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HEAVY METALS FROM THE SOIL AND MINERAL FERTILIZATION

Nicoleta MĂRIN[1], Nicoleta VRÎNCEANU[1], Naliana LUPAȘCU[2], Mihail DUMITRU[1]

[1]National Research and Development Institute for Soil Science, Agro-Chemistry and Environment - ICPA Bucharest, 61 Marasti Blvd, District 1, Bucharest, Romania
[2]National Research and Development Institute for Marine Geology and Geoecology, 304 Mamaia Blvd, Constanța, Romania

Corresponding author email: nicoleta.marin@icpa.ro

Abstract

The degree of soil loading with heavy metals (Cd, Cu, Mn, Ni, Pb, Zn) has been studied after 39 years of fertilization with nitrogen and phosphorus on a Faeoziom cambic soil in Drăgănești-Vlasca village in Teleorman. Nitrogen from nitrogen nitrate was applied at doses of 0, 50, 100, 150, 200 kgN/ha, and phosphorus from superphosphate at doses of 0, 40, 80, 120, 160 kg P/ha. The soil samples were harvested at a depth of 0-20 cm after harvesting the wheat crop. The heavy metal content did not suffer statistically significant changes following long-term fertilization with mineral fertilizers with nitrogen and phosphorus. No cadmium accumulation process was observed following the application of doses of 40-160 kg/ha P_20_5 annually for 39 years. The cadmium values in the soil oscillated between 0.9 and 1.2 mg/kg, the loading level being assessed as normal-weak, the copper values were in the low loading range, the manganese is within the range of normal-weak, and copper and manganese in the soil content are within the normal range.

***Key words**: long-term experiences, heavy metals, fertilizers.*

INTRODUCTION

Water, air and soil are the most vulnerable environmental resources, but most frequently subject to aggression by pollutants, with direct and serious consequences not only on the quality of the environment but also on the health of humans and other living creatures. The most frequent environmental pollution factors usually come from industry, but lately, agriculture is increasingly being discussed (Dumitru et al., 2003).

One of the important components of sustainable development is environmental protection.

The presence of contaminants can cause immediate or long-term danger to human, animal or plant health, which may lead to limiting or excluding land use (Dumitru et al., 2008).

Heavy metals are found in all types of soil in larger or smaller quantities up to trace levels. Once introduced into the environment as a result of anthropogenic activities, they will be present in the soil in the following forms: dissolved in the soil solution, occupying exchange positions or adsorbed specifically on the inorganic soil constituents associated with organic matter or associated with the structure of primary or secondary minerals.

Although it is a rare element, cadmium is distributed everywhere in the environment.

The cadmium concentration in the earth's crust is estimated to be between 0.08 and 0.5 Cd mg/kg.

Both in the upper horizon of the soil and in the marine sediments the content varies between 0.1-1 mg Cd/kg, in seawater is estimated a concentration of 0.02-0.25 mg/l Cd. The main sources of cadmium are the minerals of zinc (Shulte -Schrepping quoted by Kaarstad, 1991).

The main sources of cadmium in industrialized countries are:

- The natural load of soils in cadmium;

- Atmospheric deposits from the production of non-ferrous metals, iron and steel, burning of fossil fuels;
- Manure from animals with cadmium in their diet;
- From phosphorus fertilizers (Dumitru et al., 2008).

Heavy metals penetrate the depth of the soil through precipitation, through biological accumulation penetrate into plants and through consumption pass to humans and animals (Nicoleta Vrînceanu et al., 2010).

Ingested in high doses, cadmium is toxic to humans, its admissible concentration in foods in European countries is 10 µg/day cadmium, the tolerable weekly intake is 70 µg/day cadmium. Removal of cadmium from the human body occurs much more slowly than other contaminants. Around 20 years are needed to eliminate half the amount (Dumitru et al., 2008).

MATERIALS AND METHODS

The experience was located within SCDA Teleorman. For the field experiments it was used, the method of two-factor sub-division and 3 repetition parcels and consisted in 25 variants.

Fertilizers with nitrogen and phosphorus were applied, nitrogen (N) at doses of 0, 40, 80, 120, 160 N kg/ha as ammonium nitrate, phosphorus (P) at doses of 0, 40, 80, 120, 160 P kg/ha, administered from superphosphate. Soil harvesting was carried out at the end of the wheat culture vegetation period, at a depth of 0-20 cm.

The total concentrations of heavy metals were determined in the soil samples by atomic absorption spectrometry after extraction by the aqua regia - microwave digestion method (SR ISO 11047:1999).

Microwave digestion was performed using 10 mL of aqua regia (7.5 mL HCl and 2.5 mL HNO_3) at 140°C for 30 min.

