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Zinc Mobility from Polluted and Treated Soils with Pillared Materials due to Rain Water

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Abstract: Water acidity due to precipitation can fixe from zinc polluted soil an important quantity of metal, who are taken and stored by plants tissue. Using some immobilization agents in-situ represents a remediation technique for polluted soil, for reducing of zinc ions bioavailability. Using of some pillared materials obtained by polynuclear aluminum salts (R = molar ratio OH/Al = 2.3) settled onto natural zeolite with about 70% clinoptilolite, had as effect the reduction of Zn ions mobility, in contact with rains water. Pillared materials used, like tuf-Al_n action synergic for reducing the metal mobility, in respect with the tuf components and high polymer Al_n salts, at soil impact with percolated water with pH range in 5.4 – 6.5. Decreasing effects of zinc dissolution are 10-40 times higher in presence of pillared material than others used in this study, in the case of percolation with rains waters, pH between 5.4 ÷ 6.5.

1. Introduction

Zinc accumulation in soils represents a process with toxically effects for human, animals and plants. Exposed to heavy metals accumulation in soils can be chronics (during time) and appear by transfers made in foods chains. Exposure to a high concentration with immediate effects is rare but can appear.

Zn^{2+} can succeed to arrive in agricultural soils with municipal sludge at once or by compost based on municipal sludge. In the case of city wet sludge for fertilization, restrictions are imposed for annual limit of metal accumulation In case of zinc accumulation in soil, it is very difficult to be eliminate. zinc is fixed on soil components by adsorption, chemical bonds, network oxides, etc. The mobile species of Zn^{2+} are easier to be obtained, if medium pH is smaller (1,2,3).

On the other side, plants take zinc from soil by roots with fertilizers, at once. Plants take zinc until 90% from soil as Zn^{2+} and pollution type is diffusion by cell membrane.

With soil pH decreasing under 6.5, zinc is included and stored in vegetal tissues and then is directed towards animals and human or heavy polluted soils remediation, numerous physico - chemical methods or phytoremediation are applied, individual or in combination (4, 5).

This study tried to increase zinc mobility from polluted soils, applying some treatments with immobilising agents for pollutant metal. Used materials are obtained from high polimerized Al_n salts settled onto support materials like, zeolitic rocks, with about 70% clinoptilolite.

Al_n polymeric salts having an high degree of polymerization, are precursors in amorphous $Al(OH)_3$ formation. Aluminium polymers immobilize the metals ions from soil solution, making mixed complexes which then participated in time to transformation in oxy(hydroxides) precipitates (6).

Paper's objective is treatment of some polluted soils, chernozem, with zinc salts by use of amended agents , pillared materials tuff – Al_n , in order to reduce metal mobility.

2. Materials and methods

It was worked with chernozem soil type, with telluric zinc contents about 63-65 mg/kg dry soil. Soil is artificial polluted with zinc sulfate, so that final content of zinc is between 100.5 – 237.2 mg Zn/kg dry soil. Soil samples have a 1 kg dried soil, maintained previously in air 2 weeks for drying and are introduced in cylindrical vessels with 10 cm i.s. diameter. Soil height in vessels is 25 cm. Vessels have in the lower part an water emptiness cock. Soil samples are kept 30 days for equilibrium realization with zinc sulfate. The soil is wet until 50% humidity and this is maintained by periodical watering on study period.

Soil samples analysis are make by determination of total zinc quantity corresponding to analysis method ISO 11047/99. Soil samples preparation for analysis was made in accordance with ISO 11464/98. F 1 fraction defines the interchangeable quantity of zinc (ionic exchange capacity and nonspecific adsorbed) and its determination is according to the following scheme (7)

1 g soil sample dry at 35°C
grain size diameter < 2

↓

Fraction I. *Extractant A: acetic acid.*
The soil sample is mixed with 50 ml of extractant A
It is let under night, is filtering, analized be spectrophotometer
The result is express in mgZn/kg dry soil

After the equilibration period, the soils are treated with immobilizing agents for zinc, named amendments or additives:

1. Polymeric salts of Al_n e.g. PBA(Cl)-basic Al polychloride; r = 2,3; C_{final} = 0,098 M Al and PBA(NO_3)-basic Al polynitrate; r = 2,3, C_{final} = 0,114 M Al $Al_n(NO_3)$,obtained from $AlCl_N$, $Al(NO_3)_3$;
2. Pillared material – native volcanic tuff having 70% clinoptilolite solid shape tuff-Na (washed of by Cl^- ions)
3. Pillared materials, obtained from support: clinoptilolite volcanic tuff, tuff-Na shape and polymeric salts of Al_n e.g. Tuf-Al_n (Cl^-) and Tuf – $Al_n(NO^-_3)$ in solid phase.

