water

MDPI

Article

Fate and Spatial–Temporal Variation of 23 Elements at 7 Wastewater Treatment Plants in Southeast City of China

Shanshan Guo [1,2], François Nkinahamira [3], Bob Adyari [1,4], Yiqing Zhang [1,4], Anyi Hu [1] and Qian Sun [1,*]

[1] CAS Key Laboratory of Urban Pollutant Conversion, Institute of Urban Environment, Chinese Academy of Sciences, Xiamen 361021, China
[2] College of Resources and Environment, Fujian Agriculture and Forestry University, Fuzhou 350002, China
[3] State Key Laboratory of Urban Water Resource and Environment, Shenzhen Key Laboratory of Organic Pollution Prevention and Control, School of Civil and Environmental Engineering, Harbin Institute of Technology Shenzhen, Shenzhen 518055, China
[4] University of Chinese Academy of Sciences, Beijing 100049, China
* Correspondence: qsun@iue.ac.cn; Tel./Fax: +86-592-6190762

Abstract: Rapid urbanization has caused an increase in the discharge of inorganic elements into the environment; however, the knowledge about the fate and annual variations of multiple elements in wastewater treatment plants (WWTPs) is limited. To understand the distribution and change of those elements, we collected and analyzed wastewater and sludge samples from seven WWTPs in a southeast city of China. Results revealed the elemental concentration ranging from 0.06 $\mu g \cdot L^{-1}$ (Tl) to 221.90 $\mu g \cdot L^{-1}$ (Mn) in the influent, below the detection limit (Er), to 206.40 $\mu g \cdot L^{-1}$ (Mn) in the effluent, and 0.58 $mg \cdot kg^{-1}$ (Tl) to 309.30 $mg \cdot kg^{-1}$ (Zn) in the sludge. The removal analysis revealed that rare earth elements (REEs) were removed well from the wastewater with removal efficiencies ranging from 88.03% (Tm) to 97.37% (Sm), while heavy metals were poor, with removal efficiencies ranging from 10.71% (Mn) to 89.17% (Pb). The elemental flux analysis highlighted that activated sludge served as a major temporary storage site for 23 elements, while excess sludge acted as the major sink for REEs. Significant spatial variations were detected among different WWTPs. On the contrary, the temporal variations were insignificant based on the monitoring data from 2010 to 2020, indicating the satisfactory implementation of current environmental regulations.

Keywords: WWTPs; inorganic element; removal efficiency; elemental fluxes; spatial variations; annual variations

Citation: Guo, S.; Nkinahamira, F.; Adyari, B.; Zhang, Y.; Hu, A.; Sun, Q. Fate and Spatial–Temporal Variation of 23 Elements at 7 Wastewater Treatment Plants in Southeast City of China. *Water* **2023**, *15*, 1226. https://doi.org/10.3390/w15061226

Academic Editor: Andrea G. Capodaglio

Received: 4 February 2023
Revised: 15 March 2023
Accepted: 17 March 2023
Published: 21 March 2023

1. Introduction

The hazardous inorganic elements derived from industries and consumer products are increasingly deposited into the environment with increasing urbanization and population growth. These inorganic pollutants pose serious threats, such as functional impairment of vital organs and cancer, when they enter the food chain [1]. As the recipient of municipal wastewater, wastewater treatment plants (WWTPs) are central to preventing inorganic pollutants from being released into the environment. Therefore, detailed research on the pollution levels and behavior of multiple inorganic elements in WWTPs is necessary.

The occurrence and fate of heavy metals in WWTPs have been investigated around the world, such as in Greece [2], Italy [3], France [4], China [5], Turkey [6], and South Africa [7]. However, most reports focused on the heavy metals in the priority monitoring list [8], and information on the nonpriority pollutants, including critical elements such as rare earth elements (REEs), is limited. In recent years, due to their large exploitation and usage in new technology industries [9], REEs have been continuously discharged into wastewater treatment systems, raising concerns about their potential environmental impacts, including their bioaccumulation in aquatic organisms and their potential toxicity to humans and other organisms [10]. Hence, fully investigating REEs in WWTPs could help improve existing

management to reduce the release of pollutants. A few studies have focused on the REEs in sludge [11,12] and effluent samples [13], but without information on influents, evaluating their removal efficiency or their element flux values is difficult. Therefore, a simultaneous investigation of multiple elements in influent, effluent, and sludge is needed.

Removal efficiencies are calculated to evaluate the removal of inorganic elements from the aqueous phase [14]. However, evaluating elements' fate in wastewater treatment processes on the basis of the removal percentage of the dissolved phase is incomplete, because sludge adsorption is the major way to remove inorganic elements from water. As an alternative, determining elemental fluxes via material flow analysis, which considers both aqueous and solid phases, is an effective way to elucidate the fate of inorganic elements in WWTPs. Previous studies have quantified the flux of inorganic elements into WWTPs, focusing on the inflow and outflow fluxes and their mass loads in the receiving environment [15,16]. Given that adsorption is the primary means of elemental removal, evaluating the storage of elements and elucidating the complete picture of elemental fate in the wastewater treatment system without information on the activated sludge and excess sludge are difficult. Therefore, obtaining a collection of input, storage, and output information is beneficial for a clearer understanding of the distribution of inorganic elements in sewage plants.

Understanding the temporal variation of inorganic elements in WWTPs, as a long-term recipient of inorganic elements in a city, is helpful for effective control of sewage management, as confirmed by different studies. For instance, Sadiq et al. reported that the heavy metal level in the influent and sludge was mostly higher in the dry season than in the wet season; however, the opposite trends were observed for metal concentrations in the effluent [17]. In addition, our previous work revealed an insignificant temporal variation among the four sampling seasons for 52 inorganic elements in sewage sludge [18]. The information was helpful for understanding the seasonal variation of elements, but the time scale of the investigation needs to be expanded because the short-term monitoring results still had a bias in judging the temporal variation. Therefore, to obtain more accurate information about the temporal variation of elements, continuous monitoring in the same region over decades needs to be conducted to provide a detailed pollution trend of elements, facilitating pollution management, especially for areas under rapid development.

To study the fate and variation of multiple elements in a municipal wastewater system with rapid urbanization development, we collected influent, effluent, and active sludge samples from seven WWTPs in a southeastern city of China. The purpose of this study was to (1) investigate the current range of concentration for 23 inorganic elements, including heavy metals and REEs, (2) study the spatial variation of selected elements among seven WWTPs, (3) reveal the removal efficiency of each element, (4) evaluate the distribution and mass load of selected elements for a wastewater treatment system by calculating element flux, (5) understand the annual variation for elements considered in this study over 10 years. These results will provide a useful reference for urban development and sewage disposal.

