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# BIOSOLIDS AND VOLCANIC TUFF INFLUENCE OVER THE UPTAKE COEFFICIENT OF CADMIUM AND ZINC FROM POLLUTED SOILS IN MAIZE CULTIVATION

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**Abstract:**
Potentially toxic elements such as cadmium, lead and zinc can accumulate in cropland soils through fertilizer application. This study analyzes, comparatively, the uptake coefficient (UC) of cadmium and zinc in maize (Zea mays L.) destined as fodder for animals. Results indicate that the addition of biosolids can change the plant bioavailability for metals from soil. During the first phenophases of plant development, it especially accumulates cadmium into the aerial tissues. The use of the pillared volcanic tuff of type tuf-$Al_n$ as an addition to the organic fertilizer, determines metal bioaccumulation reduction in young plants.
**Keywords:**
cadmium, zinc, bioaccumulation, bioavailability, soil, Zea mays

## 1. INTRODUCTION

The long application of organic fertilizers as manure, biosolids (municipal sludge anaerobic fermented) or anorganic fertilizers based on phosphatic rocks, determines both the enrichment of the agricultural land in nutritive substances, nitrogen and phosphorus, and a gradual accumulation of cadmium, lead and zinc. [5, 8, 9].

The accumulation level of heavy metals in agricultural soils reached a point which alerted the specialists from numerous countries in Europe (England, Germany, Norway), America (USA) and Australia [1, 2, 3, 4, 12]. The statistic analysis of the gathered data regarding the transfer of these metals from soil into plants, intended for human and animal consumption, is of general concern. Researches demonstrated that in plant tissues the heavy metal quantity accumulates directly proportional with the rhythmic addition of metal in soil. Accumulation rate depends on soil characteristics, plant species, plant age, hydroclimatic conditions, and type of tillage [5].

Mankind faces, in the last years, different aspects of waste storage, especially of the increasing amounts of municipal sludge. Many countries chose as solution the reuse of these as organic fertilizers for agricultural crops, due to the high content in fertilizing agents, nitrogen, and phosphorus [2, 11, 13]. Analysis of the agricultural lands fertilized with biosolids on a long period of time shows that soils can accumulate between 0.035-33.8 mg Cd/kg of D.M. and 16-5,010 mg Zn/kg of D.M., for those cultivated with wheat, and between 0.02-2.31 mg Cd/kg of D.M. and 19-429 mg Zn/kg of D.M. for those cultivated with barley [1]. Plants can also accumulate significant quantities of heavy metals. Thus, maize can accumulate in the aerial parts between 1-9 mg Cd/kg of D.M. [12]. Metal accumulation in crops represents now one of the greatest problems of the world [2]. The addition of metal immobilizing agents in soil, such as zeolites from volcanic tuffs, can significantly reduce the bioavailability of plants for certain metals [13].

To perform this study we took under consideration the following aspects: - cadmium and zinc content increase from cropland soils as a result of some anthropic activities, as is the case of the area adjacent to the mining activity from Moldova Noua, located in south-western part of Romania; - the use over long periods of some fertilizers that annually add small quantities of toxic metals, metals that accumulated in time; - crop bioavailability to accumulate metals such as cadmium and zinc in the aerial_parts; - the soil addition of a metal immobilizing agent such as the modified domestic volcanic tuff, which can significantly reduce the content of the metal up-taken by plants from the soil solution.

## 2. MATERIALS AND METHODS

The experimental field is located at Banat's University of Agricultural Sciences and Veterinary Medicine in Timisoara (western Romania). The study was done on an experimental block comprising plots with a 13.6 $m^2$/lot surface. Cadmium, lead and zinc salts were added to the soil, in order to obtain a pollution level similar to the one determined in the analyzed soils from Moldova Noua. Maize (*Zea mays* L.) was used as a test plant. Heavy metals were applied to soil in soluble form before seeding with maize.

The variants of the treatments of the soils on which the experiments were done are:

- **V1** - variant without organic fertilizer (biosolids) addition, which comprises three categories of soil (Fig.1): M - control soil with characteristics of normal soil; P - soil polluted with cadmium, zinc and lead salts; T - soil polluted with cadmium, zinc and lead salts and amended with pillared materials, of tuff-$Al_n$ type;
- **V2** - variant of fertilized soil with organic fertilizer (biosolids), which also contains three categories of soil (Fig.2): FM - control soil; FP - polluted soil; FT - soil polluted and amended with pillared materials, of tuff-$Al_n$ type.

