

*Short Communication*

# The Binding of Heavy Metals and Arsenic in the Soil by [3-(2-Aminoethylamino)Propyl]Trimethoxysilane

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## Abstract

This paper describes the results of research concerning the binding of heavy metals and arsenic (HM+As) by [3-(2-Aminoethylamino)propyl]trimethoxysilane. The studies have been carried out on soils sampled from areas affected by emissions from the Głogów Copper Smelter and Refinery. The currently applied technique of soil stabilization of HMs by pH changing does not guarantee their permanent blocking in a sorption complex. The research aims to increase food safety in areas of industrial impact.

**Keywords:** nanotechnology, heavy metals, soil stabilization

## Introduction

Industry introduces into the environment various types of waste, whose composition and properties correspond to technological processes. The waste is usually discharged into all environmental media, i.e. air, soil, and water. This also applies to the processing of copper, realized in Głogów and Legnica Copper Smelter and Refinery. These smelters reproduce national sulfide ore. At the stage of pyrometallurgical ore processing, mainly dust waste materials are generated, while at a later stage of process gas cleaning, waste gas and liquids are produced. Dust emissions are metal oxides from a processed concentrate, while gas emissions are mostly sulfur oxides and significantly lower amounts of mist and droplets of sulfuric acid. Finally, liquid wastes are acidic scrubber liquids resulting in a purification of process gas and electrolytic acids resulting in a copper electrolytic refining process. Limit values of these wastes are defined in the integrated permit. Dust emission

is alkaline, while gas emission is strongly acidic and is responsible for the dynamics of (HM and As) release in the soil environment.

Heavy metals remain in the soil for a very long time, thus their presence in humus-arable land is particularly dangerous. These metals have toxic effects on soil microorganisms, and have a negative impact on soil properties and its agricultural usefulness. They contribute to the reduction of species diversity of soil microorganisms, resulting in a decrease in the amount of produced enzymes. It is a direct cause of the decline of soil fauna and a deterioration of soil fertility as a result of interference of organic matter mineralization and a degradation of soil structure and permeability.

Since the areas of industrial influence are large, one cannot use any method of reclamation and rehabilitation of these areas. The most common method to reduce the mobility of heavy metals in soils is chemical stabilization of soil acidity. This method leads to the conversion of heavy metals into sparingly soluble hydroxides [1-3]. However, the use of this technique does not give a full guarantee of food safety due to changes in acidic-basic equilibrium of a soil

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Table 1. The methods of extraction and forms of occurrence of heavy metals in soils.

Fraction	Form of HM occurrence	Extraction method
F1	Exchangeable metals	10 cm <sup>3</sup> 1M CH <sub>3</sub> COONH <sub>4</sub> (pH=7), shaking time 1 h, temp. 20°C
F2	Metals associated with carbonates	20 cm <sup>3</sup> 1M CH <sub>3</sub> COONa acidified by CH <sub>3</sub> COOH to pH=5, shaking time 5 h, temp. 20°C
F3	Metals associated with hydrated oxides of Fe and Mn	20 cm <sup>3</sup> 0.04M NH <sub>2</sub> OH·HCl dissolved in 25% CH <sub>3</sub> COOH, shaking time 5 h, temp. 95°C
F4	Metals associated with organic matter	5 cm <sup>3</sup> 0.02 M HNO <sub>3</sub> +5 cm <sup>3</sup> 30% H <sub>2</sub> O <sub>2</sub> (pH=2), shaking time 2 h, temp. 85°C
		5 cm <sup>3</sup> 30% H <sub>2</sub> O <sub>2</sub> (pH=2), shaking time 3 h, temp. 85°C
		10 cm <sup>3</sup> 3.2 M CH <sub>3</sub> COONH <sub>4</sub> in 20% HNO <sub>3</sub> , shaking time 0.5h, temp. 20°C
F5	Metals associated with aluminosilicates	3 cm <sup>3</sup> 10 M HNO <sub>3</sub> +3×2 cm <sup>3</sup> H <sub>2</sub> O <sub>2</sub> , shaking time 1h + 10 cm <sup>3</sup> H <sub>2</sub> O, shaking time 0.5 h, boiling temp.

sorption complex, which is caused by a progressive increase of soil acidification. Such a tendency indicates a need for continuous monitoring of these areas and taking of appropriate agricultural treatments, leading to a stabilization of pollutants in forms unavailable to plants. The disadvantage of this technique is the limited application of some crops in these areas.

