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Research article

Occurrence, geochemical fractionation, and environmental risk assessment of major and trace elements in sewage sludge

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ABSTRACT

Industrialization and accelerated population growth have created a huge amount of sewage sludge. Many studies have reported the sewage sludge as a sink of major and trace elements, but less is known about their geochemical fractionations. In order to assess the mobility, the distribution, bioavailability, and toxicity of those elements in sludge, we collected the sewage sludge samples from all the seven wastewater treatment plants in Xiamen City, China. Results revealed a strong spatial variation and the occurrence of 48 elements with concentrations ranging from 1.00×10^{-2} mg kg^{-1} (Re) to 9.03×10^{1} g kg^{-1} (Fe) on the basis of dry sludge weight. Sequential extraction procedure showed that residual and oxidizable fractions were the main geochemical fractions of most studied elements. However, Ca, Mn, Sr, and Ni were mainly bound to acid-exchangeable fractions, while Fe, Zn, Cd, Cr, Co, and V were mainly distributed in the reducible fractions. The contamination factor and risk assessment code indicated that Ni, Cu, Zn, Cd, Cr, Co, Sr, Ca, Mn, Mo, Re, and W were highly mobile with less retention time and exerted high environmental risks through sludge land application. The sludge disposal strategy should consider not only the total concentrations of a broad range of elements but also their bioavailability.

1. Introduction

The global use of major and trace elements in industries and consumer products has increased dramatically due to economic and population growth over the last decades. This increase applies to major elements such as Fe, Al, K, Na, Ca, Mg, as well as trace elements like rare earth elements (REE), precious elements (PE) and other less-studied elements, such as Nb, Ga and Tl (Vriens et al., 2017). Many studies had reported the sewage sludge as the sink of major and trace elements which were accumulated during wastewater treatment processes via precipitation, coagulation, complexation with organic matter, particle surface adsorption, and ion exchange (Pathak et al., 2009; Suanon et al., 2017). Pollution of soils, groundwater, surface water, and sediments via the metals leaching from the sludge is a big ecological problem, and its management poses a big challenge in the debate on environment safety (Fang et al., 2016; Li et al., 2017; Pathak et al., 2009).

In 2008, European Union countries produced more than 10 million tons of dry sewage sludge, of which approximately 36% was used in agriculture (Milieu Ltd. et al., 2008). In 2013, China produced 6.25 million tons of dry sewage sludge with more than 80% of which disposed of improperly (Zhen et al., 2017; Yang et al., 2015). The major challenge of sewage sludge is its high concentration of heavy metals and other trace elements that may cause metabolic disorder and chronic diseases in living organisms when their bioavailability surpasses the brink limit (Pathak et al., 2009; Suanon et al., 2017).

Although the total concentrations of elements in sewage sludge and related materials can give important information on overall pollution levels (Cantinho et al., 2015; Yang et al., 2014), previous reports have confirmed that the toxicity, mobility, bioavailability, and geochemical processes of major and trace elements in the environment depend strongly on their geochemical fractions (Miaomiao et al., 2009; Rao et al., 2007; Tessier et al., 1979). Generally, elements can exist as water-soluble; exchangeable; carbonates bound; occlude in Mn, Fe oxides and hydroxides; bound to organic matter or appear in residual fraction (Suanon et al., 2016b; Zhang et al., 2016). The acid-exchangeable fractions, comprising of water-soluble, exchangeable, and carbonate

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bound elements, are easily released into the environment and constitute the bioavailable fractions, although elements that are incorporated into residual phases appear relatively inactive (Suanon et al., 2016b). The other fractions can be relatively active or inactive based on the actual combination of physical and chemical properties (pH, temperature, C: N ration, conductivity and so on) of the sewage sludge, soil or sediment (Hass and Fine, 2010; Rao et al., 2007). Hence, geochemical fractionation through sequential extractions is vital for understanding the physical and chemical behaviors of major and trace elements in the environment in order to set up the proper strategies of sewage sludge management and disposal for sustainable development. Notably, most of the reported works on sewage sludge have been focused on the total contents of heavy metals (As, Cd, Cr, Pb, Mn, Zn, Ni, Cu) and their pollution levels (Wu et al., 2015; Yang et al., 2014). However, investigations related to geochemical fractionations of a broad range of major and trace elements in the sewage sludge appear limited and should enhance the interest of this study.

To assess the distribution and toxicity of major and trace elements, we collected 49 sewage sludge samples from all seven wastewater treatments plants (WWTPs) in Xiamen. This study aimed to (1) study the occurrence and quantify the current ranges of major and trace elements concentrations in sewage sludge, (2) investigate the distribution and geochemical fractionations as a way to understand the mobility and bioavailability of major and trace elements, in order to assess the pollution levels and ecological risks using geo-accumulation index (Igeo), contamination factor (Cf) and risk assessment code (RAC), (3) understand the spatial and temporal variations, (4) reveal the relationships between geochemical fractionations of elements and sewage sludge physicochemical properties according to correlation analysis, and (5) indicate the proper sludge disposal and elements recovery possibilities. To our knowledge, this is the first study of geochemical fractionation on a broad range of elements in the sewage sludge. The results are necessary to evaluate management options which range from sludge landfilling to elements recovery.

2. Materials and methods

2.1. Sample collection and pretreatment

Xiamen is a major city located in the southeast of China (117°53'-118°25′ E and 24°25'-24°54′N). The population of Xiamen has increased from approximately 1.31 million in 2000 to more than 3.92 million in 2016 with the urbanization rate increased from 50.4% to 89.0% (Wang et al., 2018; Xiamen Bureau of Statistics, 2001). In this study, sludge samples were collected on February 28th to March 6th, 2016 from 7 WWTPs (W1-W7), which received 92% of domestic and industrial wastewater from the Xiamen City in 2016. Table S1 in the supplementary information (SI) summarizes the details of each WWTP, including treatment processes, daily dry sludge production, the ratio of industrial to domestic wastewater. Samples were kept at 4 °C, lyophilized, and homogenized for further process.

