

RESEARCH ARTICLE

Feasibility of pXRF to evaluate chosen heavy metals in soil highly influenced by municipal waste disposal—A monitoring study of a former sewage farm

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Abstract

Sewage disposal onto agricultural land may result in the high accumulation of organic wastes, which questions the applicability of typical elemental analysis used for the soil components. To monitor the contamination status of agricultural soils at a former sedimentation basin, after the long-term cessation of wastewater irrigation, 110 locations (15–20 cm depth) and 4 boreholes (up to 100 cm depth) were sampled to determine pH, loss on ignition, and concentration of Ni, Cu, Pb, Zn, and Cr. Additionally, the applicability of portable X-ray fluorescence (pXRF) for the soil samples highly influenced by the organic wastes was evaluated. The study revealed the presence of a relatively homogenous sewage waste layer (depth of 20 cm), characterized by slightly acidic to neutral pH (6.3–7.5), high organic matter (OM) accumulation (up to 49%), and elevated concentration (mg kg^{-1}) ranges between: Pb (5–321), Cu (31–2828), Ni (10–193), Cr (14–966), and Zn (76–6639). The pXRF analysis revealed metal concentration increase in mineral samples (up to 50%). The regression models and correction factors demonstrated high correlation and significance of pXRF measurement with response to increasing OM content, with the lowest $r^2 = 0.86$ obtained for Ni. Correlation of pXRF and AES measurement illustrated element-dependent response for soils high in organics. Zn, Cu, and Cr pXRF analysis led to a slight underestimation in lower values, but overall good correlations (0.87; 0.89; and 0.88 respectively). Pb and Ni pXRF measurement revealed higher deviation from the reference in both lower and higher concentrations (0.74 and 0.70, respectively).

KEYWORDS

atomic emission spectroscopy, heavy metals, municipal sewage wastes, pollution

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1 | INTRODUCTION

Irrigation of farmland with municipal wastewater is an agricultural practice for saving scarce freshwater reservoirs, recycling of nutrients, and increasing organic matter content (Abd-Elwahed, 2018; Guo-hang et al., 2018; Hamdi et al., 2019; Sayo et al., 2020). However, especially in the past, due to lack of proper pretreatments, long-term wastewater irrigation led also to negative changes in soil physico-chemical properties and significantly increased the contaminants pool (Abd-Elwahed, 2018).

In Germany, sewage farming began in 1531 and near Berlin the activity started in 1876 (Saber et al., 2016). Until 1928, a total area of 10,000 ha. divided into 20 sewage farms, was in operation. Especially in the second half of the 19th century, due to the industrial revolution in Germany, the inhabitants' number in Berlin and neighbouring areas increased, which led to the stronger contamination of farmlands by municipal wastes (LUA, 2008). Apart from the organic contaminants being a major issue, an important role has been played by uncontrolled disposal of potentially toxic metals. According to Hamdi et al. (2019), the presence of heavy metals in sewage sludge led to soil contamination, impaired plant growth, and disrupted microorganisms' functions and development. Several studies (Blume et al., 1980; Blumenbach et al., 1991; Hoffmann, 2002; Langgemach, 1992; Scheytt et al., 2000; Witten, 2002) and regional reports (LUA, 2003; LUA, 2008) have been conducted to analyze and evaluate the content of potentially toxic metals in soil and groundwater of former sewage farms near Berlin. However, vast affected areas mostly used as fallow land or for extensive cropping are still not examined or have been evaluated many years ago. In Germany, many locations are considered 'waste sites' due to long-term deposition, which is a potential threat to groundwater and surrounding habitants. Ongoing studies are therefore crucial to monitor and assess this environmental issue, especially since the Berlin/Brandenburg metropolitan region is rapidly developing these areas which will result in major land-use changes of former sewage farms.

