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Monitoring and Studying the Behavior of Metals in an Industrial Wastewater Treatment Plant in Italy

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Abstract: Heavy metals represent a significant hazard in textile wastewater, posing a considerable risk to both the ecosystem and human health. The objective of this study was to analyze the removal efficiency of specific heavy metals in a large wastewater treatment plant (WWTP) located in Prato (Tuscany, Italy), where the main Italian textile district is based. To achieve this, the mass balance calculation approach was employed. Therefore, two monitoring campaigns were conducted, collecting wastewater and sludge samples in some specific sections of the WWTP. The concentrations of Pb, Cd, Ni, As, and Sn were consistently below the detection limits. A good removal efficiency was determined for Zn, Cu, Ba, Cr^{tot}, and Sb, in the range of 37–79%. These metals are predominantly present in particulate form, facilitating their removal through sedimentation. Conversely, boron is largely present in the dissolved phase, resulting in its complete release through the treated effluent. Subsequently, an excellent linear correlation was identified between the input load and the contaminant load removed. This demonstrated that the plant's efficiency remains unaffected by an increase in the input load at the observed contaminant concentrations. Finally, a probability law was identified that demonstrates an excellent degree of approximation in representing inlet metal concentrations. The findings of this study indicate that the treatment systems employed by the WWTP are capable of effectively removing heavy metals.

Keywords: heavy metals; mass balance; metal removal mechanism; sustainability; textile wastewater

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1. Introduction

The textile industry employs water as the primary medium for the removal of impurities, the application of dyes and finishing agents, and the generation of steam [1]. Typically, the volume of wastewater discharged represents approximately 70% of the total freshwater consumption [2]. The effluent composition is highly complex, comprising a multitude of chemical constituents, including dyes, metals, detergents, solvents, and salts. The specific composition of the effluent is influenced by several factors, including the textile process, the equipment utilized in the manufacturing facility, the type of fabric produced, the chemicals applied, the weight of the fabric, the season, and the prevailing trends in fashion [3–5].

Heavy metals are among the most deleterious constituents of textile wastewater, exerting adverse effects on both aquatic ecosystems and human health [5]. Heavy metals may occur naturally in the fiber structure or as a consequence of production and dyeing processes [6–8]. The principal heavy metal ions generated by the textile industry are chromium, cadmium, lead, zinc, tin, copper, antimony, nickel, and manganese [8]. As reported in the literature, the emission of antimony is generally associated with the presence of residues in polyester fibers [9]. Similarly, the emission of zinc into water is commonly linked to the utilization of cationic dyes (or pre-dyed yarns), bleaching with zinc dithionite, and the treatment of cellulose fibers, such as regenerated cellulose fibers, to which zinc oxide powder is added (e.g., for skin-protective hygienic and antibacterial effects). Furthermore, zinc salts are employed in the production of cellulose, residues of which remain on the fiber (e.g., lyocell, viscose, etc.). Emissions of Cu and Cr may be linked to the use of dyes [1]. Finally, the presence of a large amount of boron may also be associated with the textile industry, particularly in textile finishing operations [10]. If transferred to the environment through direct or indirect wastewater discharges, these metals can exert toxic effects through bioaccumulation in the human body, aquatic life, and natural water bodies, as well as potentially being trapped in the soil [7].

Prato, located in the Tuscany region, is a prominent global hub for textile and clothing production [11]. The Prato district was the first in the textile industry to implement a centralized wastewater treatment system, managed by the company G.I.D.A. S.p.A. (hereafter G.I.D.A.). The Baciacavallo WWTP represents the core of this treatment system, with the capacity to process both domestic and industrial wastewater, the majority of which is generated by textile industries. To date, the sewer network in Prato is comprised of two distinct lines: a separate sewer line, which collects solely industrial wastewater (since 2020); and a mixed sewer line, which collects both urban and industrial wastewater. The objective of the separate sewer line is to preclude the inadvertent discharge of industrial wastewater into the environment, particularly during storm events when combined sewer overflows can discharge untreated wastewater into receiving water bodies.

In light of these considerations, all the textile industries are allowed to discharge wastewater into the sewer system (indirect discharge) without any preliminary treatment, provided that they comply with the limits set forth by G.I.D.A. for discharging into the sewerage network.

In accordance with the revised version of the best available techniques (BAT) for the textile industry (TXT BATc), textile companies may be subject to new discharge limits based on the associated emission levels (BAT-AELs) for the indirect discharge of specific metals, unless the downstream WWTP can abate them [1]. In WWTPs where wastewater of both domestic and industrial origin is treated together, it is essential to demonstrate that the reduction in contaminants of industrial origin is not merely due to dilution but is a result of the actual capacity of the plant to achieve such a reduction. In the absence of evidence that such capacity exists, companies would be required to comply with the limits set out in TXT BATc at the point of discharge to the sewer network, which would have significant implications for their process costs. Given that the Baciacavallo WWTP treats both industrial and urban wastewater, it is essential to ascertain the plant's actual removal capacity, beyond the dilution effects associated with domestic wastewater.

However, biological wastewater treatment systems, such as the Baciacavallo WWTP, are primarily designed to remove organic matter through the action of activated sludge microorganisms [12–16] Consequently, the removal of metals is typically an indirect effect and may exhibit considerable variability [12,17]. In the majority of instances, metal removal is attributable to the partitioning of metals to the solid phase of the treatment system [16,18,19]. As a result, a considerable proportion of the metals entering the WWTP are expected to be retained in the sludge [12,13,17,20,21]. The actual removal capacity must be determined through experimental means, specifically through the implementation of mass balances, as highlighted by Yoshida et al., 2015 [18]. According to this source, the mass balance calculation approach can be utilized to ascertain the fate of contaminants and the overall removal rates of a WWTP. Nevertheless, there is a lack of studies regarding the calculation of the mass balance of a WWTP to evaluate the behavior of contaminants [12,18,21,22].