The introduction of integrated crop production and sustainable agriculture in areas affected by the industrial impact requires searching of opportunities for permanent bonding of heavy metals and arsenic in the soil. The use of agents binding metal impurities permanently will allow the proper rehabilitation of these areas, as well as restoration of food safety cultivated under specific conditions. Such solutions are possible by using nanotechnology in an agricultural environment [4-6].

### Experimental Procedures

The soil for the research studies was sampled from the impact zone of Głogów Copper Smelter and Refinery [7]. The soil was screened in order to remove solid impurities, and dried at 105°C to constant weight (soil moisture content below 0.5%). In dried and ground soil the total content of heavy metals and arsenic was determined by atomic absorption spectroscopy (AAS) after extraction with 65% HNO<sub>3</sub> [8] – Table 1. The effectiveness of binding of heavy metals and arsenic by [3-(2-Aminoethylamino)propyl] trimethoxysilane (Fig. 1) has been studied. The conditions of the research studies have been as follows: sample weight of about 25.0±0.1 g, nano-agent concentration in a solution

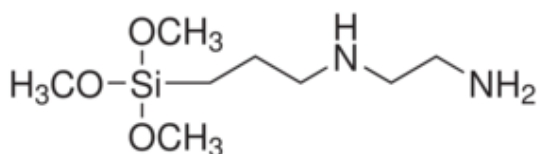


Fig. 1. Structural formula of [3-(2-Aminoethylamino)propyl] trimethoxysilane.

0.1% and 0.5%, volume of dosing nano-agent solution – 2.5 cm<sup>3</sup>, soil moisture after nano-agent introduction – 16%. The method of sample preparation: a measured volume of the agent solution was mixed thoroughly with soil and left for 4 days. The sample was mixed every day and the moisture content was maintained constantly. The reference sample (“0” sample) without nano-agent also was prepared. The soil samples were exposed to five-step Tessier sequential extraction, using for the same soil sample stronger and stronger extractants [9]. The speciation studies were limited to four sequentially defined fractions according to Table 1 and a determination of their metal content [10]. The last fraction of this method consists of metals bonded with aluminosilicates. This fraction is unavailable for plants because it requires radical agents (10 M HNO<sub>3</sub> at boiling point) to release metals.

For the sequence analysis 1.000±0.001 g of the soil sample was weighed. The individual steps of extraction were carried out in glass centrifuge tubes of 50 ml. The solution acidity was stabilized at each stage of the extraction process according to the methodology. The samples were shaken in a horizontal shaker with a thermostatic water bath having programmable temperature range from 20°C to 100°C (an accuracy of ±2°C). After each extraction step, the samples were centrifuged for 30 minutes. The supernatant was transferred to a calibrated polypropylene tube with a hermetic seal. The residual precipitate in a centrifuge tube was washed with demineralized water (5 ml) and centrifuged again for 30 minutes. The washings were pipetted and combined with the first portion of the extract. The content of heavy metals and arsenic in the solutions was determined. The solutions derived from the first three stages of the extraction were acidified with four drops of concentrated nitric acid(V). In order to determine heavy metals content in the extracts, flame absorption spectroscopy was used, while arsenic content determination used a hydride generation technique using sodium bromide and hydrochloric acid (Table 2).

On the basis of HM and As content in different fractions, the binding coefficients were calculated using equation 1 (Table 3):

Table 2. Heavy metals and arsenic content in different fractions of soil extracts.

Concentration of agent, %	F1				
	Cu	Pb	Zn	Cd	As
	mg/kg				
0	19.54	0.81	3.37	0.14	0.57
0.1	7.33	0.19	2.66	0.11	0.40
0.5	7.40	0.19	2.75	0.12	0.41
F2					
0	7.54	4.18	3.52	0.04	0.32
0.1	4.35	3.01	3.07	0.02	0.25
0.5	4.41	3.16	3.21	0.02	0.26
F3					
0	99.37	45.51	17.39	0.68	2.14
0.1	68.12	32.28	16.79	0.47	1.22
0.5	68.09	32.28	16.92	0.48	1.22
F4					
0	50.55	21.14	2.99	0.31	1.37
0.1	44.59	19.91	2.08	0.22	1.15
0.5	44.71	19.89	2.20	0.22	1.15
F5					
	64.76	24.25	7.03	0.62	3.52
(HM&As) <sub>total</sub>	242.12± 27.22	95.91± 21.51	34.30± 5.50	1.81± 0.06	7.93± 2.12

$$\eta = \frac{c_o - c_i}{c_o} \cdot 100 \quad (1)$$

...where:

