THE EFFECT OF SEWAGE SLUDGE DOSES ON MANGANESE CONTENT IN THE ECOSYSTEM LUVOSOIL AND FIELD CROPS

Nicolaie Ionescu[1], Gelu Mujea[2], Marilena Diaconu[2], Ana Iordănescu[2], Gina Mincă[1]

ABSTRACT

The sewage sludge from urban waste water treatment plants can be used as organic fertilizer due to its high content of over 25% OC (organic carbon), tN (total nitrogen) between 2-3 % and neutral pH (6,93-7,17). Besides, sludge contains manganese which, together with the one in the cultivated soil, could create conditions for occurrence of phyto-toxicity in cultivated plants. To observe the evolution of Mn contents both in the soil and the plants, we used increasing doses of sludge: 0 $t.ha^{-1}$, 5 $t.ha^{-1}$, 10 $t.ha^{-1}$, 25 $t.ha^{-1}$ and 50 $t.ha^{-1}$ together with chemical fertilizers doses on intervals 0, ½ and 1/1 of the specific need for: maize, winter wheat and soybeans. By using processed sludge doses (anaerobically digested and dewatered) together with chemical fertilizers, no statistically significant increases of total forms of Mn in the soil were recorded, as compared with the check plot, which received no sludge and chemical fertilizers. The only exception was observed for soils cultivated with soybeans. The mobile forms of manganese (Mn^{2+}) showed evident increases after sludge application. However, the three crops absorbed Mn^{2+} only in the needed and specific quantities. Thus, the maize absorbed the least Mn, with leaves containing at flowering 6.0 $mg.kg^{-1}$ d.w., and mature grains 6.7 $mg.kg^{-1}$ d.w. The sludge and especially the chemical fertilizers contributed to the growth of plants with bigger biomass, which absorbed more Mn ions, so that the correlation between the total biomass of maize and the Mn content was positive and significant. Soybeans showed a positive but not significant association between total biomass and Mn concentration and in winter wheat Mn^{2+} concentration was not correlated with total biomass.

Key words: wheat, maize, soybeans, processed sludge, luvosoil, manganese.

INTRODUCTION

In its current state, the albic luvosoil contains Mn in appreciable quantities, originating from the decomposition of ferromagnetic rocks. After iron (Fe) and aluminum (Al), manganese (Mn) represents the most abundant chemical constituent in rocks making up the earth shell (Davidescu, 1981). Soil contains transformed Mn under various forms associated with the mineral and organic part. The most common are Mn oxides and hydroxides. They can originate from the parental material or from alteration process. Both Mn crystalline and amorphous states exist under many forms, including ferromanganese balls or concretions. Their formation is based on the alternation of oxidation and reduction processes. The dominant forms of Mn in the ferromagnetic concretions composition (balls) are $Mn_2O_3.nH_2O$ (Băjescu, 1984). In order to become accessible for plants, Mn oxides and hydroxides need to be reduced to Mn^{2+} ions. Between Mn^{2+} from soil solution, Mn^{2+} changeable and superior oxides of Mn there is a dynamic balance controlled by the complexity of the reduction conditions (redox). Accessibility of Mn^{2+} depends of several factors, among which the most important are: pH, microbiological activity, organic matter (OM) and soil humidity regime. Recent researches proved that the availability of Mn^{2+} occurs in soils with pH between 5 and 6 (Tisdale, 1975). Mn^{2+} is thus present mainly in acid soils, while on neutral soils manganese is under a trivalent form (Mn^{3+}) as Mn_2O_3 and in alkaline ones (pH over 8) under tetravalent form (Mn^{4+}) in an inert oxide, MnO_2 (Baize, 1988). Luvosoil – having as characteristic the acid environment – favors the reduction processes following which manganese is in bivalent form - Mn^{2+}, available for plants absorption. The specific microbial activity here is reduced, leading to a true conservation of accessible Mn^{2+} forms. OM influences the mobility of Mn^{2+} both by having a lower affinity compared with other heavy metals, thus leaving it permanently available and by the specific decomposition degree. Due to unfavorable drainage, the reduced forms of Mn are dominant, as bacteria which decompose OM using Mn oxides as O_2 source are stimulated. The luvosoil specific to Piteşti research center contains Mn accessible to plants in relatively high concentrations. A safe source of OM for local agriculture is represented by the anaerobically digested and dehydrated sludge from Piteşti Wastewater Treatment Plant. Being qualitatively comparable with manure (Mihalache, 2006), sludge such processed represents a new source both for macro-nutrients for agricultural