2.2. Physicochemical characterization

Physicochemical parameters of the sludge samples, such as electrical conductivity (EC), pH, C, N, S, and C/N ratio, were performed. A multi-parameter meter (HACH, HQ40d) was used to measure the EC and pH in the supernatant of 1:10 (sludge: water ratio, w/v) (Suanon et al., 2016b); while macro elemental CNHS/O Analyzer (Vario MAX; Elementar, Germany) was used to measure total carbon (TC), total nitrogen (TN), and total sulfur (TS). Additionally, the C/N ratio was calculated as the ratio of the percentage of carbon over the percentage of nitrogen.

2.3. Total concentrations, geochemical fractionation, and analysis

Total elemental concentration was determined by digesting sludge sample as previously reported (Chen and Ma, 2001; Lomonte et al., 2008). In detail, 0.100 g of samples and 10 mL of aqua regia (Analytical grade HNO_3 (65%) and HCl (37%), Merck, Germany, mixture at 3:1 ratio) were put into the polytetrafluoroethylene digestion tube. The reaction mixture was kept overnight at room temperature (pre-digestion step), after which the digestion was completed under hotplate at 180 °C. The samples were filtered using a Millipore filter (0.45 μm) after cooling, then collected in a 50 mL polypropylene centrifugation tube, and diluted with ultrapure water to 50 mL. All experiments for total concentration were performed in duplicate.

Geochemical fractionations of heavy metals in sewage sludge samples were sequentially extracted using sequential extraction procedure (SEP) (Palleiro et al., 2016; Suanon et al., 2016a) with detail information provided in Table S2 in SI. This fractional method sequentially divided elements into water-soluble (F1), exchangeable (F2), carbonate-bound (F3), Fe-Mn oxides-bound (F4), organic and sulfide-bound (F5) and residual (F6). The total concentrations of Fe, Al, Na, Ca, Mg, Zn, Ti, Cu, Mn, Ba, Ce, La, Gd, Pr, and Dy were analyzed by inductively coupled plasma optical emission spectrometry (ICP-OES, PerkinElmer Optima 7000 DV, USA), while the total concentration of W, Cr, Ni, Sn, Pb, Ga, Co, V, As, Mo, Nd, Rb, Y, Sb, Nb, Sm, Ag, Er, Yb, Cs, Pd, Au, Hf, Eu, Cd, Ho, Tl, Tm, Ru, Re, Pt, Ir, and the concentrations of all studied elements in extracted solution were analyzed by inductively coupled plasma mass spectroscopy (ICP-MS, Agilent 7500CX).

For quality control, a standard solution with a known concentration of elements and an reagent blank were run at regular intervals (1 standard and 1 blank for each set of 10 samples) to assess the precision and accuracy. The recoveries of elements in certified reference sediment sample (GBW07309, GSD-9, Inspection, and Quarantine of the People's Republic of China), which was digested using the same acid digestion procedure (Chen and Ma, 2001; Lomonte et al., 2008), were in the range of 62.7–122.2%. In addition, sequential fractionation efficiency [SFE (%)] was calculated by the ratio of the sum of all fractions to the total concentration (Nemati et al., 2011). Average SFEs were in the range of 85.7–102.9%, indicating good agreement between the sum of all the fractions and the total concentration of a particular element. More information about quality assurance, recovery (R), average SFEs, and the detection limits of target elements are shown in SI (Quality assurance and Table S3).

2.4. Risk assessment

Geoaccumulation index (Igeo), contamination factor (Cf) and risk assessment code (RAC) were used to evaluate the contamination level, and environmental risk of major and trace elements in sewage sludge. *Igeo* is used to understand the current environmental status and element pollution level with respect to the natural environment. It was calculated using Eq. (1) (Yaroshevsky, 2006).

$$I_{geo} = \log_2\left(\frac{C_n}{1.5 \times B_n}\right) \quad (1)$$

where C_n is the detected concentration of element n in the sewage sludge and B_n is the geological background value of element n. Factor 1.5 is used to consider possible variations in the background data. According to Igeo classification, contamination level can be categorized as class 0, Igeo ≤ 0, unpolluted; class I, $0 < Igeo \leq 1$, weakly polluted; class II, $1 < Igeo \leq 2$, moderately polluted; class III, $2 < Igeo \leq 3$, moderately to heavily polluted; class IV, $3 < Igeo \leq 4$, heavily polluted; class V, $4 < Igeo \leq 5$, heavily to extremely polluted; class VI, $Igeo > 5$, extremely polluted.

C_f indicates the degree of element risk to the environment in relation to its retention time. The C_f is defined as the ratio of element concentration of the non-residual phase to the residual phase. C_f was

calculated via Eq. (2) (Jamali et al., 2007).

$$C_f = \frac{C_i}{C_n} \quad (2)$$

where C_f is a significant indicator of the degree of element risk to the environment. C_i and C_n indicate the non-residual and the residual fractions of the element, respectively. Risk assessment indices for Cf, with $C_f < 1$ is considered to be uncontaminated, 1–3 of low contamination, 3–6 of moderate contamination, 6–9 of considerable contamination, and over 9 of high contamination.

RAC is a common ecological risk assessment index based on its content in acid-exchangeable fractions which are weakly associated with sludge and can easily equilibrate with the aqueous phase to become rapidly bioavailable (Li et al., 2017). *RAC* was developed by Perin et al. (1985), for evaluating the mobility and bioavailability of elements in soils, sediments, and sewage sludge. RAC was calculated according to Eq. (3):

$$RAC = \left(\frac{F1 + F2 + F3}{F1 + F2 + F3 + F4 + F5 + F6}\right) \times 100\% \quad (3)$$

RAC indices can be divided into five classes: class I, $RAC \leq 1\%$, no risk; class II, $1\% < RAC \leq 10\%$, light risk; class III, $11\% < RAC \leq 30\%$, medium risk; class IV, $31\% < RAC \leq 50\%$, high risk; and class V, $RAC > 50\%$, very high risk.

