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Research article

Heavy metals in sludge during anaerobic sanitary landfill: Speciation transformation and phytotoxicity

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ABSTRACT

Sanitary landfill persists as a predominant sludge disposal method in particular in China. In this study, successive subsurface sludge samples (0.3 m deep) were collected from a bioreactor landfill unit where an anaerobic process took place during a 500 d period. The sludge samples were analyzed for total concentrations of cadmium (Cd), chromium (Cr), copper (Cu), nickel (Ni), lead (Pb) and zinc (Zn) and their species distributions, together with selected sludge chemical properties. In addition, the sludge samples were subjected to phytotoxicity testing. The results showed that the mobilities of Cd and Ni were decreased with landfill time, while the mobilities of Cr, Cu, Pb and Zn remained consistently low over the landfill period. The residual amounts of all these heavy metals were increased with landfill time, suggesting that the anaerobic sanitary landfill is an effective sludge stabilization method to reduce the ecological risk of these heavy metals. The increase in the sludge pH value with landfill time tended to promote the precipitation of heavy metals. Moreover, the sludge stabilization was found to be indicated by the formation of humic substance (HS) and volatilization of volatile matter (VM). The germination index (GI) values of barley (*Hordeum vulgare* L.) and Chinese cabbage (*Brassica rapa chinensis*) seeds grown in the 500 d anaerobically stabilized sludge were approximately 5.2- and 4.1-times higher than the values of those grown in the fresh sludge. The final sludge extract did not cause any significant inhibitory effect on the germination of the two types of seeds.

1. Introduction

In Australia, the United States (US) and European Union (EU), treated sewage sludge (biosolids) containing rich plant nutrients (predominantly nitrogen (N) and phosphorus (P)) and organic matter (OM) has been widely and legally reused as a fertilizer or soil amendment for land application (Pritchard et al., 2010; Lu et al., 2012; Peyton et al., 2016). The treatments may include composting, aerobic and anaerobic digestion, thermal drying or lime stabilization (Metcalf & Eddy Inc. et al., 2013). However, the application of sewage sludge in soil is currently limited in China largely due to its enriched concentrations of heavy metals which are non-degradable and toxic as well as tend to accumulate along the food chain (Liu et al., 2007; Dong et al., 2013; Zhang et al., 2015). Specifically, sewage sludge in China contains higher concentrations of heavy metals than that in the developed countries because municipal sewage treatment plants in China are likely to accept industrial wastewater (Fang et al., 2016). Due to its large treatment capacity, simple disposal procedure and low cost, sanitary landfill remains as a predominant sewage sludge disposal method in China (Liu et al., 2015).

It is now well recognized that the mobility and toxicity of heavy metals are depended predominately on their chemical forms, while the sole determination of their total concentrations is not enough to understand the severity of environmental damage caused by them (Amir et al., 2005; Walter et al., 2006; Nomeda et al., 2008; Thanh et al., 2015). Regarding the sanitary landfill site itself as an anaerobic bioreactor, the sewage sludge dumped in it would be subjected largely to an anaerobic stabilization process. Numerous studies have observed speciation transformation of heavy metals in sewage sludge placed into anaerobic digestion reactors. For example, a recent study of Dong et al. (2013) reported that high-solid anaerobic digestion of sewage sludge much or less increased

Abbreviation: FA, fulvic acid; GI, germination index; HA, humic acid; HS, humic substance; OM, organic matter; RRG, relative root growth; RSG, relative seed germination; TK, total potassium; TN, total nitrogen; TOC, total organic carbon; TP, total phosphorus; VM, volatile matter.

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the ratios of chromium (Cr), copper (Cu), nickel (Ni) and zinc (Zn) in mobile fractions while decreased the ratio of lead (Pb) in mobile fraction. A more recent study of Zhang et al. (2015) found that the ratios of Cr, mercury (Hg), Ni and Zn in stable fractions were increased in the phase of anaerobic digestion after thermal hydrolysis. They inferred that sulphate and other sulphur (S) compounds in the sewage sludge were transformed into S^{2-} by sulphate-reducing bacteria during anaerobic digestion. Consequently, S^{2-} formed stable sulphides with these heavy metals. Thanh et al. (2015) recently reviewed trace metal (the term specifically used in the reference) speciation in anaerobic digestion of sewage sludge and summarized that trace metal sulphides (e.g. NiS) can become a storage of and source for trace metals after anaerobic digestion. They also concluded that it is important to determine the sulphide speciation of trace metals. However, few studies have examined the changes in mobility and toxicity of heavy metals associated with different species in sewage sludge in sanitary landfill sites. In fact, the knowledge of chemical speciation of heavy metals in sewage sludge disposed in sanitary landfill sites is of great importance to assess the ecological risk of land application of stabilized sewage sludge from the sites.

The aims of this study are therefore to (a) investigate the species distributions of heavy metals in sewage sludge during anaerobic sanitary landfill and (b) evaluate the effect of anaerobic sanitary landfill on the mobility and phytotoxicity of heavy metals in sewage sludge.