2. Materials and Methods

2.1. Study Area and Sampling

Wastewater and sludge samples were collected from seven WWTPs in a southeast city, China. W1, W2, and W6 use the oxidation ditch process; W3, W4, and W5 use the anaerobic/anoxic/oxic process; while W7 uses a biological aerated filtration process. The details on treatment processes, daily processing capacity, and daily sludge production of each WWTP over six sampling days are shown in Table S1. Grab samples of influent, effluent, and sludge were collected using individual glass bottles from W1 to W7 in June 2020 (3rd, 5th, and 8th) and January 2021 (4th, 6th, and 8th).

2.2. Analytical Methods

The influent and effluent samples were stored at 4 °C after being acidified to pH < 2 by using HNO_3 (65%, analytical grade, Merck, Germany). The sludge samples were dewatered

via centrifugation (Heraeus Multifuge X1R, Thermo, Waltham, MA, USA) for 5.0 min at 8000 rpm (4 °C), then freeze-dried using a lyophilizer (FD-1A-50, Boyikang, Beijing, China). The dried sludge samples were sieved using a screen cloth (mesh size < 100 nm) and preserved at −20 °C.

Wastewater samples were prepared following the USEPA 3015A method [19]. An aliquot (9.00 mL) of influent or effluent and 1.00 mL of nitric acid (65%, analytical grade; Merck, Darmstadt, Germany) were added into a polytetrafluoroethylene digestion vessel and placed in a microwave (MASTER 40A021, CEM Corporation, Charlotte, NC, USA). During the digestion procedure, the temperature was increased to 180 ± 5 °C in 10.0 min and remained at this level for 30.0 min. Subsequently, the digested samples were filtered through a 0.45 μm Millipore filter after cooling and diluted to 20 mL with ultrapure water. The digestion of sludge samples was completed following the USEPA 3051A method [20]. Sludge sample (0.100 g) and freshly prepared reverse aqua regia (9.00 mL, analytical grade, 65% HNO_3 and 37% HCl, Merck, 3:1 mixture ratio; Merck, Germany) were mixed in a digestion tube and maintained overnight at room temperature. In a microwave system, this mixture was heated to 180 ± 5 °C for 10.0 min and maintained at that temperature for 60.0 min. Lastly, the cooled digestion solution was filtered through a 0.45 μm Millipore filter and diluted to 40 mL with ultrapure water.

Elements with relatively high concentrations in sludge, including Mn, Zn, La, and Ce, were detected by ICP-OES (PerkinElmer Optima 7000DV, Waltham, MA, USA). All elements in effluent and influent and those with relatively low concentrations in sludge (V, Co, Ga, Cr, Cd, Sb, Tl, Pb, Y, Pr, Nd, Sm, Eu, Gd, Dy, Ho, Er, Tm, and Yb) were detected by ICP-MS (Agilent 7500CX, Santa Clara, CA, USA). The external standard method was used to quantify each element, and a standard curve was prepared using a multielement standard solution (Guobiao Beijing Testing & Certification Co., Ltd., Beijing, China).

2.3. Quality Assurance and Quality Control

The instrumental blank, procedural blank, sample repetition, and elemental recovery for each sampling batch were evaluated. The elemental recovery from sludge was evaluated using a standard reference material (GBW07309, GSD-9) with the known concentration of elements under the same analytical method mentioned above. The elemental recovery from wastewater was evaluated using a matrix spike of a multielement standard solution (Guobiao Beijing Testing & Certification Co., Ltd., Beijing, China).

All the instrumental blanks were below the instrumental detection limits. All the procedural blanks were below the method detection limits, indicating the absence of contamination during the sample pretreatment and determination. Elemental recovery ranged from 80% to 120% for wastewater samples, while this was 60–130% for sludge samples (Table S2), which met the requirement of simultaneous analysis of inorganic elements in a complex matrix [21,22]. The relative standard deviation (RSD) of triplicate analysis of standard materials or spiked wastewater was in the range of 0.66–4.82% and 0.08–7.66%.

2.4. Data Processing

The removal efficiency (RE, %) for individual elements from the aqueous phase was calculated as follows:

$$\mathrm{RE}(\%) = \frac{C_{\text{influent}} - C_{\text{effluent}}}{C_{\text{influent}}} \times 100 \quad (1)$$

where C_{influent} and C_{effluent} are the concentrations of each element in the influent and effluent ($\mu g \cdot L^{-1}$), respectively.

The daily mass flux of elements in WWTPs was calculated using the following equation:

$$M_{\text{influent}} = C_{\text{influent}} \times Q_{\text{influent}} \quad (2)$$

$$M_{\text{effluent}} = C_{\text{effluent}} \times Q_{\text{effluent}} \quad (3)$$

$$M_{\text{excess sludge}} = C_{\text{activated sludge}} \times Q_{\text{excess sludge}} \quad (4)$$

$$M_{\text{storage in WWTPs}} = C_{\text{activated sludge}} \times Q_{\text{activated sludge}} \quad (5)$$

where M_{influent}, M_{effluent}, $M_{\text{excess sludge}}$, and $M_{\text{storage in WWTPs}}$ are the daily mass load of each inorganic element ($kg \cdot d^{-1}$) in influent, effluent, excess sludge, and storage in WWTPs, respectively. $C_{\text{activated sludge}}$ is the elemental concentration of each element in activated sludge ($mg \cdot kg^{-1}$). Q_{influent}, Q_{effluent}, $Q_{\text{excess sludge}}$, and $Q_{\text{activated sludge}}$ are the daily capacity of each inorganic element for influent ($m^3 \cdot d^{-1}$), effluent ($m^3 \cdot d^{-1}$), flux of excess sludge ($t \cdot d^{-1}$), and flux of activated sludge ($t \cdot d^{-1}$) in each WWTP, respectively. The values of Q_{influent}, Q_{effluent}, $Q_{\text{excess sludge}}$, and $Q_{\text{activated sludge}}$ are shown in Table S1.

2.5. Statistical Analysis

R Studio Desktop version 1.3.959 and PAST v 3.20 were applied for the statistical analysis of data. Significance level was considered when $p < 0.01$ and $p < 0.05$. Correlation analysis was applied to evaluate the correlation between removal efficiency for inorganic elements and sludge retention time (SRT), as well as the correlation among the concentrations in the influent, effluent, and sludge. Principal component analysis [23] was conducted to investigate the spatial variations of inorganic elements in the 7 WWTPs. Kruskal–Wallis one-way analysis of variance and Dunn's multiple comparisons tests [24] were used to analyze the differences in element removal efficiency, the elemental concentration of 7 WWTPs, and the annual variation of elements in 10 years.