2.5. Statistical analysis

The R Studio Desktop version 1.1.442.0 and PAST v 3.20 were used in our study for data and statistical analysis. Spearman correlation analysis was carried out to study the relationships between the sludge physicochemical properties and geochemical fractions of elements. Differences were considered to be significant if $p < 0.05$. Network analysis, which was performed in R environment using Vegan, igraph and Hmisc packages (Li et al., 2015) and visualized using Gephi (Bastian et al., 2009), were used to study the co-occurrence relationship between different elements. Co-occurrence event was considered to be a valid robust correlation if the Spearman's correlation coefficient (R^2) was greater than 0.7 and statistically significant (FDR-adjusted P-value less than 0.01). In addition, to decrease the chances of getting false-positive results, the P-values were adjusted with multiple testing corrections (Benjamini and Hochberg, 1995).

3. Results and discussion

3.1. Physicochemical characterization of the sludge

The physicochemical properties of the sludge samples are listed in Table S4. Generally, the pH values were almost neutral (range between 6.55 and 7.52). However, the pH value in W1 was significantly lower than that in the W4 ($p < 0.01$, Tukey's pairwise comparison, one-way ANOVA test). Electrical conductivity (EC) values varied between 1.933 and 8.404 $mS\,cm^{-1}$ with significant differences among samples ($p < 0.01$, ANOVA test). The TC, TN, and TS were in the range of 207.7–279.7 $g\,kg^{-1}$, 41.6–50.9 $g\,kg^{-1}$, and 6.07–20.0 $g\,kg^{-1}$, respectively. The C/N ratio ranged from 4.90 to 5.91. Remarkably, the C/N ratio was low in W7, which might be due to the high ratio of the industrial wastewater (60.0%).

3.2. The total content of target elements in the sludge

Forty-eight out of forty-nine elements were detected in the sludge samples, as shown in Fig. 1. The most abundant elements such as Fe, Al, K, Na, Ca, Mg, Ti, Zn, Mn, Cu, Sr, and Ba showed obviously high concentration, ranging from 1.17×10^2 mg kg^{-1} DS (Sr) to 9.03×10^4 mg kg^{-1} DS (Fe). Concentrations of W, Cr, Ni, Ce, La, Sn, Pb, Ga, Co, V, As, Mo, Nd, Rb, and Y ranging from 5.00×10^0 mg kg^{-1} DS (Co) to 3.53×10^3 mg kg^{-1} DS (Cr). In addition, Sb, Gd, Pr, Nb, Sm, Ag, Dy, Er, Yb, Cs, Pd, Au, Hf, Eu, Cd, Ho, Tl, Tm, Ru, Re, and Pt were detected at trace level with concentrations ranged from 1.00×10^{-2} mg kg^{-1} DS (Re) to 3.69×10^1 mg kg^{-1} DS (for Sb). Ir was below the detection limit (BLD) in all analyzed samples (Table S5).

In this study, Fe and Al showed the highest concentrations; the same results were also reported elsewhere for sludge (Tou et al., 2017; Vriens et al., 2017; Westerhoff et al., 2015). The median concentrations of Zn, Cu, Cr, and Ni in this study are 1–2 times higher than those found in samples from 107 WWTPs located in 48 cities of China; on the contrary, the median concentrations of Pb, As, and Cd are lower compared with the above-mentioned study (Yang et al., 2014). According to the regulation issued by the Chinese government for acid and alkaline soil (GB 18918-2002), the high concentration of Zn, Cu, Cr, and Ni may raise an issue when some of the sludge are used as a fertilizer in agriculture (Ministry of Environmental Protection, 2002). Regarding the REE, the concentrations were higher than those reported in Switzerland and USA (Vriens et al., 2017; Westerhoff et al., 2015), which might be related to the position of China in the production of REE, as approximately 50% of the world's REE reserves are in China (Chakhmouradian and Wall, 2012).

3.3. Co-occurrence of elements in the sludge

Network analysis tools have been widely used to explore interactions between entities or parameters (Liu et al., 2015). In this work, network analysis was conducted to explore and identify the co-occurrence among elements, as shown in Fig. 2. Very strong significant correlations ($R^2 > 0.8$) were detected between V and As; Cr, Ni, Cu and Ag; Fe and As; Co and W; Ni and Ag; As and Nb, which suggested their similar geochemical behavior or the same origins (Li et al., 2017; Palleiro et al., 2016; Tou et al., 2017). REEs positively correlated well with each other; this might be due to their similar chemical properties (Vriens et al., 2017). REEs also showed a significantly strong correlation ($R^2 > 0.7$) with Al, Fe, As, Tl, Nb, Mo, V, Ga, Rb, and Cs. The co-occurrence of REE in the sludge in this study is in good agreement with the findings of Vriens et al. (2017), which indicates that most REEs correlate relatively well in Switzerland sewage sludge. Co-occurrence provided valuable insights about the origin and pathways of the elements, including the precipitation, coagulation, adsorption, etc. onto the sludge during the wastewater treatment processes. Furthermore, co-occurrence can be used as an indicator to reduce the number of target elements, which will be useful in term of cost and time reduction.