Nowadays, the potentially toxic metals content (As, Cr, Cd, Cu, Pb, Hg, Mo, Ni, Se, and Zn) in sludge is restricted by governmental regulations like the Sludge Directive 86/278/EEC of the European Union (European Commission, 1986) and EPA Part 503 of the United States. However, in the past, when the sewage farms were operated, no such regulations were applied, resulting in disposal on agricultural soils of municipal sewage composed of unknown amount of potentially toxic elements. Even in industrialized nations with high environmental standards, former sewage farms are increasingly becoming a problem, as they are usually located in the expansion areas of growing metropolitan regions that were previously used extensively for agriculture. Typically, site screening for environmental assessment and determination of metal concentrations involve extensive sampling and laboratory analysis. When it comes to former sewage sludge farms, the most common approach is a wet chemical digestion and subsequent elemental analysis by inductively coupled plasma atomic emission spectrometry (ICP-AES) or inductively coupled plasma mass spectrometry (ICP-MS) (Abd-Elwahed, 2018; Hamdi et al., 2019; Sayo et al., 2020). ICP-AES/MS can identify both trace content and high concentrations of a vast range of elements in various matrixes, including strongly anthropogenically

influenced soil samples. This laboratory approach is generally time and cost consuming, additionally producing toxic wastes.

Due to the still ongoing and weakly restricted sewage farm irrigation in Asian (Guo-hang et al., 2018) and African (Abd-Elwahed, 2018) countries and vast areas of former sewage farms around the world that are still not properly investigated and reclaimed, there is a strong need for a quick and economic analytical method to evaluate the heavy metals concentration in soils highly influenced by municipal wastes. Portable X-ray fluorescence analysis (pXRF) is a nondestructive method, that has been used for the element's hotspot analysis since the beginning of the 2000s (Kalnicky & Singhvi, 2001; Ravansari et al., 2020; Ravansari & Lemke, 2018). The technique is based on measuring the atomic emission of X-ray fluorescence to determine both qualitative and quantitative elemental composition (Tiwari et al., 2005). Feasibility of this method for heavy metals analysis in soil has been proven in literature (Chakraborty et al., 2017; Paulette et al., 2015; Rouillon & Taylor, 2016) and standardized (USEPA, 2007). Caporale et al. (2018) have compared the metals analysis using pXRF and aqua-regia extracts (ICP) of anthropogenically influenced soil and found satisfying correlations ($R^2 > 0.9$). Similar pXRF applicability have been published by Rouillon et al. (2017) and Rouillon & Taylor (2016). However, according to our knowledge, the feasibility of this method for determination of potentially toxic element's content in soils highly influenced by municipal sewage wastes has not been evaluated before. Due to ongoing sewage disposal on the agricultural soils and thousands of still former contaminated sites, there is a necessity to evaluate the feasibility of pXRF for the soil samples highly influenced by the organic wastes.

We present a novel study that was conducted on a former sewage farm near Berlin, in Ragow. This area was used as a sedimentation basin, where solid wastes were separated from the fluid portion, which was subsequently used for field irrigation. Consequently, the amount of the deposited pollutants is much higher than on the average sewage farm soils. Therefore, the applicability of typical elemental analysis methods used for the soil components is questionable, due to the very high content of municipal sewage wastes. According to our knowledge, no such detailed evaluation of a former sedimentation basin was performed. Furthermore, the applicability of the XRF method, for the metal determination in the soil samples strongly influenced by the municipal wastes, has not been published before. Due to the fact that the sewage farming is ongoing and there are many sites still impacted in Europe, there is a necessity to adapt quick field portable methods for the site screening. The main aim of our study was to assess soil quality after long-term municipal sewage sedimentation practice. The detailed objectives were to: (a) analyze the horizontal and vertical distribution of potentially toxic metals and chosen soil properties (pH, OM, and sand fraction) on a former municipal waste sedimentation basin site; (b) compare the feasibility of common laboratory methods (MP-AES and pXRF) to evaluate elemental concentration in soil highly influenced by organic wastes; (c) elaborate on the influence of high amount of the municipal sewage waste on the elemental analysis using pXRF; and (d) define linear regression to establish metal-based linear model to predict MP-AES values using pXRF measurements as a function of organic matter.

2 | MATERIAL AND METHODS

2.1 | Study site

The study site is located near Ragow, a village within the community of Mittenwalde, Dahme-Spreewald County, which borders Berlin in the southwest (Figure 1b). From 1949 to 1990, the State of Brandenburg was a part of the German Democratic Republic (GDR) that used great amounts of municipal wastes to irrigate sewage farms located around Berlin. The study site in Ragow was flooded with sewage coming from Dahme-Spreewald County and comprises a typical sewage farm of the Berlin/Brandenburg metropolitan region. The specific study area is a 2976 m² in extent and is former sewage sedimentation basin where solid waste was separated from wastewater and the liquid subsequently used for the irrigation of surrounding agricultural fields (Figure 1a). The natural setting is typical for the Northeast German Lowlands. Soil's parent material is build up by glaciofluvial and fluvial sands of the Weichselian and Saalian glacial periods (Engelmann et al., 1992). The yearly precipitation in the region is 589 mm and the mean annual air temperature is 8.8°C (Kopp & Schwanecke, 1994).

