 3. Favourable changes in soil organic matter regime by organo-mineral fertilization
(last 5 experimental years - typical prevulosol)

Fertilisation	pH	Humus %	S_B m.e./100 g sol	Ah m.e./100 g sol	T m.e./100 g soil	V%	P-AL ppm	K-AL ppm
Unfertilised	5.80	1.90	10.0	4.0	14.0	71	9	118
$N_{50}P_{50}$	5.70	1.89	10.5	4.6	15.1	69	36	129
Manure 20 t/ha	6.30	2.36	13.0	3.6	16.6	78	34	146
Manure 20 t/ha + $N_{50}P_{50}$	6.20	2.20	13.8	3.3	17.1	80	48	158

Organo-mineral fertilization measures contribute to shaping humus content, restore and maintain nutrition, increase soil buffering capacity, and in general provide conditions close to sustainable systems, including the organic-C sequestration capacity (Rogasik et al., 2004; Nafziger and Dunker 2011; Miles and Brown, 2011; Jing et al., 2018; Johnston and Poulton, 2018; Han et al., 2021; Li et al., 2021; Christensen et al., 2022; Domnariu et al., 2022).

a. Changes in reaction (pH) and other indicators of acidity:

Changes in soil pH, whether seasonal or during plant growth, depend on the range and size of applied doses (amendments, fertilisers, etc.), the category of ions in the soil-plant system present in the rhizosphere and, last but not least, the selective uptake of crops in the growing cycle or during the growing cycle. The changes are unequivocally influenced by the soil type and, above all, its initial chemical, physical and biological indicators.

The research included analyses using specific methods to truthfully and authentically describe reaction and other indices of acidity.

Table 4. Changes of some soil acidity indices (pH, Al_{sch}, Al /S_{schB} - 100) by NP (Typical Preluvosol) fertilization

Wheat		Un-amended				Amended			
Doze NP		pH_{H2O}	Al - sch. m.e./100 g sol	$Al/S_B \cdot 100$	V%	pH_{H2O}	Al - sch. m.e./100 g sol	$Al/S_B \cdot 100$	V%
P0	N0	5.7	0.18	1.0	76	6.0	0.11	0.6	84
	N80	5.5	0.17	1.2	77	5.9	0.13	0.7	84
	N160	5.3	0.41	3.1	78	5.6	0.16	0.9	92
P80	N0	5.5	0.10	0.7	78	5.9	0.15	0.8	85
	N80	5.5	0.15	1.0	77	5.9	0.16	1.0	83
	N160	5.5	0.29	2.0	77	5.9	0.18	1.9	78
Maize		Un-amended				Amended			
P0	N0	5.7	0.17	1.6	80	6.1	0.15	0.8	85
	N100	5.5	0.26	2.3	77	5.9	0.13	0.7	85
	N200	5.3	0.54	3.3	74	5.8	0.17	1.0	81
P80	N0	5.5	0.28	1.6	80	6.0	0.15	0.8	82
	N100	5.4	0.37	2.5	75	5.9	0.15	0.9	80
	N200	5.5	0.55	3.1	74	5.8	0.13	0.8	81

Alluvial mollisol

Soya	N0	N30	N60	N90	N120	Average
P0	7.4	7.3	7.2	7.1	7.0	7.2
N80	7.3	7.2	7.1	6.9	6.8	7.1
P160	7.2	7.0	7.0	6.8	6.8	7.0
Average	7.3	7.2	7.1	6.9	6.8	7.1

Stationary NP fertilization for 20 years with ammonium nitrate and concentrated superphosphate is a determinant of soil solution acidification over time, to a higher degree in typical preluvosol versus alluvial mollisol. The effect of activating acidity is in fact the action of ammonium nitrate which, through its component ions and nitrification, protonates (with H^+ ions) the soil solution which, at pH values, has the potential to solubilise Al ions^{3+} . Process noted as specific in the category of typical and albic luvisols of NW Romania, in long-term experiments, stationarily fertilized since 1961/1962, at SCDA Livada (Rusu et al., 1972; Kurtinecz and Rusu, 2007; Kurtinecz et al., 2023).