3.4. Spatiotemporal variations of the total content of target elements

The daily variations on the total contents of the target elements were observed in a minor extent ($p > 0.05$), as shown in Fig. S1 (SI). However, strong spatial variations were observed based on a non-parametric test (Kruskal-Wallis, $p < 0.05$). Specifically, Mann-Whitney pairwise comparison indicated a significant difference ($p < 0.001$) between samples from W1, W2, and those from W5. To further understand the spatial variations, a relative distribution percentage based on the average concentration is shown in Fig. 3. It is noticeable that the total concentrations of 32 elements were highest in the sludge samples from W5 where the relative distribution of V, Co, As, and Pb reached up to 64.1%, 60.0%, 49.6%, and 45.0%, respectively. The wastewater from the manufacturing industry, including the tungsten, molybdenum, rare earth elements, and other metal related manufacture, might contribute to their high concentrations (Xiamen Bureau of Statistics, 2017). Noticeably, the highest relative distribution of Ni (44.0%) and Au (38.9%) were found to be in W4. The manufacturing cluster of spectacle frames might release these metals to the wastewater and raise a relatively high level in the sludge. In addition, principal components analysis (PCA) conducted based on the total concentrations of all the detected elements revealed that the total concentrations could be agglomerated into

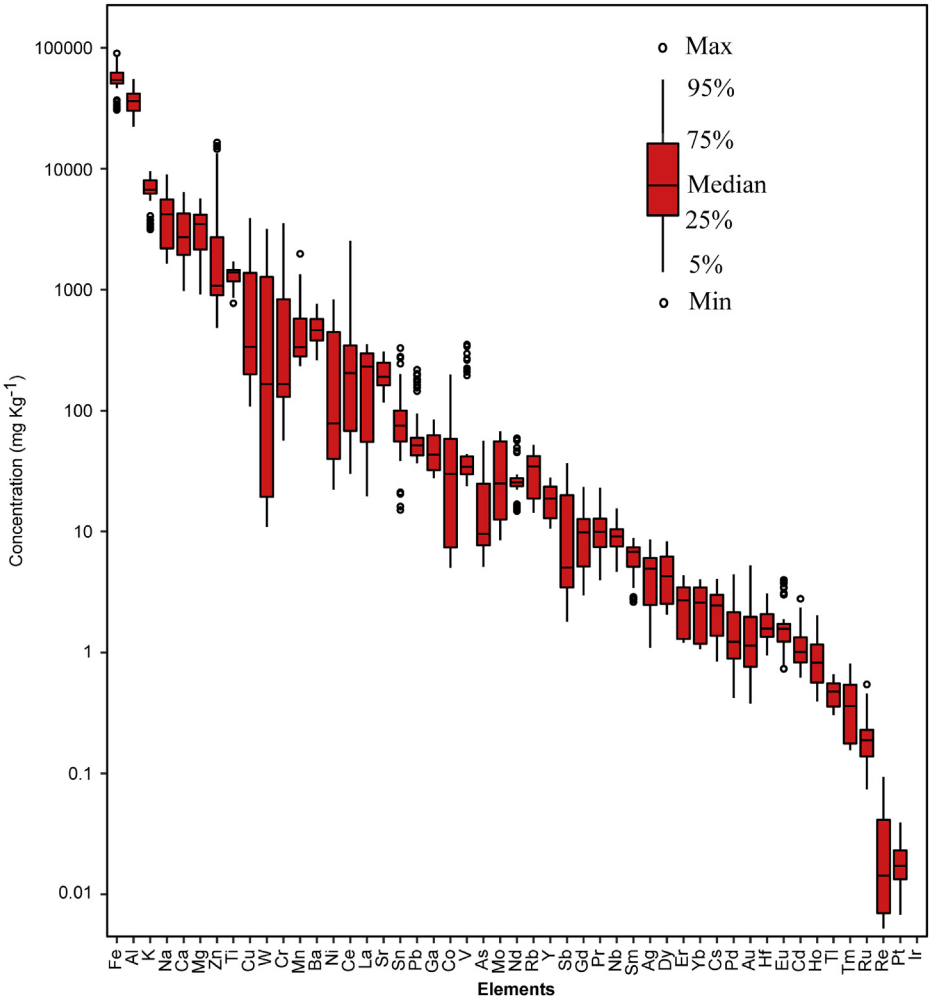

Fig. 1. Total concentrations of elements measured in sewage sludge samples.

separate groups among seven WWTPs regardless the sampling time and samples from W1 and W4 poorly correlated with PCA1 and PCA2, indicating the strong spatial variations and weak temporal variation (Figs. S2 and SI).

3.5. Distribution of geochemical fractionation in sludge samples

The determination of total elemental concentration is the most used technique in sludge quality assessment for the overall pollution level. On the other hand, it is no doubt that geochemical fractionation is a useful way to understand the mobility, bioavailability, and detail information about the toxicity of pollutants (Rao et al., 2007). Table S6 till Table S12 in SI show the average fraction concentrations of elements in samples from each WWTP, where the distribution of each fraction varies for different elements. Based on Fig. 4, some general tendencies could be noticed. Most of the studied elements, including Ag, Al, Ba, Ce, Cs, Dy, Er, Eu, Ga, Gd, Hf, Ho, La, Mo, Mn, Nb, Nd, Pb, Pr, Rb, Re, Ru, Sb, Sn, Sm, Ti, Tm, W, Y, and Yb, were mainly bounded to residual fractions (F6) and organic matter (F5). In the case of V, Tl, Au, Co, Cr, Cu, and Fe, they showed high abundance in residual, reducible, and oxidizable fractions. Ni, Cd, Zn, and Sr mostly distributed in the reducible (F4), carbonate-bound (F3), and water-soluble (F1) fractions. In addition, Ca and Mn were abundant in the water-soluble and exchangeable fractions in most samples.

Elements in the water-soluble, exchangeable, and carbonate bound fractions are more readily released into the environment and might significantly correlate with their concentrations in microorganisms (Hass and Fine, 2010). It is remarkable that the percentage distribution of Co, Cu, Mo, Ni, Rb, Re, Ru, Sb, V, and W was relatively high in water-soluble fraction (F1) in some of the sludge samples, for instance, the average percentage distribution of W was 44.4% in W6 while that of Ni in W6, Cu and Co in W2 were 26.9%, 14.4%, and 13.6%, respectively. This might be due to its presence as free ions or ions complexed with soluble organic matter (Rao et al., 2007). In the case of exchangeable fraction, the average percentage distribution of Ca, Cd, Mn, and Sr was relatively high, ranging from 15.4% (W7) to 36.1% (W3), 0.6% (W4) to 19.2% (W6), 9.2% (W5) to 26.7% (W4), and 6.0% (W6) to 17.2% (W3), respectively. Elements in this fraction are adsorbed and retained on the solid surface by relatively weak electrostatic force and could be released by ion-exchange processes. Influencing adsorption-desorption reactions, lowering of pH or changes in the ionic composition, could influence remobilization of elements from this fraction (Hass and Fine, 2010). Furthermore, the carbonate form as the first acid-extraction step is liable to change with environmental conditions. This fraction is susceptible to changes with pH; the presence of acid rain may enhance the release of these metals in sludge when applied to soils as fertilizer (Tou et al., 2017). Zn, Tl, Ba, and Ga showed a relatively high percentage in the carbonate form with the range of 28.9%–56.9%, 7.1%–28.6%, 4.0%–17.4%, and 3.07%–13.81%, respectively. Numerous literature reported that the high concentration of these elements in the first three fractions (F1, F2, and F3), may accumulate in plants and have harmful effects on the food chain (Jamali et al., 2007; Kousi et al., 2018; Rao et al., 2007; Suanon et al., 2016a).

