

Heavy metals fractionation before, during and after composting of sewage sludge with natural zeolite

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Abstract

The main limiting factor, in order to use compost in agriculture, is the total concentration of heavy metals. Natural zeolites, such as clinoptilolite, have the ability to take up and remove those metals by utilizing ion exchange. However, it is important to know about the fractionation of the heavy metals during the thermophilic phase and the maturation phase. The purpose of this work was to determine the changes in the fraction of heavy metals in sewage sludge compost in which clinoptilolite is used as a bulking agent to remove metals. The final result indicates that a significant ($p < 0.05$) percentage of the metals, which is not removed by the zeolite, is associated with the residual fraction which is considered as an inert form.

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1. Introduction

The management of sewage sludge is becoming increasingly difficult due to the presence of heavy metals. Natural zeolite is capable of removing quantities of cations from aqueous solution and from solid phase by utilizing the phenomenon of ion-exchange (Zorpas et al., 1999; Zorpas, 1999; Kesraoui Ouiki and Kavannagh, 1997). Clinoptilolite, for example, has received extensive attention due to its attractive selectivities for certain heavy metal ions such as Pb^{2+} , Zn^{2+} , Cd^{2+} , Ni^{2+} , Fe^{2+} and Mn^{2+} (Kesraoui Ouiki and Kavannagh, 1997).

At present the zeolite group includes more than 40 naturally occurring species, and is the largest group of minerals among the silicates. Before the 1960s, zeolite minerals were thought to be mainly distributed in hydrothermal veins and geodes in basalts, andesites and other volcanic

rocks (Helfferich, 1962; Tsitsishvili et al., 1992). Zeolite in such settings form large, well-shaped crystals and druses. Due to the usual small size of veins and because of polyminerality, 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 (Tsitsishvili et al., 1992). According to the bibliography prepared by Drzaj et al. (1985) in the decades of the 1980s, more than 300,000 tonnes of natural zeolites were used in world market (including 150,000 tonnes 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 are sometimes limited to single occurrences (Tsitsishvili et al., 1992).

According to Zorpas (1999), Tsitsishvili et al. (1992) and Drzaj et al. (1985), zeolites can be used as structural materials, in the paper industry, to improve soil properties, in the animal feeds industry, in wastewater treatment plants,

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for the cleaning and quality improvement of drinking water, for metal removal, etc.

This work deals with the behavior of heavy metals before, during and after sewage sludge composting with natural zeolite (clinoptilolite). In order to observe the behavior of the heavy metals, a Sequential Chemical Extraction (SCE) procedure was used. A wide variety of SCE schemes have been developed for the determination of heavy metal forms in sewage sludge (Lindau and Hossner, 1982; Pierce et al., 1982).

According to Tessier's scheme (Tessier et al., 1979), heavy metals are associated with five fractions:

- (a) the exchangeable fraction which is likely to be affected by changes in water ionic composition (e.g., in estuarine waters), as well as sorption–desorption processes,
- (b) the carbonate fraction that would be susceptible to changes of pH,
- (c) the reducible fraction that consists of iron and manganese oxides which are thermodynamically unstable under anoxic conditions,
- (d) the organic fraction that can be degraded leading to a release of soluble metals under oxidizing conditions,
- (e) the residual that contains mainly primary and secondary minerals, which may hold metals within their crystal structure. These metals are not expected to be released in solution over a reasonable time span under the conditions normally encountered in nature.

2. Materials and methods

2.1. Raw materials collection

In this study, Dewatered Anaerobically Stabilized Primary Sewage Sludge (DASPSS) was obtained from Psittalia's wastewater treatment plant (Rock Island in Saronic Gulf in Athens, Greece). At Psittalia, approximately 750,000 m³/day of municipal wastewater along with industrial wastes are subjected to primary treatment, producing approximately 250 tonnes/day of dewatered anaerobically stabilized primary sewage sludge (DASPSS) (Zorpas, 1999; Zorpas et al., 1998).

The natural zeolite, clinoptilolite, was collected from Evros (region in northern Greece); it has an ion-exchange capacity of 1.70 meq/g (Zorpas et al., 1999). In order to observe the effect of the zeolite and how the metal content of the final product varies, a range of 0–30% clinoptilolite (2.5–2.7 mm) was applied to the DASPSS (Table 1).