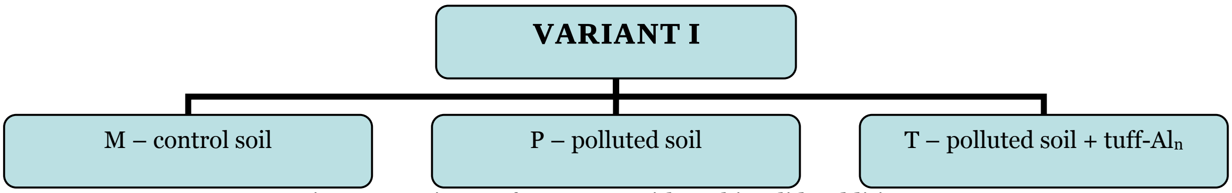


Figure.1. Variant I of treatment without biosolids addition.
M - control soil with normal soil characteristics; P- soil polluted with cadmium, zinc and lead salts;
T - soil polluted with cadmium, zinc and lead salts and amended with pillared materials of the tuff-$Al_n$ type

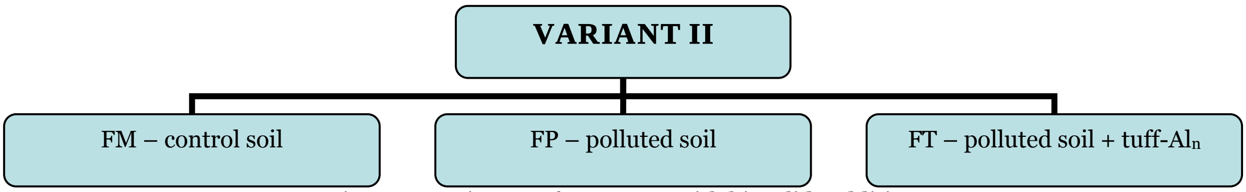


Figure.2. Variant II of treatment with biosolids addition.
MF - control soil with normal soil characteristics; FP- soil polluted with cadmium, zinc and lead salts; FT – soil polluted and amended with pillared materials of the tuff-$Al_n$ type.

Fertilization was done with organic fertilizer (biosolids). Fertilizer dose was of 30 to of D.M./ha. Table 1 shows the characteristics of biosolids for the experiment**.**

Soil analysis after the artificial heavy metal pollution and fertilization, showed the following: cadmium from polluted soil was of 1-3.4 mg/kg of D.M., zinc was of 670-720 mg/kg of D.M, lead was of 58-70 mg/kg of D.M., and the stabilized pH was of 6.2-6.3.

Metal content from the polluted soils in this experiment ranks as sensitive soils and/or less sensitive, alert level, according to the effectual norms in Romania (Table 2).

Table 1. Characteristics of the biosolids used for fertilization for the experimental plots and heavy metal quantity introduced in soil for the 30 tonnes/ha dose.

| Biosolids characteristics | Value | Addition of metals and other substances from biosolids (30 to of D.M./ha) in soil |
|---|---|---|
| pH | 5.80 | - |
| Dried matter, % | 18.3 | - |
| Humidity, % | 81.7 | - |
| Volatile substance, % | 32.0 | - |
| Extractible in ether of petroleum, mg/kg | 2.11 | - |
| Manganese, mg/kg D.M. | 536.2 | 5.89 |
| Zinc, mg/kg D.M. | 1,575 | 17.9 |
| Copper, mg/kg D.M. | 481.0 | 5.29 |
| Cadmium, mg/kg D.M. | 76.60 | 0.84 |
| Chromium, mg/kg D.M. | 1,420 | 15.62 |
| Nichel, mg/kg D.M. | 220 | 2.42 |
| Lead, mg/kg D.M. | 591 | 6.51 |
| $N_{total}$,% | 0.57 | 0.06 |
| $P_{total}$,% | 0.33 | 0.035 |
| Organic substance, % | 34.3 | 3.77 |