The solids materials exe characterized by specific area, using BET method:

- tuff – Na = 53,8 m^2/g;
- tuff-Al_n(Cl)=128 m^2/g;
- tuff-$Al_n(NO_3)$=147 m^2/g;

The soil was mixed with amending agents and was let in equilibrium 30 days.

Percolating water used are rain wates, surface waters, law acid (distilled) water. In *Table 1* are presented the characteristics of this water.

TABLE 1. Characteristics of percolated water from soils.

Water type	PH	Hardness [°d]	Conductivity [µS/cm]
Distilled water	5.0	-	6.5
Surface water Bega	6.5	6.0	260
Snow water	5.4	0.14	16
Autumn rain	6.4-6.5	0.22	10.7-41.03

Periodically, at, approximate 30 day the wet soil samples are sprinkled with percolating water and at the down side are collecte 50 ml of water which pass the studied soil layer. In percolating waters Zn containing is analyzed. Simultaneously with treated soil samples are studies a sample of polluted and not treated soil, which contains 101,5 mg Zn/kg dry soil.

Metal analysis from water extracts its made by an A.A.S. Varian spectrophotometer

3. Results and discussion

Quantities of imobilizating agent used for zinc from soil samples 1-6, are presented in table 2.

TABLE 2. Quantity of immobilization agents introduced into soil samples 1-6.

Type of immobilization agent (amendment)	Quantity		Sample symbol
	Total immobilization agent[mg/kg]	Al_n [mg/kg]	
PBA(Cl)-basic Al polychloride; r = 2,3; C_{final} = 0,098 M Al;		53	1, 6
PBA(NO$_3$)-basic Al polynitrate; r = 2,3, C_{final} = 0,114 M Al;		61	2
Tuf-Na	1 g	-	3
Tuf-Al$_n$ (Cl$^-$)	1 g	80	4
Tuf – Al$_n$(NO$^-_3$)	1 g	108.0	5

It is observed from tables nr. 3 and nr. 4 that by percolation, there are dissolved much less zinc quantities, about $10 \div 10^3$, comparatively with untreated soils.

Distilled water (pH = 5.0), weak acid, mobilizes greater zinc quantities then rain water. Also, surface water (pH = 6.5), mobilizes similar zinc quantities like those taken by weak acids waters.

In case of rain waters (pH = 6.4 – 6.5) zinc quantity is reduced in majority of cases. It is observed a decreasing of zinc quantity from waters which meet pillared materials. In this case, taken zinc is 3 times less then for soil treated with pillared material and 2-2.5 times for soil treated with Al_n polimeres, in case of water with increased acidity.

For percolation study e.g. water with pH = 6.5, decreasing of mobilizing metal in the case of treatment with pillared materials was 4-10 times, comparatively with soil treated with tuff, but in case of treatment with Al polymers, Zinc quantity decreasing from percolating waters was about 20-40 times.

TABLE 3. Total Zinc quality and fraction F1 from polluted soil and treated with amending agent.

Sample	Soil deep [cm]	Total quantity [mg Zn/kg S.U]	Mobil Zn quantity F 1		Medium mobile Zn* quality *	
			[mgZn/kgS.U[	[%]	[[mgZn/S.U.]	[%]
PBA(Cl^-)	Level 0	97,5	8,64	8,4	5,6	5,6
	Level 25	103,4	2,6	2,4		
PBA(NO_3^-)	Level 0	154	12,0	8	8,2	6,0
	Level 25	118,4	4,4	4		
Tuf-Na	Level 0	113,0	4,8	4	5,1	4,1
	Level 25	133,6	5,6	4,2		
Tuf -Al_n(Cl^-)	Level 0	237	21,6	8,6	15,6	8,2
	Level 25	139	9,8	7,5		
Tuf -Al_n(NO_3^-)	Level 0	147	14,4	10	13,2	10,2
	Level 25	112	12,0	10,3		
PBA(Cl^-)	Level 0	321	62	18,9	48,4	18,2
	Level 25	190	34,8	18,8		
Witness	Level 0	101	15,6	18,0	15,5	14,8
	Level 25	101	15,3	18,0		

*Medium quantity resulting from arithmetical mean of analyzed values at 0 and 25 level.