[1] Agricultural Research and Development Station Piteşti, Argeş County, Romania
[2] S.C. Apa-Canal 2000 S.A. Piteşti

crops: nitrogen, phosphorus, potassium, calcium etc., but also for micro-nutrients among which manganese is in concentrations close to the ones of the soil. Using digested sludge in plant nutrition and increasing the soil contents in accessible manganese, specific phytotoxicity might appear. Another element that favors the Mn^{2+} content in soil is the high rainfall, which exceeds here 700 mm per year, with water excess periods which contribute to reduced forms of Mn. The current paper presents results regarding the way maize, winter wheat and soybeans grow and develop when progressive doses of processed sewage sludge rich in manganese are applied.

MATERIAL AND METHODS

In the period 2004-2007 a complex experiment was initiated, in which plants were cultivated based on the scheme: 1st year maize, 2nd year winter wheat, 3rd year soybeans and 4th year winter wheat. In the first 2 years both for maize and winter wheat, processed sewage sludge, anaerobically digested and dewatered within Pitesti Wastewater Treatment Plant, was applied in quantities: 0 $t.ha^{-1}$, 5 $t.ha^{-1}$, 10 $t.ha^{-1}$, 25 $t.ha^{-1}$ and 50 $t.ha^{-1}$. Soybeans and winter wheat in the last years benefited from the remaining effect of previously applied sludge doses. Chemical fertilizers were used at three levels as follows: 1) without chemical fertilizers, 2) ½ of a normal dose of chemical fertilizers and 3) 1/1- complete dose of chemical fertilizers specific for each crop. Thus, for maize we used ½ of the $N_{50}P_{50}$ level, for winter wheat $N_{60}P_{40}$, for soybeans $N_{30}P_{30}$ and for winter wheat on 4th year $N_{40}P_{40}$; at level 1/1, the maize received $N_{120}P_{80}$, winter wheat $N_{120}P_{80}$, soybeans $N_{60}P_{60}$, and winter wheat on 4th year $N_{80}P_{80}$. A split-plot design with the A factor – sludge doses and the B factor – chemical fertilizers doses was used. Each plot had 100 m^2 and was replicated 3 times. Soil sampling was performed with the agricultural sampling device, in the working depth (0-20 cm) at crop flowering and maturity. Leaves samples were taken during flowering: in maize the leaves located at corn cob level, in winter wheat the upper 3 leaves, including the flag leaf and in soybeans the leaves in the central area of the plant, including those with bean-pods in formation process. Chemical analyses were performed based on recent European norms and methodologies (pH: SR ISO 11047/03; OC, %: SR ISO 14235/03; tN, %: SR ISO 11261/03; Mn: SR ISO 11047/03), both for sludge anaerobically digested and for soil and plants. Statistical analysis was performed using ANOVA, correlations and regressions.

RESULTS AND DISCUSSION

Specific cultivation eco-environment. Main characteristics of the luvosoil (Table 1) demonstrate the existence of an eco-environment very favorable for the presence of manganese in the form accessible to plants (as Mn^{2+} ions).