A certified soil reference material (ERM - CC141) was used to ensure the accuracy of the analytical data.

RESULTS AND DISCUSSIONS

A. Cadmium content in soil

The research carried out within the National Soil Quality Monitoring System 16 x 16 km revealed the following: the cadmium loading level of the soil was normal (values < 1.1 mg/kg) in 88.04% of the cases, weak (1.1-2,0 mg/kg) in 28.45% of cases, medium (2.1-3.0 mg/kg) in 2.55% of cases and strong (3.1-7.0 mg/kg) in 1% of cases (Dumitru et al., 2000).

According to the 2016 statistical yearbook in Romania, in the year of 2014, about 9 kg/ha of phosphorus were applied to agricultural land, far below plant requirements, considering that the supply level of mobile phosphorus was low:

Average phosphorus content in the 0-50 cm layer:
- extremely low < 4 mg/kg 107 sites (11.36%);
- very low 4-8 mg/kg 198 sites (21.02%);
- low 9-18 mg/kg 311 sites (33.01%);
- medium 19-36 mg/kg 195 sites (20.70%);
- high 37-72 mg/kg 89 sites (9.45%);
- very high > 72 mg/kg 42 sites (4.46%).

In order to see the difference of opinion between Romania and the Netherlands regarding phosphorus management in phosphorus mineral fertilizers, we present P-load classes in the Netherlands.

Table 1. Soil content classes in accessible phosphorus of the soil in Netherlands (Anonimous, 2015 a,b)

Phosphorus accessibility classes	Agricultural land (mg P/kg dry soil)
Class I (low accessibility of P)	<120
Class II (target areas for P)	120 - 180
Class III (moderate accessibility of P)	190 - 400
Class IV (high accessibility of P)	>410

The content of heavy metals (cadmium, cooper, manganess, nickel, lead, zinc) have not been modifical statistically significant changes following long-term fertilization with nitrogen and phosphorus.

Cadmium values fluctuated between 0.9 and 1.2 mg/kg. Thus, no cadmium accumulation process mas observed following the application of doses 40-160 kg P/ha annualy for 39 years.

Lupașcu et al. (2017) on a typical chernozem from Valu's Traian found that cadmium values fluctuated between 0.40 and 0.44 mg/kg of copper between 21 and 24 mg/kg of lead was 20 mg/kg and zinc between 83 and 84 mg/kg. The heavy metal content (cadmium, copper, lead and zinc) did not suffer statistically significant changes from long-term fertilization (44 years) with nitrogen and phosphorus.

The European Commission appreciates in the "Proposal for a Regulation of the European Parliament and of the Council on the rules for marketed CE fertilizer products available on the market and amending Regulations (EC) No 1069/2009 and (EC) No 1107/2009" Phosphorus fertilizers sold in the EU are contaminated with cadmium, typically somewhere between 32-36 mg/kg of P_2O_5.

It has been argued that 80 mg/kg of P_2O_5 is an appropriate legal cadmium contamination limit since - until recently - it was estimated an average contamination level for "non-accumulation" in the land on European farms . "Non-accumulation" means that the cadmium level in contaminated soil in farm land does not rise above current levels, because all new cadmium additions in soil are either taken up by crops (and ultimately consumed by humans or animals) or are washed from the fertile horizon of agricultural soils.

Forstner (1980) estimated that phosphorus fertilizers have a cadmium content ranging between 2 to 180 ppm.

At moderate levels of cadmium (5-10 ppm) in phosphorus fertilizers, there was no significant correlation between the applied dose and the cadmium concentration in the soil horizon after 20 years of application.

Grant et al. (2010) shows that phosphorus fertilization, especially for flax culture, tended to increase the cadmium concentration and the Cd: Zn ratio and to decrease the zinc concentration in tissues and flaxseed.

Lambert et al. (2007) found that the application of phosphorous fertilizers containing cadmium and zinc increased the cadmium concentrations in the soil solution in both field and laboratory experiments. The increase of the metal contamination level or of the applied dose has increased cadmium concentration in soil extract for field and laboratory experiments. The behavior of zinc is not closely related to cadmium. The lower zinc concentration in the soil solution is, at least in part, due to the addition of phosphorus.

Grant et al. (2013) estimated that through the increase of cadmium reserves in the soil influences the amount of cadmium accessible to crops, but the cadmium concentration in durum wheat and in flax seeds will be strongly affected by soil characteristics and environmental conditions in the season of vegetation. The type of crop and soil characteristics and climatic conditions affecting crop accesibility must be taken into account when assessing the risk of transfer of cadmium into the food chain in phosphorus fertilization.