In order to use the agrochemical data of the pH change according to the N doses (from ammonium nitrate applied with NP fertilization) and the possibility to forecast soil evolution and to determine the opportunity for reaction improvement, the values were correlated (Table 5).

Table 5. Acidification of soils (pH_{H2O}) as a function of applied N doses

Soil	Correlated regression terms X = twelve N kg s.a./ha; y = pH_{H2O}	ΔpH /kg s.a. N/ha
Typical Preluvosol		
Un-amended		
At the initiation of the experiment	y = 5.096-0.00096x	-0,00096
After 12 years of application NH_4 NO_3	y = 5.710-0.00220x	-0,00220
Amended		
After 12 years of application NH4NO3	y = 6.310-0.00260x	-0,00260
Alluvial mollisol		
At the initiation of the experiment	y = 7.780-0.00240x	-0,00240
After 12 years of application NH_4 NO_3	y = 7.350-0.00270x	-0,00270

The data presented attest the mobilization of Al ions with increasing N s.a./ha at phytotoxic levels (Al-mobile > 0.3 m.e./100 g soil and $Al/S_B \cdot 100>1$) and update the suitability of lime amendment (Table 6).

Table 6. Effect of limestone amendment on typical preluvisol (with acidity determined by fertilisation)

Wheat - production kg/ha									
NP fertilization		Un-amended	Amended	Diff. kg/ha	NP fertilization		Un-amended	Amended	Diff. kg/ha
P0	N0	3506	3589	83	P80	N0	4560	4591	31
	N40	3899	4067	168		N40	5608	5666	58
	N80	4231	4334	103		N80	5443	5757	314
	N120	3948	4360	412		N120	5254	5782	528
	N160	3905	4353	448		N160	5232	5912	680
Media		3898	4141	1214			5219	5522	1611
Maize - production kg/ha									
P0	N0	6662	7103	441	P80	N0	7113	7478	365
	N50	7509	7653	144		N50	8292	8694	402
	N100	7755	8429	674		N100	8505	8886	381
	N150	7397	8659	1262		N150	8922	9219	297
	N200	6997	7713	716		N200	8143	8762	619
Media		7264	7911	3237			8195	8808	2064

The effect of liming is due to the neutralisation process by amendments of the natural and newly created acidity by N fertilisation, with the mention that superphosphate due to the active substance, $Ca(H_2PO_4)_2$, exerts a concomitant neutralising action, due to the balance compounds P-Al and P-Fe, by which it immobilises the solubilising action of some phytotoxic factors of acidity. In this case, a higher amendment effect is perceptible in maize than in wheat, due to the higher N doses applied to maize. A positive fertilization-amendment interaction is also observed, with mutual support of efficiency and yield increases (previously proven in acidic soils of NW Romania) (Boeriu, 1969; Rusu, 1970; Kurtinecz, 1989; Kurtinecz and Ursan, 2022; Thierfelder and Mhlanga, 2022).

For the vertic clay-silt chernozem, it is also confirmed that long term, systematic and stationary application of increasing doses of N (as ammonium nitrate) causes acidification of the reaction, with the contribution of H^+ ions from the nitrification phenomenon (Table 7).

Table 7. Multiannual evolution of soil reaction (pH) to NP fertilization (Leached vertic chenrnozem - Turda)

N kg a.s./ha	Years							
	1968	1984	1995	2013	2015/%	Average 1968/2015	2022*	Diff %
0	7.72	7.63	7.44	7.00	7.00/91	7.36	8.23	-0.38/95
40	7.56	7.55	7.32	6.95	6.90/91	7.26	8.23	-0.30/96
80	7.48	7.47	7.21	6.85	6.83/91	7.16	8.22	-0.32/96
120	7.41	7.40	7.09	6.75	6.70/90	7.07	8.16	-0.34/95
160	7.33	7.33	6.98	6.63	6.61/90	6.98	8.01	-0.35/95
Background P_2O_5 - 0.40.80.120.160/M	7.50	7.48	7.21	6.84	6.81/91	7.17	8.17	-0.33/96

* - from 2020, consecutive 2 years, ammonium nitrate (33.5%N) has been replaced by nitrocalcar (CAN) (27%N, min. 7% CaO; min. 5% MgO).