Table 1. Characterization of main features of plants' cultivation eco-environment

Factors of the eco-environment	Mn, $mg.kg^{-1}$ d.w.		OC %	tN, %	pH
	absorb-able	MAC*			
Cultivated luvosoil	440	400[a]	2.03	0.191	5.14
Used fermented sludge	340	500[b]	30.11	2.242	7.06

*MAC – maximal admissible concentrations: [a]344/04, [b]NRDIPAEP

On average Mn^{2+} is found at the level of 440 $mg.kg^{-1}$ d.w., slightly above the limit set by technical requirements of Order no. 344/2004. Processed sludge (anaerobically digested, stabilized, treated and dewatered) brings itself Mn^{2+} 340 $mg.kg^{-1}$ d.w., which is under the unofficial recommendations of National Research and Development Institute of Pedology and Agrochemistry and Environment Protection (NRDIPAEP) Bucharest. On the other hand, the used sludge had some favorable features for the improvement of the soil. Thus, organic carbon (OC,%) was situated at approximately 30% in comparison with 2% of the soil, total nitrogen (tN,%) exceeded 2% (2.242%) compared to only 0.191% in the normal soil, while the sludge pH values indicate the neutral state (7.06) compared to the acid one (5.14) of the luvosoil. Therefore, the sludge can be considered as a real amendment of the soil in the area.

Influence of sludge doses and chemical fertilizers on soil manganese content. Cultivated soils have had and currently have modifications of their Mn content. Periodical investigations demonstrated Mn values between 280 and 3200 ppm total forms and approximately 300 ppm mobile forms (Swaine, 1955; Cottenie, 1977, quoted by Davidescu, 1981). A global average figure would be situated between 950 and 1000 ppm manganese (Davies, 1980, quoted by Băjescu, 1984). Of all agricultural soils the luvosoil in Piteşti research facility has Mn^{2+} contents under this average figure, yet with annual variations due to numerous cultivation factors, eco-environment factors, weather conditions etc. The 4 years of the experiment emphasized this fluctuation of soil's contents, both in terms of total forms and mobile forms of manganese (Table 2). In case of the maize, total Mn forms oscillated insignificantly around the average value of 829 $mg.kg^{-1}$ d.w. In turn, mobile forms of Mn had slight increments – some statistically significant, compared to the sample without sludge ad chemical fertilizers. The average was situated at 519 $mg.kg^{-1}$ d.w. Mn^{2+}.

Table 2. Evolution of Mn contents (Mn, $mg.kg^{-1}$ d.w.) – total forms (T.f.) and mobile forms (M.f.) in soils cultivated with maize, winter wheat and soybeans, according to sludge doses and chemical fertilizers doses used

Sludge doses	Chemical doses	Maize		Winter wheat		Soybeans		Winter wheat	
		T.f.	M.f.	T.f.	M.f.	T.f.	M.f.	T.f.	M.f.
0 $t.ha^{-1}$	B_1	822	466	747	375	815	506	892	399
	B_2	803	443	800	403	815	483	830	431
	B_3	823	449	762	372	860***	622***	919	518
5 $t.ha^{-1}$	B_1	769	508	713	433*	835**	593***	842	469
	B_2	694	440	661	406	889***	577***	855	501
	B_3	772	486	770	438*	860***	662***	928	565*
10 $t.ha^{-1}$	B_1	861	539**	771	456**	866***	586***	1050	529*
	B_2	852	576***	770	464**	926***	579***	971	578**
	B_3	821	534*	704	403	909***	670***	849	587**
25 $t.ha^{-1}$	B_1	865	554**	760	441*	981***	625***	942	486
	B_2	837	586***	807	437*	805	497	953	595**
	B_3	893	603***	731	405	830*	534***	832	454
50 $t.ha^{-1}$	B_1	892	585***	817	435*	803	434	995	561**
	B_2	826	538**	814	404	780	452	998	530*
	B_3	899	469	861*	455**	758	430	795	478
	LSD 5 %	168	51	88	49	11	8	161	127
	LSD 1 %	233	71	122	68	16	12	224	177
	LSD 0.1 %	324	99	170	96	22	16	308	243
Trial average		829	519	766	422	849	550	910	512

The soil under winter wheat, in the 2nd year of cultivation and use of digested sludge, shows variation in Mn contents, both compared to the check plots without sludge and to the average of 766 $mg.kg^{-1}$ d.w. soil. The highest value - 861 $mg.kg^{-1}$ d.w. was obtained for 50 $t.ha^{-1}$ sludge and $N_{120}P_{80}$. Mobile forms increased in most cases as the result of using both sludge and chemical fertilizers. The average for the entire experiment was 422 mg $Mn^{2+}.kg^{-1}$ d.w. soil. In the 3rd cultivation year, under soybeans, Mn values showed larger, variation, with some significant differences.