3. Results and Discussions

3.1. Concentration of Elements in WWTPs

The inorganic elements considered in this study were classified into two groups: heavy metals (Zn, Cr, Cd, Sb, Tl, Pb, Mn, Co, Ga, and V) and REEs (Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Dy, Ho, Er, Tm, and Yb). The heavy metals were a group of widely studied elements whose concentrations fluctuate considerably in WWTPs, while the REEs were a group of trace elements with similar characteristics that are often used as indicators to observe pollution in new technology industries. The concentrations of each element in the influent, effluent, and sludge are presented in Figure 1.

The influent samples demonstrated concentration differences of over three orders of magnitude between the most abundant elements (e.g., Mn and Zn, <250 $\mu g \cdot L^{-1}$) and the least abundant elements (e.g., Tl, Cd, Tm, Ho, Eu, and Yb, <0.05–0.5 $\mu g \cdot L^{-1}$). Mn (221.90 $\mu g \cdot L^{-1}$) exhibited the highest concentration among the heavy metals, followed by Zn (142.20 $\mu g \cdot L^{-1}$), Cr (22.00 $\mu g \cdot L^{-1}$), Ga (20.52 $\mu g \cdot L^{-1}$), V (7.85 $\mu g \cdot L^{-1}$), Pb (7.52 $\mu g \cdot L^{-1}$), Co (5.35 $\mu g \cdot L^{-1}$), Sb (1.14 $\mu g \cdot L^{-1}$), Cd (0.29 $\mu g \cdot L^{-1}$), and Tl (0.06 $\mu g \cdot L^{-1}$). According to Table S3, the influent concentrations of the priority substances for monitoring, including Cd, Pb, Cr, and Zn, were comparable with those in other Chinese cities (Shanghai, Chongqing) and other countries (Norway, the Czech Republic, and Italy). The most abundant elements among the REEs were Ce (16.21 $\mu g \cdot L^{-1}$), La (14.88 $\mu g \cdot L^{-1}$), Nd (4.89 $\mu g \cdot L^{-1}$), and Y (4.23 $\mu g \cdot L^{-1}$), while the concentrations of the other REEs ranged from 0.11 $\mu g \cdot L^{-1}$ (Tm) to 2.73 $\mu g \cdot L^{-1}$ (Pr).

In the effluent, the elemental median concentration was 0.89 $\mu g \cdot L^{-1}$ (Nd)–206.40 $\mu g \cdot L^{-1}$ (Mn), excluding Er, which was below the detection limit (0.005 $\mu g \cdot L^{-1}$), and the concentration difference was about two orders of magnitude. For heavy metals, Mn and Zn showed the highest quantities, just as they did in the influent. The median concentrations of the priority monitored heavy metals, namely, Zn, Cr, Pb, and Cd, were 72.40, 7.91, 0.99, and 0.15 $\mu g \cdot L^{-1}$, respectively, in discharge water (Table S3), which did not exceed the discharge standard of pollutants for municipal WWTP (GB 18918-2002) [25]. For REEs, Nd had the highest concentration, followed by Y (0.83 $\mu g \cdot L^{-1}$), Ce (0.59 $\mu g \cdot L^{-1}$), La (0.29 $\mu g \cdot L^{-1}$), and Gd (0.17 $\mu g \cdot L^{-1}$), with the rest falling below 0.1 $\mu g \cdot L^{-1}$.

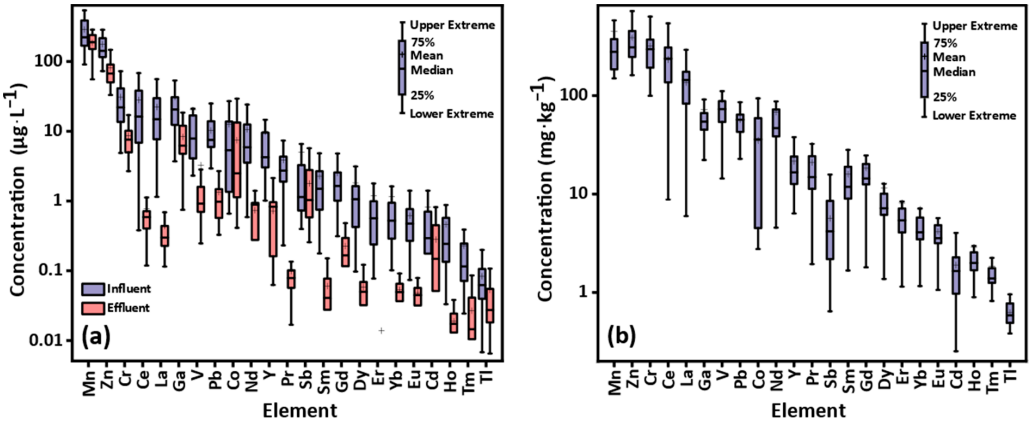

Figure 1. Element concentrations in influent and effluent (**a**) and in sludge (**b**) at 7 WWTPs (box plots show the upper extreme, lower extreme, 25th and 75th percentile, mean and median values).

The concentration span in sludge samples differed by over two orders of magnitude, in which the elements with the highest quantities were Zn, Cr, and Mn (<310 $mg \cdot kg^{-1}$) and those with the lowest quantities were Yb, Eu, Ho, Tm, and Tl (0.5–5 $mg \cdot kg^{-1}$). Among the heavy metals, Zn (309.30 $mg \cdot kg^{-1}$), Cr (296.40 $mg \cdot kg^{-1}$), Pb (56.90 $mg \cdot kg^{-1}$), and Cd (1.69 $mg \cdot kg^{-1}$) were comparable with, or lower in the present study than, studies conducted in 48 other cities in China [26], as shown in Table S3. Meanwhile, the concentrations of the REEs in sludge were in the range of 1.38 $mg \cdot kg^{-1}$ (Tm) to 237.6 $mg \cdot kg^{-1}$ (Ce) and were significantly higher (Dunn's test, $p < 0.05$) than those found in Switzerland (0.07–19.0 $mg \cdot kg^{-1}$) [16] and USA (0.02–7.35 $mg \cdot kg^{-1}$) [27]. The massive storage and extensive use of REEs in China lead to abundant REEs in sludge [28].

