The Cd mobility in incubated sewage sludge after ameliorative materials additions

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ABSTRACT

Cadmium mobility in sewage sludge amended by four types of ameliorative materials (lime, limestone, bentonite and zeolite) incubated under aerobic and anaerobic conditions for eight months was studied in the experiment. The most statistically significant decrease of available Cd extracted by 0.01 mol/l $CaCl_2$ was recorded in sludge between second and fourth months of incubation. As most effective stabilizers were found limestone and bentonite added into the sludge incubated under aerobic and anaerobic conditions respectively. The presence of air reduced Cd mobility in individual sludges more than lack of air. Cadmium was separated by sequential extraction into five fractions as water soluble, exchangeable, bound with Fe and Mn oxides, organically bound, and residual fraction. Sequential analysis showed decrease of Cd in exchangeable and oxide fractions in sludge treated by lime and limestone at the end of aerobic incubation. Cadmium was found in water soluble and exchangeable fractions in small portion, even so its content in these fractions was higher than determined in slighter 0.01 mol/l $CaCl_2$ solution.

Keywords: cadmium; sewage sludge; incubation; limestone; lime; bentonite; zeolite; sequential analysis

The problem of sludge disposal is becoming important with the increase of sewage sludge production. Recycling to land may offer an economically and environmentally sustainable option (Smith 1996). Major limitation of sewage sludge reuse is the potential release of heavy metals from the sludge and heavy metal accumulation to toxic levels in the topsoil. Total content of the element can be important in long-term assessment of sewage sludge application, but only available portion of element can immediately affect its accumulation in plant biomass (Tlustoš et al. 1998). Single and sequential extraction methods were developed for metal partitioning (Albores et al. 2000). The properties of the sludge play an important role in the availability of heavy metals in amended soils. Bioavailable forms of heavy metals in recently amended soils are most likely to be those that are bioavailable in the sewage sludge (Merrington et al. 2002). A major concern with the safe re-use of biosolids on land is the potential for release of metals from organic matter in the biosolids, due to decomposition proceeding (Stacey et al. 2001).

The increase of pH as well as clay content can sufficiently affect the mobility of cadmium in sludge and soil (Gerritse and Van Driel 1984, Ross 1994, Serrano et al. 2005). The ameliorative compounds such as lime and limestone are used for increase of pH value and consequently they can decrease heavy metals mobility and reduce the uptake of these elements by plants (Sloan and Basta 1995, Tlustoš et al. 1995). The addition of material with high sorption capacity (bentonite and zeolite) can reduce the availability of heavy metals as well (Chlopecka and Adriano 1997, Adriano 2001, Puschenreiter et al. 2005).

The main objective of our investigation was focused on determination of Cd mobility in sewage sludge amended by four types of ameliorative materials incubated under aerobic and anaerobic conditions.

MATERIAL AND METHODS

The change of cadmium mobility was investigated in an incubated pot experiment with stabilized