The average of total Mn forms was 849 $mg.kg^{-1}$ d.w., and of mobile forms 550 $mg.kg^{-1}$ d.w. Higher values of Mn content in soil can be caused by the accumulation of the 2 sludge application layers, which were then mixed with the soil in the 3rd year, during the cultivation with soybeans. In the last year, under winter wheat, total forms of Mn were high (on average 910 $mg.kg^{-1}$d.w.), but not significantly different from the check plots with no sludge applied. Mobile forms had an average for the entire experiment of 512 $mg.kg^{-1}$d.w. and showed significant increases compared to the check plots. In general, in the luvosoil eco-environment, application of processed sludge and chemical fertilizers produced slight increments of soil Mn content both in terms of total forms – more evident for soybeans – and mobile forms – for all crops.

Influence of experimental factors upon Mn contents in leaves and grains. Given the fact that the content of both total and mobile forms of Mn in the soil was high, it was expected that the absorption of Mn^{2+} would occur in the same manner. Published data are rather vague, without presenting clear cases of Mn contents in different crops. On the other hand, one thing is certain: in small quantities, of about 30-50 ppm, Mn is a micro-nutrient indispensable for plants' life (Tisdale, 1975; Hera, 1988).

Manganese is required by plants and contributes to the normal physiology of all tissues in development, while the analyzed leaves – irrespective of their stage, always show this content of the chemical micro-element Mn. The luvosoil specific to Piteşti area can provide the minimal required quantity – as feeding factor for plants, irrespective of the crop. However, high values of Mn^{2+} in soil contribute to the occurrence of phytotoxicity phenomena, and the chemical element Mn becomes the heavy metal hazardous for both plants' life and for the entire food chain.

In this case plant analyses at several moments of plant's development become very important.

Both Mn and other chemical elements, mineral salts etc. are absorbed selectively by each plant species, and the clayey-humic complex activates through a complex moderation of plants' feeding process.

Our data illustrate the way Mn was absorbed by plants. Regarding the Mn contents both in leaves and grains of the three crops, one can notice evident differences (Table 3). Maize had at flowering between 4.4 and 7.3 $mg.kg^{-1}$ d.w. Mn in its leaves. Thus, maize proves to be quite selective, having relatively low contents of Mn in the leaves during flowering. Sludge doses increased the Mn content in leaves at significant levels compared to the check, while the average Mn value of the entire experiment was situated at 6.0 $mg.kg^{-1}$d.w. The winter wheat cultivated in the two years shows higher values of Mn in leaves of over 100 $mg.kg^{-1}$ d.w. Sludge and fertilizers did not have a significant influence compared to the check, and the general average values were 128 $mg.kg^{-1}$ d.w. leaf in the first case and 118 $mg.kg^{-1}$ d.w. leaf in the second case. Soybeans, a plant with a totally different physiology, absorbed and contained Mn in leaves between 107 and 240 $mg.kg^{-1}$ d.w., with significant differences compared to the check. The average this year was of 183 mg $Mn.kg^{-1}$ d.w. leaf, being the highest among the three crops.

Table 3. Mn contents (Mn, $mg.kg^{-1}$ d.w.) in leaves and grains of three crops, according to the sludge and chemical fertilizer doses used