2.2 | Sampling

To conduct a site screening on a former sewage farm near Ragow, soil samples were collected using a 5x5 m (rows: A–B; columns: 1–10) grid at the depth of 15–20 cm (Figure 1). Prestudies (random locations field portable pXRF analysis up to 60 cm depth in June 2019) have shown that at this depth section, metal concentrations are significantly increased, presumably caused by a distinct sedimentation layer that can be observed. 110 soil samples were collected in October

2019, during dry warm weather, using 250 ml steel cylinder. Subsequently, 4 boreholes (samples taken every 10 cm up to 100 cm depth between the rows 'd' and 'e') were investigated using a hand drill. Soil samples were stored in polyethylene plastic bags and brought to laboratory for further analysis.

2.3 | Soil analysis

To evaluate water content, fresh soil mass was recorded prior to drying at 40°C for 24 hr in an oven. Subsequently, samples were sieved (2 mm) and 10 g were used for a pH analysis (0.01 M CaCl₂, 1:2.5 ratio). The amount of organic matter was determined using loss on ignition (LOI; DIN EN 13039) on samples ground using a mortar grinder RM 200. Sand fractions were analyzed according to particle size analysis using a wet sieving method.

Concentration of the chosen potentially toxic metals (Ni, Cu, Pb, Zn, Cr) was determined with a portable X-ray fluorescence (NITON XL3t) in a laboratory setting (Sut et al., 2012). Approximately, 5–10 g of dried, sieved, and ground samples (<10 µm) were placed in plastic sample cups (Spex Industries Inc.), covered with thin film for pXRF (Mylar). The measurements were performed using the built-in procedure for soil analysis. The analysis was repeated on samples after LOI. According to Johnson (2008), for the investigated elements, following detection limit (ppm) for Niton XL3t is recorded: Zn (<15); Cu (20); Ni (40); Pb (<9); and Cr (<30). The average error ($\pm 2\sigma$; ppm) is: Zn (prior LOI 49.52; after LOI 83.32); Cu (prior 36.34; after 60.34); Ni (prior 24.74; after 37.11); Pb (prior 10.42; after 17.02); and Cr (prior 21.94; after 20.33).

Subsequently, about 0.250 g of soil material was digested using 8 mL of 65% HNO₃ using a Mars G microwave system (20 min at 200°C). Ni, Cu, Pb, Zn, and Cr analysis was performed by plasma