For the vertic clay-silt chernozem, through a 47-year (1968-2015) stationary application of 1880 kg a.s. N/at the 40 kg/ha rate to 7520 kg a.s. at the 160 kg/ha rate in the 5 nitrogen gradation variants, the soil reaction (pH) changed by acidification and represents about 91% of the initial pH values, with changes between the final (2015) and initial pH values of - 0.33 reaction units.

b. Dynamic changes in the agrochemical status of essential elements:

The bioavailability regime and effect of essential elements are related to certain soil characteristics (pH, humus, initial NPK content, etc.), the range and rate applied and the uptake and requirements of the crops in the soil. Previous and recent results, in several platforms with long-standing experiments, significantly assess the effect of cumulative fertilisation on the essential nutrient regime, productivity and sustainability of farming systems (Petcu and Petcu, 2006; Powlson et al., 2014; Johnston and Poulton, 2018; Christensen et al., 2022).

The essential process highlighted in the long-term NP experiments is that of positive and significant interaction of these elements, with complementarity of particular roles and phosphorus conditioning for the quantitative and qualitative effect of nitrogen as the pivot of production per unit area (Table 8).

Table 8. Effect of NP fertilization on wheat crop (average 1972-1990);
Variety: Fundulea 29; Soil: Alluvial Mollisol

Doses N kg a.s./ha	Production kg/ha	%	Diff. kg/ha	Diff. signif.	Prod./spor per kg s.a.	Doses P_2O_5 kg a.i./ha	Production kg/ha	%	Diff. kg/ha	Diff. signif.	Prod./spor per kg s.a.
0	3577	100	-	Mt		0	4350	100	-	Mt	
40	5509	154	1939	***	138/48	40	5435	124	1086	***	136/22
80	6060	169	2483	***	76/31	80	5646	129	1296	***	74/16
120	5939	166	2362	***	49/20	120	5679	130	1329	***	47/11
160	5466	152	1889	***	34/12	160	5438	125	1088	***	34/7
Background P_2O_5 = 0-40-80-120-160						Background N = 0-40-80-120-160					
DL (5%) = 297; DL (1%) = 408						DL (0.1%) = 548					

A particular case is the amended acidic soils (typical preluvosol) in which wheat (sensitive to natural and newly created acidity by N doses) can exploit P at a different level, (not only as interaction and support for the N effect) but for the positive influence in mitigating the effects of acidity by Ca monophosphate in the superphosphate. Therefore, the significance of the P-effect in this case is due to the applied doses and subsequently it is sustained ain terms of time, it is useful to optimise the phosphate regime in the soil with P doses and on this background the NP interaction is achieved).

The mobile phosphorus regime in the soils under long-term experiments (NP, 20 years, Alba, 55 years Turda) shows a significant improvement through annual dose-dependent increases and cumulative amount of P_2O_5 over the experimental period (Table 9).