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sewage sludge obtained from three wastewater factories in the Czech Republic situated in towns of different population. Main parameters of sewage sludge before incubation are presented in Table 1. Treatments were set up in three replications for each sludge as control treatment, treatment with addition of limestone (7% of Ca w/w of sludge dry solid), treatment with addition of lime (7% of Ca w/w of sludge dry solid), treatment with addition of bentonite (30% of bentonite w/w of sludge dry solid) and treatment with addition of zeolite (30% of zeolite w/w of sludge dry solid). The Cd content in additive materials is shown in Table 2. All treatments were incubated under aerobic and anaerobic conditions in a room with controlled temperature (20°C) and relative humidity (80%). The aerobic treatments were stirred thoroughly and mass loss was checked every 14 days. The pots were refilled by water on 60% of lost weight. Material incubated under anaerobic conditions were covered by plastic bags and sealed by elastic band. The samples were taken at 0, 1, 2, 4 and 8 months and stored in the freezer (–26°C) for analyses. pH (1:20 w/v of 0.01 mol/l $CaCl_2$) – Novozamsky et al. 1993, carbon content (Sims and Haby 1971), total nitrogen (Bremner 1960), dissolved organic carbon – DOC (1:10 w/v of 0.01 mol/l $CaCl_2$) – Novozamsky et al. 1993, total Cd content (Miholová et al. 1993) and available content of Cd (1:10 w/v of 0.01 mol/l $CaCl_2$) – Novozamsky et al. 1993 – were determined in each collection. Sequential analyses of Cd (Ure et al. 1993) were determined at 0, 4 and 8 months. Sewage sludge cadmium was determined in five fractions as water soluble, exchangeable (0.1 mol/l CH_3COOH), bound with Fe and Mn oxides (0.1 mol/l $NH_2OH.HCl$), organically bound (8.8 mol/l H_2O_2 + 1 mol/l CH_3COONH_4), and residual fraction. The cadmium content in individual fractions was determined by ETA-AAS. Quality of analyses was controlled by reference material RM 12-03-12 Sludge. Certified value of this material was 1.97 ± 0.21 mg Cd/kg and obtained value was 1.83 ± 0.09 mg Cd/kg.

RESULTS AND DISCUSSION

The dry matter content of sludge I was 28% before incubation and was higher than the other ones (sludge II = 17% and sludge III = 18%). Dry matter content was not changed during the sludge incubation. The anaerobic conditions almost did not influence the decomposition of sludge. A greater loss of weight in aerobic conditions was due to intensive decomposition and release of gases (CO_2, NH_3). The length of incubation affected the structure of sewage sludge incubated under aerobic conditions in the second half of incubation.

The redox potential values in anaerobically incubated sludge decreased and gradually settled on – 440 mV (in sludge I and III after 5 days, in sludge II after 10 days). The differences between pH values were found in sludge incubated under sufficiency and lack of air (Table 3). Values of pH were higher under anaerobic than under aerobic condition. It could be caused by a decreasing of

Table 1. Main parameters of sewage sludge before incubation

Sewage sludge	I	II	III
Dry matter content (%)	28	17	18
pH ($CaCl_2$)	8.1	8.2	8.0
Total N content (% in dry matter)	3.8	5.1	4.8
Organic C content (% in dry matter)	42	42	36
Dissolved organic carbon – DOC (0.01 mol/l $CaCl_2$) (mg/kg)	2418	2593	3448
Total Cd content (mg/kg)	3.23	5.20	2.42
Cd content in $CaCl_2$ (mg/kg)	0.0011	0.0015	0.0010

Table 2. The Cd content in additive materials (mg/kg)

	Lime	Limestone	Bentonite	Zeolite
Average value	0.114	0.034	0.202	0.059
SD	0.000	0.001	0.008	0.005

Table 3. pH values (0.01 mol/l $CaCl_2$) in untreated and treated sludge incubated under aerobic and anaerobic conditions (average of three sludges); pH value before incubation = 8.1

Conditions	Aerobic incubation				Anaerobic incubation			
Months	1.	2.	4.	8.	1.	2.	4.	8.
Sludge	7.0	6.6	6.3	6.4	8.2	8.4	7.9	7.7
Sludge + limestone	7.3	7.1	7.1	7.0	8.0	8.3	8.0	7.8
Sludge + lime	8.2	8.0	7.3	7.5	11.0	10.1	9.6	8.9
Sludge + bentonite	7.2	6.5	6.4	6.5	8.1	8.3	8.0	7.9
Sludge + zeolite	7.0	6.2	6.3	6.5	7.9	8.5	7.7	7.7

microbial activity and of an accumulation of organic acids, whereby hydrogen ion concentration dropped and so pH value increased. The major decrease of carbon percentages was recorded during the first half of incubation (in sludge incubated under aerobic conditions by 43%, under anaerobic one by 25%) and was brought about enhanced microbial activity. Total nitrogen decreased substantially in aerobic treatments. It was caused mainly by ammonia volatilization (Balík et al. 1999).

