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Heavy metals leachability before, during and after composting of sewage sludge with natural clinoptilolite

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ABSTRACT

Environmental problems associated with sewage sludge disposal have prompted strict legislative actions over the past years. At the same time, the upgrading and expansion of wastewater treatment plants have greatly increased the volume of sludge generated. The major limitation of land application of sewage sludge compost is the potential high heavy metal content in relation to the metal content of the original sludge. Composting of sewage sludge with natural zeolite (clinoptilolite) can enhance its quality and suitability for agricultural use. The aim of the article is to examine the leachability of the heavy metals before, during and after the composting process of sewage sludge and clinoptilolite. The natural zeolite, clinoptilolite has the ability to uptake heavy metals in satisfactory levels. In order to estimate the metal leach ability of the final product of compost, the generalized acid neutralization capacity (GANC) procedure was used, and was found that by increasing the leachate pH, the heavy metal concentration decreases.

Keywords: Sewage sludge composting; Metals uptake; Natural zeolite; Clinoptilolite; Metal leachability

1. Introduction

The mineralization of biogenic substances is a part of the natural recycling processes, which occurs at any place where organic material is synthesized by plants and degraded by animals and microflora. Environmental problems associated with sewage sludge disposal have prompted legislative actions. At the same time, the upgrading and expansion of wastewater treatment plants have greatly increased the volume of sludge generated. The sludge is classified as difficult solid wastes that require special arrangements for disposal, because of their noxious properties.

Composting sewage sludge is being increasingly considered by many municipals throughout the world because it has several advantages over other disposal strategies. Firstly, composting can reduce the waste volume by 40–50% v/v and thus requires less land field space for disposal [1]. Secondly, pathogens can be killed due to the heat generated during the thermophilic phase [1–3]. Lastly, compost is established and can be used as a soil conditioner of resources containing in sludge. It contains major plant nutrients, such as N, P and K; micro-plant nutrient such as Cu, Fe and Zn and organic matter for improving the physical

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properties in order to have better soil aeration and water holding capacity [1,4].

At present the zeolite group includes more than 40 naturally occurring species, and is the largest group of minerals among the silicates. Before 1960s, zeolite minerals were thought to be mainly distributed in hydrothermal veins and geodes in basalts, andesites and other volcanic rocks [5,6]. Zeolite in such settings forms large, well-shaped crystals and druses. Due to the usual small size of veins and because of poly-minerality, these deposits have no practical importance, but samples of vein origin have been used to establish the properties of the mineral and the possibility of their utilization in industry [6]. In the decades of 1980s more than 300,000 t of natural zeolites were used in world market (150,000 t in Europe and 90,000 in Japan) and the most common zeolites were: clinoptilolite, mordenite, phillipsite and chapazite. Zeolite minerals are known to distribute rather unevenly in nature. Clinoptilolite, mordenite, phillipsite, chapazite, stilbite, analcime and laumontine are very common whereas offretite, paulingite, barrerite and mazzite, for example, are much rarer, and sometimes limited to single occurrences [6].

According to Zorpas [7], Tsitsishvili [6], zeolites can be used as structurally materials, in paper industry, to improved soil properties, in the animal feeds industry, in wastewater treatment plants, for the cleaning and improve the properties of the drinking water, for metal removal, etc.

The major limitation of land application of sewage sludge compost is the potential high metals contents related to the metal contents of the original sludge and the degree of dilution by the bulking agent for composting. However, much of the sludge originating from urban wastewater treatment is contaminated with heavy metals [8–13]. Theses metals, may be leached from the sludge's and enter the ecosystem, the food chain and finally the human population. Also the determination of total concentration of heavy metals cannot provide useful information about the risk of bioavailability, toxicity and the capacity for remobilization of heavy metals in the environment [14–16].

The nature zeolite, clinoptilolite has the ability to uptake those metals [17]. Zeolites have been worldwide for the last decades, either for their cation exchange or molecular sieving properties. Natural zeolites nowadays are mostly used in catalysis, in air enrichment, as filers in paper and rubber industry, in soil beneficiation, as animal feed supplements, and in water and wastewater treatment for the ammonia and heavy metal removal [18,19].

The aim of this study is to determine the leachability of the heavy metals (Cd, Cr, Cu, Fe, Mn, Ni, Zn, Pb), in the raw sludge, during the composting process and in the final compost products when natural zeolite is used in order to take up the heave metals.