Reducible fraction, which is also known as a heavy metal sink, is

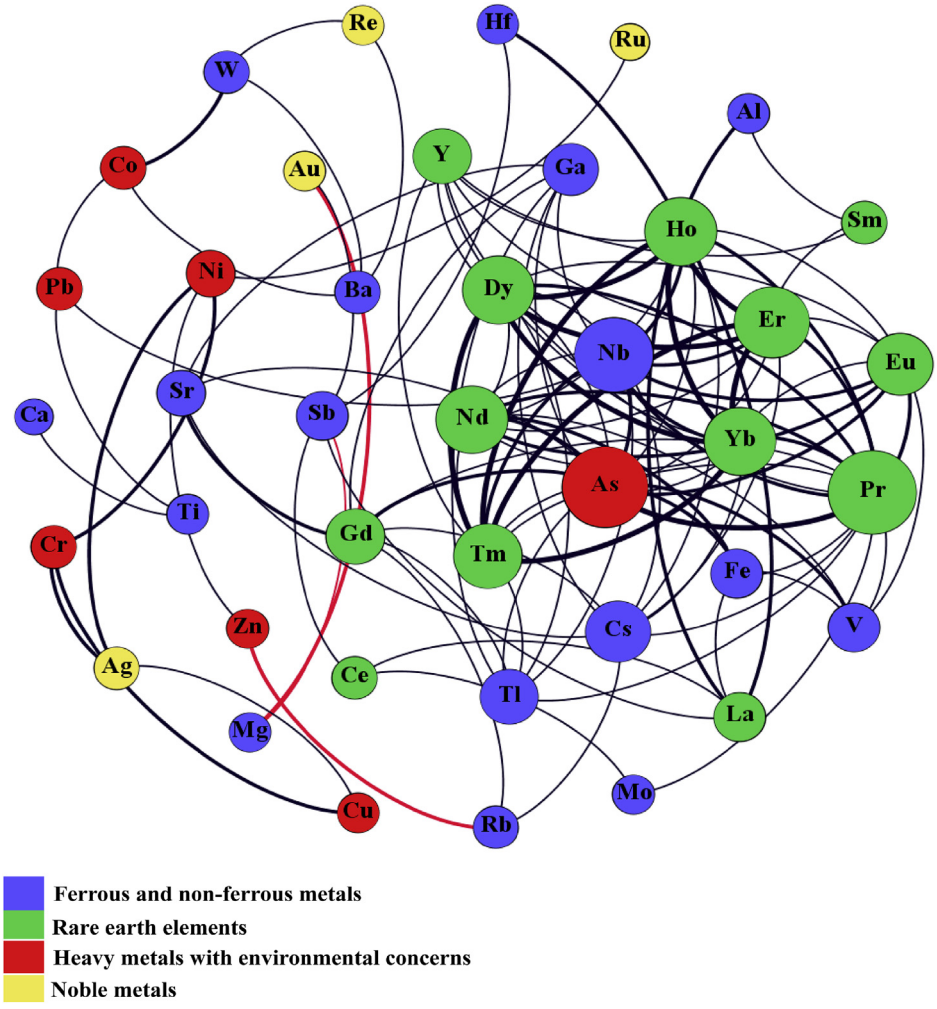

Fig. 2. The network analysis revealing the co-occurrence patterns among different studied elements. The node indicates each element, where the size of each node is proportional to the number of connections (that is, degree). The thin, medium and wide connection between two nodes (i.e. edge) are significant correlation ($p < 0.01$) and proportional to the value of Spearman's coefficients ($0.7 \leq R^2 > 0.8$), ($0.8 \leq R^2 > 0.9$), and ($0.9 \leq R^2 > 1$), respectively. The black edges represent positive correlation while red edges symbolize negative correlation. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

principally composed of the Fe – Mn oxides bound elements (Rao et al., 2007). The predominant association of Cd, Co, Cr, Ni, Zn, and Sr, in the reducible fraction, may be due to the strong sorption properties of amorphous oxyhydroxides of iron and manganese initially in the exchangeable fraction, but with the effect of time they can be transformed into less mobile, specifically adsorbed forms (Rao et al., 2007). Elements in oxidizable fraction might be attributed to complexation or bioaccumulation process with various forms of organic material such as living organisms, detritus, or coatings on mineral particles. The high degree of selectivity for divalent ions compared to monovalent ions exhibited by organic substances might be the reason of the predominance of Cu (44.1%–89.4%) and Pb (33.9%–63.5%) in oxidizable fraction as the probable binding strength order for metal ions onto organic matter being Cu > Pb > Zn > Ni > Co (Filgueiras et al., 2002). The distribution patterns of Cu and Pb are at variance with the report of Tou et al. (2017), who reported the predominance association of Cu and Pb with the reducible fraction in Shanghai sludge.