- $\eta$  – binding coefficient of HM and As in a fraction  
 $c_o$  – HM content in a fraction in sample (0) without nano-agent  
 $c_i$  – HM content in a fraction in sample (i) with nano-agent

## Results and Discussion

Trialkoxysilanes having amine functional groups are bifunctional molecules characterized by strong chemical affinity to form complexes with metal ions and the ability to form stable covalent bond with inorganic matrices having hydroxyl groups (e.g. silica, sand). In our previous paper [11] the modification of silica surface with four aliphatic acyclic amines has been described. The organic layer differed in the number of nitrogen donor atoms and chain length. Taking into consideration several parameters (pH of the aqueous solution, the amount of modified silica,

stirring time, selectivity with respect to other metal ions), it was demonstrated that the systems studied showed excellent scavenging of copper ions with much weaker nickel ones from water solutions.

Another interesting observation has been made using modified silica containing poly(ethylene oxide) 4-arm, amine-terminated unit [12]. This support under optimal conditions showed the ability of copper extraction of the order of 90%, significantly greater than that of the other coexisting ions – nickel(II) [Ni(II)], cobalt(II) [Co(II)], and manganese(II) [Mn(II)]. It is a solvent-resistant matrix and it can be reused after a regeneration process (the recovery of copper(II) ions was about 97%).

The other supports suitable for copper extraction were more complex. The inorganic cores were (Fe, Co, Ni)-encapsulated carbon nanomaterials, which were coated with cyclam-bonded silica [13]. Again the parameters of extraction procedure were optimized with respect to several factors.

The effectiveness studies of heavy metals and arsenic binding in the soil from the impact zone of Głogów Copper Smelter and Refinery by [3-(2-Aminoethylamino)propyl]trimethoxysilane nano-agent have been carried out. The total content of heavy metals and arsenic in the soil was 242.12 (±27.22) mg Cu/kg, 95.91 (±21.51) mg Pb/kg, 34.30 (±5.50) mg Zn/kg, 1.81 (0.06) mg Cd/kg and 7.93 (±2.12) mg/kg As (Table 2). Whereas copper content in extracts from four soil fractions (F1-F4, Table 1), without nano-agent addition was 177.30 mg/kg, lead – 71.63 mg/kg, zinc – 27.27 mg/kg, cadmium – 1.14 mg/kg and 4.40 mg of As/kg (Table 2). The remaining amount of the metals was permanently bound in fraction F5, which was unavailable to plants. The copper content in this fraction was 64.76 mg/kg (26.75%), lead – 24.26 mg/kg (25.30%), zinc – 7.03 mg/kg (20.50%), cadmium – 0.62 mg/kg (34.19%), and 3.52 mg of As/kg that was 44.45% of the total content in the soil (Table 2, Fig. 2). The average content of impurities associated with aluminosilicates was about 30.24% of the total content of HM and As in the soil.

The studies of heavy metal and arsenic content in the extracts after the addition of 0.1% solution of [3-(2-Aminoethylamino)propyl]trimethoxysilane (2.5 ml) have shown different degrees of permanent bonding of impurities in the individual fractions (Fig. 3). Copper was the most

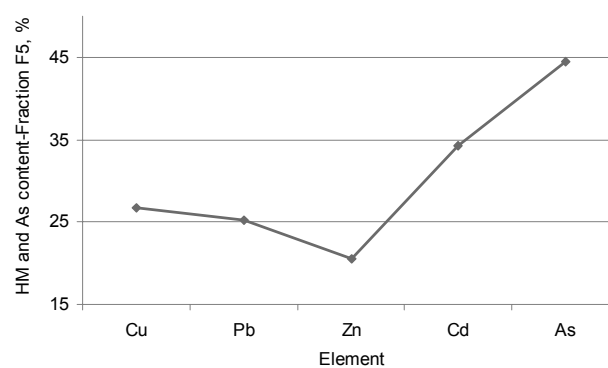


Fig. 2. HM and As content in fraction F5 associated with aluminosilicates and unavailable for plants.