TABLE 4. Zinc mobilized quantity from 1-6 soils samples by percolating water with pH between 5.0-6,5.

Sample	Water 1 (distilled water) pH = 5,0		Water 2 (surface water) pH = 6,5		Water 3 (snow water) pH = 5,4		Water 4 (autumn water) pH = 6,4		Water 5 (autumn water) pH = 6,5	
	mgZn/ sample	%	mgZn/ sample	%	mgZn/ sample	%	mgZn/ sample	%	mgZn/ sample	%
PBA(Cl^-)	0,04	0,6	0,04	0,6	0,025	0,44	0,023	0,4	0,07	1,0
PBA(NO_3^-)	0,24	0,9	0,045	0,6	0,009	0,12	0,018	0,3	0,05	0,6
Tuf-Na	0,04	0,8	0,035	0,7	0,006	0,12	0,025	0,5	0,03	0,7
Tuf -Al_n(Cl^-)	0,06	0,4	0,035	0,25	0,004	0,026	0,025	0,16	0,02	0,13
Tuf -Al_n(NO_3^-)	0,07	0,5	0,05	0,4	0,002	0,015	0,019	0,15	0,023	0,17
PBA(Cl^-)	0,13	0,3	0,2	0,4	0,164	0,34	0,12	0,25	0,54	1,12
Witness	1,7	10,8	1,9	12,1	1,6	10,2	1,3	8,3	1,35	8,65

In *Table 5* are presents the pH variation of the waters used in percolated of soil from sample 1-6.

TABLE 5. pH-variation of percolated water for the soil who was treated by amendments.

Sample	Medium Quantity of Zinc - F 1 [mg Zn/kg dried soil]	Type of amendments	Water pH after percolation of 25 cm of soil				
			Water 1 $pH_{initial}$ 5	Water 2 $pH_{initial}$ 6,5	Water 3 $pH_{initial}$ 5,4	Water 4 $pH_{initial}$ 6,4	Water 5 $pH_{initial}$ 6,5
1	5,6	PBA (Cl^-)	5,1	6,1	6,3	6,2	6,2
2	8,2	PBA(NO3)	5,0	5,8	6,3	6,3	6,2
3	5,1	Tuf – Na	5,0	6,0	6,4	6,0	6,0
4	15,6	Tuf– Al_{13}(Cl)	5,4	6,1	6,1	6,1	6,0
5	13,2	Tuf–Al_{13}(NO_3^-)	5,1	5,9	6,5	6,3	6,0
6	48,4	PBA (Cl^-)	5,5	6,1	6,4	6,0	5,8

Due to buffered effects of used agents for treatment, at percolation with natural waters (surface and rain waters) of polluted and treated soil samples with reagents consisting of tuff and tuff - pillared with aluminium polymer salts, water pH after soil passing is 6 ± 0,5, a phenomenon which is not produced in case of distilled water.

4. Conclusions

The presence of natural pillared materials, consisting of native vulcanic tuff with aluminium polymer salts, decrease zinc quantity from percolating waters up to 10-40 times, comparatively with others materials used for treatment, in case of waters with pH = 6,5.

Synergic effect is strong for weak acid waters (pH = 5.0), when zinc mobility is reduced about 2.5 times comparatively with other treatments and more then 20 times comparatively with a polluted and untreated soil.

The presence of Al_n aggregates in soils polluted with metal decreases zinc ions mobility, adsorbed or interchangeble, in contact with rain waters at pH = 6,4.–6.5.

Pillared material, volcanic tuff containing 70 % clinoptilolite, in presence of soils polluted with zinc and exposed to rains, has a similar effect with that of Al_n polymer salts, to decrease zinc mobility from fraction of matrix which generates mobile ions.

Treatment agents which contain aluminium polymer salts, native volcanic tuff in form tuff – Na, and pillared materials have in study conditions, buffered effects for rain waters.

Zinc mobilizing phenomenon of some soil components are interdepedend both to amendments .nature and percolate water characteristcs.

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