Table 1
Chemical analysis of clinoptilolite

Component	Mean value of 20 samples	
	mol/100 g	% W/W
SiO_2	1.151 ± 0.025	69.396 ± 0.660
Al_2O_3	0.112 ± 0.001	11.551 ± 0.045
Fe_2O_3	0.002 ± 0.0002	0.384 ± 0.016
Na_2O	0.080 ± 0.001	4.980 ± 0.027
H_2O	0.495 ± 0.005	8.955 ± 0.039
K_2O	0.028 ± 0.002	2.753 ± 0.086
CaO	0.035 ± 0.002	1.981 ± 0.049
Total		100

2. Materials and methods

2.1. Sewage sludge collection

Dewatered anaerobically stabilized primary sewage sludge (DASPSS) was collected from the Psittalia wastewater treatment plant in Athens. The samples were air-dried at room temperature and prepared in order to determine the heavy metals contents (Cd, Cr, Cu, Fe, Mn, Ni, Pb and Zn). The natural zeolite, clinoptilolite was collected from Evros (region in northern Greece) and analyzed for chemical composition (Table 1). The above analysis gives an ion-exchange capacity of 1.70 meq/g. In order to observe the effect of the zeolite and how the metal content of the final products vary, a range of 0–30% clinoptilolite was applied to the DASPSS (Table 2).

Table 2
Prepared samples for composting

Sample	Clinoptilolite (%)	DASPSS (%)[a]
Ao	0	100
A1	5	95
A2	10	90
A3	15	85
A4	20	80
A5	25	75
A6	30	70

[a] DASPSS, dewatered anaerobically stabilized primary sewage sludge.

Table 3
Metals content in DASPSS and compost

Metal[a]	Cured compost[b]							
	DASPSS	A0	A1	A2	A3	A4	A5	A6
Cd	0.002 ± 0.0005	0.002 ± 0.0001	nd[c]	nd	nd	nd	nd	nd
Cr	0.552 ± 0.025	0.578 ± 0.023	0.552 ± 0.023	0.550 ± 0.023	0.542 ± 0.020	0.501 ± 0.024	0.488 ± 0.025	0.478 ± 0.025
Cu	0.258 ± 0.005	0.205 ± 0.005	0.265 ± 0.006	0.184 ± 0.006	0.181 ± 0.004	0.172 ± 0.004	0.163 ± 0.006	0.140 ± 0.007
Fe	5.098 ± 0.310	4.118 ± 0.225	3.963 ± 0.170	3.838 ± 0.125	3.217 ± 0.125	3.191 ± 0.150	2.999 ± 0.150	2.673 ± 0.100
Ni	0.041 ± 0.003	0.045 ± 0.003	0.040 ± 0.002	0.038 ± 0.001	0.038 ± 0.001	0.034 ± 0.001	0.019 ± 0.002	0.018 ± 0.001
Mn	0.150 ± 0.003	0.168 ± 0.005	0.150 ± 0.003	0.149 ± 0.003	0.139 ± 0.002	0.136 ± 0.003	0.136 ± 0.002	0.114 ± 0.001
Pb	0.326 ± 0.004	0.335 ± 0.004	0.199 ± 0.004	0.187 ± 0.003	0.178 ± 0.002	0.177 ± 0.003	0.157 ± 0.004	0.145 ± 0.005
Zn	1.739 ± 0.028	1.801 ± 0.030	1.400 ± 0.045	1.216 ± 0.037	1.117 ± 0.040	1.083 ± 0.035	1.027 ± 0.025	0.938 ± 0.027

[a] mg/g dry sludge; zeolite has been removed from the final products.
[b] Mean value of 20 samples ± standard deviation.
[c] nd, not detected.

2.2. Composting process

The composting process was carried out in the Laboratory using an In-Vessel reactor of 50 L activated volume, and according to the Rutgers Strategy [3,7]. According to the Rutgers Strategy the thermophilic phase in the reactor lasted for 15 days, the temperature was set to approximately 60–65 °C in the center of the reactor and the moisture was in the range of 40–50%. After the thermophilic period in which the organic material was biodegraded, the compost was piled into an enclosed package where it remained for about 4 months to mature.

Twenty grams of compost samples were taken from the reactor on the 5th day, on the 15th, and on the 30th day and at the final stage 150 of maturity, in order to estimate the leachability of the heavy metals Cd, Cr, Cu, Fe, Mn, Ni, Pb and Zn.