In this study, mass balance calculations were conducted to analyze the fate of specific metals and metalloids, primarily originating from industrial (textile) processes. The objective was to verify that the removal of these contaminants was a consequence of an effective treatment process and not merely a dilution effect with domestic wastewater. The ultimate goals were twofold: firstly, to prevent textile companies from being compelled to adhere to new limitations on sewer discharge, and secondly, to prevent irreparable harm to the natural environment and human health. To this end, an extensive one-year monitoring campaign was conducted to study the behavior of the following metals: As, Pb, Cd, Ni, Zn, Cu, Sn, Se, Mn, Ba, B, Cr^{tot}, and Sb. Additionally, an intensive one-week monitoring campaign was conducted with a more rigorous sampling procedure. The main novelty of this work focused on the behavior of metals and metalloids in a WWTP that treats both domestic and textile wastewater. Furthermore, the impact of the sampling procedure on the observed outcomes was illustrated.

This article is a revised and expanded version of a paper entitled "Monitoring and studying the behavior of metals in a large wastewater treatment plant in Italy" [23], which was presented at the sixth IWA International Conference on Eco-Technologies for Wastewater Treatment, Girona (Spain), 26–29 June 2023.

2. Materials and Methods

This study focuses on the Baciacavallo WWTP, which aims to process both domestic and industrial (mainly textile) wastewater, with an average inflow capacity of approximately 100,000 m^3/d. The facility was constructed to cater to a population equivalent (PE) of 900,000, with industrial wastewater representing approximately 70% of the total inflow [24]. The industrial wastewater is primarily derived from textile industries and is partially collected via a dedicated sewer system. The plant is illustrated in Figure 1 and comprises several stages for the treatment of water, including coarse and fine screening, grit removal, primary sedimentation, equalization, biological oxidation/nitrification, coagulation–flocculation–sedimentation, and final ozonation. After treatment, the water is discharged into both a surface water body and the refining section for recycling in the textile district. Secondary and tertiary sludges are recycled in the primary settler. The primary sludge is then sent to the sludge treatment section. Sludge treatment includes gravity thickeners, centrifuges, and final incineration; thickener overflow and centrate from dewatering are also recycled in the primary sedimentation unit.

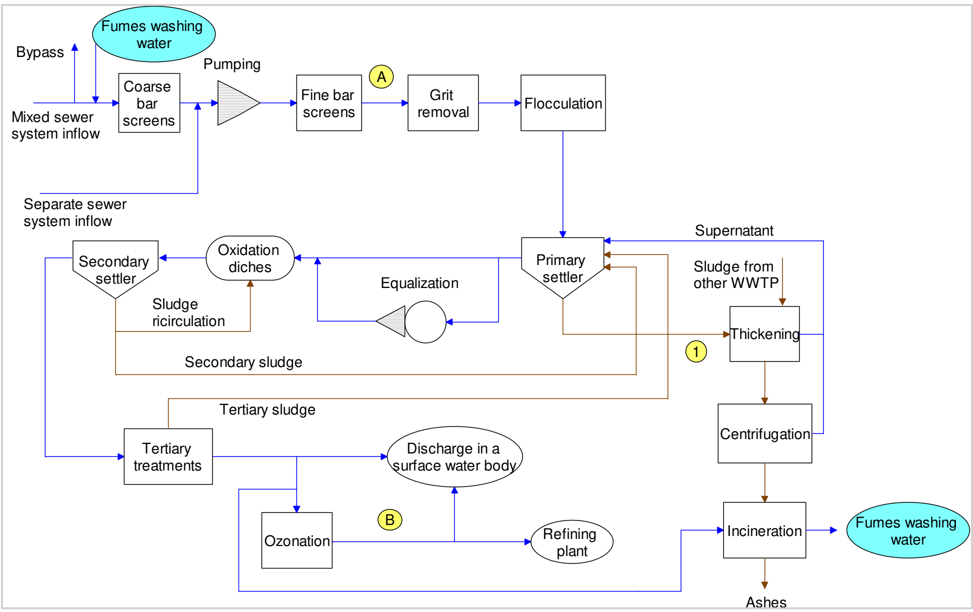


Figure 1. Flowchart of Baciacavallo WWTP. The yellow labels show the sampling points: (A) influent of the WWTP; (B) effluent of the WWTP; (1) primary sludge.

2.1. Sampling

Two monitoring campaigns were conducted between October 2021 and October 2022 to assess the removal efficiency and perform a mass balance. The sampling points of wastewater and sludge were identified through the utilization of existing samplers and flow meters situated along the wastewater and sludge treatment lines. For each section, both the flow rate and the concentration of contaminants were determined.

The extensive monitoring campaign entailed the collection of wastewater samples on a weekly basis for 12 months. Sampling was temporarily halted in August 2022 due to the necessity of undertaking maintenance operations on the plant. Composite samples of wastewater were taken from the plant's influent and effluent at 24 h (Figure 1), without consideration of the estimated hydraulic retention time (HRT) of approximately 24 h for the WWTP. Furthermore, no sludge samples were obtained during this campaign.

In May 2022, an intensive monitoring campaign was conducted over eight consecutive days, including the weekend. During this period, wastewater and sludge samples were collected from the sections indicated in Figure 1. In this instance, 24 h composite samples were collected with a 24 h delay between the influent and the effluent, thus permitting correspondence between influent and effluent samples, which is essential for mass balance calculations [12]. In addition to wastewater, grab samples of mixed sludge (primary, secondary, and tertiary sludge) extracted from the primary sedimentation tank were collected.