The mobility of cadmium in sewage sludge sample was determined by 0.01 mol/l $CaCl_2$ solution, which belongs to leaching agents the best correlated with cadmium content in plants. That knowledge was confirmed by De Vries (1983) who used a lot of leaching agents to evaluate twenty sewage sludges for applicability into agricultural land. The 0.01 mol/l $CaCl_2$ solution correlated very closely with cadmium available to plants (McBride et al. 2004).

Figure 1 illustrates the process of available Cd changes in sludge during eight months of aerobic incubation. After one month of rapid increase, the available Cd content gradually decreased (except of sludge with bentonite). The similar content of available Cd was found out in individual treatments at the end of incubation. It was especially evident in sludge I (Figure 1a). Minimal contents of available Cd were detected at the beginning and at the end of incubation in sludge III (0.0067 to 0.0139 mg Cd/kg of dry matter in first month and 0.0023–0.0143 mg/kg of dry matter after eight months of incubation, Figure 1c). This sludge contained the lowest amount of total and available cadmium before the incubation of all used sludges as well. Zorpas et al. (2000) composted sewage

Table 4. The values of available Cd contents at the beginning and at the end of aerobic and anaerobic incubation of individual treatments (average value of three sludges)

Treatment	mg Cd/kg of dry matter	
	at the beginning of incubation (1^{st} month)	at the end of incubation (8^{th} month)
A – untreated sludge	0.0300 ± 0.0150	0.0098 ± 0.0100
An – untreated sludge	0.0211 ± 0.0074	0.0201 ± 0.0112
A – sludge + limestone	0.0256 ± 0.0101	0.0095 ± 0.0029
An – sludge + limestone	0.0246 ± 0.0114	0.0052 ± 0.0059
A – sludge + lime	0.0316 ± 0.0126	0.0075 ± 0.0054
An – sludge + lime	0.0175 ± 0.0040	0.0118 ± 0.0045
A – sludge + bentonite	0.0062 ± 0.0040	0.0117 ± 0.0057
An – sludge + bentonite	0.0154 ± 0.0045	0.0045 ± 0.0020
A – sludge + zeolite	0.0161 ± 0.0048	0.0113 ± 0.0045
An – sludge + zeolite	0.0165 ± 0.0037	0.0058 ± 0.0052