2.3. Methods of analysis

For the determination of total metal concentration, a known quantity (1 g) of sample was digested with 10 mL of conc. HNO_3 and 2 mL of conc. H_2SO_4 as described by Zorpas et al. [20]. After the completion of the digestion, the samples were vacuum filtered and the filtrate was used for the determination of heavy metal concentration by atomic absorption spectroscopy, using a Perkin Elmer 2380 spectrophotometer (Norwalk, Connecticut, USA).

The generalized acid neutralization capacity (GANC) test procedure was used for the estimation of the leachability of metals from the sludge and compost samples [7,21]. This test is a single batch procedure that utilizes a series of sludge samples extracted with increasingly acidic leachant. A known quantity (1 g) of sludge sample is placed in a series of 100 mL polyethylene bottles. Twenty milliliters of liquid is added to each bottle. A declining amount of distilled water is added to each bottle followed by an increasing amount of 2 N acetic acid. This process produces a series of bottles containing increasing equivalents of acid per kilogram of samples but the same total liquid volume (20 mL). The mixtures were tumbled in rotating extractors for 48 h and then were let to stand for 15 min. Following, in the supernatant the pH was measured and the metal concentrations were determined by atomic absorption spectroscopy, using a Perkin Elmer 2380 spectrophotometer, (Norwalk, Connecticut, USA). Leachants strength starts out at the 0 equivalents of acetic acid and is increased until pH is below 5 for three consecutive equivalents.

It is important to know that, for the characterization of all the compost samples the zeolites have been removed from the final products.

3. Results and discussions

Table 3 presents the metal content in DASPSS and in the final compost products. When comparing the metal content of the Ao, sewage sludge compost with no zeolite and DASPSS sample, it may be observed that the concentration of chromium, nickel, manganese, lead and zinc appeared increased while that of copper and iron decreased. Composting can concentrate or dilute the heavy metals present in sewage sludge. This change in metal concentration depends on the metal loss through leaching and on the overall concentration of metals due to organic matter destruction [22]. As it is observed, in Table 3, natural clinoptilolite has the ability to exchange sodium and potassium. It is also clearly seen that with the increasing amount of zeolite the