2.2. Sample Analysis

G.I.D.A.'s internal laboratory analyzed various metals and non-metals. Among the metals were Cr, Cu, Ni, Zn, Ba, Cd, Mn, and Pb, while the non-metals included Se. The laboratory also analyzed semimetals, such as As, B, and Sb. The wastewater samples were subjected to digestion with 69% HNO_3 in ultrapure water (obtained with the Thermo Scientific™ Barnstead™ MicroPure™ Water Purification System (Waltham, MA, USA)), using the CEM™ MARS-6™ (Matthews, NC, USA) microwave digestion system, in accordance with the APAT IRSA-CNR 3010B standard [25]. Atomic emission spectrometry inductively coupled to an argon plasma with an optical detector was employed for the determination, utilizing the ICP-OES Thermo Fischer Scientific™ instrument iCAP™ 7200 Duo, in accordance with the APAT IRSA-CNR 3020 standard [25]. Quantification was conducted with the aid of external CRM AccuStandard™ (New Haven, CT, USA) and LabMix24™ Ultra Scientific™ (North Kingstown, RI, USA) calibration control. The limits of detection (LOD) are presented in Table 1.

Table 1. Limits of detection of the chemical species analyzed through the analytical instrument used by the in-house laboratory of the WWTP (expressed in mg/L).

Chemical Species	Limit of Detection
Antimony (Sb)	0.02
Total Chromium (Cr^{tot})	0.01
Copper (Cu)	0.05
Nickel (Ni)	0.05
Zinc (Zn)	0.01
Arsenic (As)	0.02
Barium (Ba)	0.1
Boron (B)	0.01
Cadmium (Cd)	0.01
Manganese (Mn)	0.05
Lead (Pb)	0.05
Selenium (Se)	0.002
Tin (Sn)	0.02

During the intensive monitoring campaign, the partitioning of the species between the particulate and dissolved phases was determined. The dissolved concentrations were subsequently analyzed after filtration of the wastewater through a filter with a 0.45 μm pore size [12,21]. The particulate concentrations were calculated as the difference between the total concentration and the dissolved one. Finally, the primary sludge was characterized as having a dry matter content of 2%. It was assimilated in water and analyzed by using the same method applied to the wastewater.

Furthermore, the analysis of wastewater requires the daily determination of the concentration of specific constituents. These include pH, chemical oxygen demand (COD), biochemical oxygen demand (BOD), total suspended solids (TSS), total nitrogen (TN), nitrate ($N–NO_3^-$), nitrite ($N–NO_2^-$), ammonia ($N–NH_4^+$), and total phosphorus (TP).

2.3. Material Flow Analysis

The arithmetic mean of the available values was calculated for each month of the extensive monitoring campaign to facilitate comparison of the concentrations of metals in the influent and effluent of the WWTP. In instances where the concentration was found to be below the detection limits, a concentration value equal to half of that limit was assigned [26]. During the one-week monitoring campaign, the comparison between inlet and outlet was calculated using the daily mean concentration values. The removal efficiency (*RE*) of the plant was then calculated using Equation (1) [12,17,22,27]:

$$RE\ [\%] = (C_i - C_e)/C_i \quad (1)$$

where

C_i = mean concentration of metal in the influent, [mg/L]
C_e = mean concentration of metal in the effluent, [mg/L]

Subsequently, a mass balance of the plant was conducted, whereby the metal load in the influent and effluent was calculated using Equations (2)–(4). Finally, an attempt was made to establish a correlation between the influent mass load and the removed mass load.

$$M_i = Q_i * C_i \quad (2)$$

$$M_e = Q_e * C_e \quad (3)$$

$$Removal = M_i - M_e \quad (4)$$

where

Q_i = influent flow rate, [m^3/d]
Q_e = effluent flow rate, [m^3/d]
M_i = metal load in the influent, [g/d]
M_e = metal load in the effluent, [g/d]

To guarantee the precision of the intensive monitoring campaign outcomes, a comparison was conducted between the mass of metal at the inlet (calculated using Equation (2)) and the mass of metal at the outlet. The latter was estimated by summing the amount of metal in the effluent with the amount of metal that was in the sludge, as illustrated in the following calculation method:

$$M_{out} = Q_e * C_e + Q_{sludge\ I} * C_{sludge\ I} \quad (5)$$

where

$Q_{sludge\ I}$ = mixed sludge flow rate, [m^3/d]
$C_{sludge\ I}$ = mixed sludge metal concentration, [mg/L]

The trends in influent and effluent flow rates during the one-week monitoring campaign are presented in Figure S1. It is highlighted that the mass balance was conducted on a weekly basis, rather than on a daily basis, to take account of fluctuations generated by the equalization process.

2.4. Statistical Analysis of Quality Data

To conclude the study, the probability distribution that most accurately represents the data set was identified. In the context of water purification, data quality is typically observed to fall within the parameters of either a normal or log-normal distribution. In this study, the concentration of metal species at the inlet was examined to ascertain the most appropriate distribution type. Probability charts were employed to achieve this. The charts plot the observed experimental data on a straight line that corresponds to a specific probability distribution, such as a normal or log-normal distribution [28]. All data processing was conducted using the Microsoft Excel 2024 software program.

3. Results

3.1. Extensive Monitoring Campaign

The wastewater entering the WWTP is characterized by a significant industrial contribution from the textile industry of Prato. The principal parameters of the wastewater are reported in Table 2.

Table 2. Characteristics of the influent of the Baciacavallo WWTP (obtained from a 24 h composite sample) during the extensive monitoring campaign.

Parameter	Value			U.M.
	Mean ± STD	Maximum	Minimum	
pH	7.96 ± 0.16	8.49	7.26	-
TSS	126 ± 73	532	10	[mg/L]
COD	301 ± 134	994	40	[mg/L]
BOD	124 ± 42	280	43	[mg/L]
TN	36 ± 11	69	13	[mg/L]
$N\text{-}NO_2^-$	0.51 ± 0.38	2.17	0.05	[mg/L]
$N\text{-}NO_3^-$	2.35 ± 1.15	7.43	0.11	[mg/L]
$N\text{-}NH_4^+$	24 ± 8	47	5	[mg/L]
TP	3 ± 0.84	6	1	[mg/L]

Regarding metals, the concentrations of Pb, Cd, Ni, As, and Sn in the raw wastewater remain consistently below the LOD. Therefore, these levels are considered negligible when evaluating the plant's capability for water purification.