3.2. Spatial Variation of Elements in Seven WWTPs

In influent (Figures 2a and S1a–c), a spatial variation of elemental concentrations was observed in W1 and W5 compared with the other WWTPs. The spatial variation in W1 could be attributed to the high concentrations of REEs (Dunn's test, $p < 0.05$), while that in W5 might be due to the high concentrations of heavy metals, including V, Sb, and Cd. For example, the concentrations of V and Sb in W5 were 98.41 and 179.1 $\mu g \cdot L^{-1}$, respectively, whereas these were only in the range of 4.78–11.05 and 31.49–114.20 $\mu g \cdot L^{-1}$, respectively, in the other WWTPs. The concentrations of Y and Er in W1 were 40.32 and 4.07 $\mu g \cdot L^{-1}$, respectively, whereas they were only in the range of 4.46–9.82 and 0.30–0.71 $\mu g \cdot L^{-1}$, respectively, in the other WWTPs. In addition, a strong correlation was observed among the REEs (R^2 = 0.5–1.0, Figure S2a). The similar usage and source might lead to their co-occurrence and their high concentrations in W1.

Significant spatial variations in elemental concentrations were also observed in sludge (Figures 2b and S1d–f). W7 was separated from the other WWTPs because of the low concentrations of REEs and heavy metals. W1 was separated because of the high REE content (Dunn's test, $p < 0.05$). The high concentrations of REEs in the influent, together with the high adsorption tendency of REEs in the sludge [28], led to the significantly high concentrations in the sludge in W1.

In the effluent, the spatial variations in elemental concentrations were observed (Figures 2c and S1g–i). W5 was separated from the other WWTPs because of the high concentration of heavy metals, while W4 formed an independent group given the low proportions of elements. Notably, the proportion of REEs in the effluent was lower than that in the influent and sludge. Moreover, REEs had a positive correlation in sludge (R^2 = 0.9–1.0, Figure S2b) and a weak correlation in effluent (R^2 = 0.1–0.5, Figure S2b), indicating that REEs were preferred for adsorption by sludge in W1.

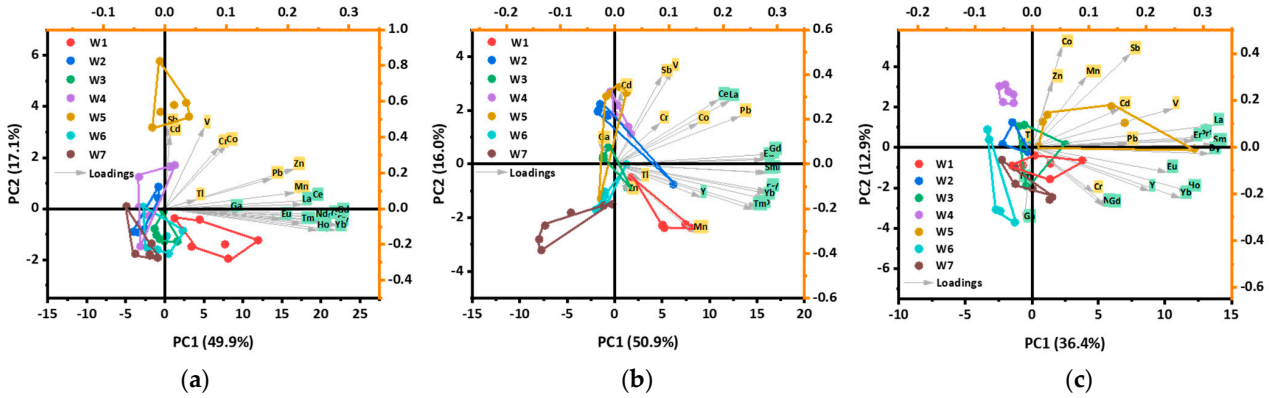

Figure 2. Principal component analysis for 23 elements in influent (**a**), sludge (**b**), and effluent (**c**) at 7 WWTPs. Arrows indicate 23 elements. Dots indicate WWTP: red—W1, blue—W2, green—W3, purple—W4, goldenrod—W5, cyan—W6, and brown—W7. Letters with a yellow background are heavy metals, whereas those with a green background are REEs.

3.3. Removal Efficiency for Elements

The removal efficiencies for 23 elements from the aqueous phase in the seven WWTPs are shown in Figure 3 and Table S4. REEs were efficiently removed from the wastewater with removal efficiency rates in the range of 88.03% (Tm) to 97.37% (Sm). Among the heavy metals, V and Pb were efficiently removed, with median removal efficiencies of 83.96% and 89.17%, respectively. The removal efficiencies for Cr, Ga, Cd, Zn, Tl, and Sb were 65.75%, 64.93%, 53.00%, 51.75%, 46.24%, and 31.61%, respectively. On the contrary, limited removal of Co (27.66%) and Mn (10.71%) was achieved. A previous study showed that Cd, Zn, Tl, Sb, Co, and Mn were mainly present in the soluble fraction; thus, these elements were hardly removed by precipitation in the primary sedimentation treatment [29,30]. In our previous study, Cd, Zn, Tl, Co, and Mn mainly existed in the water-soluble, exchangeable, and carbonate phases in the sludge [28]. Therefore, these elements might be released as dissolved ions to the aquatic phase after adsorption in sludge. Moreover, the addition of flocculant (such as $FeCl_3$), which remained one of the key treatment processes for removing impurities (primarily suspended particles) in WWTPs [31], might increase the concentration of inorganic elements (Co) in effluent [32], consequently causing low removal efficiencies. When focusing on each sewage treatment plant, the median values of removal efficiencies for 23 elements were 96.61% (W1), 80.43% (W2), 86.72% (W3), 87.24% (W4), 90.27% (W5), 90.49% (W6), and 79.59% (W7). Significantly high efficiencies were observed in W1, while significantly low efficiencies were observed in W7 (Dunn's test, $p < 0.05$, Table S4). SRT, which is the average residence time of microorganisms in aeration pools [33], might be related to the difference in the removal efficiency rates of the seven WWTPs. Figure S3 shows a negative correlation ($r = -0.36$, $p < 0.01$) between removal efficiencies and SRTs. The SRTs of W1–W7 were 11.10, 16.50, 13.03, 20.95, 17.00, 15.70, and ~30 d, respectively. Sterritt et al. showed similar results; the removal rate for heavy metals decreased with increasing sludge age [34]. The long SRT in W7 indicated the slow growth of biomass, which could reduce the elemental adsorption and increase the elemental concentrations in the wastewater [34]. The long SRT might also decrease extracellular polymer substances (EPS) [35], thereby decreasing elemental adsorption on the EPS or biomass. By contrast, the short SRT in W1 indicated the fast growth of biomass and, consequently, the high removal of inorganic elements via adsorption. In addition, a bio-absorption study indicated that the adsorption capacity of sludge increased with increasing concentration of inorganic elements because the concentration gradient is an important driving force for the transfer of elements between the aqueous and solid phases; that is, the concentration is proportional to the mass transfer effect [36]. For example, the concentration of Y (with a concentration percentage of 60% and a removal rate of 97.51%) in W1 was higher than that in other

WWTPs (with a concentration percentage below 10% and a removal rate of 75.37–97.03%), so the high concentration of Y in W1 was more likely to be adsorbed by sludge.

