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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.

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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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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

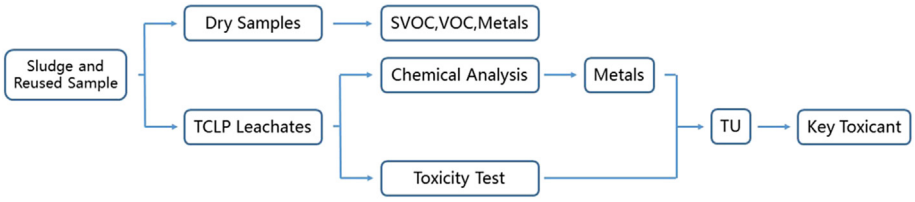

Fig. 1. Steps of chemical and biological analysis.

calculation of TUs.

2.2. Leaching tests

Potential for residues to be leached from materials made from reused sludges and their toxic potencies of leachates were assessed use of the leaching procedure (TCLP), which has been used widely to assess sludge leachate (Qian et al., 2009). Due to differences in acidities and alkalinities and buffering capacities of sludges, two buffers with pHs of 4.9 ± 0.05 (buffer 1) and 2.9 ± 0.05 (buffer 2) were used. Buffers 1 and 2 were prepared by adding 64.3 mL of 1 mol/L sodium hydroxide (NaOH) containing 5.7 mL of glacial acetic acid and 5.7 mL of glacial acetic acid respectively to 1 L deionized water. When pH of sludge was less than 5, buffer 1 was used, while when pH of sludge was greater than 5, buffer 2 was used. A mass of 20 g of sludge was paced in a 500 mL pp bottle. After adding 400 mL buffer, the bottle solution was shaken for 18 ± 2 h at 0.18 ± 0.001 × g. After shaking, samples were allowed to stand for 15 ± 5 min. Samples were then centrifuged for 30 min at 4616 × g. After centrifugation, the supernatant was pipetted into a wide-mouth plastic bottle stored at 4 °C. Part of the sample was used for instrumental analysis, while the other was used for testing of toxicity.

2.3. Toxicity testing

The water flea (*D. magna*) was used as a sensitive test organism to determine toxic potencies of leachates from sludges or materials made from sludges to aquatic organisms (Fjällborg et al., 2005) and (Marttinen et al., 2002). *D. magna* (<24 h old) were exposed acutely to leachates of sludge. Plastic, six-well Nunc plates (multi-dish, Nulge Nunc international products) were used as exposure vessels, with 10 mL of test solution in each well. Temperature was maintained at 22 ± 1 °C and tests were conducted with a light cycle of 16 h light and 8 h darkness. Each sample was diluted to form a gradient of nine concentrations, dilution ratios of which were: 1, 2, 4, 8, 16, 32, 64, 128 and 256. Each concentration included four replicates. Mobility of *D. magna* was determined after 48 h, and proportions of immobile individuals were compared to the untreated, control. Each test was accompanied by negative controls (dilution water) and a positive control, which was a range of concentrations of potassium dichromate ($K_2Cr_2O_7$). Results of the negative and positive controls were used to assess sensitivity of *D. magna* and to correct for differences among exposures. No immobility was observed in the negative control.

2.4. Identification and quantification of contaminants

2.4.1. Preparation of samples

Ten grams of sludge or brick (wet mass) were lyophilized. Samples were Soxhelt extracted with n-hexane/acetone (1:1,v/v) for 16 h according to criteria described by US EPA method 3540C (USEPA, 1996). Extracts were concentrated to approximately 25 mL by use of rotary vacuum evaporation and then were solvent-exchanged by use of n-hexane. Extracts were then purified by Florisil column, which had been pre-activated for 12 h at 180 °C, and were then eluted with 10 mL of n-hexane/acetone (4:1, v/v). Volumes of eluents were then reduced to 1.0 mL under 30 °C water bath by nitrogen. Headspace was used for injection of VOCs determination.

2.4.2. PAHs

Sixteen priority PAHs were quantified by use of a Thermo-Fischer, series II gas chromatography (GC), equipped with a triple quadrupole mass spectrometer operated in multiple reaction monitoring (MRM) mode. The carrier gas was Helium, and the flow rate was 1.0 mL/min. When quantifying PAHs, a pulsed, splitless injector was used to inject 1.5 μL of extract. An Rtx-5MS column (30 m × 0.25 mm, film thickness 0.25 μm) was used for chemical separation of leachates. Inlet temperature was 250 °C. Initial oven temperature was 80 °C, which was held for 2 min, then increased to 180 °C at 15 °C/min, held at 180 °C for 15 min, then heated to 300 °C at a rate of increase of 15 °C/min then held at 300 °C for 5 min.

2.4.3. SVOC and VOC full scan

GC-mass spectrometry (MS) was used to identify and quantify semi-volatile organic compounds in leachates. After injecting organic extracts of leachates into a GC with a narrow-bore fused-silica capillary column, the GC column was temperature-programmed to separate analytes, which are then detected by use of a MS connected to the GC. Analytes eluted from the capillary column were introduced into the mass spectrometer via a jet separator or a direct connection. Identification of target analytes was accomplished by comparing their mass spectra with electron impact (or electron impact-like) spectra of authentic standards.