Table 3 presents the mean concentrations of the specified heavy metals at the plant's inlet and outlet. The relative abundance of the elements in the raw wastewater follows the general order: Se < Mn < Cr^{tot} < Cu < Ba < Zn < B < Sb.

Table 3. Inlet and outlet concentrations (mg/L) and removal efficiency (%) of metal, calculated for the extensive and intensive monitoring campaigns (mean ± STD).

		Extensive Monitoring Campaign			Intensive Monitoring Campaign		
	D. Lgs. 152/2006 [29]	C_{in}	C_{out}	RE	C_{in}	C_{out}	RE
	[mg/L]	[mg/L]	[mg/L]	[%]	[mg/L]	[mg/L]	[%]
Zn	0.5	0.15 ± 0.03	0.05 ± 0.02	66 ± 11	0.13 ± 0.03	0.03 ± 0.01	76 ± 12
Cu	0.1	0.05 ± 0.02	<0.05	37 ± 20	0.06 ± 0.01	<0.05	57 ± 8
Mn	2.0	0.04 ± 0.02	0.05 ± 0.02	31 ± 33	0.04 ± 0.02	0.06 ± 0.05	6 ± 11
Se	0.03	0.007 ± 0.007	0.003 ± 0.001	52 ± 32	0.003 ± 0.003	0.002 ± 0.001	31 ± 40
Ba	20	0.12 ± 0.01	<0.1	58 ± 3	0.14 ± 0.01	<0.1	63 ± 3
B	2.0	0.16 ± 0.08	0.14 ± 0.05	14 ± 12	0.17 ± 0.01	0.15 ± 0.01	13 ± 6
Cr^{tot}	2.0	0.04 ± 0.01	0.01 ± 0.003	79 ± 6	0.04 ± 0.01	0.01 ± 0.005	78 ± 11
Sb	-	0.35 ± 0.39	0.08 ± 0.03	68 ± 15	0.26 ± 0.09	0.10 ± 0.01	58 ± 21

Additionally, Table 3 reports the mean RE. The efficiency of removal for species such as Zn, Se, Ba, Cr^{tot}, and Sb was found to be greater than 50% (66%, 52%, 58%, 79%, and 68%, respectively). Regarding Cu, the mean removal efficiency was found to be below 40%. Mn exhibited negative removal efficiencies in numerous instances, resulting in an average removal of 31 ± 33%. This result is attributable to two factors: the proximity to the LOD of both inlet and outlet concentrations, and the sampling procedure, which does not account for the HRT of the plant. Lastly, the lowest concentration reduction was observed for B, with an average of 14 ± 12%. Overall, the removal of metal is satisfactory and compliant with surface water discharge limits (D. Lgs. 152/2006 [29]).

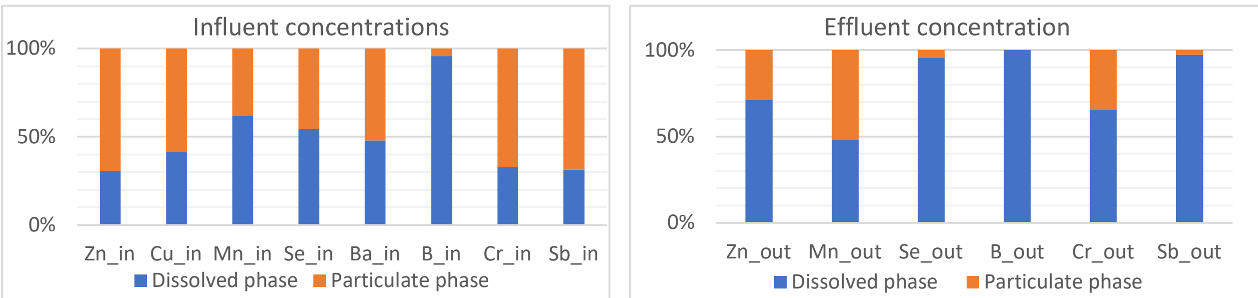
3.2. Intensive Monitoring Campaign

The results of the intensive monitoring campaign demonstrate that the concentrations of Pb, Cd, Ni, As, and Sn are consistently below the LOD. As illustrated in Table 3, the relative abundance of all other species in the raw wastewater follows the general order: Se < Mn < Cr^{tot} < Cu < Zn < Ba < B < Sb. A comparison of these results with those of the extensive monitoring campaign reveals enhanced average removal efficiencies for metals such as Zn, Cu, and Ba (76%, 57%, and 63%, respectively). It has been demonstrated that the removal of chrome and antimony is more than 50% efficient. Finally, the lowest average concentration reductions were observed for B and Se at 13 ± 6% and 31 ± 40%, respectively. Mn exhibited negative removal efficiencies in numerous instances due to the proximity of its measured concentrations at both the inlet and outlet to the LOD, resulting in an average removal of 6 ± 11%.

In general, the reduction in metal concentration achieved by the Baciacavallo WWTP is satisfactory and within the limits set for discharges to surface water bodies.

3.3. Speciation of Metals

During the intensive monitoring campaign, it was planned to measure not only the total species concentration but also the concentration in the dissolved phase. Figure 2 illustrates the distribution of metals between the dissolved and particulate phases in the inlet and outlet sections of the plant.



(**a**) (**b**)

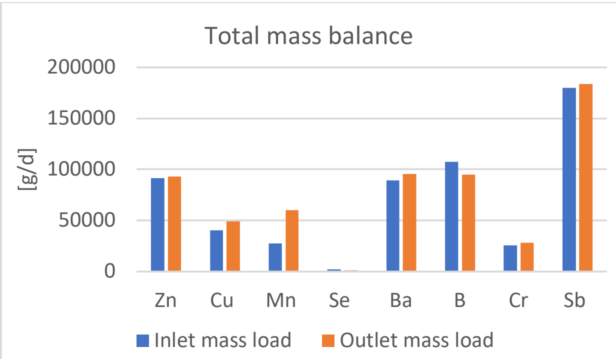
Figure 2. Distribution of metal concentrations in the influent (**a**) and effluent (**b**) between the dissolved phase and the particulate phase.

