Chemosphere 168 (2017) 191–198

Contents lists available at ScienceDirect

Chemosphere

journal homepage: www.elsevier.com/locate/chemosphere

Bioassay directed identification of toxicants in sludge and related reused materials from industrial wastewater treatment plants in the Yangtze River Delta

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HIGHLIGHTS

- Reused approaches resulted in reduced concentrations of metals in leachates.
- TUs of sludge leachates are still greater than 1.0 after being reused.
- Cr and Ni contributed most to the total toxicity followed by Zn and Cu.
- Making sludge into bricks reduced more toxicity than landfills.
- Combining bioassays and instrumental analysis make better evaluation of sludge.

ARTICLE INFO

Article history:
Received 28 April 2016
Received in revised form
26 September 2016
Accepted 13 October 2016
Available online 23 October 2016

Handling Editor: Jian-Ying Hu

Keywords:
Sewage
Metals
Leaching test
Toxicity
The Yangtze River Delta
Treatment

ABSTRACT

Industrialized development of the Yangtze River Delta, China, has resulted in larger amounts of wastes, including sludges from treatment of these wastes. Methods to manage and dispose, including reuse were urgently needed. Sludge and reused products were collected from two largest factories, KEYUAN and HENGJIA where treated sludges were turned into bricks or sludge cake to be placed in landfills, respectively. Metals and organic compounds were quantified in sludges and leachates assessed by use of toxicity characterized leaching procedure (TCLP) while acute toxicity was determined by *Daphnia magna*. Nine metals were detected in all raw sludges with concentrations of Cr and Ni exceeding Chinese standards. For sludge leachate, concentrations of metals were all less than Chinese standards, which changed little after being made into cake by HENGJIA, but were significantly less after being made into brick by KEYUAN. Toxicity units (TU) for all samples are greater than 1.0 indicating that they are potentially toxic to aquatic organisms. TUs changed little after being made into filter cake, but were 10-fold less after being made into bricks. Cr and Ni contributed most to the total toxicity followed by Zn and Cu. Making of sludges into K-brick 1 resulted in better inactivation of contaminants, which resulted in less toxic potencies. So that is the recommended method for handling of industrial sludges. To further assure their safe reuse, additional research on identification of key toxicants and potential hazards, based on additional endpoints, by combining bio-tests and chemical analysis should be done for reused sludges.

1. Introduction

Sewage sludge is a byproduct of biological wastewater treatment, that is one alternative, being considered as an important source of secondary pollution. On average, total production of

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http://dx.doi.org/10.1016/j.chemosphere.2016.10.046
0045-6535/

sludge in China increased 13% annually over the past ten years and currently amounts to more than 6 million tons of dry solids (DS) produced annually (Yang et al., 2015). In China, wastewater from industrial parks are treated in wastewater treatment plants (WWTPs) where their proportion as approximately 35.0% (Feng et al., 2015). This can result in greater concentrations of heavy metals and organic contaminants in sewage sludge. Among industrial parks, chemical plants in the downstream reaches of the Yangtze River produce approximately 0.6 million tons DS of sludge, which is approximately 10% of the total produced annually in China (Yang et al., 2015). Relatively great concentrations of cadmium (Cd), mercury (Hg) and copper (Cu) have been reported in sludges of seven wastewater treatment plants in downstream reaches of the Yangtze River. This resulted in those sludges needing to be managed as hazardous wastes (Li et al., 2013). Contaminations of polycyclic aromatic hydrocarbons (PAHs) (Shen et al., 2007; Zhao and Zhu, 2010), polychlorinated biphenyls (PCBs) and organochlorine pesticides (OCPs) (Shen et al., 2006) and polybrominated diphenyl ethers (PBDEs) (Xiang et al., 2013) have been detected in sludges of WWTPs in the Yangtze River Delta. A wide variety of pollutants can be detected in sludges and relative proportions of constituents vary depending on the industries and processes discharging to treatment plants. However, the commonly used techniques for treatment of sludges, such as anaerobic digestion and aerobic composting are ineffective to remove these pollutants which seriously limited how they could be disposed. In China, standards have been promulgated for some of the more common contaminants, such as metals, they are not available for many of the organic constituents of sludges.