Table 9. Change in mobile phosphorus content (SCDA Turda vertic clay-silt chernozem)

Fertilisation* P/NP	P - AL ppm	Fertilisation N/NP	P - AL** ppm	Other NP formulas	P - AL ppm
0	23.8	0	133.1	N0P0	23.8
40	126.5	50	154.7	N100P0	61.4
80	139.1	100	140.0	N100P40	143.7
120	147.9	150	130.0	N100P80	144.7
160	141.0	200	132.4	N100P120 N100P160	149.4 155.4
* - var. fertilization N0 f 200 kg s.a./ha			** - var. fertilisation **P_2O_5 – 0-160 kg s.a./ha**		

In terms of the phosphate regime (both for the preluvosol and chernozem), for all NP variants, the soil undergoes an essential change from the poorly supplied (by 5-6 ppm in the preluvosol and poorly-medium supplied (by 18-23 ppm in the chernozem) to the well supplied (by about 60-70 ppm in the preluvosol) and very well supplied (by about 130-140 ppm in the chernozem), thus exhibiting a substantially improved mobile phosphorus regime. These positive changes in the phosphate regime due to rational and long-term application of fertilizers of various sorts, primarily phosphate or organic ones, have been frequently noted and interpreted for the purpose of real nutrient management (Jing et al., 2018; Johnston and Poulton, 2019).

Deepening these positive changes in the phosphate regime led to results related to the evolution of the monophosphate anion $(H_2PO_4^-)$ from superphosphate in soils into non-occluded mineral phosphates (P-Al, P-Fe, P-Ca) that are annually maintained by P fertilization from NP and that "feed" mobile and bioaccessible forms of phosphates for the soil solution and plant nutrition (Table 10).

Table 10. Content of non-occlusive forms of phosphates (P-Al, P-Fe, P-Ca)
by long-term applications of concentrated superphosphate (0-40-80-120-160 kg P_2O_5/ha) (after 20 years)

Preluvosol	pH	P-AL ppm	Non-occluded mineral phosphates (ppm)/% of Σ			
			P-Al	P-Fe	P-Ca	Σ
Wheat - un-amended						
P0N0 -160	5.5	5.1	15/5	47/15	273/82	335
P80N0-160	5.5	32.8	60/13	94/20	306/67	460
Wheat - amended						
P0N0 -160	5.9	6.4	20/7	58/20	212/73	290
P80N0-160	5.9	31.3	61/14	111/25	260/61	432
Soy - amended						
P0N0 -120	6.1	5.2	16/6	32/11	232/83	280
P80N0-120	6.1	25.1	48/12	63/16	290/72	401
Alluvial Mollisol - Wheat						
P0N0 -160	7.4	13.0	13/4	22/7	288/89	323
P80N0-160	7.3	45.0	35/7	75/15	365/78	475
Vertic chernozem - Wheat						
P0N0 - 160	7.4	15.2	21/6	22/6	317/88	360
P80N0-160	7.5	78.8	32/6	46/9	418/65	496

The improvement of the phosphate regime is quantitatively dependent on the dose and amount of phosphate accumulated, but there is also a qualitative improvement due to the particular soil characteristics. In this context, the reaction and base saturation of the two soils with pH>7 (alluvial mollisol and chernozem) favour the improvement of the phosphate regime mainly due to calcium phosphates (P-Ca) with better bioavailability.

Mobile potassium regime

The improvement dynamics for K-mobile resources in the 2 soils, typical preluvosol and alluvial mollisol, is due to and supported by annual applications of K fertilization (potassium salt, 40% K_2O s.a.) on a differentiated agrochemical background. The differences between the two soils are noticeable in the distribution and reallocation of the applied potassium between the essential forms in the soil (unchangeable and exchangeable), which support the supply of bioavailable K^+ ions to the soil and plant solution. It is a currently updated perception about the different support for potassium application in relation to soil form dynamics and specific plant consumption (Kurtinecz, 1989; Krauss, 1997; Hera, 2008; Chen et al., 2020).

From this point of view, the soil-specific and/or technology-specific nonexchangeable K- exchangeable K- soluble K dynamic model can justify the often different crop response to potassium supply and application (Table 11).