Gao et al. (2011) estimated an increase of concentration and accumulation of cadmium in durum wheat strains immediately after phosphorus fertilization, primarily, as a result of the reduction of competition between zinc and cadmium for plant absorption, of the improvement of cadmium translocation from the root to the stem and improvement of root development , more than the effect of direct cadmium addition with the phosphorus fertilizer. In the short term, the application of phosphorus fertilizers can increase the cadmium concentration in crops, unrelated to cadmium concentration in fertilizers. An optimal fertilization strategy, such as in combination with zinc application, is of great importance to reduce cadmium concentration and accumulation in crops.

Hong et al. (2010) selected seven phosphorus materials (commercial phosphorus fertilizer - mixture of phosphates, mixture of phosphates and superphosphates and phosphate rock, phosphorus chemicals - $Ca[H_2PO_4]_2{\cdot}H_2O$, $[NH_4]_2HPO_4$, KH_2PO_4 and K_2HPO_4) selected for the incubation test, the mixture of phosphates, Ca $[H_2PO_4]_2 \cdot H_2O$, KH_2PO_4 and K_2HPO_4 significantly decreased the extractable cadmium concentration in NH_4OAc (plant accessible form) with increase of the applied doses . The selected phosphorus sources were mixed with contaminated soil with 0, 200, 400, 800 and 1600 P/kg. In particular, K_2HPO_4 was found to be the most effective, mainly due to the increase of the negative charge produced by soil pH and phosphorus adsorption. Phosphorus induced a relief of cadmium extraction which can be attributed primarily to cadmium immobilization due to the increase in soil pH and negative charge, not the precipitation of cadmium phosphate, and therefore alkaline phosphorus materials such as K_2HPO_4 can be effective in immobilizing cadmium in soil.

Corguinha et al. (2012) show that a major concern in assessing health risk is cadmium consumption, and food intake is an important route of exposure. Although the addition of phosphorus fertilizer can increase cadmium content in soils, its transfer to the plant varies according to the management system. They evaluated the cadmium contents of different potato types fertilized with 560 kg P_2O_5/ha and in soybeans cultivated in different soil management systems with long-term application of different management systems and where they were applied high doses of phosphorus fertilizer. The largest amount of cadmium remains in the potato peel (23-781 μg/kg bw) compared to the tuber (14-43 μg/kg bw), and the values vary according to type and area. For soybeans, the grain content ranged from 10 to 30 μg/kg b.w. in rotational experiments and 23-28 μg/kg b.w. for soils that received different doses of calcium carbonate amendments. All the cadmium content found in the crops studied is in line with the Codex alimentarius guide, so there is no risk to human health.

The Health Risks and Environment Committee (2015) shows that phosphate fertilizers used in the EU had an average content of 36 mg Cd/kg P_2O_5.

Working Group of the Council of the European Commission quoting Smolders and Six (2013) presents on 20-21 September 2016 sources of cadmium in agricultural soils: manure 0.01 g Cd ha^{-1} $year^{-1}$, sludge from municipal wastewater treatment plants 0.05 g Cd $ha^{-1}year^{-1}$, the amendments with calcium carbonate 0.09 g Cd $ha^{-1}year^{-1}$, atmospheric deposits 0.35 g Cd $ha^{-1}year^{-1}$ and phosphorus fertilizers 0.8 g Cd $ha^{-1}year^{-1}$ (where the average dose of phosphorus fertilizer was 100 kg P_2O_5/ha).

The concentration of Cd in phosphate rocks varies greatly with origin, e.g. eruptive phosphate rocks have lower Cd concentrations (0.07-0.25 mg Cd/kg rock) compared to sedimentary rocks (0.01 - 2.60 mg Cd/kg rock). The smallest concentrations of metals are generally found in phosphate rocks from the Scandinavian countries, while the highest values were found in Nauru, Togo and Morocco, where the values varied between 2 and 1500 mg Cd/kg P_2O_5.

Smolders (2013) estimates that an average contamination level of 80 mg/kg P_2O_5 leads to soil growth increase with 3% after 100 years, a contamination level of Cd of 60 mg/kg was estimated to result in a decrease of 7% over the same period of time, a contamination level of 40 mg/kg P_2O_5 leads to a 14% decrease after 100 years, a 20 mg/kg P_2O_5 contamination level leads to a 20% decrease after 100 years.

However, the Working Group of Technical Harmonization proposes in 2016, the following limits for cadmium in phosphorus fertilizers : 60 mg Cd/kg P_2O_5 (initial limit value after application of the Regulation), 40 mg Cd/kg P_2O_5 (three years after the application date of the Regulation) and 20 mg Cd/kg P_2O_5 (12 years after the application date of the Regulation).