A – aerobic incubation, An – anaerobic incubation

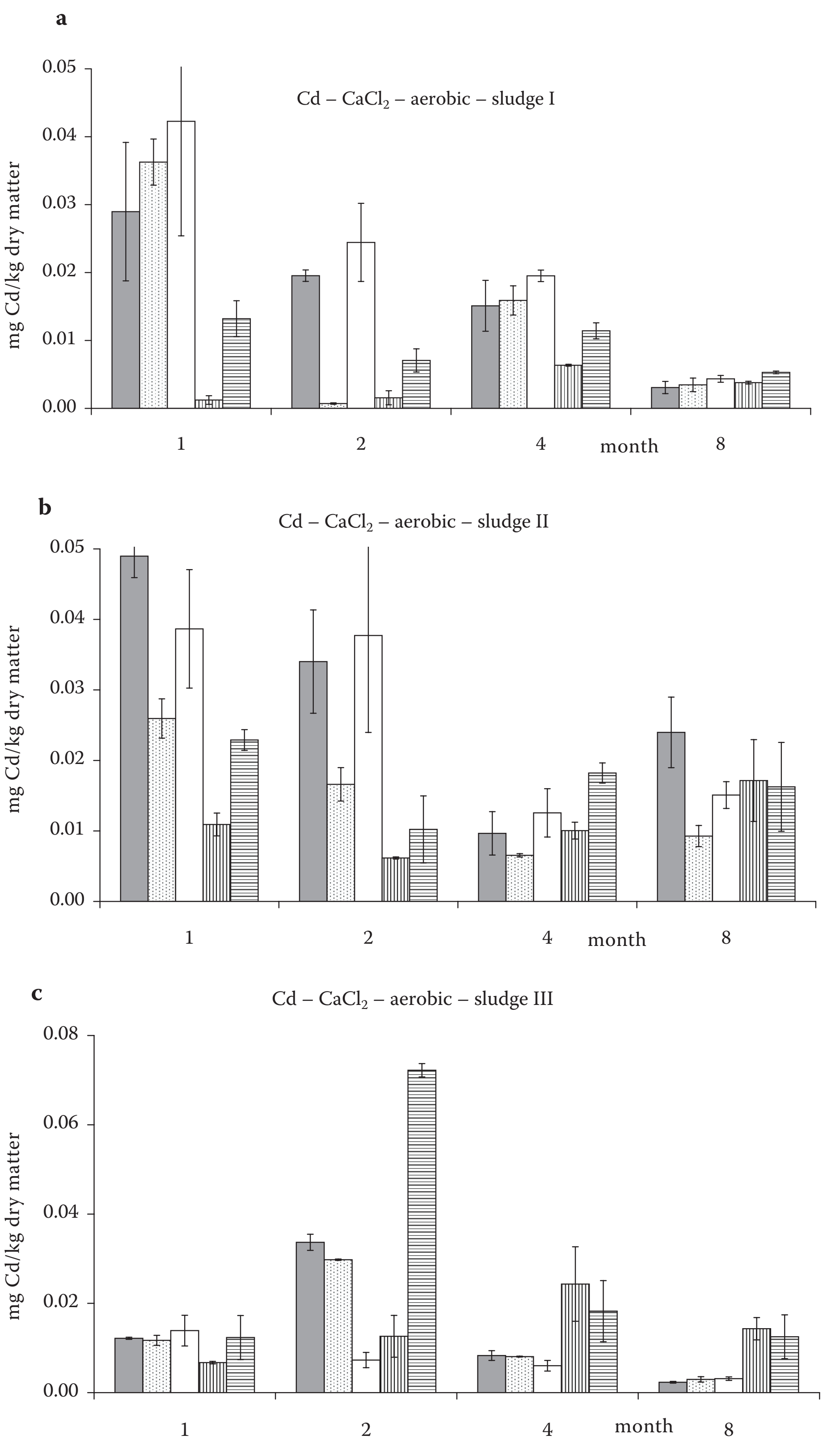

Figure 1. The Cd availability in sewage sludge during 8 months of aerobic incubation (mg Cd/kg)

Explanations to the figure (from left):
1st bar: sludge
2nd bar: sludge + limestone
3rd bar: sludge + lime
4th bar: sludge + bentonite
5th bar: sludge + zeolite

sludge with various rates of zeolite (clinoptilolit) during five months. They concluded the decrease of heavy metal's contents (determined in HNO_3 solution) in compost in dependent on the amount of added natural zeolite. They found out that the use of 20–25% w/w of clinoptilolite during the composting process appears to immobilize all available Cd.

The changes of Cd content during anaerobic incubation depended on the origin of sludge