2.2. Composting process

The composting process was carried out in the laboratory using an in-vessel reactor of 1 m³ (active) volume (Zorpas, 1999; Finstein et al., 1992). An aeration system consisted of an air fan for air supply, an air flow meter

Table 1
Prepared samples for composting

Sample	Clinoptilolite, % w/w	DASPSS, % w/w
S0:	0	100
S1:	5	95
S2:	10	90
S3:	15	85
S4:	20	80
S5:	25	75
S6:	30	70

and an air humidity meter. A temperature indicator controller was used to control the operation of the fan in order to maintain the temperature at about 60 °C, according to the following principle: minimum air flow (2.3 m³ per m³ active volume) was provided at low temperature (<30 °C) and maximum air flow (28 m³ per m³ active volume) was provided at high temperature (>60 °C). The minimum air flow corresponds to the minimum oxygen demand for the micro-organisms and the maximum to the necessary air for cooling. The moisture was in the range of 40–50%. The thermophilic phase lasted for 15 days in the reactor. After the thermophilic period in which the organic material was biodegraded, the compost was placed in an enclosed vessel (package) where it matured for approximately 4 months.

2.3. Methods of analysis

For determining the total metal concentration, a known quantity (1 g) of sample was digested with 10 ml of conc. HNO₃ according to Zorpas et al. (1998). After the completion of the digestion, the samples were vacuum filtered and the filtrate was used for the determination of heavy metal concentration by flame atomic absorption spectroscopy, using a Perkin Elmer 2380 spectrophotometer.

The chemical forms of heavy metals were determined by the use of the sequential extraction procedure of Tessier et al., 1979. A known quantity (1 g) of each sample was treated with 1 M CH₃COONa for 1 h at room temperature and at pH 8.2 to extract the exchangeable phase; and 1 M CH₃COONa for 5 h at room temperature and at pH 5.0 to extract the carbonate phase. Using 0.04 M NH₂OH · HCl in 25% v/v CH₃COOH for 6 h at 96 °C, the fraction bound to Fe–Mn oxides was extracted. To extract the organic fraction 0.02 M HNO₃ and 30% w/v H₂O₂ was used for 2 h at 85 °C and pH 2.0, followed by the addition of 3.2 M CH₃COONH₄ in 20% w/v HNO₃ with 30% w/v H₂O₂ for 3 h at 85 °C. The final residue was digested with conc. HF and conc. HNO₃ for 1 h at room temperature to extract the residual fraction. Between each extraction, the samples were centrifuged (5000 rpm for 30 min) and filtered. The filtrate was used for the determination of heavy metal concentration by atomic absorption spectroscopy, using a Perkin Elmer 2380 spectrophotometer.

The linear range of analysis for each metal is 2.0 mg/l for Cd (sensitivity 0.028 mg/l), 5.0 mg/l for Cr (sensitivity

0.078 mg/l), 3.5 mg/l for Cu (sensitivity 0.12 mg/l), 5.0 for Fe (sensitivity 0.10 mg/l), 2.0 for Ni (sensitivity 0.14 mg/l), 2.0 mg/l for Mn (sensitivity 0.052 mg/l), 20.0 mg/l for Pb (sensitivity 0.028 mg/l), 1.0 for Zn (sensitivity 0.018 mg/l), 2.0 mg/l for K (sensitivity 0.043 mg/l), 0.50 mg/l Mg (sensitivity 0.0078 mg/l), and 1.0 mg/l for Na (sensitivity 0.012 mg/l).

For the characterization of all compost samples, the zeolites were manually removed from the final products using sieving (the diameters of the sieve were ≤ 2.3 mm). Also, three shambles for all the parameters were analyzed.

For the statistical analysis, Taylor's statistical techniques were used for data analysis and specifically the mean and 95% confidence interval (CI) (Taylor, 1990).