The General Secretary Council considered that if the limit of 60 mg Cd/kg P_2O_5 was introduced, even in the absence of an available decadmiation tehnologies, most sources of phosphorus fertilizer usually used in the EC could still be used. When introducing a limit of 40 mg Cd/kg P_2O_5 will require specific efforts from the EU fertilizer industry, namely the introduction of an available decadmiation tehnologies.

Rietra et al. (2017) felt that in the EU only 55% of cadmium taken up by people in the total diet is related to cadmium in the soil. A reduction of

50% of cadmium in soil is estimated to reduce the uptake of cadmium in the diet by 18%. Based on these calculations, cadmium limits for phosphorus fertilizers will have little impact on levels of cadmium in the soil on a time scale of 20-50 years. Taking into account even smaller responses to the crop taking of such limited changes in cadmium levels in the soil, it is estimated that a reduction in cadmium levels in fertilizers will have a marginally lower exposure to cadmium in the diet, in Europe.

Six and Smolders (2014) estimate that the use of phosphorus fertilizers in the EU 27 + 1 has fallen by 40% over the past 15 years.

They studied cadmium leaching in 151 soils covering a wide range of European soils properties, and noticed no tendency in cadmium accumulation time following application of manure, compost, urban sludge and calcium carbonate, all of which on large-scale are small sources of cadmium.

The modeling of future long-term changes in cadmium concentrations in the upper horizon of agricultural soils cultivated with cereals or potatoes will result in a 15% decrease in cadmium concentrations in soil over the next 100 years.

Bolan et al. (2003) showed that the application of KH_2PO_4 increased pH and surface charge, the effect being more pronounced in soils dominated by variable load components.

This process induces the addition of specifically adsorbed anions resulting in increased sequestration of the added cations, thus reducing their accessibility in plants. Addition of phosphates improves cadmium immobilization, as shown by increased adsorption, cadmium redistribution to less accessible fractions, and decreasing accessibility for plants.

In fact, if we consider the 80 mg Cd/kg P_2O_5 content, we would apply 100 kg of P_2O_5/year for 100 years without losing anything in the applied cadmium could increase the cadmium content by 0.267 mg/kg , which does not represent any risk to the environment.

Under these circumstances, I wonder why we need to change the limit of cadmium that can accompany phosphorus from mineral fertilizers?

B. Copper content in soil

The research carried out within the National Soil Quality Monitoring System 16 x 16 km revealed the following: copper loading was normal (< 21 mg/kg) in 57.43% of cases, low (21-40 mg/kg) in 36.67% of cases, medium (41-100 mg/kg) in 5.31% of cases (101-200 mg/kg) in 0.83% and very high (201-400 mg/kg) 0.11% of cases (Dumitru et al., 2000).

Li et al. (2007) showed that after 16 years of fertilization with different fertilizers, the concentrations of Cu, Fe and Mn extractable in DTPA were not significantly altered, while soil-soluble Zn was slightly higher in all treatments compared to unfertilized control. Treatments with NP, NPK, ½ fertilized organic plus half fertilized with N, and organically fertilized, led to increased wheat and corn production and organic matter levels in the soil, which also led to an increase in Zn and Fe extract in DTPA.

Maintaining or increasing organic matter in the soil is very important in providing micronutrients accessible to crops.

Through long-term fertilization with phosphorus, nitrogen or nitrogen and phosphorus has not produced statistically significant changes in the copper content of the faeoziom in Drăgănești Vlașca.

Copper values have been recorded in the low level field. Data in the literature does not show changes in the soil content of copper under the influence of mineral fertilization with nitrogen and phosphorus.