Sludge doses	Chemical doses	Concentration within the leaf				Concentration within the grains			
		maize	wheat	soybeans	wheat	maize	wheat	soybeans	wheat
0 $t.ha^{-1}$	B_1	4.4	127	130	121	8.4	84	43	81
	B_2	5.2	105	107	112	7.4	77	40	77
	B_3	5.8	107	116	112	7.4	94	39	60
5 $t.ha^{-1}$	B_1	5.3	136	141	127	6.4	104	38	73
	B_2	5.5	129	206	126	6.8	100	37	80
	B_3	6.4*	131	214	102	6.8	87	46	74
10 $t.ha^{-1}$	B_1	5.6	145	230*	134	5.6	103	47	80
	B_2	6.0	110	234*	117	5.7	91	32^0	76
	B_3	7.0**	140	209	120	6.0	94	37	60
25 $t.ha^{-1}$	B_1	5.9	122	161	115	6.1	105	41	65
	B_2	6.2*	143	180	118	6.1	106	39	69
	B_3	7.2*	138	240*	124	7.0	89	44	70
50 $t.ha^{-1}$	B_1	6.2*	131	205	110	7.0	102	42	53
	B_2	6.8**	138	216	113	6.0	104	35	58
	B_3	7.3**	116	157	114	7.3	88	42	67
	LSD 5 %	1.7	30	96	17	5.9	18	9	19
	LSD 1 %	2.4	42	134	24	8.1	25	13	26
	LSD 0.1 %	3.3	57	184	33	11.3	35	17	36
Average of the trial		6.0	128	183	118	6.7	95	40	70

Mn contents of mature grains were also specific to the crops. Maize showed the lowest concentrations, not significantly different compared to the check and with an average of 6.7 mg $Mn.kg^{-1}$ d.w. grains. Winter wheat in the two cultivation years contained Mn at different levels, not differentiated statistically from the check, with average values of 95 $mg.kg^{-1}$ d.w. in the 2nd year (2005) and of only 70 $mg.kg^{-1}$ d.w. in the last cultivation year. This differentiation occurred due to the weather conditions in the last year (2007) which interfered with the normal Mn migration in the grains. Soybeans had the least concentrations of Mn, without evident differences compared to the unfertilized check (no organic-mineral fertilizers) and with an average on the entire experiment of only 40 $mg.kg^{-1}$ d.w. grains.

Correlations between Mn contents in plants and total produced biomass. Some trends of Mn contents can be noticed, regarding the biomass produced by the three crops, (Figure 1).