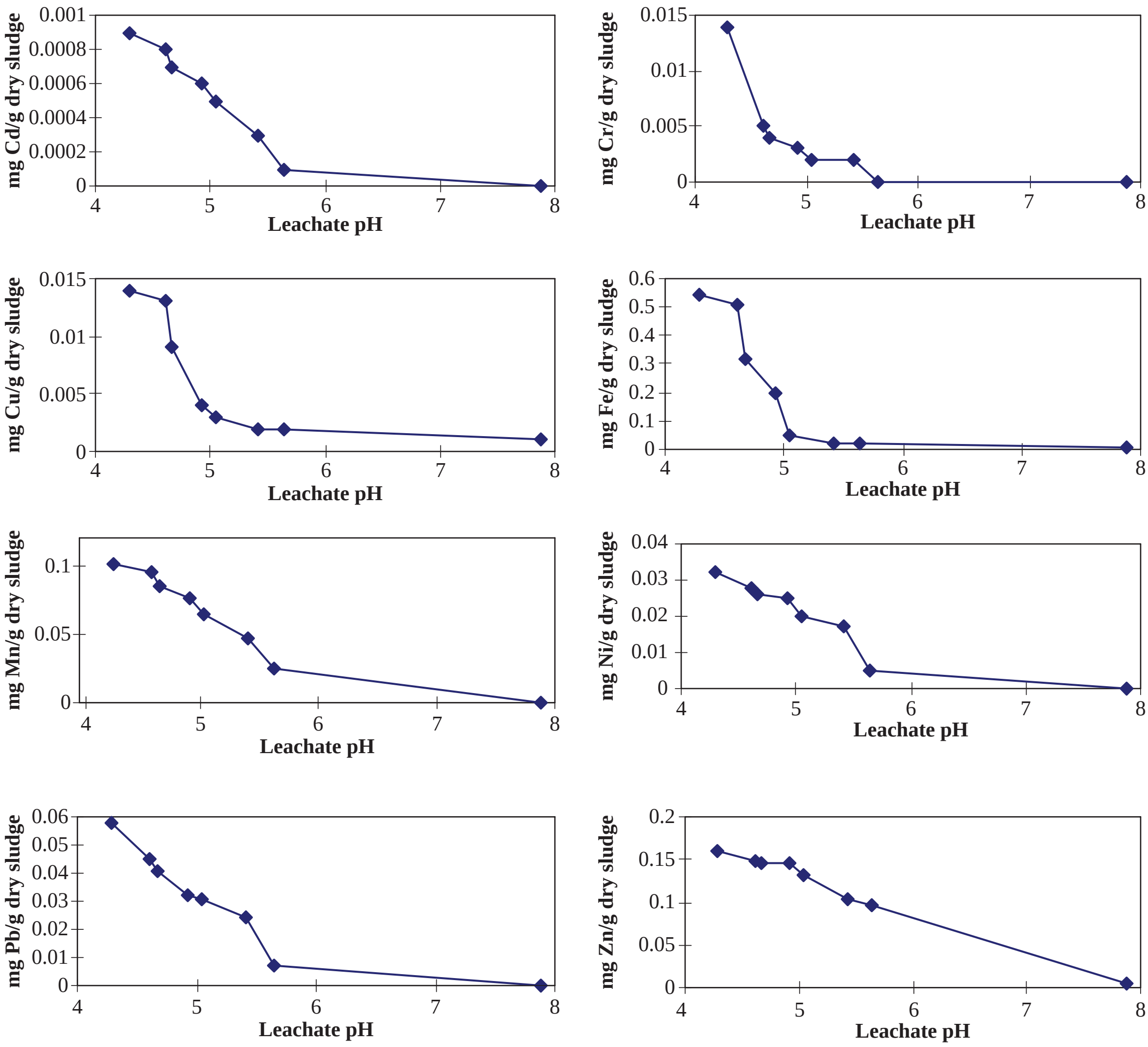

Fig. 1. Generalized acid neutralization capacity (GANC) metals releases to leachates from primary sludge samples as a function of pH of leachate.

concentrations of all heavy metals content in the compost samples decreases while the concentration of sodium and potassium increases. It is seen that in samples A5 and A6 containing 25–30% of clinoptilolite maximum metal uptaken and specifically 28–45% of Cu, 10–15% of Cr, 41–47% of Fe, 100% of Cd, 9–24% of Mn, 50–55% of Ni and Pb and 40–46% of Zn.

The GANC test was applied in the raw sludge (DASPSS), in sewage sludge compost with no clinoptilolite (Ao) and in the A5 and A6 samples where maximum metal was uptaken, after the 5, 15 days (during the thermophilic phase), 30 days (during the mesophilic phase) and 150 days of maturity (final product).

Fig. 1 presents the metals leachability before the composting process (in raw materials). The GANC test results showed that by increasing the leachate pH, the heavy metals concentration in leachates was decreased. It was observed that at pH greater than 5 the metal amount in leachate was decreased. This phenomenon can be explained by the fact that, the metal load was not bound to the exchangeable and carbonate fractions [17].

Fig. 2a–g presents the metals leachability during the composting process for A5 compost sample. It is obvious that the zeolite has a different selectivity during the first 30 days of composting. This is due to the fact that, the pH during the composting process is initially low, due to the acid formation, then increases and in the final stage of the composting process remains constant. Also, due to the high temperature and the amount of moisture the mobile forms of the metals move faster.

However, it is obvious that zeolite seems to be constant for most of the metals after 15 days.