Regarding the inlet of the plant (Figure 2a), most of the metals, except for manganese, selenium, and boron, are predominantly present in the particulate phase (lead, cadmium, nickel, arsenic, and tin were not considered since they are characterized by concentrations below the LOD). Boron is predominantly in the dissolved phase, comprising over 95% of the total concentration. In contrast, zinc, chromium, and antimony are primarily present in the particulate phase (>70%).

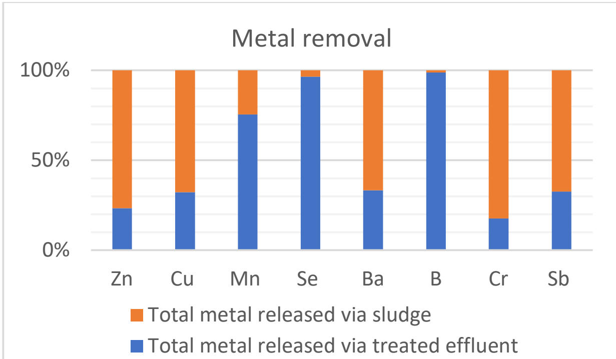
Concerning the effluent, the concentrations of copper and barium are not reported, as they are under the LOD. Figure 2b illustrates that most of the metals exhibit a higher dissolved concentration, except for manganese. This result is consistent with the findings of Karvelas et al., 2003 [12], who observed an increase in the dissolved concentration of metals in the inlet and outlet compared to their total concentration.

3.4. Removal Mechanisms and Correlation Analysis

As illustrated in Figure 3a, the graph depicts the findings of the mass balance. Apart from Mn, the comparison of the influent and effluent mass loads yielded a largely satisfactory outcome for all the metals under consideration. The discrepancies are within the range of 2% to 22%. The results indicate that the monitoring campaign was conducted with high reliability and consistency.



(**a**)

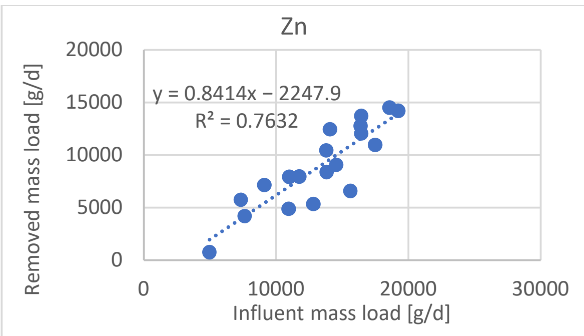


(**b**)

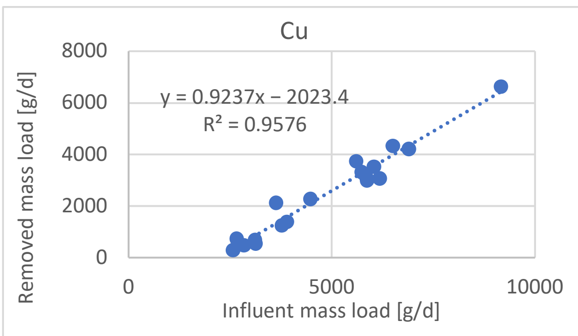
Figure 3. Total mass balance of Baciacavallo WWTP (**a**) and release of metals from the WWTP via the treated effluent and the sludge streams (**b**).

For most metals, the release via sludge is expected to be a more significant phenomenon than that via the treated effluent [12]. In this study, the relative importance of the two release processes was calculated and the values are presented in Figure 3b. The percentage of sludge removal varies significantly, with values ranging from 1% for boron to 82% for chromium. The removal of zinc, copper, barium, chromium, and antimony is predominantly accomplished through sludge (>65%), whereas manganese, selenium, and boron are primarily removed by treated effluent (>75%).

Subsequently, a linear correlation was established between the incoming contaminant load and the contaminant load removed from the plant based on the available experimental data, as illustrated in Figure 4.



(**a**)



(**b**)