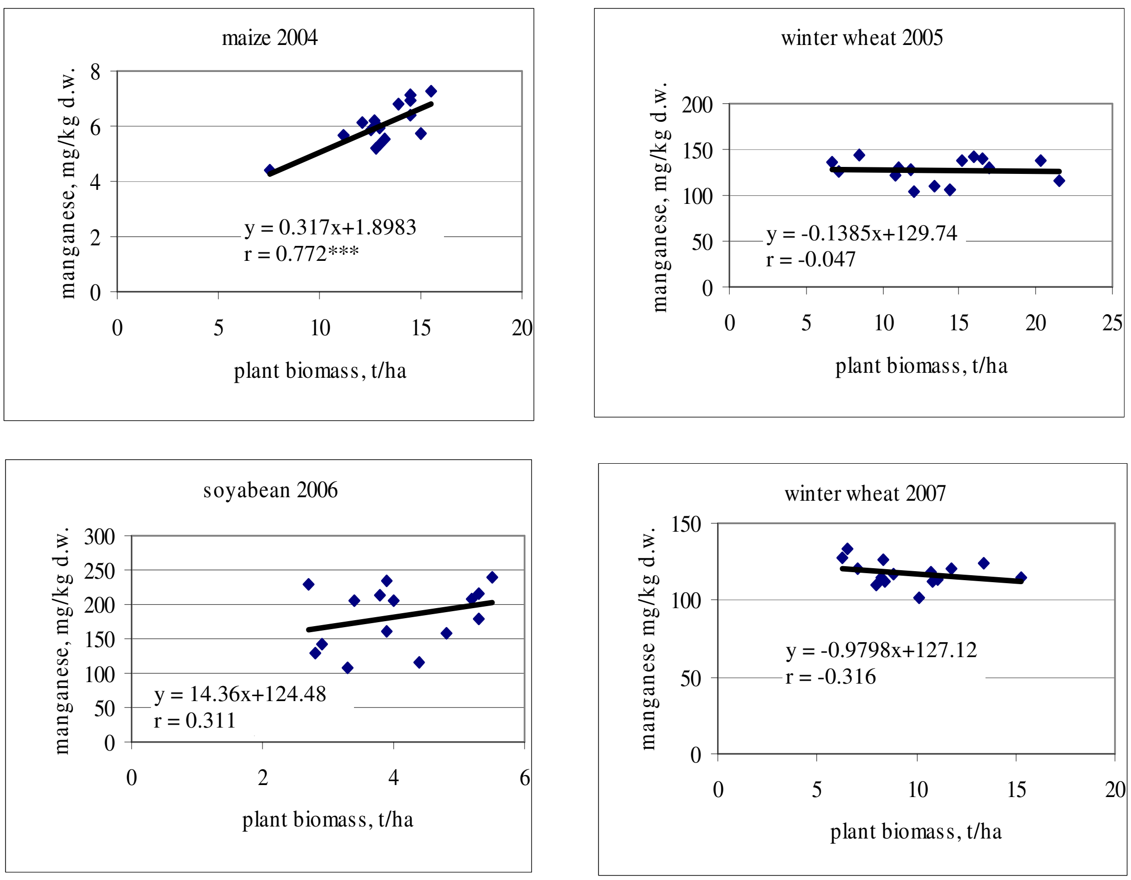

Figure 1. Relations between total biomass production and Mn content in plants leaves

In maize and soybeans, positive correlations were noticed, which suggest that at higher biomass the two crops accumulated higher Mn quantities. However, only in maize, the correlation was statistically significant. For the two years with winter wheat the correlations were not significant and the trend was even negative. Therefore the correlations emphasize the maize as the plant absorbing increasing quantities of Mn in direct relation with formation of total vegetative mass, while in winter wheat the micro-nutrient once absorbed at the beginning of vegetation proved to be sufficient, irrespective of the formed biomass.

Correlations between grain yield and Mn contents in grains were different in comparison with the ones of leaves (Figure 2).