Chinese standard HJ 643–2013 (MEP, 2013) GC-MS was used to determine the concentration of volatile compounds in leachate. Volatile compounds were introduced into the GC by the purge and trap method or by other methods. Effluent from the trap was sent to an injection port operating in the split mode for injection to a narrow-bore capillary column. The column was temperature-programmed to separate analytes, which were then detected by use of a MS interfaced to the GC. Analytes eluted from the capillary column were introduced into the mass spectrometer via a jet separator or a direct connection. (Wide-bore capillary columns normally require a jet separator, whereas narrow-bore capillary columns may be directly interfaced to the ion source). Identification of target analytes was accomplished by comparing their mass spectra with mass spectra of authentic standards.

2.4.4. Metals

Lyophilized sludges (0.5 g) were treated with 10 mL *aqua regia* for 2 h under gentle reflux on a stirring heater. The suspension was left to cool, diluted with double-deionized water, and filtered for determination of concentrations of metals. Quantifications of Cu, Zn, Cd, Pb, Cr, Hg, Be, Ni, Ag, As, Se in leachates of sludge were made by use of an inductively coupled plasma mass spectrometry (ICP-MS) measurements which was performed using an Optima 5300DV

(Perkin Elmer, Akron, US) with wavelengths of 170–800 nm. Limits of detection varied among elements and ranged from 0.001 to 0.1 mg/L.

2.5. Calculation of toxic units

To evaluate toxic potencies of leachates and determine relative contributions of various metals to the overall toxic potencies of leachates, the TU approach was employed. First, TU were calculated for each sample Eq. (1).

$$\mathrm{TU\ (sample)} = 100\%/\mathrm{IC_{50}(or\ EC_{50})of\ sample} \quad (1)$$

The IC_{50} (or EC_{50}) in the formula is the diluted multiples or the enrichment ratios when half of the test organisms have toxic effect. For each compound in the leachate, the TU was calculated Eq. (2).

$$\mathrm{TU\ (Compound}\ i) = \mathrm{Concentration}(i)/\mathrm{IC_{50(}}_{i)}(\mathrm{or\ EC_{50}}(i)\big) \quad (2)$$

The $IC_{50\ (i)}$ (or $EC_{50(i)}$) is the concentration of compound *i* when half of the test organisms were affected.

Larger TUs mean a larger proportion of toxicity. The TU method has been widely used in evaluations of mixtures of toxicants by several countries (Fjällborg et al., 2005) and (Tsarpali et al., 2012).

2.6. Data analyses

Acute immobilization (lethality) of *D. magna* expressed as EC_{50} with units of equivalents of leachate of sludge was calculated by use of Graphpad Prism 06. Values were reported as mean ± SD (n = 4). Levene's Test and Shapiro-Wilks normality test were used to test the homogeneity of variances and normality of data. If data did not meet the assumptions of parametric statistical tests, they were log-transformed. One-way analysis of variance (ANOVA) was used to analyze significant differences between samples and control and between various sludges and leachates. The significance (p) was controlled below 0.05, respectively. Also, the statistics power analyzed by Power and Precision 2.0 (Biostat Inc., Englewood, NJ, USA) was higher than 0.8.

3. Results and discussion

3.1. Chemical characterization of sludge

Concentrations of metals including: As, Ba, Be, Cd, Cr, Cu, Ni, Se and Zn in sludge are shown in Table 1. Hg and Se were not detectable in any samples of sludge. Mean concentrations of Cr and Ni were approximately 6.0×10^3 and 1.0×10^4 mg/kg, dm, respectively, which were greater than those of other metals. Concentrations of Ag and Be were less than 1 mg/kg, dm, which were less than those of other metals. Concentrations of Cr, Ni, Zn and Cu in HENGJIA raw sludge were from 2 to 50 times greater than those in KEYUAN raw sludge. The reason for this observation was that raw sludges generated by HENGJIA were mainly from water treatment plants of small-scale plants including chemical processing, electroplating and metalwork factories which is mainly engaged in petrochemical raw material production and metal-plating. Thus, concentrations of metals in wastewater were relatively great due to characteristics of the various industries, including: poor treatment and outdated recycle technology, which led to greater concentrations of contaminants in raw sludges. However, raw sludges treated at KEYUAN were mainly from large-scale factories, which had updated recycle processing by ion exchange. Thus, concentrations of contaminants in sludges at KEYUAN were relatively small. Qualities of sludges were directly affected by process and scales of production at each facility.