3. Results and discussion

Table 2 presents the results of the metal content in dewatered anaerobically stabilized primary sewage sludge (DASPSS) and in the final compost products. As expected, the total concentration of heavy metals increased during the composting procedure (Sample S0:

Table 2
Metals content in DASPSS and compost

Metals*	DASPSS	Compost ^a – final product after 150 days						
		S0	S1	S2	S3	S4	S5	S6
Cd	2	2	nd	nd	nd	nd	nd	nd
Cr	552	578	552	550	542	501	488	478
Cu	258	205	265	184	181	172	163	140
Fe	5098	4118	3963	3838	3217	3191	2999	2673
Ni	41	45	40	38	38	34	19	18
Mn	150	168	150	149	139	136	136	114
Pb	326	335	199	187	178	177	157	145
Zn	1739	1801	1400	1216	1117	1083	1027	938
K	723	772	772	902	965	1121	1215	1235
Mg	1132	796	786	738	695	620	589	538
Na	724	732	783	796	865	901	1011	1121

All value in dried matter, nd: not detected.

^a Significant different at $p < 0.05$.

* mg/kg dry sludge.

sewage sludge compost with no zeolite and DASPSS sample). The concentration of chromium, nickel, manganese, lead and zinc appeared to increase while that of copper and iron decreased. This result occurred mainly because of losses of mass that occurred during composting. This outcome is supported by a number of published papers (Garcia-Delgado et al., 1994; Wagner et al., 1990; He et al., 1992).

As observed in Table 2, natural clinoptilolite has the ability to exchange sodium and potassium. It is also clearly seen that with an increasing amount of zeolite, the concentrations of all heavy metals in the compost samples decrease, while the concentrations of sodium and potassium increase. It is seen that in samples S5 and S6 containing 25% and 30% of clinoptilolite (respectively), metal uptake is highest 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 sequential extraction procedure was utilized to the raw sludge, to the S0 cured compost and to the S5 (during and after the composting process).

The metal partitioning in the DASPSS sample, as determined by sequential chemical extraction, is shown in Figs. 1–7. A significant ($p < 0.05$) amount of Cr and Cu are bound to the organic and residual fractions with less than 2% in the exchangeable and the carbonate fractions. Almost 60% of Mn is bound to the reducible fraction. Iron and Pb were found to be bound in the reducible and residual fractions (about 95% for the Fe and 83% for the Pb). Only Ni and Zn were found in substantial proportions in all phases.

Comparing the results with the raw materials and the S0 cured compost (Figs. 1–7), it is evident that Cd, Fe and Zn are not affected during the composting process. Additionally, Cr seems to be transformed from the reducible fraction and the organic fraction to the residual fraction. The organic fraction of Cu changes to other fractions, especially residual and exchangeable. The residual fraction increased from 27.53% to 45.37% and exchangeable from 1.55% to 10.22%. Approximately, 72% of the Pb was found to be bound in the residual fraction. A substantial percentage

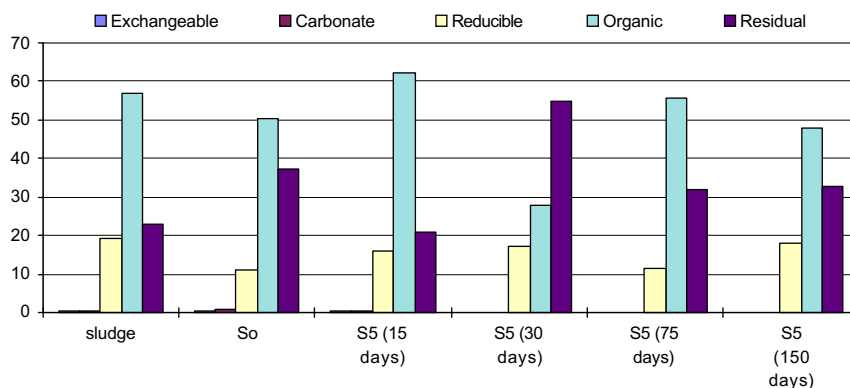


Fig. 1. Cr concentration before, during and after the composting process (%).