Table 2. Reference values for metals in soils, according to MAPPM 756/1997, in mg/kg of D.M.

| Element | Normal values | Alert level | | Intervention level | |
|---|---|---|---|---|---|
| | | Sensitive soils | Soils less sensitive | Sensitive soils | Soils less sensitive |
| Cadmium | 1 | 3 | 5 | 5 | 10 |
| Lead | 20 | 50 | 250 | 100 | 1,000 |
| Zinc | 100 | 300 | 700 | 600 | 1,500 |

Soils from the T and FT categories were amended with a quantity of 2 to/ha of pillared domestic volcanic tuff, of tuff-$Al_n$ type (ECOIND patent) [6].

After the geochemical stabilization for 30 days, the fertilized and amended polluted soils were seeded with forage maize. Analysis of plant metal accumulation from aerial tissues of plant parts (stem, leaves, and grains) was done on dried plants. Plant sampling was done accordingly to the methodology described in STAS 9597/1-74, and the sample analysis was done accordingly to STAS 9597/17-86. Plant extract analysis was done by using a spectrophotometer with atomic absorption, Varian Spectra AAS.

The comparative analysis of metal bioaccumulation from aerial tissue of plants was done through the uptake coefficient by plants, designated as UC (uptake coefficient) [7, 10]

The uptake coefficient is obtained by the ratio between the metal quantity accumulated in plant tissues that are grown on adjacent soils with anthropic activities and the metal quantity from the same part of the plant, grown on the unpolluted, control soil:

$$UC = Q_P / Q_M$$

where: Qp – metal concentration accumulated in tissues of the plant grown on polluted soils;

Om – metal concentration accumulated in the tissues of the same plant grown on the unpolluted, control soil.

## 3. RESULTS AND DISCUSSIONS

The following tables present data regarding the accumulation level of cadmium and zinc in the aerial parts of maize (*Zea mays* L.) destined for animal forage.

From sample analysis of the aerial parts of the plants, resulted that lead was absent. Probably the two metals, cadmium and zinc, were competitively assimilated, and lead was more difficult to be accessed by plants in the presence of the other two.

Table 3 shows the cadmium and zinc quantities, periodically accumulated in the aerial parts of the forage maize (*Zea mays* L.)

Table 3. Cadmium and zinc quantities accumulated in the aerial parts of forage maize (*Zea mays L.*) in two successive phenophases

| Treatment | Soil category | Zinc (mg/kg of D.M.) | | Cadmium (mg/kg of D.M.) | |
|---|---|---|---|---|---|
| | | First phenophase | Second phenophase | First phenophase | Second phenophase |
| Without fertilization with biosolids | **M** - control | 4.20 | 4.20 | 0.025 * | 0.025* |
| | **P** - polluted | 14.2 | 10.5 | 0.380 | 0.500 |
| | **T** - polluted + amended | 9.65 | 14.7 | 0.320 | 0.380 |
| Fertilization with biosolids | **FM** - control | 2.80 | 8.63 | 0.570 | 0.700 |
| | **FP** - polluted | 12.8 | 14.50 | 1.300 | 1.470 |
| | **FT** - polluted + amended | 3.12 | 5.00 | 1.200 | 1.417 |

* the determined quantity of cadmium in plant tissues obtained on unpolluted soils can originate from atmospheric deposits, or from transport of the pollutant by the abundant rainfalls from the 2008 spring, from the plots with polluted soil in those unpolluted.

**Zinc** accumulates differently in the aerial parts, depending on the plant growth level and treatment type. In the variants without biosolids fertilization, zinc quantity remains constant (4.2 mg/kg) in plants grown on the control soil. In plants grown on polluted soil (P) the quantity of zinc in the second phenophase, at plant maturity, is lower (10.5 mg/kg) compared to the first phenophase when the plant is immature (14.2 mg/kg).

Addition of tuff-$Al_n$ in the variant of no-biosolids soil, reduced the bioaccumulation level of zinc with 32% in the first phenophase, from 14.2 mg/kg to 9.65 mg/kg.

Addition of biosolids had a synergetic effect in the variant of the treatment with biosolids-pillared tuff to decrease bioaccumulation, up to 75%, (from 12.8 mg/kg to 3.12 mg/kg) for zinc accumulation in plant tissue.