Concentrations of Cr and Ni in all raw sludges exceed standards for metals in sludges (Table 2). In HENGJIA, concentrations of metals were all less after sludges were used to make conditioned soil. Rates of reduction of concentrations of Cr, Ni, Zn and Cu are 46%, 83%, 69% and 56%, respectively. In KEYUAN, concentrations of metals in sludge were also less after sludge was used to make bricks. Rates of reductions in concentrations of Cr, Ni and Cu are 99%, 99% and 80% for K-brick 1 and 70%, 69% and 18% for K-brick 2. Concentrations of metals had been significantly removed both in HENGJIA and KEYUAN compared to those in raw sludges, which indicated that waste acid treatment followed by neutralization and related precipitation process, efficiently removed or immobilized contaminants. Moreover, making sludge into K-brick 1, resulted in greater reduction of metals in leachates, than making sludge into K-brick 2. The reason for the significant reduction in K-brick 1 is that K-brick 1 was made of raw sludge with water content 12% which means it was mixed with more materials which resulted in significant dilution of metals. After making sludge into K-brick1, rates of removal for all metals were greater than 80%. Concentrations of Cr and Ni in the HENGJIA product were more than 200-fold greater than that in K-brick 1 from KEYUAN. Thus, making sludge into K-brick 1 by KEYUAN resulted in lesser concentrations of metals in sludges than did making sludge into thickened sludge cake by HENGJIA. Thus, it is recommended that making sludge into brick is the preferred option. The reason for this is potentially due to mixing with related materials and high-temperature thermal process. This result is consistent with those of previous studies which indicated that the process involved in producing bricks from sludge immobilizes toxic and hazardous materials by thermal treatment (Turovskiy and Mathai, 2006). Concentrations of metals were significantly reduced after being made into K-brick 1, and all concentrations of metals in bricks were less than all the standards listed in Table 2. Thus, making sludge into K-brick 1 is a good way to reuse sludges. However, standards on toxic substances in reused products including bricks and muds are not available. For thickened sludge cake produced by HENGJIA, Cr and Ni still exceeded standards for agricultural use and landfill (CJ/T 249, 2007; CJ/T 309, 2009). So concentrations of both Cr and Ni would need to be further reduced before the sludge could be used for landfill.

Concentrations of PAHs in all sludges were less than their limits of detections Table S2 in the supporting information. Full scans of VOC and SVOC detected no organic compounds except for m-xylene in sample H-raw 1.74%. The limits of detection of VOCs and SVOCs were listed in Table S3 and Table S4 in the supporting information. Raw sludges of these two factories were mainly from electroplating and metalworking industries, with limited numbers of petrochemical industries were included. Thus, PAHs, VOCs and SVOCs were not main contaminants in raw sludges. M-xylene, used for production of isophthalic acid, m-toluic acid and isophthalonitrile, and is also used for synthesis of medicine, spice and dye, might be from the chemical plants. Xylene can irritate eyes and upper respiratory tract. M-xylene is the only organic compound detected in raw sludge and the concentration was reduced to less than the limit of detection in reused products.

3.2. Toxicity identification for sludge leachates

To better evaluate hazards posed by sludges and products made from those sludges, toxicities of leachates of sludges were measured by use of an *in vivo* bioassay. The EC_{50} of the reference toxicant, K_2CrO_4, to *D. magna* was $1.3 \pm 5.0 \times 10^{-2}$ mg/L, which met requirements of ISO 6431 (ISO, 1996) for a valid test. Toxic

Table 1
Mean concentrations of metals and metalloids in sludges and products (mg/kg, dm).

Metal (mg/kg)	H-raw 1.38%	SD	H-raw 1.74%	SD	H-thickened	SD	K-raw	SD	K-brick 1	SD	K-brick 2	SD
Ag	8.52×10^{-2}	1.70×10^{-2}	6.16×10^{-2}	8.50×10^{-3}	N.D.		N.D.		N.D.		N.D.	
As	2.30×10^{1}	2.4	2.22×10^{1}	3.86	1.56×10^{1}	2.48	5.12×10^{1}	3.87	3.33	8.60×10^{-1}	2.70×10^{1}	2.65
Ba	4.76×10^{1}	1.7	5.51×10^{1}	5.17	3.04×10^{1}	5.13	2.85×10^{2}	7.10×10^{1}	6.38×10^{1}	2.76	1.78×10^{2}	5.40×10^{1}
Be	2.17×10^{-1}	5.60×10^{-2}	2.25×10^{-1}	6.60×10^{-2}	6.47×10^{-2}	7.60×10^{-3}	4.87×10^{-2}	3.20×10^{-3}	3.63×10^{-1}	5.40×10^{-2}	5.43×10^{-1}	6.90×10^{-2}
Cd	9.13	9.80×10^{-1}	9.81	1.43	5.49	2.70×10^{-1}	5.56	1.70×10^{-1}	6.97×10^{-1}	9.70×10^{-2}	3.13	7.60×10^{-1}
Cr	1.97×10^{4}	6.26×10^{2}	1.84×10^{4}	7.38×10^{2}	1.07×10^{4}	1.04×10^{3}	9.20×10^{3}	1.20×10^{3}	4.4×10^{1}	2.73	5.64×10^{3}	9.63×10^{2}
Cu	1.47×10^{3}	1.03×10^{2}	1.51×10^{3}	6.60×10^{1}	6.40×10^{2}	38.00	2.91×10^{2}	3.20×10^{1}	5.67	8.70×10^{-1}	3.44×10^{2}	7.60×10^{1}
Ni	1.15×10^{4}	8.23×10^{2}	1.40×10^{4}	6.59×10^{2}	2.00×10^{3}	3.79×10^{2}	4.05×10^{3}	7.63×10^{2}	1.75×10^{1}	1.25	4.00×10^{3}	9.55×10^{2}
Pb	2.70×10^{1}	9.60×10^{-1}	3.32×10^{1}	6.98	1.81×10^{1}	1.17	1.97×10^{1}	2.80	1.69	3.40×10^{-1}	2.54×10^{1}	2.77
Zn	2.87×10^{3}	93	3.35×10^{3}	6.39×10^{2}	8.98×10^{2}	4.50×10^{1}	6.27×10^{1}	4.50	1.26×10^{1}	5.40×10^{-1}	5.13×10^{1}	3.69