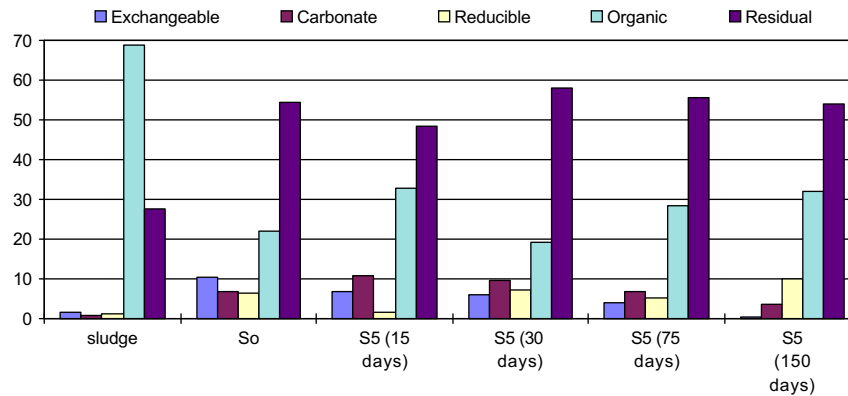


Fig. 2. Cu concentration before, during and after the composting process (%).

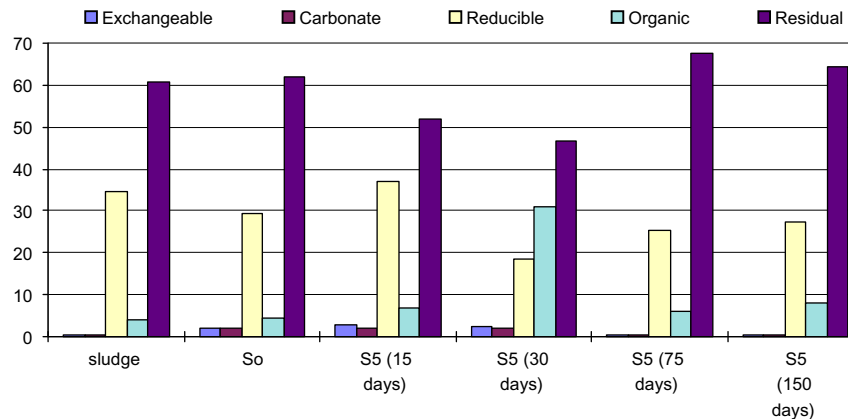


Fig. 3. Fe concentration before, during and after the composting process (%).

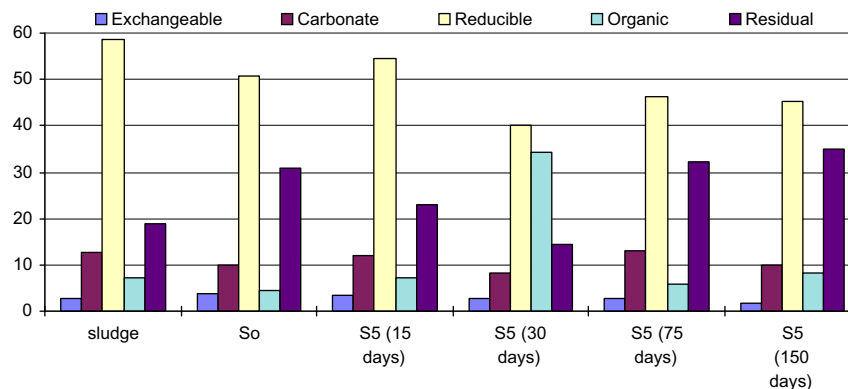


Fig. 4. Mn concentration before, during and after the composting process (%).

of Mn was removed from the reducible, carbonate and organic fractions and transferred to the residual fraction.

As observed in Figs. 1–7, zeolite has the ability to take up all of the metals content bound in the exchangeable and carbonate fraction. More specifically:

3.1. For Cr

In Fig. 1, the percentage of Cr is higher in organic phase during the thermophilic phase than the other fractions. After the thermophilic phase, Cr seems to be

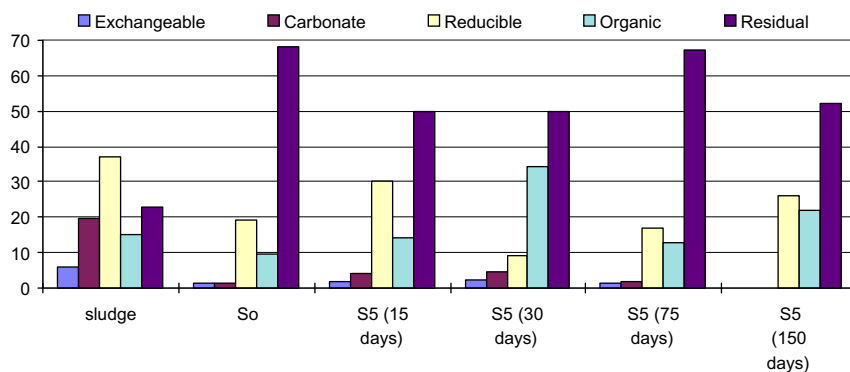


Fig. 5. Ni concentration before, during and after the composting process (%).