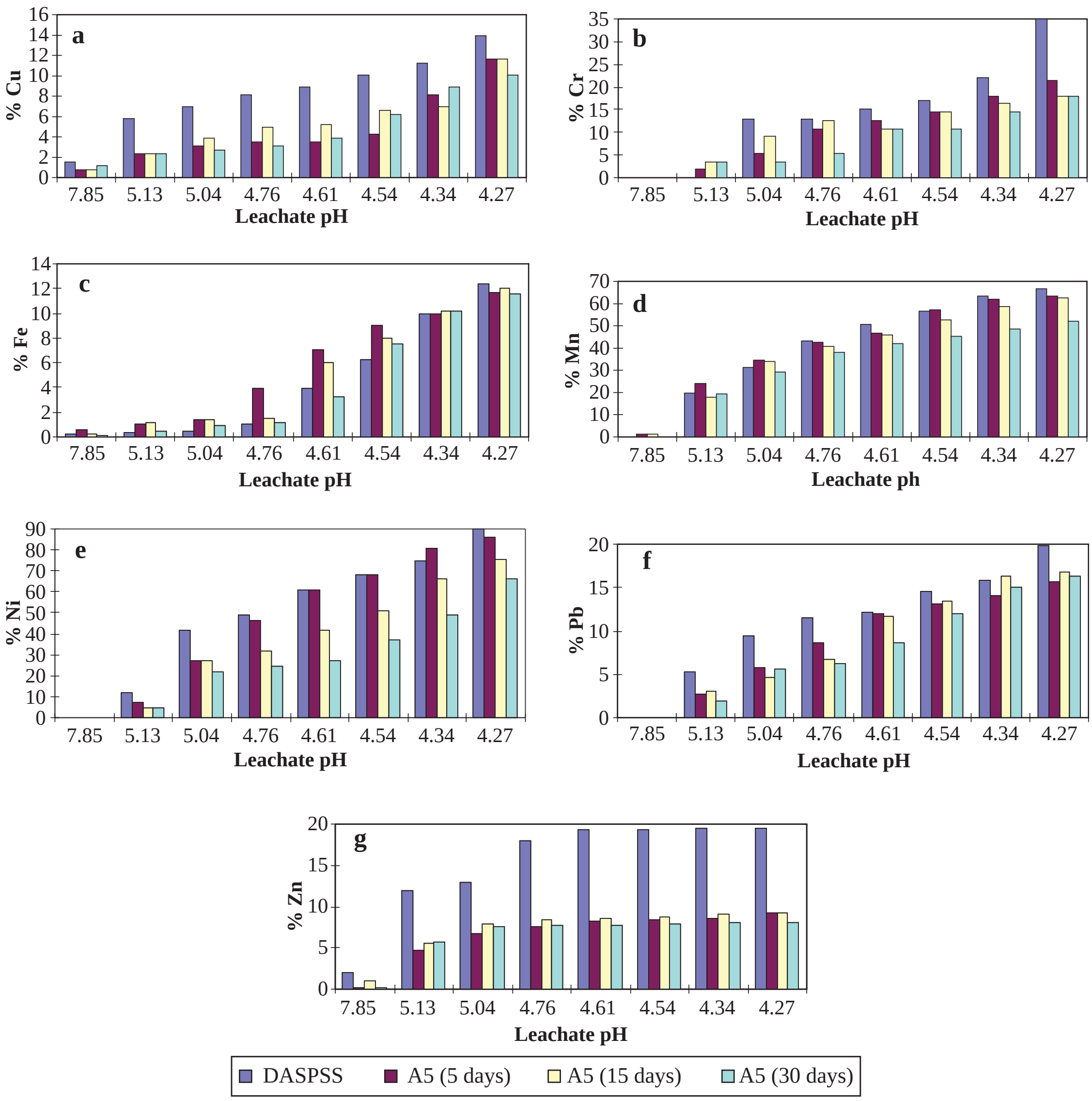

Fig. 2. GANC metals releases to leachates from A5 compost sample as a function of pH of leachate, during the first step of composting.

Fig. 3 shows that by increasing the leachate pH, a decrease to the heavy metal concentration is caused. According to Fig. 3 zeolite bounds a significant ($p < 0.05$) amount of heavy metals at pH lower than 4.5. Specifically zeolite bounds 100 % of Cd in A5 and A6 compost sample, 98% of Cr, 92–95% of Cu (A5 and A6, respectively), almost 90 % of Fe and Zn, 50–60% of Mn (A5 and A6, respectively), almost 50% of Ni, and 82–88% of Pb (A5 and A6, respectively).

4. Conclusion

The most significant problem for the use of composts produced from sewage sludge, for agricultural purposes, is the presence of the heavy metals. Heavy metals in small concentrations consist valuable trace elements for the plants' developments; in higher concentrations they become phytotoxic and toxic agents for the human health. Zeolites synthetic or natural ones have the ability to uptake heavy metals by ion exchange. According to this characteristic, while the amount of natural zeolite (clinoptilolite) increases the concentration of heavy metals decrease. It was found that 25–30% of clinoptilolite can uptake 28–45% of Cu, 10–15% of Cr, 41–47% of Fe, 100% of Cd, 9–24% of Mn, 50–55% of Ni and Pb and 40–46% of Zn. Using the GANC procedure was found that by increasing the leachate pH, the heavy metal concentration was