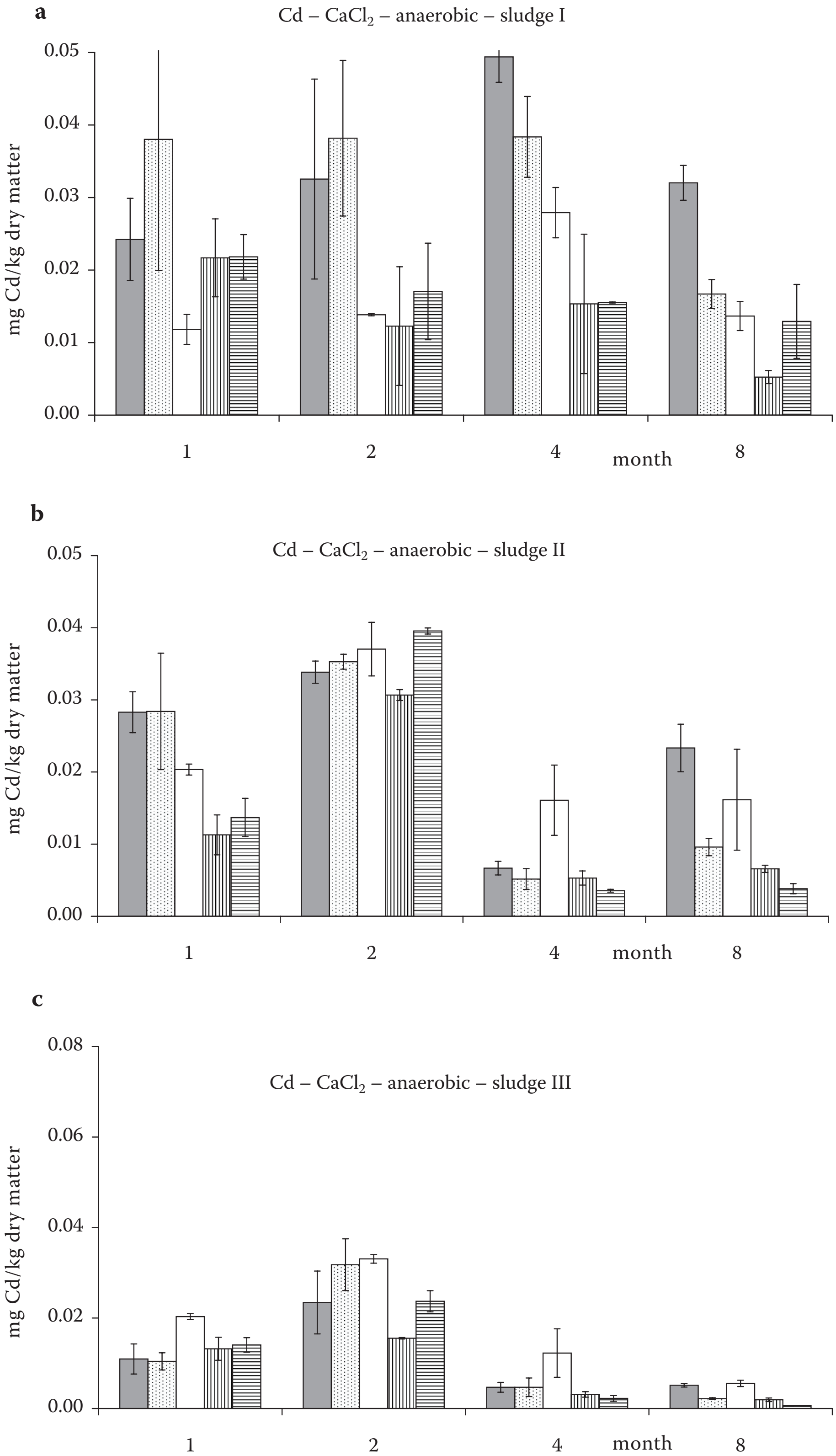

Figure 2. The Cd availability in sewage sludge during 8 months of anaerobic incubation (mg Cd/kg)

Explanations to the figure (from left):
1st bar: sludge
2nd bar: sludge + limestone
3rd bar: sludge + lime
4th bar: sludge + bentonite
5th bar: sludge + zeolite

(Figure 2). The substantial changes among treatments were observed in sludge I (Figure 2a). The addition of bentonite decreased the amount of available Cd content in sludges most significantly under lack of air. The high binding capacity of bentonite published by other authors (Sims and Boswell 1978, Arnfalk et al. 1996) was confirmed in this experiment.