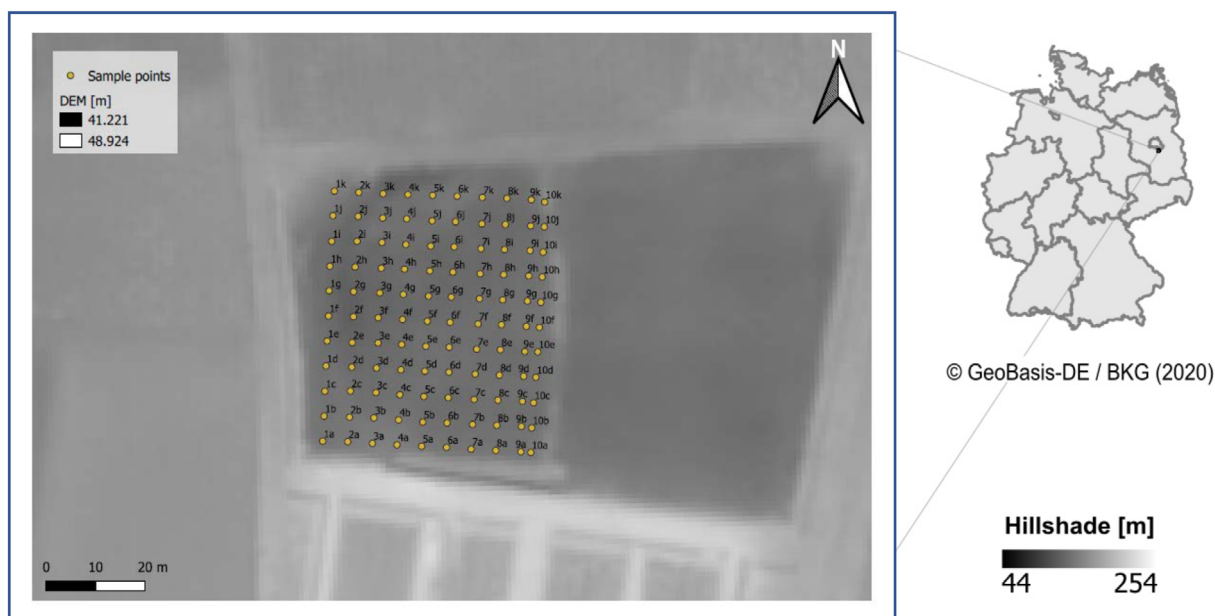


FIGURE 1 (a) Sampling scheme at the former sewage farm near Ragow, Germany; circles indicating 100 cm deep boreholes and (b) map of the Brandenburg Counties [Colour figure can be viewed at [wileyonlinelibrary.com](https://onlinelibrary.wiley.com)]

atomic emission spectrometry (Agilent 4100 MP-AES) (Sut-Lohmann et al., 2020). All the measurements were conducted using two replicates, and certified reference materials Merck Certipur™ were used to control soil analysis quality and instruments calibration. Following detection limits for the analyzed elements (ppm) using AES were obtained: Zn (0.7); Cu (0.1); Ni (0.4); Pb (0.4); and Cr (0.12).

2.4 | Data analysis

The geographical location (longitudinal and latitudinal) of the study site was obtained using GPS. Subsequently, the data were imported to Google Maps API to create maps. The spatial visualization was

performed in R software using 'ggmap' to combine spatial data of Google Maps with graphics of 'ggplot2' (Kahle & Wickham, 2013). The acquired results from soil analysis were visualized in the form of distribution maps (Figure 2). Site screening data visualization, correlations, linear regression, and regression model were performed using R software. Correlation analysis was performed to demonstrate relationship of the chosen metal's concentration to soil OM content and pH.

Linear regression approach was used to evaluate linear relationship between the p-XRF values (prior to LOI) and the AES values as an independent variable. Statistical parameters for the linear regression models were calculated to determine the significance of the correlations including coefficient of determination (r^2), Pearson's correlation