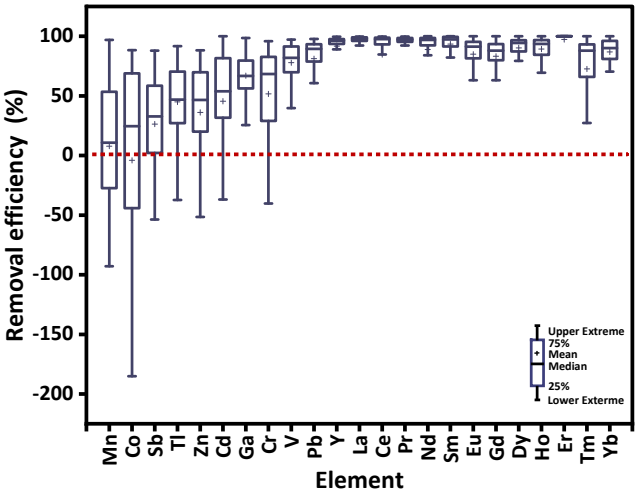

Figure 3. Overall removal efficiency of 23 elements at 7 WWTPs (box plots show the upper extreme, lower extreme, 25th and 75th percentile, mean and median values).

3.4. Elemental Flux

The element fluxes (total mass loads of inorganic elements) of the seven WWTPs were calculated and extrapolated to the elemental fluxes of the whole municipal sewage treatment system, as shown in Figure 4. The total inflow flux value of inorganic elements was 570 kg·d^{-1}, of which the inflow flux values of W1–W7 were 104, 36, 45, 47, 126, 104, and 108 kg·d^{-1}, respectively. Industrial production was the main source of inorganic elements of wastewater in W1 and W5, which promoted the increase in inorganic pollution concentration in raw wastewater. Therefore, the high element flux in W1 and W5 was attributed to a high mass load per cubic meter of water in the influent, which was 11.6 kg·m^{-3} (W1) and 10.0 kg·m^{-3} (W5), respectively. Although the mass load per ton of water for W6 (4.3 kg·m^{-3}) and W7 (4.1 kg·m^{-3}) was low, the inflow flux was comparable with or higher than other WWTPs, which was mainly caused by the large volume of wastewater. In addition, the heavy metals flux was 7–9 times the REE flux, which might be related to the extensive use of heavy metals and the presence of elements with high abundance in the crust, such as Mn [37]. Regarding heavy metals, the flux of W5 was 126 kg·d^{-1} higher than those in other WWTPs (37–104 kg·d^{-1}). Meanwhile the highest REE flux was found in W1 (20 kg·d^{-1}), which had values in the range of 3–15 kg·d^{-1}.

In terms of outflow, the total inorganic element flux value was 563 kg·d^{-1}, of which the element flux values via the excess sludge and effluent were 268 and 295 kg·d^{-1}, respectively. Heavy metals were comparable in effluent and excess sludge, with daily loads of 292 and 188 kg, respectively. REEs were mostly adsorbed in excess sludge with a daily load of 80 kg; this was higher than that in the effluent (3 kg·d^{-1}). Hence, excess sludge was an essential sink for REEs in WWTPs. REEs are critical metals with high value, and recycling them from sludge had become a hot topic; for example, PCDP-M-SHM performed well in the extraction of REEs from industrial sludge [38]. Therefore, further development of recycling technology might be an excellent solution to reduce the pollution of REEs in solid waste. Moreover, the total inorganic element flux value of storage was 1852 kg·d^{-1}, which was higher than the inflow and outflow. This finding indicated that the sludge in the sewage treatment plant was a sink for storing inorganic elements and was the main temporary storage site for inorganic elements in urban areas. Ensuring the operation and management of WWTPs is essential to prevent inorganic element contamination and promote urban sustainability. The development of a dynamic cost model to optimize operation technology and economy [39], the use of a machine learning model to complete pollutant process

analysis [40], and the construction of a wireless sensor network to synchronize water quality monitoring and management [41] are some useful tools reported for optimizing the management of WWTPs. In the future, we can utilize modeling methods, intelligent management techniques, and other tools to strengthen the management of inorganic elements in WWTPs to avoid unnecessary environmental impacts.

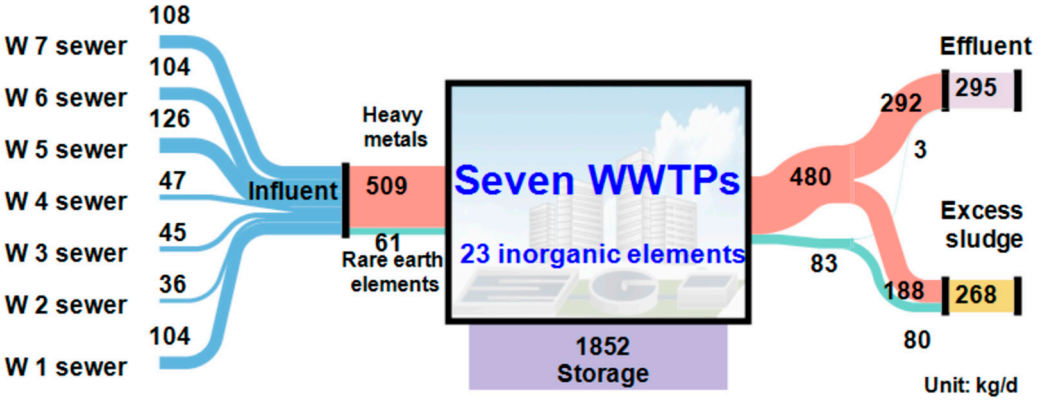

Figure 4. Elemental flux at 7 WWTPs (unit was kg·d^{-1}). The flow from sewer to WWTP represents inflow of elements, while the flow discharged from WWTP represents the output of elements from effluent and excess sludge. Storage gives an indication on elemental flow saved in WWTP. The 23 elements are classified as heavy metals and REEs. Heavy metals (light coral) including Zn, Cr, Cd, Sb, Tl, Pb, Mn, Co, Ga, and V; REEs (aquamarine) including Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Dy, Ho, Er, Tm, and Yb.