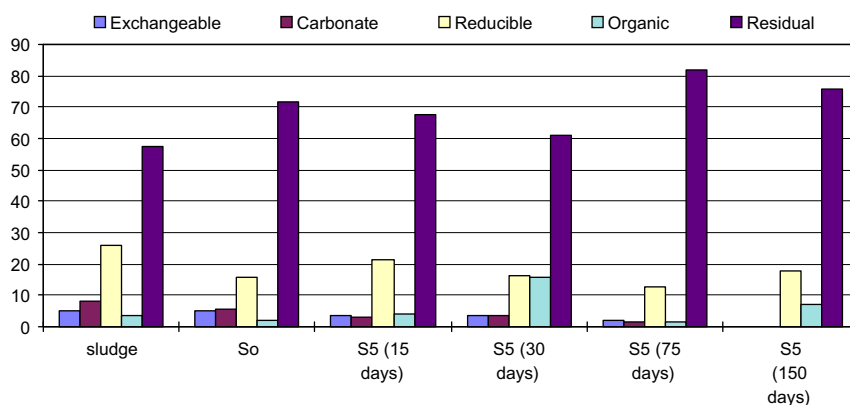


Fig. 6. Pb concentration before, during and after the composting process (%).

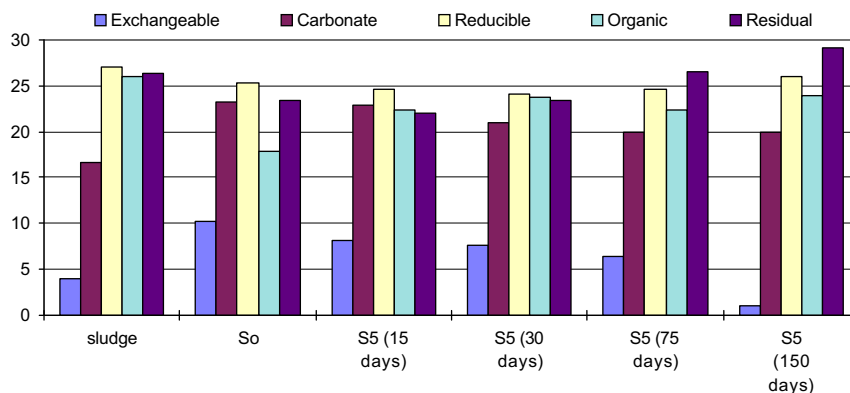


Fig. 7. Zn concentration before, during and after the composting process (%).

transferred to the residual fraction while at the end of the maturity period (after 150 days) zeolite binds all of the readily available metal (metals which are associated with mobile forms). It is obvious that the behavior of Cr is different in 30–70 and 150 days. This phenomenon may be due to the effect of zeolite, which has the ability to absorb and exchange metals.

3.2. For Cu

In Fig. 2, the changes in the percentage of each fraction of Cu are presented. Before the composting process, Cu was associated with the organic fraction while at the first step of composting it seems to be transferred to the exchangeable, carbonate and residual fractions. After the

Table 3

Metal content in the five chemical phase, presented in order of decreasing concentration, for each metal examined

Cr	Organic (47.74%)	Residual (32.75%)	Reducible (18.08%)	Carbonate (1.01%)	Exchangeable (0.42%)
Cu	Residual (54%)	Organic (32.06%)	Reducible (9.94%)	Carbonate (3.50%)	Exchangeable (0.5%)
Fe	Residual (64.19%)	Reducible (27.21%)	Organic (7.95%)	Carbonate (0.38%)	Exchangeable (0.27%)
Mn	Reducible (45.15%)	Residual (35%)	Carbonate (10%)	Organic (8.13%)	Exchangeable (1.72%)
Ni	Residual (52%)	Reducible (22%)	Organic (26%)	Carbonate (<0.02%)	Exchangeable (<0.01%)
Pb	Residual (75.55%)	Reducible (15.58%)	Organic (6.87%)	Carbonate (0.00%)	Exchangeable (0.00%)
Zn	Residual (29.1%)	Reducible (26.03%)	Organic (23.96%)	Carbonate (20%)	Exchangeable (1%)

maturity period, Cu was observed to be associated with the residual and organic fractions (54% and 32%, respectively).