**Cadmium** is introduced in soil through biosolids addition. In time, it accumulates in the aerial parts of plants. Addition of biosolids will determine the increase of cadmium accumulation in plants up to 71% in the first phenophase (from 0.38 mg/kg to 1.3 mg/kg) and up to 66% in the second phenophase (from 0.50 mg/kg to 1.47 mg/kg). Addition of the pillared tuff-$Al_n$ in the experimental variant that doesn't use fertilization with biosolids, doesn't limit cadmium bioaccumulation in the aerial parts of plants, the quantitative values being similar (0.38 mg/kg; 0.32 mg/kg). This situation can be noticed in advanced phases of plant development, in the second phenophase, of maize harvest for forage, recording similar values ((0.50 mg/kg; 0.38 mg/kg).) When adding pillared tuff (tuff-$Al_n$) to the experimental plots, fertilized with biosolids, no effects on the bioaccumulation reduction could be noticed, values being similar (1.47 mg/kg in variant FP; 1.41 mg/kg in variant FT). Biosolids have components with no limitation effect for metal bioaccumulation in plant tissue.[6]. The forage maize biomass shows significant quantities of cadmium (1.2 mg/kg; 1.4 mg/kg), which makes it unusable as food for animals.

Tables 4, 5, and 6, show the values of the uptake coefficient of cadmium and zinc from polluted soils, unfertilized and fertilized with biosolids, with and without amendments that immobilize metals in soil of the Tuff-$Al_n$ type compared to control soils.

Table 4 shows the uptake coefficient for cadmium and zinc from polluted soils compared to the unpolluted soils (UC= $Q_P/Q_M$) for forage maize in the first phenophase, when the height of plants is of 20-30 cm. The uptake coefficient (UC) is reported to the quantity of metal accumulated in plants cultivated on common soils, unfertilized, unpolluted, and non-amended.

Table 4. Uptake coefficient of cadmium and zinc by forage maize (*Zea mays L.*), in the first phenophase

| Treatment | Experimental variant | Uptake coefficients (UC) | |
|---|---|---|---|
| | | Cd | Zn |
| Without addition of biosolids | **P** – polluted soil | 14.4 | 3.80 |
| | **T** – polluted soil and treated with Tuff-$Al_n$ | 12.8 | 2.28 |
| With addition of biosolids | **FM** – normal soil | 22.8 | 0.70 |
| | **FP** – polluted soil | 33.0 | 3.16 |
| | **FT** – polluted soil and treated with Tuff-$Al_n$ | 24.0 | 0.65 |

From the data presented in table 4, we can see that when grown on soil with significant quantities of metals (cadmium and zinc), the cultivated plants, under such conditions, will uptake, in the aerial tissues, higher quantities of metals than the plants cultivated on unpolluted, normal soils.

Thus, in the case of zinc, the uptake coefficient was of 2.28 – 3.80 and for cadmium it was ten times higher (UC= 33).

Biosolids addition needed to fertilize the soil, did not modify the uptake coefficient for zinc (UC=3.80 in variant P and UC=3.16 in variant FP) in plant tissues, but it also favored a higher accumulation of cadmium.

Thus, the uptake coefficient for cadmium increases twice (UC=33.0 in the variant FP) compared to the similar variant, of polluted and unfertilized soil (UC=14.4 in variant P).

Table 5 shows the uptake coefficient for cadmium and zinc from polluted soils compared to the unpolluted soils (UC = $Q_P/Q_M$ ) for forage maize in the second phenophase, when the height of plant is of 50-70 cm.

Table 5. The uptake coefficient for cadmium and zinc by the forage maize (*Zea mays L.*), in the second phenophase

| Treatment | Experimental variant | Uptake coefficient (UC) | |
|---|---|---|---|
| | | Cd | Zn |
| Without addition of biosolids | **P** – polluted soil | 20.0 | 2.50 |
| | **T** – polluted soil and treated with Tuff-$Al_n$ | 15.2 | 3.50 |
| With addition of biosolids | **FM** – normal soil | 28.0 | 1.98 |
| | **FP** – polluted soil | 16.0 | 3.45 |
| | **FT** – polluted soil and treated with Tuff-$Al_n$ | 13.0 | 1.25 |

In the second phase of plant development, when forage maize is harvested, it can be observed that zinc is taken in the same proportion as in the first phase, reporting it to the plants cultivated on the control soil. For zinc bioaccumulation, in treatment variant without addition of biosolids UC is of 2.5 – 3.5, and in the ones with biosolids UC was of 3.45.