3.5. Annual Variations of Elements in Sludge

Annual variations of elemental concentrations were investigated by revisiting the information on the sludge samples from W3, W4, and W7 in 2010, 2014, and 2016 based on previous studies. There was no significant difference in the elemental concentrations in the sewage sludge over the period of 2010–2020 (Kruskal–Wallis test; Dunn's test, $p > 0.05$, as shown in Figure 5). A low annual variation was observed for Ga, Mn, and Cd, with RSD in the range of 10–22%. Similarly, a stable trend was observed in heavy metals, such as Cr, Pb, and Zn. This phenomenon was possibly the result of balancing the heavy metal concentration of sludge by increasing biomass because the concentration of heavy metals per unit weight of activated sludge will be diluted by the growing biomass, regardless of whether heavy metals were continually accumulated by the expanding activated sludge [42]. In the case of REEs in the sewage sludge, no significant difference was found from 2010 to 2020 (Kruskal–Wallis test; Dunn's test, $p > 0.05$). Although the REEs' related industrial production grows fast in China, the stable trend over the past 10 years indicated the proper control of REEs released via wastewater discharge in the southeast city of China. The "Emission Standards of Pollutants from Rare Earths Industry" (GB 26451-2011) issued by the Ministry of Ecology and Environment of the People's Republic of China in 2011 regulated the amount of industrial wastewater containing REEs. The government had also introduced a sufficient policy to promote cleaner production in the REE industry [43]. REEs in discharged wastewater have been effectively controlled since then, which has prevented the increase in REE concentrations in sewage sludge. A similar situation was demonstrated by the findings of the Norwegian WWTP that the heavy metal content in sludge was controlled by introducing policies [44]. The above results indicated that the current management policies of the southeastern city in China could effectively control the emissions of inorganic elements, and further management should be strengthened in the future to reduce the environmental hazards caused by the sludge disposal process.

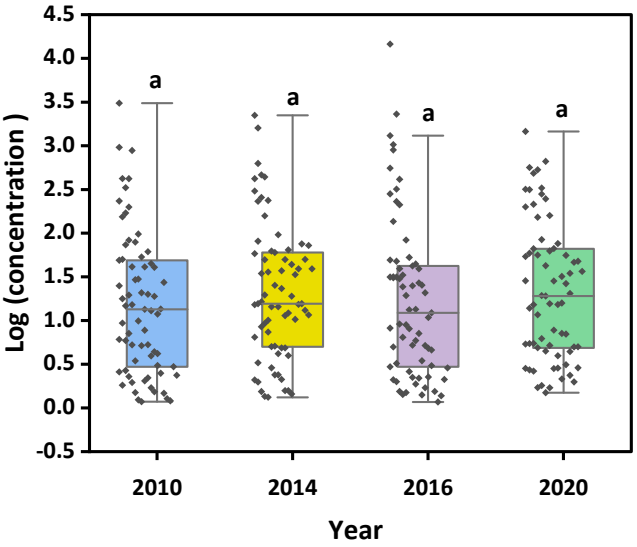

Figure 5. Annual variation of inorganic elements concentration between 2010 and 2020 in sewage sludge. The same letter indicates no statistical difference (Kruskal–Wallis test; Dunn's test, $p > 0.05$).

4. Conclusions

This study investigated the fate and spatial–temporal variations of 23 elements in seven WWTPs in a southeast city of China. Strong concentration differences of 2–3 orders of magnitude were detected for the 23 elements in the influent, effluent, and sludge, with a heavy metal content that was generally higher than the REE content. Mn and Zn dominated among the heavy metals, while Ce, La, Nd, and Y were the most abundant elements among the REEs. Significant spatial differences were also observed, in which W1 showed significantly high concentrations of REEs, and W5 showed significantly high concentrations of heavy metals. The element flux analysis demonstrated the fate of the 23 elements in the sewage treatment system of the southeast city. REEs were mainly distributed in sludge and discharged in the way of excess sludge, while heavy metals were unstable and equally discharged from effluent and residual sludge. The removal efficiency analysis also proved that the removal efficiencies for REEs from the wastewater were good, whereas those for heavy metals were poor. Activated sludge was the major temporary storage site for inorganic elements in the southeast city in China, which had the largest storage of inorganic elements and was a non-negligible unit. Based on the data from 2010, 2014, 2016, and 2020, there was no significant annual variation in the elemental concentration of sludge in the past 10 years, indicating that the current environmental protection policy was effective and that inorganic elements were controllable. In the future, for the sustainable development of the environment and economy, effective control of WWTPs, removal of harmful elements, and recovery of valuable elements are necessary before inorganic elements go beyond the range controllable by WWTPs.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/w15061226/s1, Figure S1: Relative percentage of inorganic elements in influent (a–c), sludge (d–f), and effluent (g–i) in 7 WWTPs. Different letters indicate statistically different (Kruskal-Wallis test; Dunn's test, $p < 0.05$); Figure S2: Correlation analysis among elements in influent (a), effluent (upper triangular) and sludge (lower triangular) (b). Figure S3: Relationship of sludge retention time and elemental removal efficiency in seven WWTPs. Table S1: Performance of each WWTP during the sampling days. Table S2: Elemental recoveries and analytical standard deviations in aqueous and sludge (n = 3). Table S3: Median concentrations of target elements, unit: μg·L−1. Table S4: Median value of removal efficiency of target elements, unit: $\mu g \cdot L^{-1}$.

Author Contributions: Conceptualization, S.G. and Q.S.; investigation, S.G.; resources, Q.S.; writing—original draft preparation, S.G.; writing—review and editing, F.N., B.A. and Y.Z.; supervision, A.H., F.N. and Q.S.; funding acquisition, A.H. and Q.S. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the National Key R&D Program of China (2022YFE0120300), CAS Youth Interdisciplinary Team (JCTD-2021-13), the STS Project of Fujian-CAS (2021T3059, 2021T3014), and the Youth Innovation Project of Xiamen (3502Z20206093).