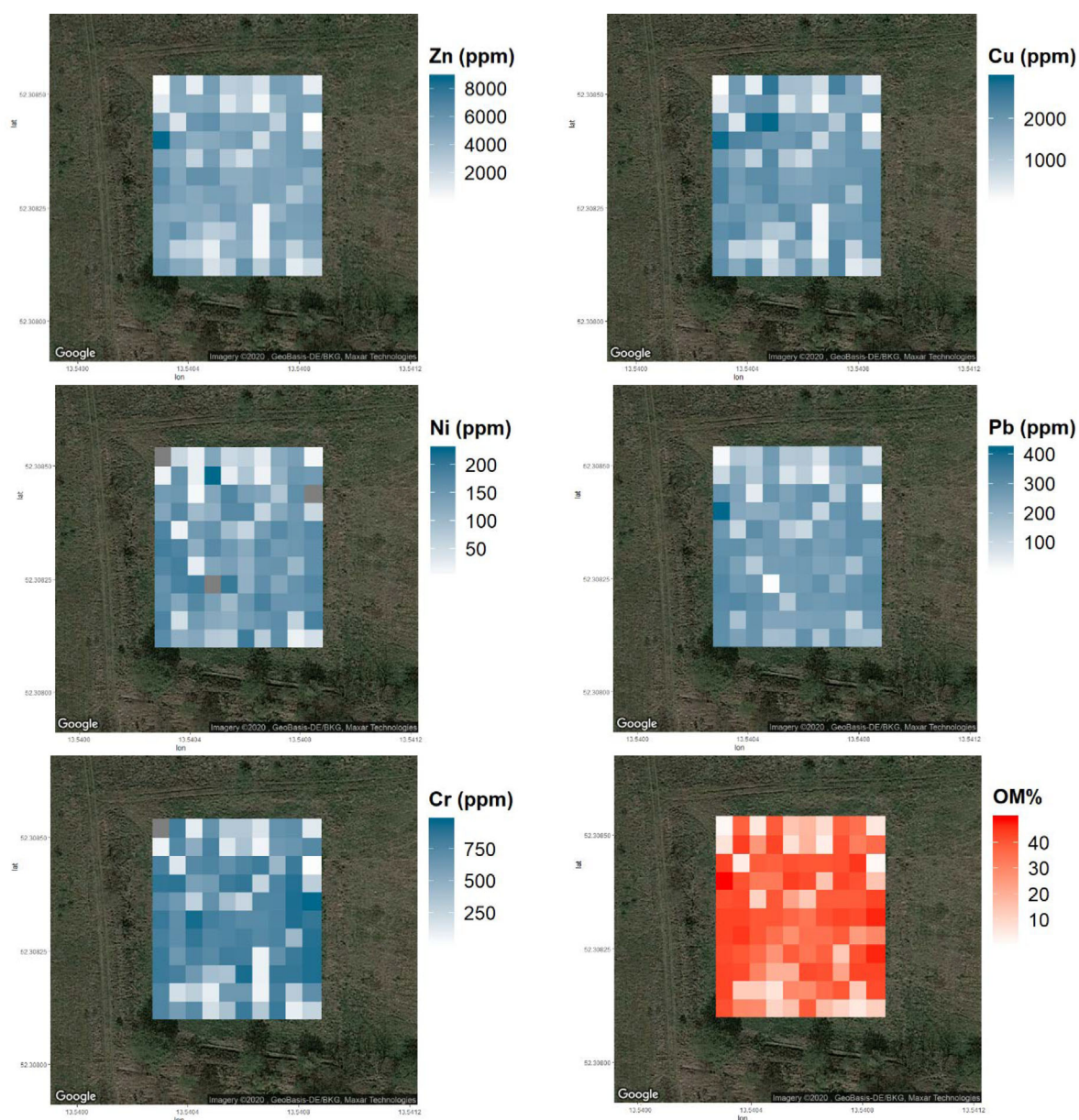


FIGURE 2 Spatial distribution of the potentially toxic metals (mg kg^{-1}) and organic matter (OM) (%) at the depth of 20 cm (atomic emission spectrometry [AES] values) [Colour figure can be viewed at [wileyonlinelibrary.com](https://onlinelibrary.com)]

coefficient (r), and probability value (p -value) for null hypothesis significance testing.

$$r^2 = 1 - \frac{\sum_{i=1}^n (\text{Obs}_i - \text{Pred}_i)^2}{\sum_{i=1}^n (\text{Obs}_i - \overline{\text{Obs}})^2} = 1 - \frac{\text{SSE}}{\text{SST}} \quad (1)$$

Where:

SSE—sum of the squared error,

SST—total sum of squares.

$$r = \frac{\sum (x_i - \bar{x})(y_i - \bar{y})}{\sqrt{\sum (x_i - \bar{x})^2 \sum (y_i - \bar{y})^2}} \quad (2)$$

Where:

x_i — x -variable in a sample.

\bar{x} —mean of the values of the x -variable.

y_i — y -variable in a sample.

\bar{y} —mean of the values of the y -variable.

To find an empirical correlation of the element's concentration using pXRF prior to pXRF after LOI values as a function of OM, the following equation was applied:

$$C_m' = \text{intercept} + (\alpha * C_m) + (\beta * \text{OM}\%) \quad (3)$$

Where:

C_m' —metal concentration after LOI (mg kg^{-1}).

C_m —metal concentration prior LOI (mg kg^{-1}).

Intercept, α and β —constant for each metal.

OM—organic matter content (%).

The predictive performance was evaluated using correlation coefficient (r^2) and probability value (p). Subsequently, Equation (4) was applied to find the correction factor for each element:

$$x = \frac{M_{(\text{before LOI})}}{M_{(\text{after LOI})} - (M_{(\text{before LOI})} \times \frac{\text{OM}}{100})} \quad (4)$$

Where:

x is the correction factor.

$M_{(\text{before LOI})}$ —metal concentration prior to LOI (mg kg^{-1}).

$M_{(\text{after LOI})}$ —metal concentration after LOI (mg kg^{-1}).

OM—organic matter content (%).