H-raw 1.38%: HENGJIA condition tank with Ni 1.38%; H-raw 1.74%: HENGJIA condition tank with Ni 1.74%; H-thickened: Thickened sludge cake of HENGJIA.
K-raw: Material of KEYUAN; K-brick 1: KEYUAN brick with water 12%; K-brick 2: KEYUAN brick with water 50%.
N.D.: Not detected.

potencies of leachates of sludges are shown in Table 5. Toxic units of all leachates of sludges were greater than 1.0, which means that they would pose acute hazards to aquatic organisms. There are no officially recommended methods or criteria for evaluation and classification of sludge and the reused materials regarding their toxicity. Based on the toxicity classification system (TCS) proposed by Persoone, sludge and reused materials, whose TUs are between 1 and 10 (Persoone, 1999), exhibited significant ecotoxicity. TU of K-brick 2 was similar to that of K-brick 1 but was 1.76-fold less than that of H-thickened, which further emphasized that making brick is better than thickened sludge cake placed into landfills. At HENGJIA, TUs in raw sludge and products in which it was used were similar, which indicated that removal of bioavailable metals was limited. TU of H-thickened was greater than 1.0, which indicates that hazards posed when used in landfill should be further considered. When sludge from KEYUAN was used to make K-brick 1 or K-brick 2, TU were reduced 10-fold. But TUs of leachates from bricks were still greater than 1.0, which indicated that leaching from bricks made from sludge from KEYUAN still posed some hazard. Leachate is important for evaluation of hazard since it provides an estimate of the bio-available fraction that could contribute to toxicity if for instance bricks were washed by rainfall. Chemical analyses characterized the bulk matrix of the sludge or products derived from the sludge, but evaluation of toxicity of leachates increased the realism and insight into the true hazards posed by contaminants in sludges, especially when it is used as landfill (Utilization, 2012). Thus, more attention should be paid to identifying hazards of materials made from sludges. The potential for contaminants in leachates to migrate from sludges placed in landfills is great, as is the release of toxic materials due to disturbances in the future. Placing sludges in landfills is inherently more hazardous than immobilized contaminants, especially metals in bricks. While it is true that metals could be leached from bricks and become available, the rate of release is much slower and would result in much less exposure at any given time (Kadir et al., 2016). The release would not be instantaneous. Thus, while ultimately once the brick is dissolved as will ultimately happen, releasing all of the metals, the rate of release would result in lesser hazard at any point in time.

Table 2
Standards for metals in sludges.

Standard	pH	Content (mg/kg)				
		Cu	Pb	Ni	Cr	Zn
GB18918-2002	<6.5	800	300	100	600	2000
	≥6.5	1500	1000	200	1000	3000
GB4284-1984	<6.5	250	300	100	600	500
	≥6.5	500	1000	200	1000	1000
America		4300	840	420	1200	7500
Germany		800	900	200	900	2500
European Union		1750	1200	400	1000	4000

GB18919-2002: Discharge standard of pollutants for multiple wastewater treatment plant.
GB4282-1984: Control standards for pollutants in sludge from agricultural use.
America: US EPA. 40CFR Part 503. Standards for the use or disposal of sewage sludge, 1992.
Germany: The Federal Republic of Germany. AbfklarV. Sewage Sludge Ordinance, 1992.
European Union: (Directive 86/278/EEC) Council directive of 12 June 1986 on the protection of the environment, and in particular of the soil, when sewage sludge is used in agriculture, 1986.