Moreover, Ag, Re, Sm, Tm, and W had the similar dominance for the organic fraction in most samples with average percentages of 82.7% (W7), 59.2% (W4), 48.9% (W1), 52.3% (W4) and 76.9%(W4),

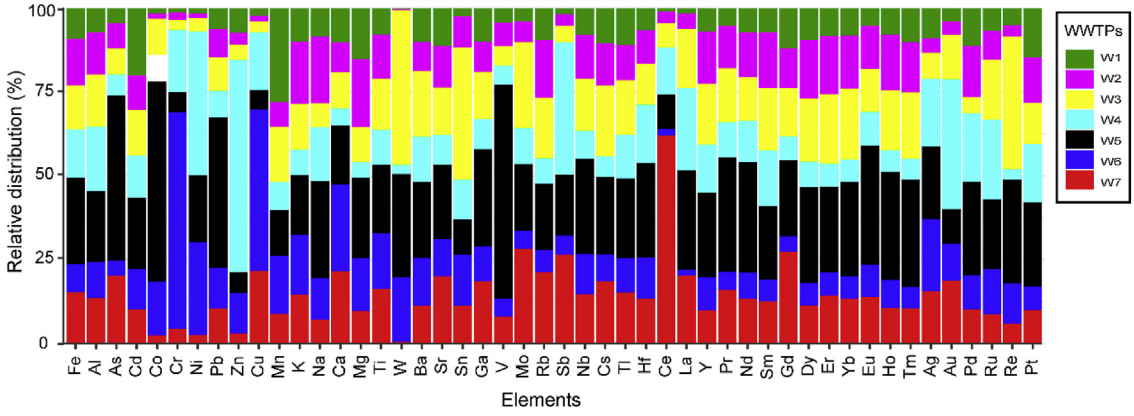

Fig. 3. Spatial variations of relative distribution for the total concentration of the target elements.

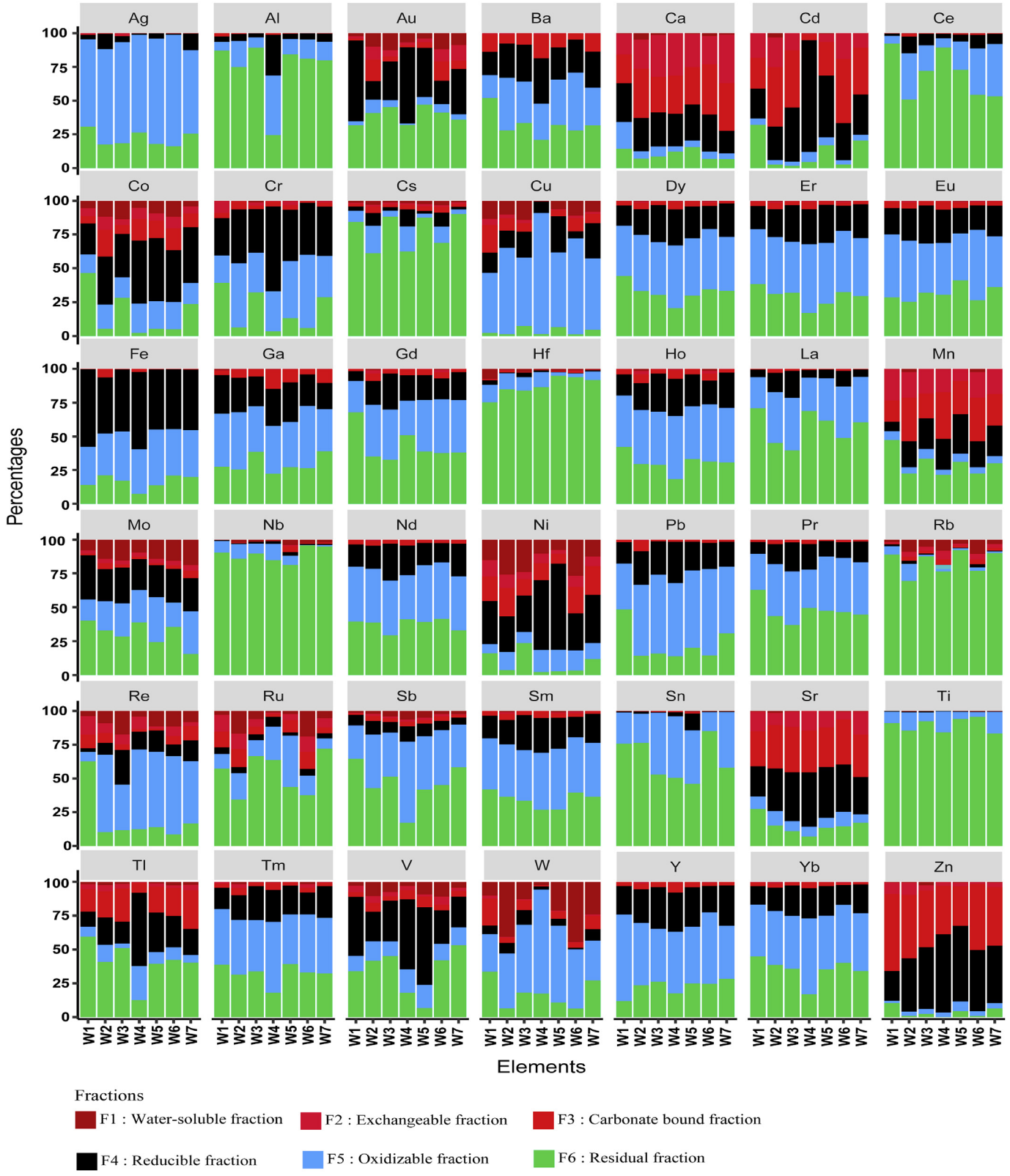

Fig. 4. Spatial distribution of different elemental fractions in sludge samples.

respectively. Elements bounded to organic and sulfide material are supposed to remain in the sludge for longer periods compared to the reducible fraction but may be mobilized by decomposition processes (Tessier et al., 1979). The residual fraction, which is usually attributed to chemical elements within the mineral lattice, was reported to be stable and hardly affected by environmental factors (Hass and Fine, 2010; Kousi et al., 2018). Thereby, the predominant association of Au, Al, Ce, Cs, Hf, La, Nb, Pr, Rb, Sn, Ti with the residual fraction is an indication of their stability in the sewage sludge.