To compare the feasibility of pXRF to determine the elements concentration in soils highly influenced by municipal wastes, the values of pXRF prior to LOI were compared to AES results using a linear regression and correlation (r , r^2 , and p) applying a following equation:

$$C_m' = \text{intercept} + (\alpha * C_m) \quad (5)$$

Where:

C_m' , metal concentration by XRF measurement (mg kg^{-1}).

C_m , metal concentration by AES measurement (mg kg^{-1}).

Intercept and α —constant.

TABLE 1 Chosen soil properties (pH, organic matter [OM], and WC) and potentially toxic metals concentrations, measured using atomic emission spectrometry (AES) and portable X-ray fluorescence (pXRF) [prior and after loss on ignition (LOI)] of horizontal samples presented as a mean and standard deviation values ($n = 110$)

AES	Zn		Cu		Ni		Pb				
	Prior	pXRF After	Prior	pXRF After	Prior	pXRF After	Prior	pXRF After			
4211 ± 1731	4161 ± 1676	7816 ± 3830	1645 ± 695	1569 ± 647	2962 ± 1448	126 ± 52	160 ± 54	316 ± 145	229 ± 80	221 ± 76	410 ± 175
AES	Cr (mg kg^{-1})		OM		%		WC ^a		pH		
616 ± 269	Prior	pXRF After	654 ± 289	31.24 ± 13.15	5.62 ± 2.43	6.88 ± 0.18					

^aWater content

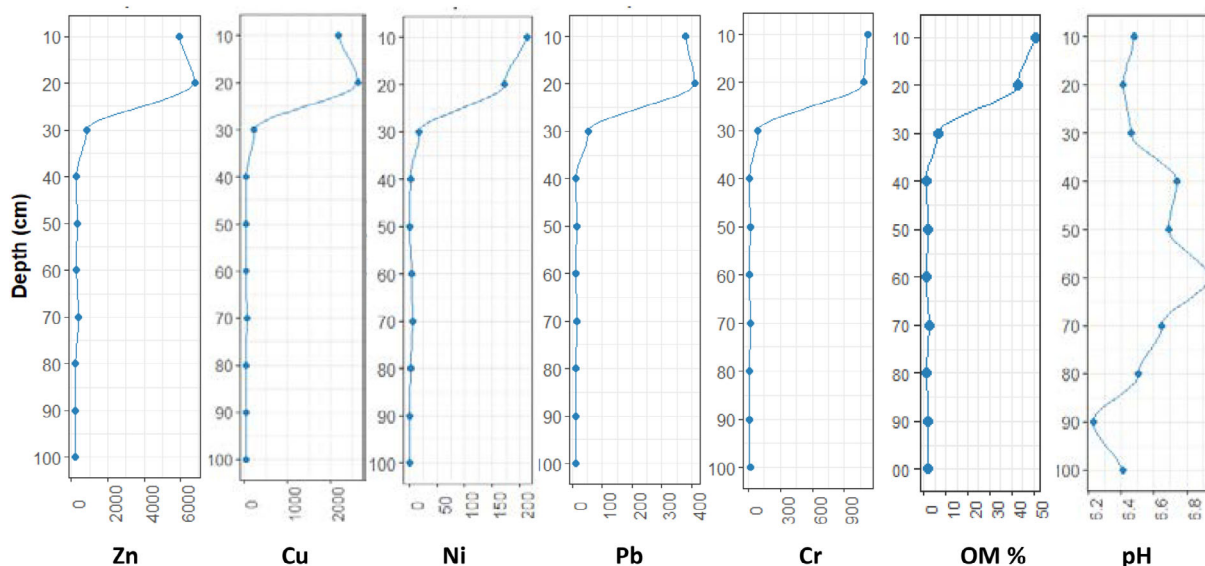


FIGURE 3 Vertical visualization of the chosen soil properties and potentially toxic metals concentration distribution (mg kg^{-1}) in the sampling point 1D [atomic emission spectrometry [(AES) values] [Colour figure can be viewed at wileyonlinelibrary.com]