3.3. Concentrations of metals in leachates

Concentrations of As, Ba, Be, Cd, Cr, Cu, Ni, Se and Zn in TCLP leachates are shown in Table 3. Concentrations of Ni, Zn, Cr and Cu were greater than concentrations of other metals in all leachates of sludges, with mean concentrations of 57, 1.07, 0.62 and 0.65 mg/L, respectively. These results were consistent with distributions of total amounts in sludges. Ni was detected in all leachates and has a greater leaching efficiency. For Cr, Cu and Zn, K-raw had a greater leaching efficiency, while for Ni, H-thickened had a greater leaching efficiency than other samples. For Cr and Ni, which exhibit greater concentrations in sludges, rates of leaching were less than 1% and 4% for HENGJIA dewatered sludge cake, were 5% and 4% for K-brick 1 and were all less than 1% in K-brick 2. Therefore, contaminants in K-brick 2 were less bio-accessible. Higher intensity, burning process, lower water percentage and more materials add to the mixture all contribute to lesser bio-accessibility. In sludges from KEYUAN, concentrations of all metals in leachates were significantly less after being made into bricks. The decrease was on average, 90% for both K-brick 1 and K-brick 2. Thus, making sludge into bricks reduced leaching of metals more than making HENGJIA sludge into dewatered filter cake.

Predicted TUs of raw sludges, which were calculated based on the EC_{50} and concentrations of these metals ranged from 0.71 to 78.15 in Table 4 and Table 5. Raw sludge in KEYUAN had a higher predicted TU than raw sludge in HENGJIA, while reused products in KEYUAN exhibited less TU than products made from sludges from HENGJIA. Predicted TU could not be accounted for by concentrations of metals which indicated the importance of combining chemical analysis with toxicity tests. Concentrations of Cr and Ni to predicted TU contributed over 90% of the toxicity of leachates of K-raw sludge, while Cr contributed more than 10% of the TU of leachates of both kinds of HENGJIA raw sludge. However,

Table 3
Concentrations of metals in TCLP Leachates.

Metal (mg/L)	H-raw 1.38%	SD	H-raw 1.74%	SD	H-thickened	SD	K-raw	SD	K-brick 1	SD	K-brick 2	SD
As	7.47×10^{-3}	5.60×10^{-3}	N.D.		N.D.		N.D.		N.D.		N.D.	
Ba	3.40×10^{-2}	1.37×10^{-2}	N.D.		N.D.		N.D.		N.D.		N.D.	
Be	N.D.		N.D.		1.10×10^{-3}	6.10×10^{-4}	1.08×10^{-2}	6.70×10^{-3}	N.D.		N.D.	
Cd	N.D.		N.D.		2.83×10^{-2}	9.80×10^{-3}	N.D.		N.D.		N.D.	
Cr	4.75×10^{-2}	8.90×10^{-2}	9.57×10^{-2}	7.80×10^{-3}	1.01×10^{-1}	5.20×10^{-3}	2.85×10^{0}	2.60×10^{-1}	2.16×10^{-2}	6.70×10^{-3}	4.32×10^{-1}	7.60×10^{-2}
Cu	2.05×10^{-2}	1.20×10^{-2}	2.17×10^{-2}	6.70×10^{-3}	1.47×10^{0}	1.20×10^{-1}	2.38×10^{0}	5.40×10^{-1}	N.D.		N.D.	
Ni	7.84×10^{-2}	2.60×10^{-2}	8.62×10^{-2}	1.56×10^{-2}	7.61×10^{1}	3.47×10^{0}	2.64×10^{2}	2.70×10^{1}	6.21×10^{-2}	3.90×10^{-3}	8.83×10^{-2}	1.30×10^{-2}
Se	N.D.		N.D.		2.11×10^{-2}	1.70×10^{-3}	8.71×10^{-3}	1.60×10^{-3}	N.D.		N.D.	
Zn	N.D.		N.D.		4.40×10^{0}	3.60×10^{-2}	1.99×10^{0}	3.60×10^{-2}	N.D.		N.D.	

H-raw 1.38%: HENGJIA condition tank with Ni 1.38%; H-raw 1.74%: HENGJIA condition tank with Ni 1.74%; H-thickened: Thickened sludge cake of HENGJIA.
K-raw: Material of KEYUAN; K-brick 1: KEYUAN brick with water 12%; K-brick 2: KEYUAN brick with water 50%.
N.D.: Not detected.

Table 4
EC_{50} of metals for *Daphnia magna*.

Metals	EC_{50} (μg/L)	Reference
As	4501	Elnabarawy et al., 1986
Cd	129	Stuhlbacher et al., 1993
Cr	70	Dorn et al., 1993
Cu	1390	Natale et al., 2007
Ni	7590	Khangarot and Ray, 1989
Zn	4367	Muyssen et al., 2002

concentrations of metals in leachates of raw sludge were distributed differently. In leachate of raw sludge from HENGJIA, concentrations of Ni were almost the same as those of Cr, while the contribution of Ni to TU was almost 90-fold less than that of Cr. In leachate of raw sludge from KEYUAN, the concentration of Ni was 92-fold greater than that of Cr, while contribution of Cr and Ni to TU were almost the same. Thus, concentration is not enough to explain hazard, the potential toxicity is also needed. Moreover, in leachate of H-thickened, Ni contributed more than 70% of the predicted TU followed by Cr, Zn and Cu. Cr also contributed almost 100% of the predicted toxicity in leachate of K-brick 1. After sludge from KEYUAN was made into bricks, predicted TU of Cr and Ni was reduced by 89% and 99%, respectively.