Table 3. The binding coefficients (HM and As) in different fractions of soil extracts.

Binding	$\eta$ , %							
	F1		F2		F3		F4	
Fraction	0.1	0.5	0.1	0.5	0.1	0.5	0.1	0.5
Concentration of agent (%)	0.1	0.5	0.1	0.5	0.1	0.5	0.1	0.5
Cu	62.47	62.13	42.27	41.44	31.44	31.48	11.78	11.55
Pb	76.66	76.08	27.88	24.24	29.05	29.06	5.80	5.91
Zn	21.02	18.29	12.66	11.64	3.44	2.70	30.27	26.29
Cd	24.12	19.21	40.90	39.88	31.24	29.55	27.15	27.63
As	29.29	27.90	21.81	18.01	42.51	42.48	15.49	15.41

strongly bounded in fraction F1 (Fig. 3). In the following fractions, the binding efficiency of copper decreases gradually and was lowest in fraction F4. The decrease of the effectiveness of copper binding in fractions F1-F4 is almost linear. Copper binding coefficient was 62.47% in fraction F1, 42.27% in F2, 31.44% in F3, and lowest (11.78%) in F4. The similar tendency was observed for lead, which was the most strongly bound in fraction F1 (Fig. 3). The binding effectiveness steadily decreased in subsequent fractions and was the weakest for fraction F4. The lead binding coefficient was 76.66% in fraction F1, which was even higher than the one for copper. In the case of F2 and F3 the binding coefficients were similar and were 27.88% (F2) and 29.05% (F3), while for F4 – only 5.80% (the lowest value). Zinc was bound differently in the individual fractions. The strongest binding was observed for fraction F4 (30.27%). The binding coefficient for fraction F1 was 21.02% and it decreased in subsequent fractions to reach the smallest value for F3 (3.44%).

A quite different binding nature was observed for cadmium. The highest value was obtained for fraction F2 (40.90%), while the lowest for F1 (24.12%). In the case of fractions F3 and F4, the binding coefficients were 31.24% (F2) and 27.15% (F3). Arsenic demonstrated the highest coefficient in fraction F3 (42.51%), while the lowest for F4 (15.49%). In the cases of fractions F1 and F2, the coefficients were 29.29% (F1) and 21.81% (F2).

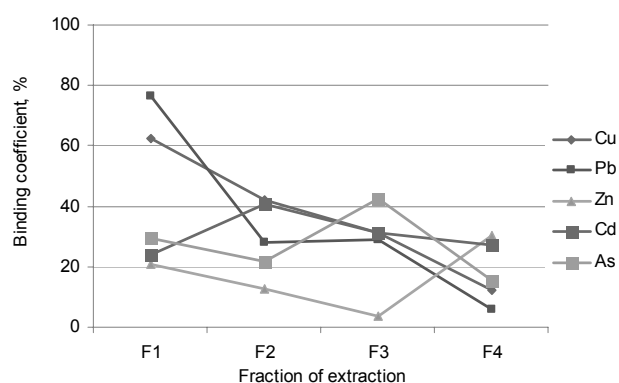


Fig. 3. The binding coefficients of HM and As in individual soil fractions.

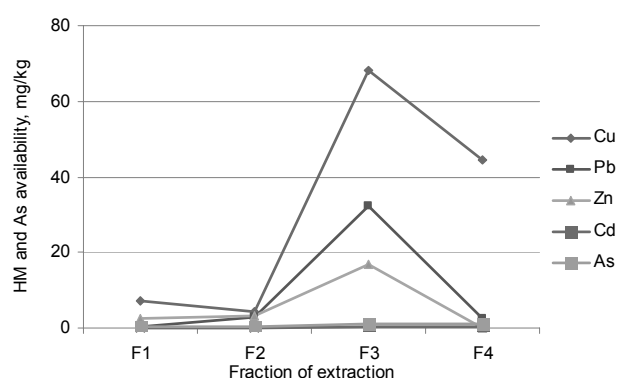


Fig. 4. The availability of HM and As in the individual fractions.