3 | RESULTS

In Table 1, the concentrations of measured elements are presented using AES and pXRF (prior and after LOI). The higher the elements concentration was, the greater the standard deviation obtained (Table 1). The analysis represents following concentration (mg kg^{-1}) ranges: Pb (5–321); Cu (31–2828); Ni (10–193); Cr (14–966); and Zn (76–6639). From the AES measurement, the following order is noticed: $\text{Zn} > \text{Cu} > \text{Cr} > \text{Pb} > \text{Ni}$. Table 1 reveals a strong increase in potentially toxic elements content in samples after LOI, where analogous raise is observed for all studied metals, except Cr. Site screening revealed rather homogeneous horizontal distribution of potentially toxic elements as presented in Figure 2. However, a few hot spot points (1h, 10d, 10f, etc.), where high OM and metals contents can be observed. On-the-other-hand, this points characterized by low OM content (1k or 10i) reveal lower elements concentrations (Figure 2). Elevation of the area visible in Figure 1 might have also influenced the distribution and accumulation of the wastes in the former sedimentation basin site, resulting in the greater deposition at point: 10b in comparison to 10a; 2k in comparison to 1k; and 9k to 10k. Figure 3 illustrates borehole sampling in the point 1D, where presence of the waste layer (up to 30 cm depth) is confirmed, which is characterized by increased OM content (up to 48%), slightly acidic pH (about 6.4) and elevated concentrations of chosen metals, which subsequently decrease by depth.

Figure 4 closely visualizes the pXRF (prior to LOI) and AES correlations, using linear regression approach, for chosen elements [Equation (5)]. The linear correlation parameters for comparison of pXRF (prior to LOI) and AES values are visible in Table 2. Pb pXRF concentrations mainly undershoot the reference AES measurement in the lower range, whereas the higher concentrations were slightly overestimated (Figure 4). The lowest correlation of 0.70 was obtained for

the Ni (Table 2), which agrees with deviation from the reference visible in Figure 4 characterized by stronger points scattering, for both lower and higher concentration range.

In this study, a regression model was applied to find an empirical correlation between the amount of organic matter and potentially toxic metals concentration, using Equation (3) (material and methods). The regression coefficients, slopes, probability values, and intercept related to metal concentration prior to LOI and OM, respectively, for each element are summarized in Table 2. Zn, Cu, and Cr pXRF response in the lower values underestimate the reference values, but overall revealing good correlations (0.87, 0.89, and 0.88, respectively) as presented in Table 2. For each element, p and r^2 values indicate high correlation and significance of the prior and after LOI pXRF measurement with response to increasing OM content. As already indicated in Table 2, obtained regression shows high correlation for each element, with the lowest r^2 revealed for Ni.

In Table 2, the determination coefficients (R^2) illustrating percentage of the total variation in the data (pH, OM, and element concentration) defined by the linear regression of the mean value are presented. Table 2 indicates positive correlations of the OM contents and concentrations of the potentially toxic elements, whereas the highest correlation is obtained for Cr and Ni, and the lowest for Pb. Zn, Cu, and Pb showed no correlation with the pH values, whereas analogously to previous result, Cr and Ni showed the highest correlation.

Additionally in Table 2, the correction factors obtained using Equation (4) to modify pXRF results according to OM content are presented. It can be noticed that Cu, Zn, Ni, and Pb show similar results. The lowest correction factor was obtained for Ni and the highest for Cr. In Figure 5, the AES, pXRF (after LOI), and modified values calculated using OM-based correction factors are plotted, revealing considerable differences among the elements. Almost for all elements, except Cr, it can be noticed that pXRF (after LOI) values are