3.4. Potency balance analysis

Results of a potency balance analyses indicated that metals especially Cr and Ni contributed significantly to TU (Fig. 2). Metals in sludge from KEYUAN were primary toxicants in both raw sludge and bricks. Cr contributed most of the TU in sludges from KEYUAN, which contributed more than 95% of the TU in leachates of K-brick 1 and K-brick 2 and contributed more than 50% of the toxicity of K-raw. Alternatively, for H-raw 1.38% and H-raw 1.74%, metals contributed 13% and 39% of TU, respectively, which indicated that, unquantified substances contributed to TU. The reason that VOCs and SVOCs failed to identify the key toxicants is probably that the detection limit of VOCs was poor in full scan mode. After acidification, organic toxicants were removed and metals became key toxicants in H-thickened. Ni and Cr contributed most of the TU with contributions of 72% and 10% respectively. The results indicated that metals especially Cr and Ni are primary toxicants in thickened sludge cake used in landfills and bricks containing sludge.

3.5. Suggestions for sustainable reuse of sludge

Since regulations for reused sludges are generally lacking in China, even all around the world, it is essential to improve regulations and developing methods and criteria for assessment of hazard of products, made in part from. Chemical analysis alone is not able to provide a reasonable assessment of potential hazard unless evaluation of toxic effect and identification of toxicants are included. To enhance safer reuse of sludge, identification of key toxicants in raw sludge should be done to provide advises on choosing proper reuse technology and reuse products. Leaching toxicity should also be considered to verify potential toxicity in actual application. Also, researches on different removal rate of related reuse methods should be done. Results of this study show that after treatment with waste acid and mixed with other materials, actual TU in leachates of thickened sludge cake reduced 7% while reduced 90% on average in leachates of reused bricks. Meanwhile, TU contributed by Cr and Ni in leachates from bricks were 89% and 99% less than sludges from KEYUAN while TU in leachates of sludge cake made from raw sludge at HENGJIA were not significantly less than those in the raw sludges. Therefore, compared to making sludge into thickened sludge cake, making sludge into bricks exhibits higher removal rates of various contaminants.

Table 5
Measured and predicted toxicities of TCLP Leachates.

Sample	Actual TU	Predict TU								
		As	Ba	Be	Cd	Cr	Cu	Ni	Se	Zn
H-raw 1.38%	5.65	1.66×10^{-3}	3.09×10^{-3}	N.D.	N.D.	6.79×10^{-1}	1.47×10^{-2}	1.03×10^{-2}	N.D.	N.D.
H-raw 1.74%	3.62	N.D.	N.D.	N.D.	N.D.	1.37	1.56×10^{-2}	1.14×10^{-2}	N.D.	N.D.
H-thickened	5.26	N.D.	N.D.	4.78×10^{-2}	2.19×10^{-1}	1.44	1.05	1.00×10^{1}	2.97×10^{-2}	5.72
K-raw	3.22×10^{1}	N.D.	3.90×10^{-3}	4.70×10^{-1}	N.D.	4.07×10^{1}	1.71	3.48×10^{1}	1.23×10^{-2}	4.56×10^{-1}
K-brick 1	3.15	N.D.	3.02×10^{-3}	N.D.	N.D.	N.D.	N.D.	9×10^{-4}	N.D.	N.D.
K-brick 2	2.99	N.D.	2.1×10^{-3}	N.D.	N.D.	6.17	N.D.	1.16×10^{-2}	N.D.	N.D.

H-raw 1.38%: HENGJIA condition tank with Ni 1.38%; H-raw 1.74%: HENGJIA condition tank with Ni 1.74%; H-thickened: Thickened sludge cake of HENGJIA.
K-raw: Material of KEYUAN; K-brick 1: KEYUAN brick with water 12%; K-brick 2: KEYUAN brick with water 50%; N.D.
N.D.: Not detected.