Figure 4. *Cont.*

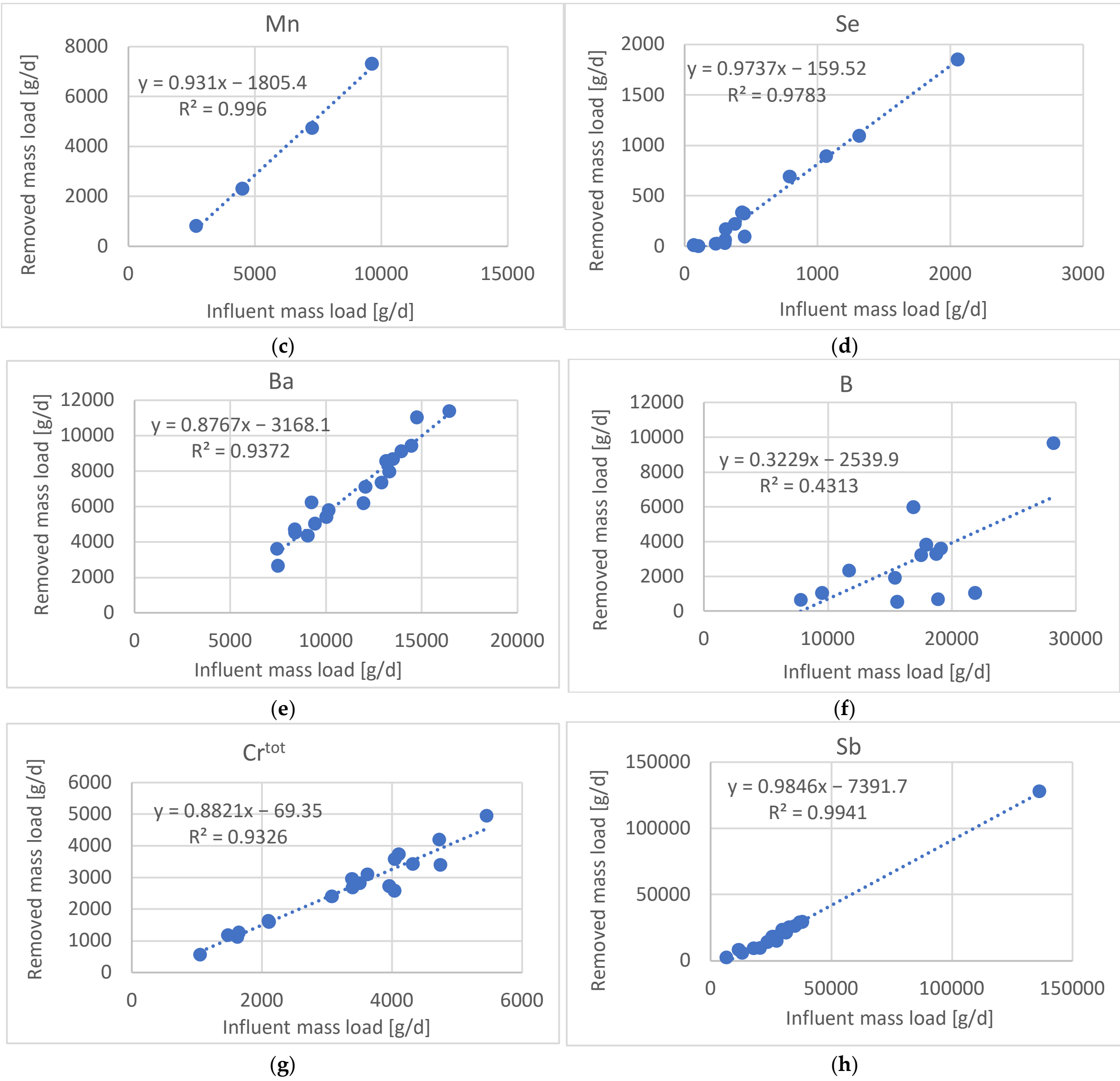


Figure 4. Correlation between the metal load removal and the WWTP's influent load: (**a**) zinc, (**b**) copper, (**c**) manganese, (**d**) selenium, (**e**) barium, (**f**) boron, (**g**) chromium, (**h**) antimony.

As illustrated in the graphs, B exhibits the poorest correlation (R^2 = 0.43), which may be attributed to it having the lowest abatement in terms of loading due to its prevalence in the dissolved phase. Copper, manganese, selenium, barium, chromium, and antimony are distinguished by an excellent correlation (R^2 > 0.9). Finally, zinc is characterized by a fairly good correlation (R^2 = 0.76).

3.5. Statistical Analysis

Figure 5 illustrates the probability and non-exceedance probability charts for the metal species identified in the TXT Bref document [1] as characteristics of the textile industry (all other heavy metals are reported in Figure S3). It can be observed that the inlet concentrations of these species are better described by a normal distribution.

The results in Figure S2 demonstrate that from October 2021 to October 2022, 95% of Zn levels were above 0.08 mg/L, with only 5% exceeding 0.20 mg/L. In the case of copper, 95% of values were higher than 0.03 mg/L, while only 5% exceeded 0.09 mg/L. Similarly, 95% of Cr values were higher than 0.02 mg/L, while only 5% of values were higher than 0.05 mg/L. Finally, 95% of Sb values were above 0.05 mg/L, while only 5% were above 0.41 mg/L.