Table 2. Heavy metals content in cambic faeoziom from SCDA Teleorman

Variants	Cd (mg/kg)	Cu (mg/kg)	Mn (mg/kg)	Ni (mg/kg)	Pb (mg/kg)	Zn (mg/kg)
Control	1.00	28	884	37	18.7	76
N50	1.06	33	981	40	19.6	85
N100	0.93	30	829	34	17.7	69
N150	0.95	30	846	34	18.0	72
N200	1.02	30	896	36	19.4	77
P50	1.20	32	969	47	19.8	91
P50 N50	0.91	30	855	35	16.0	69
P50 N100	105	30	927	36	17.5	77
P50 N150	1.09	32	937	39	19.0	80
P50 N200	1.10	29	929	38	19.2	80
P100	1.02	31	942	37	19.2	78
P100N50	1.23	32	962	42	20.8	85
P100N100	0.95	28	829	32	15.2	69
P100N150	0.89	28	895	34	17.3	73
P100N200	1.15	33	971	41	21.0	84
P150	0.98	27	888	37	18.7	75
P150N50	1.16	31	1001	40	21.5	83
P150 N100	0.97	27	875	35	16.1	74
P150N150	0.94	27	872	35	17.9	74
P150N200	0.949	28	831	35	16.9	71
P200	0.88	27	829	34	15.1	71
P200N50	1.17	32	963	43	21.0	86
P200 N100	1.00	29	892	37	17.6	78
P200N150	0.97	28	862	34	15.5	78
P200N200	1.07	29	945	38	17.2	80
DL 5%	0.29 mg/kg	6 mg/kg	191 mg/kg	10 mg/kg	6 mg/kg	18 mg/kg
DL 1%	0.39 mg/kg	8 mg/kg	255 mg/kg	14 mg/kg	8 mg/kg	24 mg/kg
DL 0,1%	0.51 mg/kg	11 mg/kg	335 mg/kg	19 mg/kg	11 mg/kg	32 mg/kg

C. Manganese content in the soil

After iron, manganese is the most abundant heavy metal in the earth's crust. Total Mn reserves vary greatly due to the diversity of soil cover from 10-10000 mg/ kg of soil. Excessive potentially toxic manganese content for plants, may occur under the conditions of systematic application of acidifying fertilizers to soils with low buffering capacity. Unlike Cu and Al that accumulate mostly in the roots, manganese is translocated into the plant aerial part. Symptoms of leaf toxicity occur at concentrations above 300 mg/kg (Băjescu et al., 1984).

The research carried out under the National Soil Quality Monitoring System showed the following: the degree of loading with manganese was normal (< 901 mg/kg) in 93.20% of the cases, low (901-1100 mg/ kg) in 3,4% of the cases, average (1101-1500 mg/kg) in 2,23% of cases and strong (1501-2000 mg/kg) in 0.11% of cases (Dumitru et al., 2000).

The data presented in table 2 did not reveal statistically significant changes in total manganese content in the soil under the influence of fertilization with nitrogen, phosphorus or nitrogen and phosphorus. Data from the literature does not provide informations on the influence of mineral fertilization with nitrogen and phosphorus on the total content of manganese in the soil. Manganese values ranged from normal to low loading.

D. Nickel content determination in soil

The research carried out under the National Soil Quality Monitoring System showed the following: the degree of soil nickel loading was normal (< 21 mg/kg) in 21.87% of cases, low (21-30 mg/kg) in 29.82% of cases, mean (31-50 mg/kg) in 37.79% of cases, strong (51-100 mg/kg) in 9.55% of cases and very strong (101-300 mg/kg) in 0.32% of cases.

There were no statistically significant changes in soil nickel content under the influence of mineral fertilization with nitrogen, phosphorus or nitrogen and phosphorus. The soil nickel content was found in the average loading range with this element. In the literature, we have not found data on the influence of mineral fertilization with nitrogen and phosphorus on soil content in nickel.

E. Lead content in soil

Research into the National Soil Quality Monitoring System revealed the following: lead load was normal (< 21 mg/kg) in 22.72% of cases, low (21-40 mg/kg) in 57,32% of cases, medium (41-101 mg/kg) in 18.47% of cases and strong (101-300 mg/kg) in 0.53% of the cases (Dumitru et al., 2000).

The data obtained in long-term experience revealed no statistically growth of lead in the soil under the influence of mineral fertilization with nitrogen and phosphorus. The lead load level was maintained within the normal range.

F. Zinc content in soil

The research carried out within the National Soil Quality Monitoring System revealed the following: The soil load in zinc was normal (< 101 mg/kg) in 78,54% of the weak (101-150 mg/kg) in 9.45% of cases; average (151-300 mg/kg) in 11.04%.

The data presented in table 2 do not reveal statistically significant changes in the zinc concentration in the soil under the influence of mineral fertilization with nitrogen and phosphorus. All values fall within the normal supply range.

IV. CONCLUSIONS

No cadmium accumulation process was observed following the application of doses of 40-160 kg/ha P_2O_5 annually for 39 years.

For a content of 80 mg Cd/kg P_2O_5, the application of 100 kg P_2O_5/year for 100 years without losing any of cadmium applied could increase soil contents of cadmium with 0.267 mg/kg, which is not a risk to the environment.

Although ammonium nitrate has an acidic physiological reaction, the application of doses up to 200 kgN/ha for 39 years has not resulted in statistically assured accumulations of manganese in the soil;

The long-term application of ammonium nitrate and superphosphate does not lead to the accumulation of heavy metals in the soil.

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