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IMPLICATIONS OF SEQUENTIAL REPARTITION OF ZINC IN POLLUTED AND TUFF TREATED SOILS CROPPED TO CORN

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ABSTRACT

Remediation of soils polluted with metals by engineering techniques, such as the use of pillared clay, e.g. tuff pillared with aluminum polynuclear salts, was studied on experimental corn areas, for 6 months. Obtained results are as follows:

- *Polluted and treated soils, uncropped, contained up to 55% of the total zinc, bound in oxides networks, and 7-10% as mobile zinc from structures which allow ion exchange, and unspecific adsorption, respectively (iron and manganese hydro(oxides) site surfaces);*
- *By cropping polluted soils containing zinc, with plants having affinity for this metal, considerable modification of the metal distribution occurs in soil components: enzymatic equipments of the plant allow zinc to dissolve from the organic compounds and its transition to easily bioavailable forms of interchangeable zinc, unspecifically adsorbed;*
- *Treatment of zinc polluted soils with pillared materials of Al-coated tuff was efficient during the study period, with respect to bioavailability alteration by decreasing zinc amount bound to the aerial vegetative organs of the plants, up to 50%.*

KEYWORDS:
pillared clay, aluminum polyhydroxides, volcanic tuff, immobilization of zinc

1. INTRODUCTION

The consequences of soil metal accumulation resides in modifications occurring at soil characteristics level and crops cultivated on contaminated soils level.

The main effects due to pollution with heavy metals are: pH alteration, excessive metal accumulation determining soil content modifications, such as nutrient content, humus content, etc., and excessive metal accumulations in different parts of the plants cultivated on these soils.

Soil heavy metal pollution is very severe in some areas due to mining activities, such as: Baia Mare, Zlatna, Copşa Mică, etc. It has been proved that metals coming from anthropogenic sources tend to be more mobile than those from pedogenic or lithogenic sources, thus more accessible to crops.

The use of certain additives and organic or inorganic agricultural amendments to modify the metal species migration in soils and metal species repartition on the basic components of the soil, influences the bioavailability level of different metal species accumulated by plants during the vegetative period [1-7]. In such a complex environment as the soil, it is difficult to appreciate the mechanism by which metal species bind to different soil components and, especially, the laws governing the shifting of settled balances under germination and vegetative activity development conditions (it is known the fact that roots may influence through their own exudates the mobility of some chemical species from soil).

Our researches had as main objective the study of the alterations occurring in the sequential distribution of zinc on the basic soil components when cropping corn (*Zea mays*) on polluted soils and polluted and treated soils, respectively. The study comprises two parts:

- Zinc sequential distribution analysis, in time, on four soil main fractions: fraction F I – interchangeable ionic species, fraction F II – species adsorbed on the surface of iron and manganese hydroxides and oxides, fraction F III – species bound to organic components and fraction F IV – species retained in the trapping oxidic nets;
- Study of zinc accumulation in the aerial parts of corn (stem, leaves, inflorescence, and stalks) after a 6-month vegetation period.

2. MATERIALS AND METHODS

Analyses were done on non-polluted, polluted, and polluted and treated soils. Soil parcels were contaminated with zinc salts to a high load level (670 mg Zn/kg of soil). Dumitru et al. [8] consider a high load level values ranging between 301-700 mg Zn/kg of dried soil. Part of the contaminated parcels were amended with organic additives based on native volcanic tuff coated with trivalent metal polynucleated salts with high level of polymerization. The study was done on 6 soil parcels of 13.5 sqm/parcel. Parcels were prepared for seeding according to the following work frame:

- Distribution on parcels 1,2,4,5 of a 1% solution of zinc chloride. After drying, the soil was tilled for homogenizing and let to equilibrate for 7 days.
- Treatment of parcels 1 and 5 with coated materials based on native volcanic tuff with dimensions $\leq$ 0.1 mm, with depositions of salts highly polymerized of trivalent metals. The material used as amendment was introduced under the furrow. Amendment quantity was of 2 g/kg of dried soil. The soil was let to equilibrate for 14 days.
- The soil was seeded with corn placed on two rows for each parcel, with 75 cm distance between rows and 35 cm between plants.

Arrangement of crops in experimental parcels are presented in fig. 1.

PARCEL 3 *Non-polluted, control soil*	*PARCEL 4* *Polluted soil*
PARCEL 2 *Polluted soil*	*PARCEL 5* *Polluted and treated soil*
PARCEL 1 *Polluted and treated soil*	*PARCEL 6* *Non-polluted, control soil*

FIG. 1. ARRANGEMENT OF CROPS IN EXPERIMENTAL PARCELS FROM FIELDS RESEARCH AND DEVELOPMENT CENTER

The analysis of zinc sequentially distributed on the four soil fractions F I, F II, F III, F IV was done according to the method described by M. Kaasalainen and M. Yli-Halla [9] and presented in previous papers [10]. Soil sample preparation for analysis is done according to ISO 11464-98. Total zinc quantity was determined according to ISO 11047-99. Sequential analysis of the metal distributed on the F I-F IV soil fractions was done at 3 months and 6 months, respectively, from treatment.