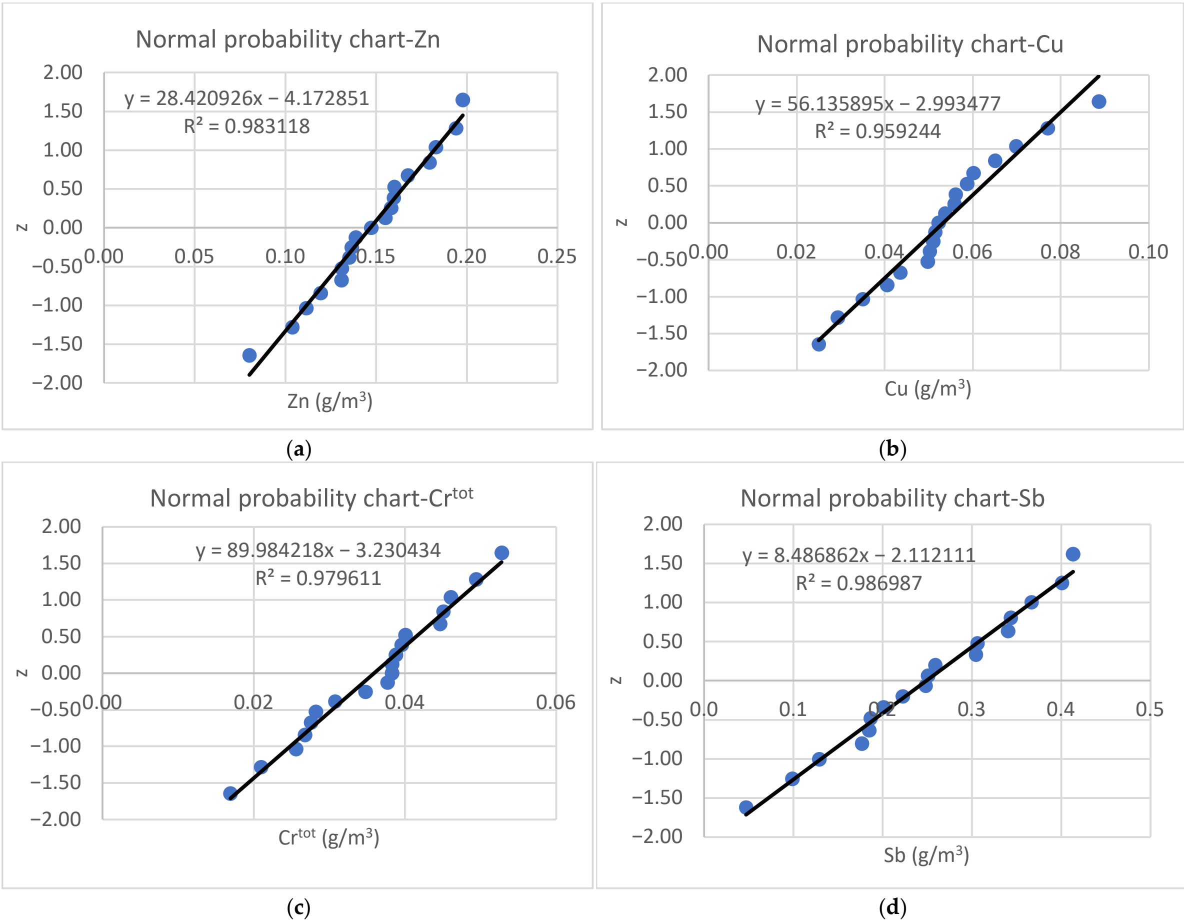


Figure 5. Normal probability charts for Zn (**a**), Cu (**b**), Cr^{tot} (**c**), and Sb (**d**).

4. Discussion

4.1. Extensive Monitoring Campaign

The results regarding the removal efficiencies of the plant are not aligned with the findings in the existing literature, which are themselves contradictory. In a study conducted by Oliveira et al., 2007 [30], the RE for Cr, Cu, Mn, and Zn was found to be 17, 44, 11, and 45%, respectively. As reported by Chanpiwat et al., 2010 [15], the RE for Cu, Mn, and Zn was approximately 60%, 50%, and 50%, respectively. As indicated by Gulyás et al., 2015 [31], the RE for Cr, Cu, and Mn was 13%, 13%, and 50%, respectively. In their study, Zhou et al., 2018 [26], assert that the mean removal efficiency in WWTPs in China for Cr, Cu, Mn, Zn, and Se is, respectively, 70%, 53%, 43%, 66%, and 63%. Du et al., 2020 [22], achieved a Cr removal rate of 64%. El Hammoudani et al., 2021 [17], concluded that their WWTP was able to remove Cr, Cu, Mn, Zn, and Ba with an efficiency of almost 35% for Cr, 75% for Cu, 78% for Mn, 85% for Zn, and 68% for Ba.

The contradictory results may be attributed to several factors, including the different types of wastewater, the actual differences in metal removal determined by varying operating conditions, and the discrepancies in analytical techniques employed for measuring metal concentrations.

As Cantinho et al., 2016 [16], have observed, the removal efficiency is contingent upon the sampling procedure, including the duration of the sampling campaign, the number and location of sampled points, the frequency of sampling, and the type of sample. The following paragraph elucidates the significance of the sampling procedure through a comparative analysis of the results obtained from the two distinct monitoring campaigns.

4.2. Intensive Monitoring Campaign

As reported by Karvelas et al., 2003 [12], the RE for Cr, Cu, Mn, and Zn was 50%, 58%, 72%, and 43%, respectively. Conversely, Busetti et al., 2005 [14], observed a RE of 87% for Cr, 93% for Cu, 61% for Mn, 75% for Zn, and 85% for Ba. As previously indicated, comparisons between the removal efficiencies of WWTPs may yield conflicting results due to the influence of numerous factors on the removal rate of heavy metals. These factors include the type of metal, concentration at the inlet, interaction with microbes in the WWTP, and the treatment processes that are employed [26].

The most interesting aspect pertains to the comparison with the results from the extensive monitoring campaign. Notable discrepancies exist in the removal efficiency of various elements, including Zn (76% vs. 66%), Cu (57% vs. 37%), Ba (63% vs. 58%), Mn (6% vs. 31%), Se (31% vs. 52%), and Sb (58% vs. 68%). For the remaining species (B and Cr^{tot}) the removal efficiencies were essentially identical, thereby conferring upon the findings a robust and reliable character. It can be assumed that the species exhibiting the greatest discrepancies are those displaying the highest degree of variability. These species may be particularly susceptible to being impacted by the sampling method. These findings highlight the importance of the sampling procedure and the use of asynchronous flow rates.

4.3. Speciation of Metals

The efficiency of metal removal is contingent upon the initial concentration of metals in the raw water and the composition and characteristics of the influent [15]. As stated by Cantinho et al., 2016 [16], and Rodrigo Sanz et al., 2021 [19], the metal removal efficiencies in WWTPs are linked to the partitioning of metals between the liquid and solid phases. Accordingly, the speciation of metals in the influent wastewater is a crucial factor in determining their potential removal through various technological processes. For instance, metals associated with particulate matter can be effectively removed through settling [21], which may explain the observed reduction in particulate concentration from the inlet to the outlet of the plant for most of the species under consideration.

4.4. Removal Mechanisms and Correlation Analysis

The principal mechanism typically considered for metal removal is adsorption, which involves the transfer of the micropollutant, based on equilibrium mechanisms, between dissolved and solid compartments. In the absence of biodegradation, all heavy metals present in untreated wastewater are ultimately retained in either the sludge or the treated effluent [12].

As illustrated in Figure 3b, the metals that are predominantly adsorbed on the sludge (zinc, copper, barium, chromium, and antimony) are those that have a higher inlet particulate concentration. These results are in accordance with the findings documented in the existing literature. Karvelas et al., 2003 [12], observed that over 50% of copper and zinc was released via sludge. Furthermore, Yoshida et al., 2015 [18], discovered that over 50% of barium, copper, chromium, antimony, and zinc was released through sludge.