Treatment and disposal of sludge is time-consuming and expensive. According to a survey, treatment of sludge costs approximately $10–31 USD/t DS, which means in China, billions of dollars are spent annually for treatment and disposition of sludge, especially in downstream reaches of the Yangtze River. Historically, over 80% of the sludge has not been disposed of in what would not be considered an appropriate manner that would be sustainably safe for the environment. Increasing amounts of sludge pose threats to the environment (Feng et al., 2015). Since there are various pollutants in sludge, inappropriate utilization might result in release of toxic substances. Thus, potential toxicities of sludges and the reused materials need to be considered. Therefore, sustainable reuse of sludge is urgently needed. To improve management of sludges, various technologies for recycling have been utilized to make constructed soil, cement and bricks (Ahmad et al., 2016; Rahman et al., 2015). Recently, sludge from industrial parks along downstream reaches of the Yangtze River have mainly been processed into soil conditioners or have been incinerated. Also they have been used to manufacture building materials, such as bricks and cement blocks. Even when formed into useful materials, in which contaminants are more immobilized, chemical wastes or ashes from incineration can still leach from more recalcitrant materials like bricks or concrete (Lu et al., 2016). Reuse is only recommended when bioavailabilities and hazards posed by major contaminants have been assessed and it has been determined that immobilization is appropriate.

Identification of toxicants and overall toxic potencies of sludges are critical to allow for appropriate treatments and potential reuses. While in China, few criteria are available for evaluation of potential effects and overall safety of toxicants in reused sludges, some standards are available for raw sludges. In Europe, identification of hazards of sludges currently consists of only 14 chemical-physical properties and concentrations of 7 metals (EU, 1986). Quantification of target chemicals can only describe part of the potential hazard to humans and the environment. Since there are so many potential contaminants in sludges and there might also be degradation products of these constituents occurring in mixtures, it is difficult to predict potential adverse effects from this type of bottom-up approach, based on criteria for individual chemicals. Even if it were possible to identify and quantify every chemical in the mixture, toxicological information would be required for each and every compound, not to mention how they would behave and what their toxic potencies would be in a complex mixture. Alternatively, a top down approach that measures adverse effects, expressed as toxic units (TU) and integrates effects and potential interactions can be used in conjunction with instrumental analyses. However, toxicity tests alone simply provide an estimate of effects and do not identify the key contaminants. Without knowledge of the causes of toxicity, it is difficult to manage it. Thus a combination of analytical and bio-analytical analyses, in an effects-directed fractionation and identification process, is an effective way of identifying critical substances in sludges so that the most appropriate methods of treatment and ultimate disposal can be applied.

Effect-directed analysis (EDA), which combines chemical analysis and with evaluation of toxicity (Burgess et al., 2013), can be used in hazard evaluation and identification of toxicants. EDA has been successfully used to identify key toxicants in waters (Brack et al., 2016; Grung et al., 2007), sediments (Brack and Schirmer, 2003), (Schwab et al., 2009; Hecker and Giesy, 2011), soils (Legler et al., 2011) and drinking water (Shi et al., 2012), while few studies have focused on sludges (Guo et al., 2014). As far as we know, EDA has never been used previously to identify toxicants in materials containing sludges that can be safely used for beneficial purposes. The purpose of this study was to combine EDA to assess hazard and identify critical contaminants in industrial sludges and related reused materials.

2. Materials and methods

2.1. Collection and processing of samples

Samples of sludge were collected during various procedures at two largest sludge reuse factories KEYUAN and HENGJIA, which are located in the downstream region of the Yangtze River. At KEYUAN, raw sludge (K-raw) is treated with waste acid and after neutralization of sludge, it is mixed with mud, coal ash and slag, which is then used to make two types of bricks, K-brick 1 and K-brick 2, which were made of fired sludge contain 12% or 50% water, respectively. At HENGJIA, conditioned raw sludge with 1.74% Ni (H-raw-1.74%) or 1.38% Ni (H-raw-1.38%) are mixed with lime to precipitate Mg, Mn and Fe, then thickened into sludge cake (H-thickened), which was then disposed of by placing it into landfills.

One kilogram samples of sludge and products made from sludge, were collected directly from the residual sludge pool 3 times in one day. Samples were collected by use of a wooden scoop and placed in brown glass bottles. Detailed information for sludges is shown in Table S1 of the supporting information. Mixed samples of sludges and product samples were transported on ice to the laboratory within 24 h. Sludges used for instrumental analysis were lyophilized, then ground and passed through a 0.4 mm sieve. Metals and organic compounds were then quantified by use of a standardized protocols (Fig. 1). Raw sludges were separated into two portions. In one portion, sludge and reused samples were first freeze dried (lyophilized), then extracted and concentrations of PAHs, volatile organic compounds (VOCs), semi-volatile organic compounds (SVOCs) and metals determined. In the other portions of sludges or materials made from sludges were to produce leachates, which were then evaluated by use of the TCLP protocol. The leachates were evaluated by use of chemical analysis and toxicity tests based on *D. Magna*. Key toxicants were further determined by calculating contributions to toxic potencies by