Analysis of plant zinc accumulation in the aerial parts of the plants (stem, leaves, inflorescence, and stalks) was done after 6 months of vegetation, on dried plants. Plant sampling was done according to the methodology described in STAS 9597/1-74, and the sample analysis was done according to STAS 9597/17-86.

Plant and soil extracts analysis was done using a spectrophotometer with atomic absorption, Varian Spectra AAS.

3. RESULTS AND DISCUSSIONS

Analyzing soil extracts from fractions F I – F IV, after 3 months and 6 months of vegetation, respectively, one can notice that for the control parcel, plants consume the soil zinc exclusively from F I and F II, and up to 40% from F III, the organic fraction, as it is presented in table 1.

For the polluted parcels and those polluted and treated, plants take from soil a greater quantity of zinc. Soil zinc reduction is up to 90% of the initial quantity. Zinc is taken from fractions F I – F III. Zinc cannot be dislocated from fraction F IV. Moreover, in this soil component slight accumulations occur for this metal species.

Tables 2 and 3 show the zinc quantities determined in the 4 fractions for the above-mentioned intervals. From table 2 data one can notice that after 6 months corn plants extract from soil up to 90% of the zinc quantity.

Initial concentration of zinc in the polluted soil was of 670 mg/kg of dried soil.

Table 3 data show a similar situation, only that at 3 months, zinc values in F III are twice as much as those of the organic fraction of the polluted soils.

It is known that corn plants extract from soil, for metabolic reasons, significant zinc quantities. In our experiment, the coated materials used as amendment immobilized in soil considerable quantities of zinc. But, in the so-known crisis periods, when the mobile species were depleted, plants managed trough their own exudates to up-take zinc species more tightly bound such as those of the organic type. Initial concentration of zinc was of 63.9 – 64.2 mg/kg of dried soil.

TABLE 1. SEQUENTIAL DISTRIBUTION OF ZINC, IN TIME, IN THE CONTROL PARCELS

Crt. Nr.	Soil type	Sampling period	Fraction sum FI + FII + FIII + FIV	Fraction I		Fraction II		Fraction III		Fraction IV	
				mgZn/ kg of dried soil	%	mgZn/ kg of dried soil	%	mgZn/ kg of dried soil	%	mgZn/ kg of dried soil	%
1	*Parcel 3 Non-polluted, control soil*	3 months	64.3	4.8	*7.5*	6.4	*10.0*	35.0	*54.5*	18.1	*28.0*
2		6 months	-	-	-	-	-	-	-	-	-
3	*Parcel 6 Non-polluted, control soil*	3 months	63.8	4.4	*6.8*	4.1	*8.2*	32.5	*50.0*	22.0	*35.0*
4		6 months	40.6	0.2	*0.5*	0.9	*2.2*	19.5	*48.0*	20.0	*49.3*

TABLE 2. SEQUENTIAL DISTRIBUTION OF ZINC, IN TIME, IN THE POLLUTED AND UNTREATED PARCELS

Crt. Nr.	Soil type	Sampling period	Fraction sum FI + FII + FIII + FIV	Fraction I		Fraction II		Fraction III		Fraction IV	
				mgZn/ kg of dried soil	%	mgZn/ kg of dried soil	%	mgZn/ kg of dried soil	%	mgZn/ kg of dried soil	%
1	Parcel 2 Polluted soil	3 months	430.0	136.0	31.6	196.0	45.6	85.0	19.8	13.0	3.0
2		6 months	82.0	22.0	26.8	23.0	28.0	19.0	23.2	18.0	22.0
3	Parcel 4 Polluted soil	3 months	339.5	144.0	42.4	120.0	35.3	62.5	18.5	13.0	3.8
4		6 months	86.0	24.0	27.9	29.0	33.7	16.0	18.6	17.0	19.8

Initial concentration of zinc in the polluted soil was of 670 mg/kg of dried soil. In the polluted and treated soils, but uncultivated, due to specific soil biochemistry, zinc sequential distribution evolves in time differently compared to that of the soils cultivated with corn. Our observations are presented in table 4.

Observing the quantity of zinc accumulated during a 6 months period in plants, it can be emphasized that for the soil treated with amendments, corn aerial parts accumulated zinc in quantities under the admitted limit of 100 mg/kg of dried matter, whereas in the polluted soil, the accumulated zinc quantity exceeds with 27% the admitted limit.

Zinc quantity found in the plants cultivated on the polluted and treated soils is 12% greater than that of the plants cultivated on non-polluted soils. In the second part of the research were analyzed the values of zinc concentrated in the aerial parts of the plants, data are shown in table 5.