The presence of air decreased available Cd content in individual sludges more than lack of air. The higher Cd values were found predominantly at the beginning of aerobic incubation than anaerobic one. The available content of this element dropped regularly and strongly under the presence of air (except of bentonite treatment). Individual values are presented in Table 4.

The most dynamic drop of available cadmium was recorded between second and fourth month of incubation. The period of four months seems to be economically useful. The limestone and the bentonite were found as the most effective materials added into sludge incubated under aerobic and anaerobic conditions respectively. The highest available Cd content was found in untreated sludge.

Tlustoš et al. (2001) found that the available Cd content (determined by 1 mol/l NH_4NO_3) regularly increased during eight months of aerobic incubation in untreated sludge and in sludge with addition of bentonite as well. The addition of bentonite into anaerobically incubated sludge decreased the available Cd content.

Fluctuation of Cd contents among main fractions during incubation was determined by sequential extraction procedure before (0 month), in half (4 months) and at the end of incubation (8 months).

Figure 3 illustrates the average distribution of Cd in three sludges amended by ameliorative materials. Water soluble and exchangeable Cd fractions belong to the most available fractions for plants. The element in the other fractions is bound stronger and is hardly available for plants.

The presence of air (Figure 3a) led to an increase of Cd content in available fractions in untreated sludge during the incubation. Growth of Cd content in oxide fraction was recorded in the sludge (6.5 times more in half of incubation compare to time zero). On the contrary, cadmium portion in organic and residual fractions decreased (in