3.6. Effects of sludge physicochemical properties on geochemical fractions

The physicochemical properties could influence the mobility and availability of elements in sludge. Spearman's correlation matrix analysis is shown in SI Fig. S3, where the blue and red colors show the positive and negative correlation, respectively, with the deeper color indicating the stronger correlation. Results indicated that pH was negatively correlated with water-soluble fractions ratio of Ca, Cr, Fe, Sr, Pb, Ru, La, and Ce. This is in agreement with the previous report where low pH value of sludge was in favor of high bioavailability (Liang et al., 2013). The carbonate fraction ratio of Pb showed a significant positive correlation ($R^2 > 0.8$; $p < 0.05$) with the ratio of industrial to domestic wastewater (IWR) suggesting its potential industrial source. It is worth noting that most of the REE fractions ratio (except residual fractions ratio of La and Pr) negatively correlate with the ratio of industrial to domestic wastewater (IWR) suggesting the dust or soils might be the main sources. Our results were consistent with the findings of Westerhoff and his co-workers who reported that the crustal soil materials, which presented in sludge through urban runoff/stormwater or other sources, might be the main source to REE compared to industrial contribution (Westerhoff et al., 2015).

3.7. Pollution levels and ecological risk

3.7.1. Igeo

The *Igeo* was calculated using Eq. (1) and the results are shown in Fig. 5(a). In general, *Igeo* was negative for most of the studied elements (*Igeo* ≤ 1). However, there were moderate to extreme contamination of sludge with As, Pb, Cd, Mo, Sb, Sn, W, Ag, Re, Ru, Pd, Pt, and Au in all the WWTPs. The accumulation of precious metals (Ag, Re, Ru, Pd, Pt, and Au) in the sludge was previously reported (*Igeo* ≤ 4) (Suanon et al., 2017). In addition, Cr and Ni showed moderate to extreme pollution (2 ≤ *Igeo* ≤ 5) in the sludge samples from W4 and W6, while the accumulation of Ni varied from moderate to heavy pollution in W4, W5, and W6 (1 ≤ *Igeo* ≤ 3) as shown in Fig. S4.

3.7.2. C_f

The C_f calculated using Eq. (2) is provided in Fig. 5 (b). Generally, Al, Rb, Cs, Ti, Nb, Sn, La, Ce, and Hf exhibited no contamination (Cf < 1). V, Ga, Mo, Sb, Ba, Tl, Ru, Pr, Nd, Sm, Eu, Gd, Dy, Ho, Er, Tm, Yb, and Au showed low contamination, while Ag, Re, Pb, Y, and W showed moderate contamination. On the other hand, Ca, Cr, Fe, Co, and Sr exhibited considerable contamination, whereas Ni, Cu, Zn, and Cd exhibited high contamination (Cf > 9) and high mobility. Even though Ca, Fe and Sr are essential elements in living organisms; they might be harmful to the ecosystem at such low retention time (Coup and Campbell, 1964; Höllriegl and München, 2011; Šourek et al., 1978). It is noteworthy that the highest mobility of elements was mainly observed in W4 with the Cf values of 27, 40, 44, 640, 13, 6, and 6 for Cr, Co, Ni, Zn, Sr, Tl, and Pb, respectively (Fig. S5.), indicating the potential environmental risks in W4.

3.7.3. RAC

To better understand the bioavailability and risks that the detected elements can cause when sludge have contact with the external environment, *RAC* values were calculated using Eq. (3) and the results were depicted in Fig. 5 (c) and Fig. S6. Generally, Mn, Ni, Zn, Sr, Cd, and Ca are highly bioavailable; hence, they exhibited high ecological risk. V, Co, Cu, Mo, Ba, Re, Tl, Ru, W, and Au posed a medium risk, while Cr, Pb, Sb, Cs, Nb, and REEs posed a light risk. Considering the elements with great environmental concerns, the average RAC values of 45.5 for Zn, 38.8 for Ni, 35.4 for Cd, 26.2 for Co, 16.7 for Cu, 6.4 for Cr, and 1.4 for Pb were observed. These elements showed high bioavailability after land application and may pose a harmful impact on human and other living organisms through the food chain. In contrast, elements like Al, Fe, Ag, Ti, Sn, La, and Ce posed no risk, even if some of them showed strong to very strong contamination through *Igeo index*. The Variances among these indices are due to their different targets. The RAC takes into account the bioavailable fractions of elements and ignores the total concentration, while the *Igeo* focuses on the total concentration of elements. (Huang and Yuan, 2016; Yuan et al., 2015).

3.8. Recovery of valuable elements from sludge

In 2013, China improperly disposed more than 80% of sewage sludge which caused the wasting of resources, soils contamination, and other serious environmental pollution. As for proper disposal, 13.4% was sanitarily landfilled, 2.4% was used in agriculture as soil fertilizer after being stabilized through anaerobic digestion, dewatering and/or drying; 0.36% of the sewage sludge was incinerated, while 0.24% was used as building materials (Yang et al., 2015). Currently, agricultural application and landfilling are the most economical way for sludge disposal, but the high concentrations of toxic elements are big issues. To overcome that problem, the recycling possibility of those elements has been investigated (Nancharaiah et al., 2016; Westerhoff et al., 2015). The recovery process would be in favor of elements with high potential economic values, high concentrations in sludge, high RAC for environmental risks in terms of their mobility and bioavailability, or high Cf considering their retention time. For instance, Zn, Cu, Ni, Co, Cr, Mn, Cd, W, and Mo, which have low retention time, high mobility and high bioavailability fractions indicating their considerable ecological risks, should be recovered or stabilized prior to the sludge application. Different techniques such as phytoremediation, bioremediation, electrokinetics, vitrification, sludge flushing, immobilization, sludge washing, solidification, surface capping, and encapsulation can be helpful for remediation of those contaminated sludge (Babel and del Mundo Dacera, 2006; Cieślik et al., 2015; Liu et al., 2018; Nancharaiah et al., 2016). Although the precious elements showed low environmental risks, their recovery is recommended in terms of their economic values (Table S13). For example, the Au concentration in the sludge from W4 was 5.25 mg/kg, which was even higher than that in some of the gold mines (Basov, 2015), with the economic value of Au in the sludge of W4 reaching $205/ton. Thus, the recovery of elements with the high economic value might be worthwhile for both recyclable uses of resources and contaminant remediation purposes. In the case of REEs and elements like Cs, Nb, Rb, Hf, V, Tl, Sr, considering their limited risk together with their low accumulation in most of the sludge samples (Fig. 5 (a)), their recovery is not suggested due to the high cost of energy and purification (Nancharaiah et al., 2016; Westerhoff et al., 2015).