The determination of a retention factor is very important in determining availability and bioavailability of these pollutants by plants. This is essential in the development of agricultural treatments for the areas of the influence of Głogów Copper Smelter and Refinery. Knowledge of the binding coefficients allows us to estimate the scale and mechanism of crop threats by determination of the content and availability of individual metals in a soil solution (Fig. 4). In some parts being in the area of influence of Głogów Copper Smelter and Refinery may be deposited about 382 mg HM+As/kg in the soil. In the fractions available for plants there are about 282 mg HM/kg (approximately 177 mg Cu/kg, 72 mg Pb/kg, 27 mg Zn/kg, 1 mg Cd/kg and 5 mg As/kg). The rest of harmful deposits is not available for plants. Its release requires radical chemical conditions that are not the soil conditions. The use of [3-(2-Aminoethylamino)propyl]trimethoxysilane nano-agent can permanently reduce the availability to plants of all studied contaminants by about 29.4%, i.e. up to about 208 mg/kg (approximately 124 mg Cu/kg, 55 mg Pb/kg, 25 mg Zn/kg, 1 mg Cd/kg, and 3.0 mg As/kg).

The best average binding in four studied fractions by the nano-agent was as follows: for copper (37.12%), lead (34.85%), cadmium (30.85%), arsenic (27.28%), and zinc (16.85%).

The studies demonstrated that increasing the concentration of the nano-agent from 0.1% to 0.5% had no significant

Table 4. The binding coefficients (HM and As) in different fractions of soil extracts for 3-Aminopropyltrimethoxysilane (P1) [6] and [3-(2-Aminoethylamino)propyl] trimethoxysilane (P2). The concentration of nano-agent in the soil is 0.1%.

Binding	$\eta$ , %							
	F1		F2		F3		F4	
Fraction	P1	P2	P1	P2	P1	P2	P1	P2
Cu	48.00	62.47	28.69	42.27	19.08	31.44	11.33	11.78
Pb	48.55	76.66	19.88	27.88	11.43	29.05	1.81	5.80
Zn	9.41	21.02	13.18	12.66	1.36	3.44	29.89	30.27
Cd	12.48	24.12	25.97	40.90	28.28	31.24	24.44	27.15
As	18.47	29.29	11.47	21.81	12.89	42.51	4.48	15.49

effect on the binding efficiency of heavy metals and arsenic – Tables 2 and 3. Slight differences in the coefficients (Table 3) were in the range of measurement error.

The [3-(2-aminoethylamino)propyl]trimethoxysilane (P2) is characterized by better binding properties of these durable impurities than previously tested 3-aminopropyltrimethoxysilane (P1) [6] (Table 4 and Fig. 5). The average percentage of permanent bonds contaminants tested was about 30%, and 3-aminopropyltrimethoxysilane was about 19%. The P2 is approximately 2.3 times, more efficient than P1 is bound in arsenic.

### Conclusions

- [3-(2-Aminoethylamino)propyl]trimethoxysilane nano-agent demonstrated a good efficiency of Cu, Pb, Zn, Cd, and As binding in the soil.
- The tested preparation showed different binding efficiency of the individual elements depending on their form in the soil.
- The highest percentage of binding by [3-(2-Aminoethylamino)propyl]trimethoxysilane was observed for copper and lead, and the lowest for zinc.
- Increasing the concentration of the nano-agent in the range of 0.1 and 0.5% does not affect the percentage of binding of heavy metals and arsenic.

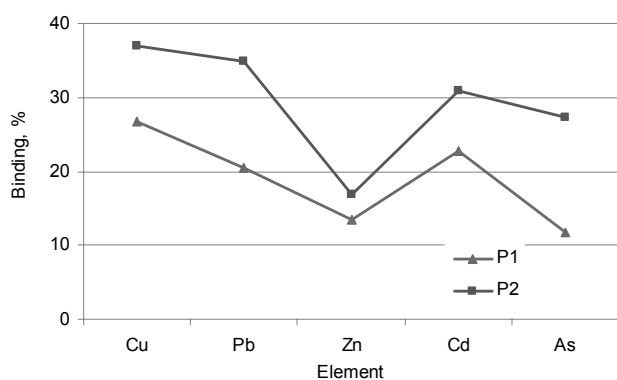


Fig. 5. The effect of HM and As binding in the soil depending on the nano-agent. P1 – 3-Aminopropyltrimethoxysilane, P2 – [3-(2-Aminoethylamino)propyl]trimethoxysilane.

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