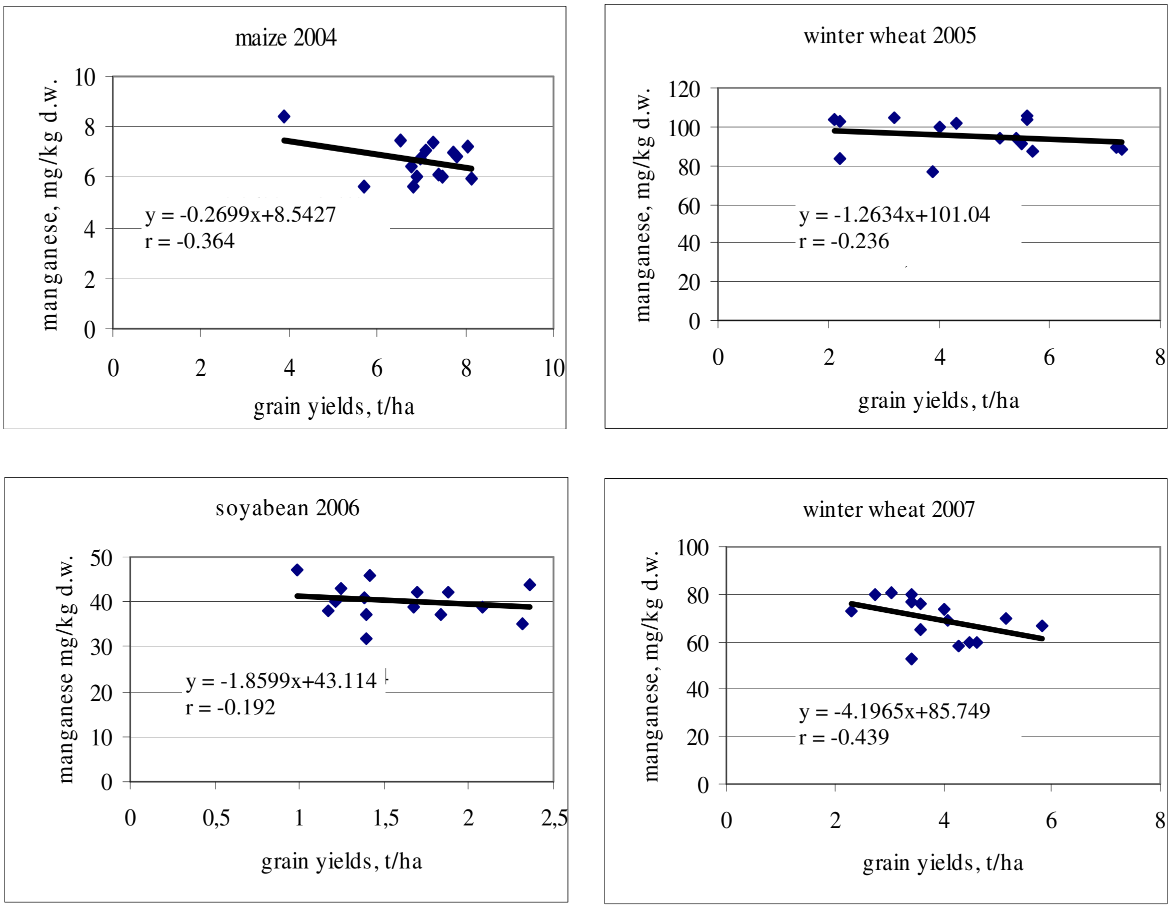

Figure 2. Correlations between grain yield and Mn content in grains

Thus, in all crops there was a trend for Mn contents to be negatively associated with grain yield, but correlations were not significant. Correlation coefficients were: r = -0.439 in case of winter wheat in the last cultivation year, r = -0.364 at maize, r = -0.236 in case of winter wheat in the 2nd cultivation year, and only r = -0.192 in case of soybeans. The reason for these negative trends can be the fact that, at maturity plants do not need anymore high concentrations of Mn^{+2} – as in the case of intense vegetative growth.

CONCLUSIONS

Using processed sludge (anaerobically digested and dewatered) improves the luvosoil eco-environment: it increases the organic matter content, increases the nitrogen supply and the pH values. At the same time, there occurs a completion of soil contents in Mn^{2+}.

Soil analyses in the 4 experimenting years show a slight increase of the total Mn forms following application of sludge and fertilizers – average values between 766 and 910 $mg.kg^{-1}$ d.w. Mobile forms of Mn were significantly increased compared to the check, and the average values obtained – between 422 and 550 $mg.kg^{-1}$ d.w. suggest possible negative influence upon the absorption of the heavy metals by the plants.

Both leaves during flowering and grains at maturity show Mn content differentiated both according to the crops and to the studied factors. Maize had the lowest levels of Mn both in leaves and grains – average figures being 6.0 and 6.7 $mg.kg^{-1}$ d.w. respectively. Sludge and chemical fertilizers significantly modified the Mn content in leaves. Soybean contained the lowest concentration of Mn in leaves, with possible positive influence of sludge and mineral fertilizers. Winter wheat contained Mn over 100 $mg.kg^{-1}$ d.w. in leaves and between

70 and 95 mg.kg^{-1} d.w. in grains. There were not significant differences between treatments.

Our results on Mn^{2+} concentrations are considerably different from the forecasts based on previously published data, presented by specialized literature (Table 4). This emphasizes the need for experiments performed in concrete cultivation conditions, to take into account the specificity of the crop, with its characteristics in the absorption and use of manganese (as Mn^{2+}) during vegetation.

Table 4. Manganese concentrations in several crops (Mn^{2+}, mg.kg^{-1} d.w.)

Crop	Value required in development phase*	Determinations performed on cultivation plants	
		At flowering – in leaves	At maturity – in grains
Maize	40	6	7
Winter wheat	35	123	83
Soybean	30	183	40

* YARA estimates.

Multi-annual observations did not prove major phytotoxicity phenomena due to higher but also fluctuating Mn concentrations in soil. Processed sludge has a contribution in the case of this heavy metal, but under the limits recommended by NRDIPAEP Bucharest and does not influence its absorption over the needs.

Study of correlations between Mn concentration and total biomass showed that only the maize absorbed Mn in direct and significant relation with biomass; soybeans showed only a positive trend, and winter wheat showed a negative but not significant trend. At maturity, Mn was no longer necessary, so that Mn concentration in grains showed a negative but nor significant relationship with grain yield.

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