4. Conclusions

In this study, the occurrence, fractionation, and environmental risk assessment of 49 elements in sewage sludge were investigated in seven WWTPs located in Xiamen City, China. Forty-eight elements were detected with strong spatial variations, where most elements had the highest total concentrations in W5. Network analysis revealed the co-occurrence among specific elements, especially among the REEs. The residual and oxidizable fractions turned out to be the major geochemical fractions of most studied elements. However, Ca, Mn, Sr, and Ni showed high mobility with the average portions of acid-exchangeable fractions (including the water-soluble fraction, exchangeable fraction, and carbonate bound fraction) of 55.2%, 44.3%, 43.1%, and 38.5%. Spearman's correlation between physicochemical properties and geochemical fractions ratio of detected elements suggested lithogenic source as the primary origin of most REE. The risk assessment based on the Cf and RAC indicated that Ni, Cu, Zn, Cd, Cr, Co, Sr, Ca, Mn, Mo, Re, and W were highly mobile with less retention time and might exert high risks. Hence, for the sake of environment and economy, effective remediation or recovery of valuable metals are urgently required before the contact of sludge with the external environment.

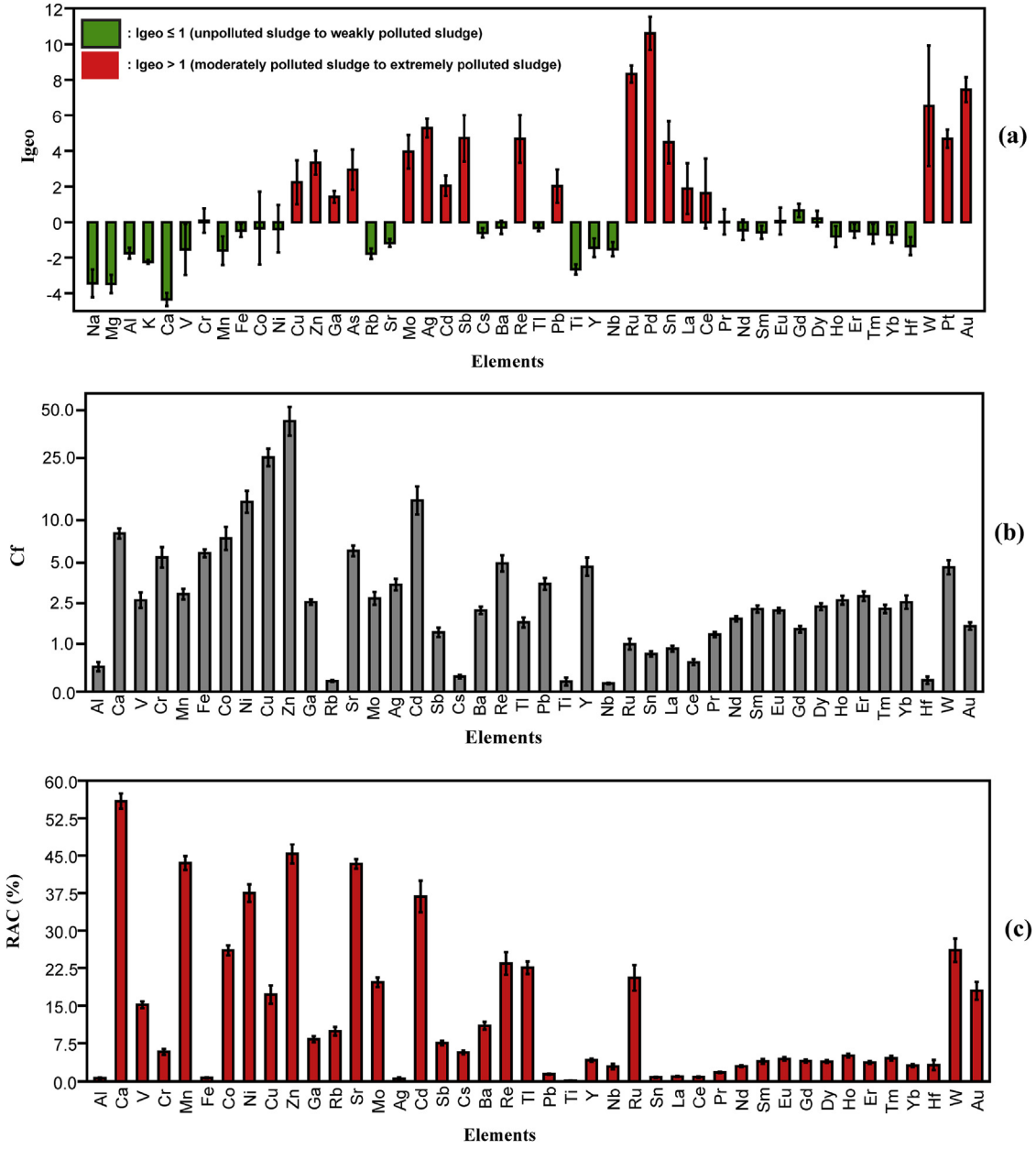

Fig. 5. (a) Geoaccumulation index (I_{geo}), (b) contamination factor (C_f) and (c) risk assessment code (*RAC*) for detected elements in Xiamen WWTPs.

Declarations of interest

None.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jenvman.2019.109427.

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