3.3. For Fe and Mn

Iron and Mn have a similar behavior in all phases during the composting period. At the end of the maturity period, 65% of Fe was associated with the residual fraction while 35% and 45% of Mn was associated with the residual fraction and the reducible fraction, respectively.

3.4. For Ni

Fig. 5 presents the changes in all fractions for Ni during composting period. Before the composting process, nickel was found to be associated with the reducible fraction (36%) and the residual fraction (23%). During the thermophilic phase, it was observed that zeolite binds a significant ($p < 0.05$) amount of the metal that was associated with exchangeable and carbonate fractions. After 150 days, the clinoptilolite has taken up the metals bound in the exchangeable and carbonate fractions, while the rest of the metal was found to be bound with the residual fraction (52%). This phenomenon may be due to the effect of zeolite, which has the ability to absorb and exchange selectively different amounts of metals. According to some researchers, metals could be attributed to the formation of metal–humus complex during composting (Tiquia et al., 1997).

3.5. For Pb

As seen in Fig. 6, 57% of the Pb was associated with the residual fraction and 25% with the organic fraction. The available lead, at the first step of composting, was taken up from the zeolite, and the rest of the metal seems to be transferred to the more stable fractions. After 150 days of maturity, zeolite binds all of the available metal. More than 70% is associated with the residual fraction.

3.6. For Zn

In the case of Zn, zeolite binds a significant ($p < 0.05$) amount from the exchangeable fraction while the other fraction has a similar behavior.

The metal content in the five chemical phases (Table 3) may be presented in order of decreasing concentration, for each metal examined:

Cr:	organic	residual	reducible	carbonate	exchangeable
	>	>	>	>	
Cu:	residual	organic	reducible	carbonate	exchangeable
	>	>	>	>	
Fe:	residual	reducible	organic	>	carbonate exchangeable
	>	>		>	
Mn:	reducible	residual	carbonate	organic	>
	>	>	>		exchangeable
Ni:	residual	reducible	organic	>	carbonate exchangeable
	>	>		>	
Pb:	residual	reducible	organic	>	carbonate exchangeable
	>	>		=	
Zn:	residual	reducible	organic	>	carbonate exchangeable
	>	>		>	

Comparing the results with studies carried out before (Angelides and Gibbs, 1989; Rudd et al., 1988; Brennan, 1991; Garcia-Delgado et al., 1994), it is concluded that chromium and copper were found in similar proportions in all fractions while iron was mainly associated with the residual and reducible forms. Nickel has been observed to have substantial proportions in all phases, whereas zinc was mostly found in the organic and reducible fractions. As far as lead is concerned, over 90% was in the reducible, organic and residual fractions.

4. Conclusions

Zeolite has the ability to take up a significant ($p < 0.05$) amount of the metals associated with the mobile forms such as the exchangeable and the carbonate fraction.

The changes that are observed in metal partitioning of the sewage sludge compost are the results of: the thermophilic phase of composting, which is the first step of composting and affects the exchangeable fraction. During the first step of composting, we have changes in the pH value (acetic acid formation) and in ammonia content (affected by the action of the proteolytic bacterial and by the temperature) (Zorpas et al., 1999). Also the pH changes, which occurs in the beginning of the composting process, and affects the exchangeable and carbonate fractions. The pH changes may be due to acid formation during the decomposition of organic matter contained in the sludge.

One of the limiting factors for land application of composted sewage sludge application to soils is the heavy metal content. The fact that the clinoptilolite binds almost all of

the available metal from the exchangeable and the carbonate fractions (except Zn) might be important. Based on this fact, materials such as sewage sludge can be used in agriculture with no problems. Also, in case of acid rain, clinoptilolite has the ability to retain the heavy metals and not let them pass into the groundwater, taking into account that the rest of the metals concentrations are associated with an inert form.

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