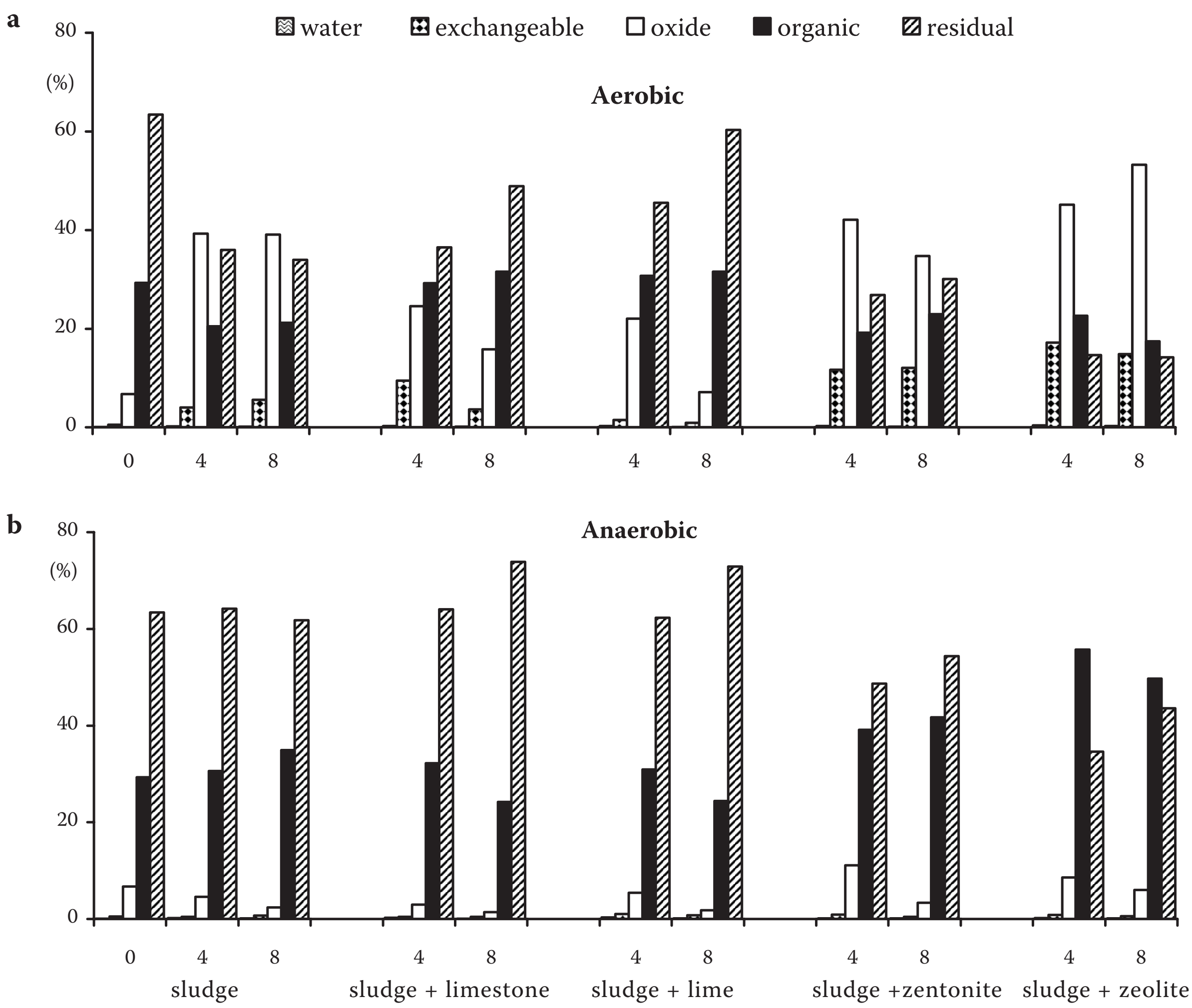

Figure 3. The fluctuation of Cd in main fractions (%) during eight months of aerobic (a) and anaerobic (b) incubation of treated sewage sludge (0, 4 and 8 months) – average of 3 sludges

organic fraction from 29% and residual from 63% before incubation to 21% and 34% at the end of incubation, respectively). This drop was caused by intensive decomposition of organic matter under the presence of air and the translocation of Cd into labile fractions. The similar Cd distribution process found Tlustoš et al. (2001) in sludges from five water treatment plants. The Cd portion in water soluble, exchangeable and oxide fractions decreased in sludge treated with limestone and lime in our experiment because of higher pH value of the mixture (Wong et al. 2000). The highest portion was apparent in residual fraction. The addition of lime increased Cd transformation into unavailable fractions more than limestone. Sewage sludge treated with bentonite and zeolite showed the highest Cd content (from all treatments) in available fractions (in average 14% of total Cd content) and in oxide fraction.

The content of available Cd reached low values in untreated sludge incubated under anaerobic condition (Figure 3b) – (0.17% in water soluble and 0.59% in exchangeable fractions of total content). Cadmium was found in water soluble and exchangeable fractions in a small portion, even so its content was higher than determined in 0.01 mol/l $CaCl_2$ solution. The differences between lower content of Cd released by 0.01 mol/l $CaCl_2$ and higher Cd content in exchangeable fraction released by acetic acid were caused by different extraction capacity of both solutions. Cadmium portion decreased in oxide fraction during the storage at all treatments. The majority of Cd content was bound in organic and residual fractions. This effect relates in the case of organic fraction with the increase of adsorb sites due the dissociation of carboxylic acids in the sludge with higher pH value. Increased Cd content in residual fraction was probably caused by Cd precipitation into CdS form. Cadmium bond with sulfide is the most important form of strong immobilization under anaerobic condition. The addition of limestone and lime decreased Cd content in organic fraction at the end of anaerobic incubation (to 24% of total Cd content). Residual fraction of this element uniquely prevailed in these treatments (after eight months of incubation composed 73% of total Cd content). Sewage sludge treated by bentonite distinguished itself by steady Cd portion in organic fraction (40%). The highest portion of Cd was found in this fraction in sludge with addition of zeolite (52%). The sludge treated by this ameliorative material contained the least Cd portion from all treatments in residual fraction (in fourth month of incubation 34% and in eighth month 43% of total Cd content).

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