Table 11. Synthetic representation of potassium dynamics in preluvosol and alluvial mollisol

Soil/plant/ fertilisation	N0P0			N80P60			N160P120		
	K-AL ppm	Non-exchangeable K ppm	Report	K-AL ppm	Non-exchangeable K ppm	Report	K-AL ppm	Non-exchangeable K ppm	Report
Amended preluvosol - Maize									
K - 0-40-80-120-160	131	759	5,8	141	781	5,6	143	744	5,2
Alluvial Mollisol - Maize									
K - 0-40-80-120-160	146	946	6,3	157	1047	6,7	148	993	6,7

This dynamic can support that the constant effect of potassium application and productivity in plant yields are higher in preluvosols that is capped in non-exchangeable fixation and availability for plant consumption compared to alluvial mollisol, which has higher affinity in non-exchangeable fixation and limiting ion mobilization (due also to a lighter texture) (Table 12).

Table 12. The influence of NPK fertilization on corn (average 20 years)

Typical Preluvosol					Alluvial mollisol			
H5 308	Doses K_2O kg/ha	Production kg/ha	Diff.	Signif. diff.	Doses K_2O kg/ha	Production kg/ha	Diff.	Signif. diff.
N80P60	0	8035	-	Mt	0	8333	-	Mt
	40	8388	353	-	40	8722	389	-
	80	9162	1127	***	80	9003	670	*
	120	9294	1249	***	120	9140	807	**
	160	8879	844	**	160	8821	488	-
N160P120	0	7648	-	Mt	0	8345	-	Mt
	40	8404	756	*	40	8686	361	-
	80	8610	962	**	80	9120	775	*
	120	9102	1454	***	120	9275	930	**
	160	8914	1266	***	160	8612	267	-

Under these conditions, in addition to the K forms dynamics, controlled by stationary applications, it is advocated to promote the effect of its application and its role in preventing Ca/K interference phenomena that may occur when amending and re-amending soils (the case of amended preluvosol) and, last but not least, the role of nutrient balance that it exerts in the NPK system, especially in relation to high doses of N. On the other hand, it is possible to explain the reduced response of alluvial mollisols to potassium application by their high fertility qualities and properties - better supply of K, more active dynamics of its forms, higher humus content, groundwater supply in some years, base saturation, etc.

CONCLUSIONS

The modelling of soil agrochemical indicators - pH, humus, N, P, K content, etc. - following pedological and agrochemical studies are applied to the field, as objectives for the implementation of sustainability principles and measures for the farming system. Long-term stationary experimentation shows essential changes in these indicators with probity and applicative value, mainly due to the duration of experimentation and the multitude of natural and anthropogenic challenges applied.

In the present research, the following conclusions could be summarised:

- NP fertilisation attributes a key role to these elements, to direct interactions but also to environmental factors. Nitrogen is a quantitative and qualitative determinant, phosphorus enhances its effect. High and excessive doses of N, applied disproportionately to P, lead to acidification effects and, in amendable soils, to the opportunity for amendment, which is enhanced by toxic acidity factors. In this case, pH, Al-molecular content and the ratio of S /Al_{Bmobil} -100 are the deciding factors. Amendments and rational fertilisation of acidic soils (in these experiments preluvosol) are sustainable fertility protection and modelling measures with mutually reinforcing effects;
- K fertilisation in the NPK regime balances nutrition and promotes the effect of each component. Improved K supply status over a long period of time, the realignment of the chemical forms of this element in the soil and the dynamics of these forms control the availability of this element in the soil and in the plants. Obviously, crop requirements are an essential differentiation criterion.
- Organo-mineral fertilisation is a key feature of sustainable measures as it shapes C and humus content, increases C sequestration capacity and controls crop nutrition in a complex manner.

All the above-mentioned observations have proved their probity and applicability due to the long term experiments carried out on typical alluvial mollisol and preluvosol (20 years, Băcăinți - OSPA Alba), with analytically controlled stationary points and subsequently also in the experiments carried out on the vertical clay-silt chernozem (synonymous with the vertical phaeozem), 52 years, at SCDA Turda. Their results, alongside with the other data from active experiments, formulate and define the need for long-term stationary experiments and through this method the formulation of basic principles in the protection of fertility, environment and consumers within a sustainable system.

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