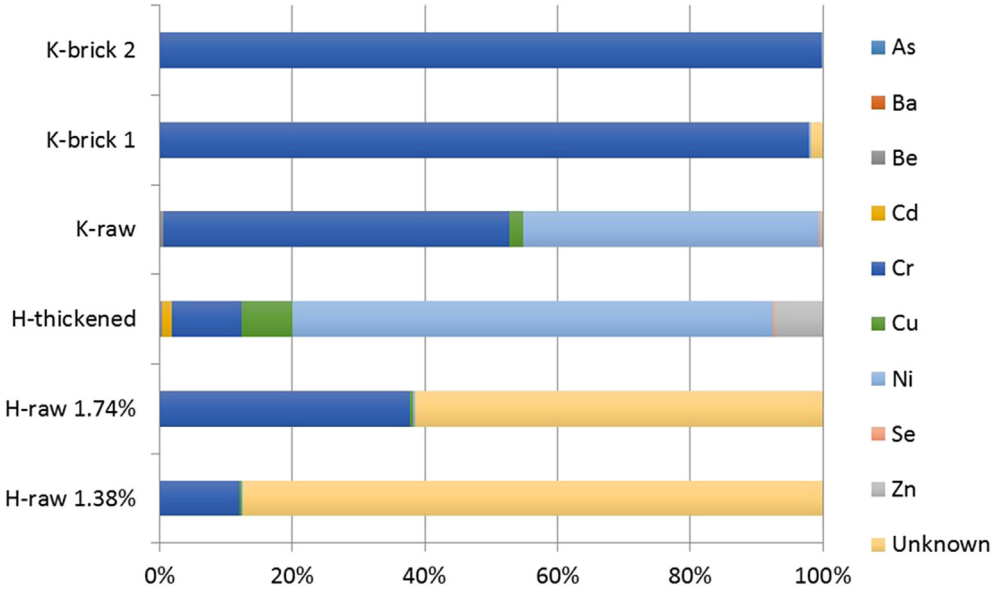

Fig. 2. Toxicity contribution of each metal in sludge leachate. H-raw 1.38%: HENGJIA condition tank with Ni 1.38%; H-raw 1.74%: HENGJIA condition tank with Ni 1.74%; H-thickened: Thickened sludge cake of HENGJIA; K-raw: Material of KEYUAN; K-brick 1: KEYUAN brick with water 12%; K-brick 2: KEYUAN brick with water 50%.

4. Conclusions

Results of this study showed that metals were detectable in all samples of raw sludges and products made from sludges. Concentrations of metals in raw sludge exceed most of the standards from jurisdictions all over the world, especially for Ni and Cr. Based on acute lethality of sludge leachates to *D. magna*, all sludge leachates had TU greater than 1.0, and are potentially toxic to organisms. Ni and Cr contribute over 90% of the toxicity in all sludge leachates from KEYUAN and contribute over 80% in leachate of H-thickened sludge. After evaluating the two approaches for recycling sludge, leachates were still toxic, but concentrations of metals were less than standards. Making sludge into bricks can reduce hazard more than using it to produce thickened sludge cake for placement into landfills. Thus, making bricks is a better way of reusing sludge.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.chemosphere.2016.10.046.

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Supporting Information

"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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Table S1. Detail characteristics of raw sludges in HENGJIA and KEYUAN.

Categories	HENGJIA	KEYUAN
Color	red	brown
pH Range	7.22-9.60	8.78-9.4
Water Content (%) Range	56.57-75.93	55.02-74.64
Water Treatment Process	neutralization	neutralization
Dewatered Method	filter-press	filter-press
Precipitator	poly acrylamide	lime, aluminum polychloride

Table S2. Quality control and limit of quantification (LOQ) of 16 priority PAHs.

	LOQ (ng/g)	Procedural recovery Recovery±RSD (%)	Matrix spike recovery Recovery±RSD (%)
Nap	0.63	68±4%	77±11%
Acy	0.13	104±6%	102±9%
Ace	0.22	105±4%	104±8%
Flu	0.17	82±7%	89±9%
Phe	0.13	93±5%	96±5%
Ant	0.15	81±8%	86±6%
Flt	0.17	84±3%	90±8%
Pyr	0.28	89±4%	95±11%
B[a]A	0.44	90±8%	95±8%
Chr	0.72	86±9%	93±11%
B[b]F	0.15	98±3%	101±9%
B[k]F	0.13	96±4%	100±7%
B[a]P	0.17	92±6%	98±8%
Ind	0.13	98±8%	102±9%
DBA	0.17	92±3%	97±10%
B[ghi]P	0.15	99±5%	105±8%

16 priority polycyclic aromatic hydrocarbons (PAHs) including: Naphthalene(Nap), Acenaphthylene(Acy), Acenaphthene(Ace), Fluorene(Flu), Phenanthrene(Phe), Chrysene(Chr), Indeno(1,2,3-cd)pyrene(Ind), Anthracene(Ant), Fluoranthene(Flt), Pyrene(Pyr), Benzo(a)anthracene(B[a]A), Benzo(b)fluoranthene(B[b]F), Benzo(k)fluoranthene(B[k]F), Benzo(a)pyrene(B[a]P), Dibenzo(a,b)anthracene(DBA) and Bnezo(g,hi)perylene(B[ghi]P). RSD: Relative standard deviation.

Table S3. Limit of detection (LOD) of VOCs full scan.