TABLE 3. SEQUENTIAL DISTRIBUTION OF ZINC, IN TIME, IN THE POLLUTED AND TREATED PARCELS

Crt. Nr.	Soil type	Sampling period	Fraction sum FI + FII + FIII + FIV	**Fraction** I		Fraction II		Fraction III		Fraction IV	
				mgZn/ kg of dried soil	%	mgZn/ kg of dried soil	%	mgZn/ kg of dried soil	%	mgZn/ kg of dried soil	%
1	Parcel 1 Polluted and treated soil	3 months	376.3	100.0	26.6	92.8	24.7	170.0	45.1	13.5	3.6
2		6 months	73.0	15.0	20.5	20.0	27.4	18.0	24.7	20.0	27.4
3	Parcel 5 Polluted and treated soil	3 months	324.0	114.0	35.2	102.8	31.7	94.0	29.0	13.2	4.1
4		6 months	66.2	16.7	25.2	13.4	20.3	17.1	25.8	19.0	28.7

TABLE 4. ZINC SEQUENTIAL DISTRIBUTION ON THE COMPONENTS OF TWO SOILS POLLUTED WITH ZINC AND TREATED WITH AL_N-TUFF AFTER 6 MONTHS FROM TREATMENT

Soil sample		Zinc quantity in F I %	Zinc quantity in F II %	Zinc quantity in F III %	Zinc quantity in F IV %
Soil 1	8.6	15.7	20.6	55.8	
Soil 2	10.0	7.0	44.0	39.0	
Soil 1	7.5	16.0	54.0	22.5	
Soil 2	10.3	7.5	49.0	33.2	
Mean	9.1	11.5	42	38	

TABLE 5. ZINC BIOACCUMULATED QUANTITY IN THE AERIAL PARTS OF CORN AFTER 6 MONTHS OF VEGETATION.

Sample	Soil type	Dried matter %	Zinc content (mg/kg)		
			Green mass	D. M.	Ash
3	Non-polluted	39.1	38.4	42.5	-
6	Non-polluted	33.3	13.5	42.6	290.7
mean	-	33.3	15.5	42.6	290.7
2	Polluted	33.7	78.7	122.5	1,406.7
4	Polluted	32.8	68.3	126.8	1,416.0
mean	-	33.2	74.0	125	1,411.3
1	Treated	39.0	36.3	64	459.3
5	Treated	53.0	27.5	52.4	750.4
mean	-	46	32.0	58.0	552.8

Even though zinc was transferred in plants in a proportion of 90% from the analyzed soils, we noticed in the plants cultivated on soils treated with amendments, quantities 40% less than those found for the polluted soils.

We need to mention that seed germination was 10% better than that in the case of the polluted soil. As well, plants cultivated on treated soils were more vigorous so that zinc quantity transferred from soil could distribute to a greater vegetative mass.

The effect of the used amendments was first noticed on the seed germination capacity and the vegetative development capacity of the plants. Seed germination occurred as follows: 74-82% on the non-polluted parcels, 72-77% on polluted parcels and 78-87% on polluted and treated parcels. Zinc pollution had as effect the inhibition of seed germination on the polluted soil with 5% more than the non-polluted soil. Plants were less vigorous, light greened than those cultivated on polluted and treated soil where plants were intense green colored.

4. CONCLUSIONS

1. The amendments represented by coated tuff included in soil act favorably, increasing the germination capacity of corn seeds with 5% than that of seeds sown in non-polluted soils and with 10% than that of the seeds sown on polluted and treated soils.
2. Plants cultivated on the polluted and treated soil parcels had more vigorous roots, greater biomass, dark greened leaves, unlike those cultivated on untreated soils that were less vigorous and had discolored leaves. Corn plants cultivated on treated soils showed an

increase of the dried matter quantity up to 25%, than those cultivated on non-polluted or polluted soils.

3. After 3 months of vegetation F III soil fraction (the organic component) retains an immobilized quantity of zinc for the amended soils two times greater than that for the polluted soils. After 6 months of vegetation, for the two types of soil – treated and polluted, residual zinc content of the organic component is similar, meaning that the plant is able to satisfy its zinc requirements solubilizing it from soil components that bind it more tightly. Corn plants consumed the reserves from the organic fraction in their "crisis" periods when, presumably, the other mobile metal species were assimilated.
4. Plants cultivated on amended soils contain zinc under the admitted limits (up to 52.4 mg Zn/kg of dried soil), whereas plants sampled from the polluted soils contain quantities exceeding with 26% the admitted limits. Treatment of zinc-polluted soils with pillared materials of Al-coated tuff was efficient during the study period, with respect to bioavailability alteration by decreasing zinc amount bound to the aerial vegetative organs of the plants, up to 50%.
5. Polluted and amended soils, but not cultivated, contain up to 55% of the total zinc as immobile species, blocked in oxidic nets.

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