Data Availability Statement: The data presented in this study are available in the article. Further information is available upon request from the corresponding author. Refs [45–47] are cited in Supplementary Materials.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Briffa, J.; Sinagra, E.; Blundell, R. Heavy metal pollution in the environment and their toxicological effects on humans. *Heliyon* **2020**, *6*, e04691. [CrossRef] [PubMed]
2. Karvelas, M.; Katsoyiannis, A.; Samara, C. Occurrence and fate of heavy metals in the wastewater treatment process. *Chemosphere* **2003**, *53*, 1201–1210. [CrossRef] [PubMed]
3. Busetti, F.; Badoer, S.; Cuomo, M.; Rubino, B.; Traverso, P. Occurrence and removal of potentially toxic metals and heavy metals in the wastewater treatment plant of Fusina (Venice, Italy). *Ind. Eng. Chem. Res.* **2005**, *44*, 9264–9272. [CrossRef]
4. Buzier, R.; Tusseau-Vuillemin, M.-H.; dit Meriadec, C.M.; Rousselot, O.; Mouchel, J.-M. Trace metal speciation and fluxes within a major French wastewater treatment plant: Impact of the successive treatments stages. *Chemosphere* **2006**, *65*, 2419–2426. [CrossRef]
5. Feng, J.; Chen, X.; Jia, L.; Liu, Q.; Chen, X.; Han, D.; Cheng, J. Effluent concentration and removal efficiency of nine heavy metals in secondary treatment plants in Shanghai, China. *Environ. Sci. Pollut. Res.* **2018**, *25*, 17058–17065. [CrossRef] [PubMed]
6. ÜStün, G.E. Occurrence and removal of metals in urban wastewater treatment plants. *J. Hazard. Mater.* **2009**, *172*, 833–838. [CrossRef]
7. Iloms, E.; Ololade, O.O.; Ogola, H.J.O.; Selvarajan, R. Investigating industrial effluent impact on municipal wastewater treatment plant in Vaal, South Africa. *Int. J. Environ. Res. Public Health* **2020**, *17*, 1096. [CrossRef] [PubMed]
8. US EPA. Toxic and Priority Pollutants under the Clean Water Act /US EPA. Available online: https://www.epa.gov/eg/toxic-and-priority-pollutants-under-clean-water-act (accessed on 24 January 2021).
9. Cobelo-García, A.; Filella, M.; Croot, P.; Frazzoli, C.; Du Laing, G.; Ospina-Alvarez, N.; Rauch, S.; Salaun, P.; Schäfer, J.; Zimmermann, S. COST action TD1407: Network on technology-critical elements (NOTICE)—From environmental processes to human health threats. *Environ. Sci. Pollut. Res.* **2015**, *22*, 15188–15194. [CrossRef] [PubMed]
10. Gwenzi, W.; Mangori, L.; Danha, C.; Chaukura, N.; Dunjana, N.; Sanganyado, E. Sources, behaviour, and environmental and human health risks of high-technology rare earth elements as emerging contaminants. *Sci. Total Environ.* **2018**, *636*, 299–313. [CrossRef]
11. Kaegi, R.; Gogos, A.; Voegelin, A.; Hug, S.J.; Winkel, L.H.E.; Buser, A.M.; Berg, M. Quantification of individual Rare Earth Elements from industrial sources in sewage sludge. *Water Res. X* **2021**, *11*, 100092. [CrossRef]
12. Gogos, A.; Wielinski, J.; Voegelin, A.; Kammer, F.v.d.; Kaegi, R. Quantification of anthropogenic and geogenic Ce in sewage sludge based on Ce oxidation state and rare earth element patterns. *Water Res. X* **2020**, *9*, 100059. [CrossRef] [PubMed]
13. Atinkpahoun, C.N.H.; Pons, M.-N.; Louis, P.; Leclerc, J.-P.; Soclo, H.H. Rare earth elements (REE) in the urban wastewater of Cotonou (Benin, West Africa). *Chemosphere* **2020**, *251*, 126398. [CrossRef] [PubMed]
14. Choubert, J.M.; Pomiès, M.; Martin Ruel, S.; Coquery, M. Influent concentrations and removal performances of metals through municipal wastewater treatment processes. *Water Sci. Technol.* **2011**, *63*, 1967–1973. [CrossRef] [PubMed]
15. Du, P.; Zhang, L.; Ma, Y.; Li, X.; Wang, Z.; Mao, K.; Wang, N.; Li, Y.; He, J.; Zhang, X.; et al. Occurrence and fate of heavy metals in municipal wastewater in Heilongjiang province, China: A monthly reconnaissance from 2015 to 2017. *Water* **2020**, *12*, 728. [CrossRef]
16. Vriens, B.; Voegelin, A.; Hug, S.J.; Kaegi, R.; Winkel, L.H.E.; Buser, A.M.; Berg, M. Quantification of element fluxes in wastewaters: A nationwide survey in switzerland. *Environ. Sci. Technol.* **2017**, *51*, 10943–10953. [CrossRef]
17. Sadiq, S.T.; Yaşa, İ.; Ali, S.F.; Eren, A.E.; Turky, A.N. Occurrence, seasonal changes and removal efficiency assessment of heavy metals in urban wastewater treatment plant. *J. Asian Sci. Res.* **2019**, *9*, 48–55. [CrossRef]
18. Suanon, F.; Sun, Q.; Yang, X.; Chi, Q.; Mulla, S.I.; Mama, D.; Yu, C.-P. Assessment of the occurrence, spatiotemporal variations and geoaccumulation of fifty-two inorganic elements in sewage sludge: A sludge management revisit. *Sci. Rep.* **2017**, *7*, 5698. [CrossRef]
19. EPA. *Method 3015A (SW-846): Microwave Assisted Acid Digestion of Aqueous Samples and Extracts*; EPA: Washington, DC, USA, 2007.
20. EPA. *Method 3051A (SW-846): Microwave Assisted Acid Digestion of Sediments, Sludges, and Oils*; EPA: Washington, DC, USA, 2007.