Chemical Name	CAS No.	LOD((μg/kg)
Vinyl chloride	75-01-4	1.5
1,1-dichloroethene	75-35-4	0.8
Methylene chloride	75-09-2	2.6
Trans-1,2-dichloroethene	156-60-5	0.9
1,1-dichloroethane	75-34-3	1.6
Cis-1,2-dichloroethene	156-59-2	0.9
Chloroform	67-66-3	1.5
1,1,1-trichloroethane	71-55-6	1.1
Carbon tetrachloride	56-23-5	2.1
1,2-dichloroethane	107-06-2	1.3
Benzene	71-43-2	1.6
Trichloroethene	79-01-6	0.9
1,2-dichloropropane	78-87-5	1.9
Bromodichloromethane	75-27-4	1.1
Toluene	108-88-3	2.0
1,1,2-trichloroethane	79-00-5	1.4
Tetrachloroethylene	127-18-4	0.8
Dibromochloromethane	124-48-1	0.9
1,2-dibromoethane	106-93-4	1.5
Chlorobenzene	108-90-7	1.1
1,1,1,2-tetrachloroethane	630-20-6	1.0
Ethylbenzene	100-41-4	1.2
m, p -xylene	108-38-3/106-42-3	3.6
o-xylene	95-47-6	1.3
Styrene	100-42-5	1.6
Bromoform	75-25-2	1.7
1,1,2,2-tetrachloroethane	79-34-5	1.0
1,2,3-trichloropropane	96-18-4	1.0
1,3,5-trimethylbenzene	108-67-8	1.5
1,2,4-trimethylbenzene	95-63-6	1.5
1,3-dichlorobenzene	541-73-1	1.1
1,4-dichlorobenzene	106-46-7	1.2
1,2-dichlorobenzene	95-50-1	1.0
1,2,4-trichlorobenzene	120-82-1	0.8
Hexachlorobutadiene	87-68-3	1.0

VOCs: volatile organic compounds

Table S4 Limit of detection (LOD) of SVOCs full scan

Chemical Name	CAS No.	LOD(μg/kg)
N-Nitrosodimethylamine	621-64-7	451
Phenol, 2-fluoro-	367-12-4	326
Phenol-D6	13127-88-3	424
Phenol	108-95-2	512
Bis(2-chloroethyl)ether	111-44-4	428
2-Chlorophenol	95-57-8	400
Benzene, 1,3-dichloro	541-73-1	414
Benzene, 1,4-dichloro-	106-46-7	412
Benzene, 1,4-dichloro-	95-50-1	304
2-methyl-Phenol	95-48-7	645
Bis(2-chloroisopropyl)ther	108-60-1	382
Hexachloroethane	118-74-1	349
N-Nitrosodi-n-propylamine	621-64-7	431
4-Methylphenol	106-44-5	814
Nitrobenzene-D5	4165-60-0	366
Benzene, nitro-	98-95-3	333
Isophorone	78-59-1	387
2-Nitrophenol	88-75-5	446
2,4-dimethylphenol	105-67-9	736
Methane, bis(2-chloroethoxy)-	111-91-1	285
Phenol, 2,4-dichloro-	120-83-2	510
Benzene, 1,2,4-trichloro-	120-82-1	308
Naphthalene	92-20-3	363
4-Chloroaniline	106-47-8	333
1,3-Butadiene,1,1,2,3,4,4-hexachlor-	87-68-3	339
Phenol, 4-chloro-3-methyl-	59-50-7	547
2-methyl-naphthalene	91-57-6	419
1,3-Cyclopentadiene,1,2,3,4,5,5-hexachloro-	77-47-4	457
Phenol, 2,4,6-trichloro-	88-06-2	555
2,4,5-trochlorophenol	95-95-4	682
1,1'-Biphenyl, 2-fluoro-	321-60-8	368
Naphthalene, 2-chloro-	91-58-7	251
2-Nitroaniline	88-74-4	831
Acenaphthylene	208-96-8	449
Dimethyl phthalate	131-11-3	577
2,6-Dinitrotoluene	606-20-2	887
3-Nitroaniline	99-09-2	736
2,4-Dinitrophenol	51-28-5	941

Acenaphthene	83-32-9	308
Dibenzofuran	132-64-9	354
4-Nitrophenol	100-02-7	746
2,4-Dinitrotoluene	121-14-2	707
Fluorene	86-73-7	507
Diethyl Phthalate	84-66-2	746
4-Chlorophenyl phenyl ether	7005-72-3	433
4-Nitroaniline	100-01-6	476
4,6-dinitro-2-methylphenol	534-52-1	966
Azobenzene	103-33-3	491
2,4,6-Tribromophenol	118-79-6	694
4-Bromophenyl phenyl ether	101-55-3	563
Hexachlorobenzene	118-74-1	353
Pentachlorophenol	87-86-5	826
Phenanthrene	85-01-8	545
Anthracene	120-12-7	512
Carbazole	86-74-8	801
Dibutyl phthalate	84-74-2	821
Fluoranthene	206-44-0	634
Pyrene	129-00-0	632
p-Terphenyl-d14	1718-51-0	551
Benzyl butyl phthalate	85-68-7	684
Benz[a]anthracene	56-55-3	889
Chrysene	218-01-9	592
Bis(2-ethylhexyl)phthalate	117-81-7	1068
Di-n-octyl phthalate	117-84-0	973
Benzo[b]fluoranthene	205-99-2	831
Benzo[k]fluoranthene	207-08-9	764
Benzo[a]pyrene	50-32-8	939
Indeno[1,2,3-cd]pyrene	193-39-5	952
Dibenz[a,h]anthracene	53-70-3	1070
Benzo[ghi]perylene	191-24-2	880

SVOCs: semi-volatile organic compounds.