2. Material and methods

2.1. Landfilling and sampling

The sewage sludge (hereafter referred to as sludge) used in this study was sourced from the Bailonggang Wastewater Treatment Plant in Shanghai, China. It was landfilled in the Shanghai Refuse Landfill. In this region (referred to the Nanhui weather station), the mean maximum temperature is 20.1 °C, ranging from 8.3 °C in January to 31.1 °C in July; the mean minimum temperature is 13.0 °C, ranging from 1.3 °C in January to 24.9 °C both in July and August (National Meteorological Information Center, 2012). A total of approximately 1800 t fresh sludge was placed in the bioreactor landfill unit in August. The permeability coefficient of the sludge was 1.18×10^{-8}–2.07×10^{-8} (100 kPa). The top and bottom areas of the unit were 1024 m^2 (32 m × 32 m) and 100 m^2 (10 m × 10 m), respectively. The height of the unit was 6 m, which was equally divided into three layers by the ladder shape of the landfill slope. High-density polyethylene (HDPE) textured geomembranes were used to seal the top of the unit. Between each layer, tri-planar geocomposites were used to accelerate drainage and concretion. In order to collect representative anaerobically stabilized sludge, the 0–0.1 m deep surface sludge was removed first, and then 0.3 m deep subsurface sludge samples were collected on Day 0, 60, 120, 180, 230, 270, 300, 360, 400, 450 and 500, respectively. Each main sludge sample consisted of six subsamples taken randomly at the same depth of 0.3 m, mixed and homogenized to form a representative sample. All the sludge samples were air-dried at 40 °C, ground in an agate mill, and passed through a 0.63 mm stainless steel sieve for subsequent analyses.

2.2. Chemical analyses

Sludge sample pH was determined by the 1:10 solid/water (*w*/*v*) suspension method using a MeterLab® pH meter. Volatile matter (VM) content in the sludge sample was determined by the incineration method at 600 °C for 3 h in a muffle furnace. Total organic carbon (TOC), N and S contents in the sludge sample were determined by the dry combustion method using a Vario EL III CNS element analyzer. Total P content in the sludge sample was determined by the microwave digestion method using a UV755B ultraviolet spectrophotometer (Hu et al., 2008). Total potassium (K) content in the sludge sample was determined by the microwave digestion method using a Perkin Elmer Optima 2100 DV inductively coupled plasma-atomic emission spectrometry (ICP-AES) (Hu et al., 2008).

Total concentrations of heavy metals (cadmium (Cd), Cr, Cu, Ni, Pb and Zn) in the sludge sample were determined by first digesting the sample using the HCl-HNO_3-HF-$HClO_4$ (1:4:1:1 *v*/*v*) method (Zhao et al., 2013). The acid digestion suspension was then filtered (0.45 μm), and the filtrate was measured to determine total heavy metal concentrations using a Perkin Elmer Optima 2100 DV ICP-AES. Reagent blanks and a standard reference material (Community Bureau of Reference (BCR) No. 40), representing 10% and 10% of the total sample population, respectively, were incorporated in the analysis to detect contamination and assess precision and accuracy. The results showed no signs of contamination and revealed that the precision (relative standard deviation) and accuracy (per cent difference (%D)) of the analysis were generally <10%.

Humic acid (HA) and fulvic acid (FA) contents in the sludge sample were determined by the standardized method of the International Humic Substances Society (IHSS) (Lamar et al., 2014). Humic substance (HS) content was the sum of HA content and FA content.

2.3. Sequential extractions

Species of heavy metals (Cd, Cr, Cu, Ni, Pb and Zn) in the sludge sample were determined by the five-step extraction procedure proposed by Campanella et al. (1995), which operationally separates heavy metals into six fractions, *viz.*, exchangeable and carbonate fraction (E1), Fe/Mn oxides fraction (F2), organic matter fraction (O3), humic compounds fraction (H4), sulphide fraction (S5) and residual fraction (R6). The extraction procedure was repeated twice. Compared with the method of Tessier et al. (1979), this method can distinguish the heavy metal fraction bound to OM from that fraction present in the sulphide form, allowing a more reliable speciation of heavy metals.

2.4. Phytotoxicity tests

The sludge sample was ground to <100 μm, and extracted with deionized water at a solid/water ratio of 1:10 (*w*/*v*). The suspension was then filtered, and a 5 mL aliquot of the filtrate was transferred to a petri dish with Whatman® Grade No. 1 ashless filter paper covering its bottom. A total of ten barley (*Hordeum vulgare* L.) and Chinese cabbage (*Brassica rapa chinensis*) seeds were placed on the filter paper, respectively, and then incubated in dark at 25 °C and 75% humidity for 48 h. Each sludge sample had two replicates. The barley and Chinese cabbage seeds incubated with deionized water solely under the same condition were prepared as controls. Relative seed germination (RSG) rate, relative root growth (RRG) rate and germination index (GI) were calculated using the following equations:

$$RSG(\%) = \frac{SGN_{sludge}}{SGN_{control}} \times 100$$

Where SGN—seed germination number.