In the case of cadmium could be observed that, along with the plant growth, the plant will uptake from the polluted soil higher quantities of metal. The accumulation level in tissues increases over 20 times compared to the accumulation in the plant tissues cultivated on unfertilized, normal soils. Biosolids addition will not determine significant changes in the UC values.

Table 6 shows the values for the uptake coefficient for cadmium and zinc in the case of domestic volcanic tuff - Tuff-$Al_{n,}$ type addition to polluted soils fertilized or unfertilized with biosolids, in the two growth phenophases of plants.

Table 6. Uptake coefficient for cadmium and zinc determined for the addition of Tuff-$Al_n$ to polluted soils, unfertilized (V1) and fertilized with biosolids (V2).

| Treatment | Experimental variant | Uptake coefficient (UC) | | | |
|---|---|---|---|---|---|
| | | First phenophase | | Second phenophase | |
| | | Cd | Zn | Cd | Zn |
| V1- Without addition of biosolids | T – soil polluted and treated with Tuff-$Al_n$* | 0.84 | 0.66 | 0.76 | 1.34 |
| V2- With addition of biosolids | FT – soil polluted and treated with Tuff-$Al_n$** | 0.75 | 0.2 | 0.27 | 0.34 |

*UC = quantity of metal from plants grown on polluted soil with addition of Tuff-$Al_n$ / quantity of metal from plants grown on polluted soil without addition of Tuff-$Al_n$.
**UC = quantity of metal from plants grown on polluted and fertilized soil with addition of Tuff-$Al_n$ / quantity of metal from plants grown on polluted and fertilized soil without addition of Tuff-$Al_n$.

Addition of Tuff-$Al_n$ to polluted soils, unfertilized with biosolids, determines the reduction of the uptake coefficient of metals by plants from soils polluted and treated with Tuff-$Al_n$, compared to those without addition of Tuff-$Al_n$ .

It can be observed that, in the first phenophase, both cadmium and zinc accumulate to a sub-unitary level of UC= 0.66 – 0.84 in the case of plants grown on areas polluted and treated with volcanic tuff. In the second phenophase, the cadmium accumulation maintains within the same range (UC= 0.76), but increases for the accumulation of zinc (UC= 1.34).

In the second case, when the soil is polluted and fertilized with biosolids, the addition of pillared tuff determined at first the decrease of the accumulated metal quantity.

In the advanced phases of plant growth, the metal quantity uptake decreased, the uptake coefficient being only 0.27 – 0.34.

Sub-unitary value of UC demonstrates the efficiency of pillared domestic volcanic tuff - Tuff-$Al_{n,}$ type, as amendment of soils polluted with heavy metals and fertilized or not with biosolids. It also demonstrates the difference between plants cultivated on amended soils with Tuff-$Al_{n,}$ and those grown on similar soils untreated with the metal immobilization agent based on pillared domestic volcanic tuff - Tuff-$Al_n$ type.

## 4. CONCLUSIONS

The presented data are the result of an experiment regarding biosolids use as organic fertilizer and of the volcanic tuff - Tuff-$Al_n$ type as amendment to soils artificially polluted with cadmium, lead and zinc, in order to reduce their bioaccumulation in forage maize (*Zea mays L*).

Values of the obtained uptake coefficients (UC) for cadmium and zinc depend on the affinity of plants for a certain metal, of the metal mobility in soils and the variant of treatment compared to the control soil (unpolluted).

Addition of volcanic tuff - Tuff-$Al_n$ type, influenced the uptake coefficient for cadmium and zinc, compared to the control soil, especially when the polluted soil was associated with biosolids.

Generally, pillared material Tuff-$Al_{n,}$ reduced cadmium and zinc transfer from soil to plant tissues, both in the first and second phenophases.

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