21. Hassan, N.M.; Rasmussen, P.E.; Dabek-Zlotorzynska, E.; Celo, V.; Chen, H. Analysis of environmental samples using microwave-assisted acid digestion and inductively coupled plasma mass spectrometry: Maximizing total element recoveries. *Water Air Soil Pollut.* **2007**, *178*, 323–334. [CrossRef]
22. Salles, F.J.; Sato, A.P.S.; Luz, M.S.; Fávaro, D.I.T.; Ferreira, F.J.; da Silva Paganini, W.; Olympio, K.P.K. The environmental impact of informal and home productive arrangement in the jewelry and fashion jewelry chain on sanitary sewer system. *Environ. Sci. Pollut. Res.* **2018**, *25*, 10701–10713. [CrossRef]
23. Santarsiero, A.; Veschetti, E.; Donati, G.; Ottaviani, M. Heavy metal distribution in wastewater from a treatment plant. *Microchem. J.* **1998**, *59*, 219–227. [CrossRef]
24. Dunn, O.J. Multiple comparisons using rank sums. *Technometrics* **1964**, *6*, 241–252. [CrossRef]
25. Ministry of Environmental Protection of the People's Republic of China (MOEP). *Discharge Standard of Pollutants for Municipal Wastewater Treatment Plant (GB18918-2002)*; MOEP: Beijing, China, 2002. (In Chinese).
26. Yang, J.; Lei, M.; Chen, T.; Gao, D.; Zheng, G.; Guo, G.; Lee, D. Current status and developing trends of the contents of heavy metals in sewage sludges in China. *Front. Environ. Sci. Eng.* **2014**, *8*, 719–728. [CrossRef]
27. Westerhoff, P.; Lee, S.; Yang, Y.; Gordon, G.W.; Hristovski, K.; Halden, R.U.; Herckes, P. Characterization, recovery opportunities, and valuation of metals in municipal sludges from U.S. wastewater treatment plants nationwide. *Environ. Sci. Technol.* **2015**, *49*, 9479–9488. [CrossRef] [PubMed]
28. Nkinahamira, F.; Suanon, F.; Chi, Q.; Li, Y.; Feng, M.; Huang, X.; Yu, C.-P.; Sun, Q. Occurrence, geochemical fractionation, and environmental risk assessment of major and trace elements in sewage sludge. *J. Environ. Manag.* **2019**, *249*, 109427. [CrossRef] [PubMed]
29. Stephenson, T.; Lester, J. Heavy metal behaviour during the activated sludge process I. Extent of soluble and insoluble metal removal. *Sci. Total. Environ.* **1987**, *63*, 199–214. [CrossRef]
30. Hargreaves, A.J.; Vale, P.; Whelan, J.; Constantino, C.; Dotro, G.; Cartmell, E. Mercury and antimony in wastewater: Fate and treatment. *Water Air Soil Pollut.* **2016**, *227*, 89. [CrossRef]
31. Jiang, J.-Q. The role of coagulation in water treatment. *Curr. Opin. Chem. Eng.* **2015**, *8*, 36–44. [CrossRef]
32. Farkas, J.; Polesel, F.; Kjos, M.; Carvalho, P.A.; Ciesielski, T.; Flores-Alsina, X.; Hansen, S.F.; Booth, A.M. Monitoring and modelling of influent patterns, phase distribution and removal of 20 elements in two primary wastewater treatment plants in Norway. *Sci. Total Environ.* **2020**, *725*, 138420. [CrossRef]
33. Sun, C.; Zhang, B.; Chen, Z.; Qin, W.; Wen, X. Sludge retention time affects the microbial community structure: A large-scale sampling of aeration tanks throughout China. *Environ. Pollut.* **2020**, *261*, 114140. [CrossRef]
34. Sterritt, R.M.; Brown, M.J.; Lester, J.N. Metal removal by adsorption and precipitation in the activated sludge process. *Environ. Pollut. Ser. A Ecol. Biol.* **1981**, *24*, 313–323. [CrossRef]
35. Ahmed, Z.; Cho, J.; Lim, B.-R.; Song, K.-G.; Ahn, K.-H. Effects of sludge retention time on membrane fouling and microbial community structure in a membrane bioreactor. *J. Membr. Sci.* **2007**, *287*, 211–218. [CrossRef]
36. Sassi, M.; Bestani, B.; Said, A.H.; Benderdouche, N.; Guibal, E. Removal of heavy metal ions from aqueous solutions by a local dairy sludge as a biosorbant. *Desalination* **2010**, *262*, 243–250. [CrossRef]
37. Fleischer, M. The abundance and distribution of the chemical elements in the earth's crust. *J. Chem. Educ.* **1954**, *31*, 446–455. [CrossRef]
38. Nkinahamira, F.; Alsbaiee, A.; Wang, Y.; Yang, X.; Chen, T.-Y.; Cao, M.; Feng, M.; Sun, Q.; Yu, C.-P. Recovery and purification of rare earth elements from wastewater and sludge using a porous magnetic composite of β-cyclodextrin and silica doped with PC88A. *Sep. Purif. Technol.* **2021**, *266*, 118589. [CrossRef]
39. Martínez, R.; Vela, N.; el Aatik, A.; Murray, E.; Roche, P.; Navarro, J.M. On the use of an IoT integrated system for water quality monitoring and management in wastewater treatment plants. *Water* **2020**, *12*, 1096. [CrossRef]
40. Hernández-Chover, V.; Castellet-Viciano, L.; Hernández-Sancho, F. Cost analysis of the facilities deterioration in wastewater treatment plants: A dynamic approach. *Sustain. Cities Soc.* **2019**, *49*, 101613. [CrossRef]
41. Wang, D.; Thunéll, S.; Lindberg, U.; Jiang, L.; Trygg, J.; Tysklind, M. Towards better process management in wastewater treatment plants: Process analytics based on SHAP values for tree-based machine learning methods. *J. Environ. Manag.* **2022**, *301*, 113941. [CrossRef]
42. Sağ, Y.; Tatar, B.; Kutsal, T. Biosorption of Pb(II) and Cu(II) by activated sludge in batch and continuous-flow stirred reactors. *Bioresour. Technol.* **2003**, *87*, 27–33. [CrossRef]
43. Chai, S.; Zhang, Z.; Ge, J. Evolution of environmental policy for China's rare earths: Comparing central and local government policies. *Resour. Policy* **2020**, *68*, 101786. [CrossRef]
44. Paulsrud, B.; Nedland, K.T. Strategy for land application of sewage sludge in Norway. *Water Sci. Technol.* **1997**, *36*, 283–290. [CrossRef]
45. Xie, Y.; Zhang, T.; Xu, C.L.; Hui, Y.F.; Ou Yang, W.J. Study on Variation Trends of Heavy Metals Contents in Process of Sludge Energy Utilization. *Adv. Mater. Res.* **2013**, *610–613*, 198–202. [CrossRef]

46. Feng, J.; Jia, L.; Liu, Q.Z.; Chen, X.L.; Cheng, J.P. Source identification of heavy metals in sewage sludge and the effect of influent characteristics: a case study from China. *Urban Water J.* **2018**, *15*, 1–7. [CrossRef]
47. Drozdova, J.; Raclavska, H.; Raclavsky, K.; Skrobankova, H. Heavy metals in domestic wastewater with respect to urban population in Ostrava, Czech Republic. *Water Environ. J.* **2019**, *33*, 77–85. [CrossRef]