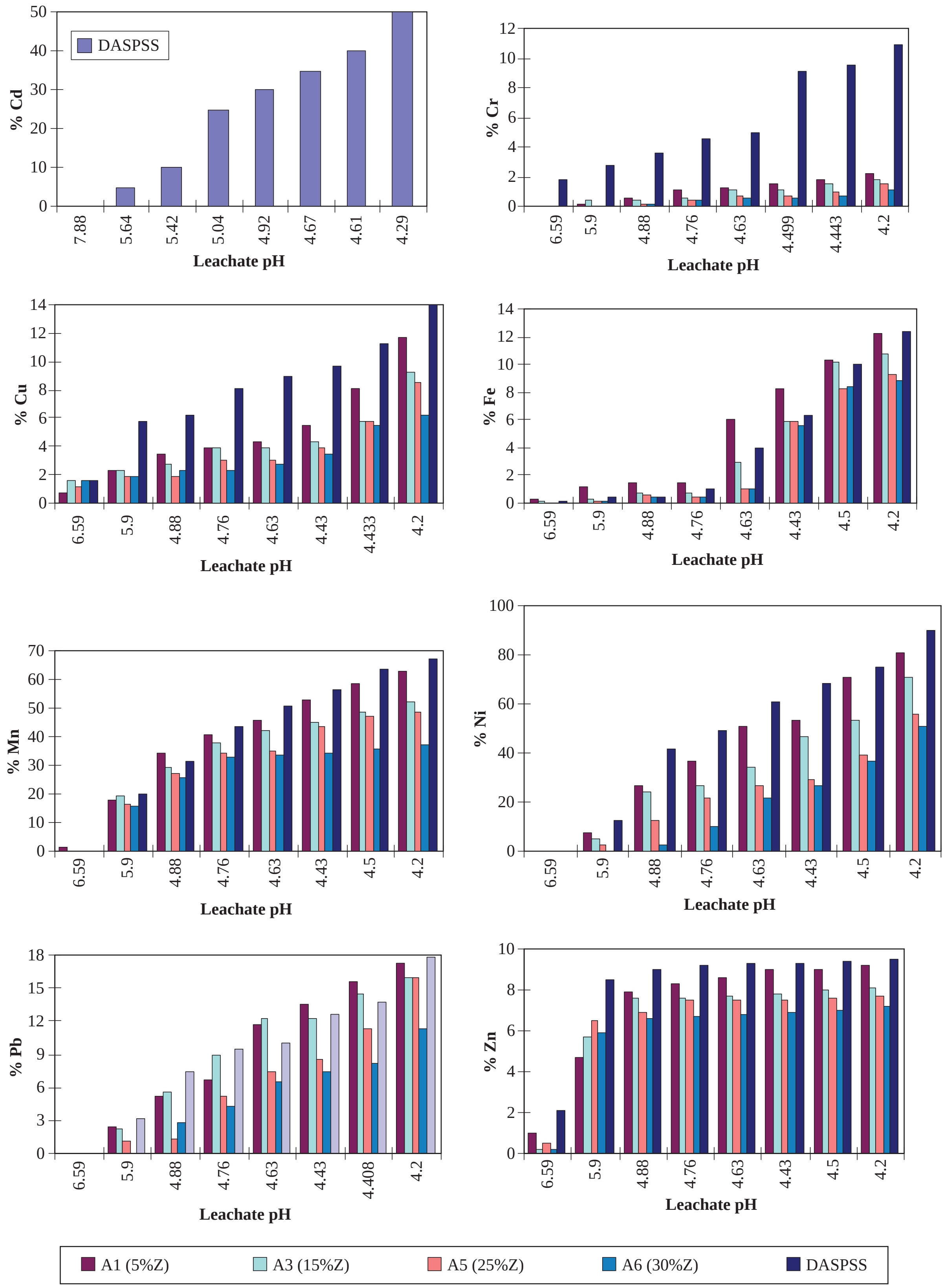

Fig. 3. GANC metals releases to leachates from A1, A3, A5 and A6 compost sample as a function of pH of leachate after from 150 days of maturity.

decreased. The GANC test procedure showed that in the case of toxic rain the zeolite had the ability to retain the heavy metals and not let them to pass in the ground water.

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