To substantiate this hypothesis, an investigation was conducted to ascertain a potential correlation between the removal of organic matter, expressed in terms of COD, and the removal of metals, using data collected during the intensive monitoring campaign. As illustrated in Figure S4, the correlation is linear for metals such as zinc, copper, barium, chromium, and antimony. This result corroborates the assertion that these metal species are predominantly removed by sludge.

Concerning boron, there is a distinct predominance of the dissolved phase over that of the particulate matter, as illustrated in Figure 2. This may explain why it is almost entirely released via the treated effluent (Figure 3b), which results in the lowest abatement in terms of loading.

Finally, the results of the linear correlation analysis indicate that the plant can withstand fluctuations in influent loading without any adverse impact on its performance. Since the primary mechanism of metal removal from a sewage treatment plant is adsorption onto the sludge [16], the data presented in Figure 4 suggest that the sludge is not yet saturated and can still effectively remove the targeted metals from the water under current influent loads.

It is noteworthy that the performance of adsorbents is dependent upon a multitude of factors, one of which is pH, which plays a pivotal role in determining the effectiveness of pollutant removal [32,33]. In this work, the pH values of wastewater entering the WWTP were found to be stable during both the extensive and intensive monitoring campaigns. Consequently, no correlation was identified between inlet pH and removal efficiencies. In addition, as reported in Table S1, the pH values observed along the wastewater treatment sections were found to be almost constant, suggesting that this parameter did not influence the removal efficiencies of metals.

4.5. Statistical Analysis

Figure 5 illustrates the probability maps of the observed data, with the abscissa representing input concentration values (x) and the ordinate depicting the reduced variable (z). The right-hand graphs present a comparison between the empirical probability of non-exceedance ($P_N(x)$) and the Gaussian cumulative distribution function relative to the observed data set. In the absence of a robust correlation in the left-hand graphs, a discrepancy between the two curves is evident. The data for manganese, selenium, and barium indicate that the log-normal distribution provides a superior fit to the data, as indicated by the higher R^2 values. In contrast, the other species are better described by a normal distribution (Figure S3).

The use of probability charts represents a valuable diagnostic tool for the effective management of sewage treatment plants. The charts facilitate the monitoring of the recurrence of specific concentration values at the inlet of the plant, thereby enabling the identification of potential issues in specific sections of the plant.

5. Conclusions

A comprehensive study was conducted to ascertain the removal efficiency of several heavy metals and metalloids in the Baciacavallo WWTP in Prato (Italy).

The levels of lead (Pb), cadmium (Cd), nickel (Ni), arsenic (As), and tin (Sn) are typically below the limits of detection. The most significant species identified in the wastewater are zinc (Zn), copper (Cu), manganese (Mn), selenium (Se), barium (Ba), total chromium (Cr^{tot}), and antimony (Sb), which are typically associated with industrial wastewater. For these contaminants, a probability law (normal or log-normal) was identified as an adequate representation of the random variable "plant inlet concentration."

The intensive campaign yielded markedly different results than the extensive campaign, demonstrating clear distinctions in removal efficiency for Zn (76% vs. 66%), Cu (57% vs. 37%), Ba (63% vs. 58%), Mn (6% vs. 31%), Se (31% vs. 52%), and Sb (58% vs. 68%). For the remaining species (B and Cr^{tot}), the removal efficiencies were essentially coincident.

The results obtained from the intensive monitoring campaign are reliable, as evidenced by a comparison of the weekly inlet mass load with the weekly outlet mass load, which is calculated as the sum of the mass load in the effluent and the mass load in the sludge. It can be assumed that the species for which a high difference in removal efficiency was observed in comparison to the findings of the annual monitoring campaign are those exhibiting a greater degree of variability. The behavior of these species may be influenced by the sampling methods employed. It is therefore pertinent to consider the sampling procedure and the use of asynchronous flow rates. For instance, monitoring campaigns frequently indicated a negative removal of manganese. This may be attributed to the concentration values being near the limit of detection during both extensive and intensive monitoring campaigns. Nevertheless, the negative removals obtained during the extensive monitoring campaign can also be attributed to concentration values in the effluent being higher than those entering the WWTP, a phenomenon that occurs due to synchronous sampling.

The WWTP is capable of effectively removing Zn, Cu, Ba, Cr^{tot}, and Sb. This is because these elements are predominantly present in a particulate form and are therefore released from the WWTP through the sludge stream, which accounts for over 50% of the removal. This result is also corroborated by the linear correlation observed between the removed COD mass load and the removed metal mass load. In contrast, B is present in the dissolved phase and is predominantly discharged with the final effluent stream, resulting in the lowest level of abatement.

In conclusion, the monitoring campaigns have demonstrated that the WWTP can comply with the discharge limits prescribed by Italian legislation. Furthermore, the excellent linear correlation values between the load removed and the load entering the plant indicate that the WWTP is well-suited to treat the incoming contaminant loads.

The present study was conducted with a specific focus on the inlet and outlet of the WWTP. Further study is necessary to understand how each treatment section of the plant affects the metal removal. Additionally, further investigation is required to determine the adsorption capacity of sludge, specifically through the determination of adsorption isotherms. Furthermore, an examination of scanning electron microscopy (SEM) images of the sludge would be a valuable addition to the study, allowing for a detailed observation of its structure and confirmation of its adsorption capacity.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/w16223164/s1, Figure S1: Influent and effluent flow rate trends during the intensive monitoring campaign; Figure S2: Normal probability of non-exceedance for Zn (a), Cu (b), Cr^{tot}(c), and Sb (d); Figure S3: Normal and log-normal probability charts and probability of non-exceedance for the specified heavy metals; Figure S4: Correlation between the metal load removal and the removed COD: (a) zinc, (b) copper, (c) barium, (d) chromium, (e) antimony; Table S1: pH trends along the wastewater treatment plant.

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