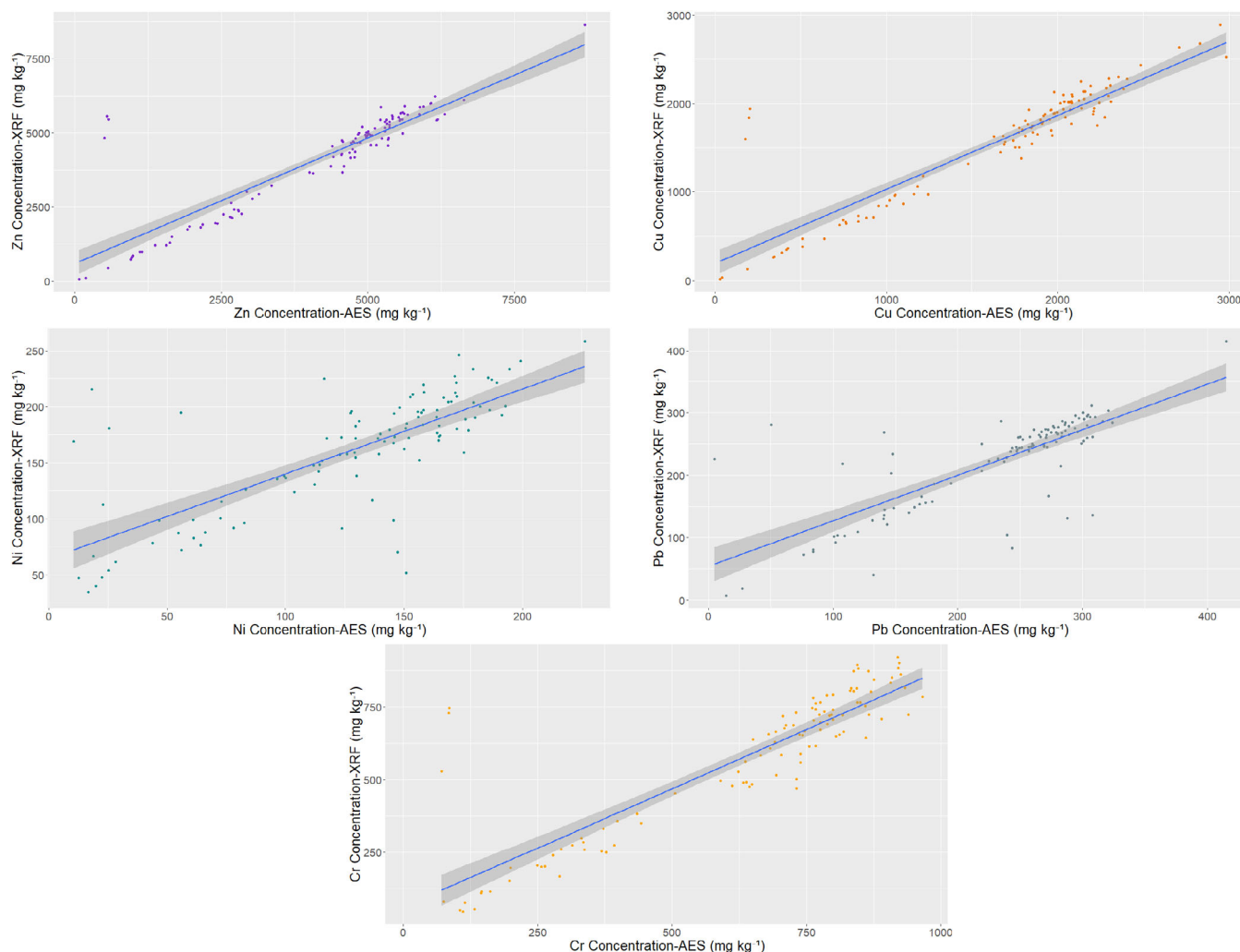


FIGURE 4 Correlation of the portable X-ray fluorescence (pXRF) [prior to loss on ignition (LOI)] and atomic emission spectrometry (AES) values (mg kg^{-1}) for the analyzed heavy metals [Colour figure can be viewed at wileyonlinelibrary.com]

TABLE 2 The determination coefficients (R^2) illustrating percentage of the total variation in the data (pH, organic matter (OM) and element concentration) defined by the linear regression of the mean value; correlation parameters for comparison of portable X-ray fluorescence (pXRF) (prior to loss on ignition [LOI]) and AES values for the chosen elements; regression model parameters for pXRF elemental analysis regarding OM content and correction factors obtained using Equation (4) to modify pXRF results according to OM content

	Zn	Cu	Ni	Pb	Cr
Determination coefficients					
OM (%)	0.62	0.58	0.95	0.43	0.99
pH	0.01	0.01	0.78	0.00	0.98
Linear regression parameters					
<i>p</i> -value	<2.2e-16	<2.2e-16	<2.2e-16	<2.2e-16	<2.2e-16
r^2	0.7674	0.8091	0.5607	0.5995	0.7669
<i>r</i>	0.8760	0.8989	0.7002	0.7402	0.8866
Regression model parameters					
Intercept	-1506.49	-590.78	-101.13	-99.84	-31.60
Slope α	2.11	2.13	1.90	1.86	1.08
Slope β	17.27	2.13	3.39	2.93	2.09
r^2	0.95	0.95	0.86	0.95	0.97
<i>p</i> -values	<2.22e-16	<2.22e-16	<2.22e-16	<2.22e-16	<2.22e-16
Factor	0.51	0.51	0.48	0.52	0.86

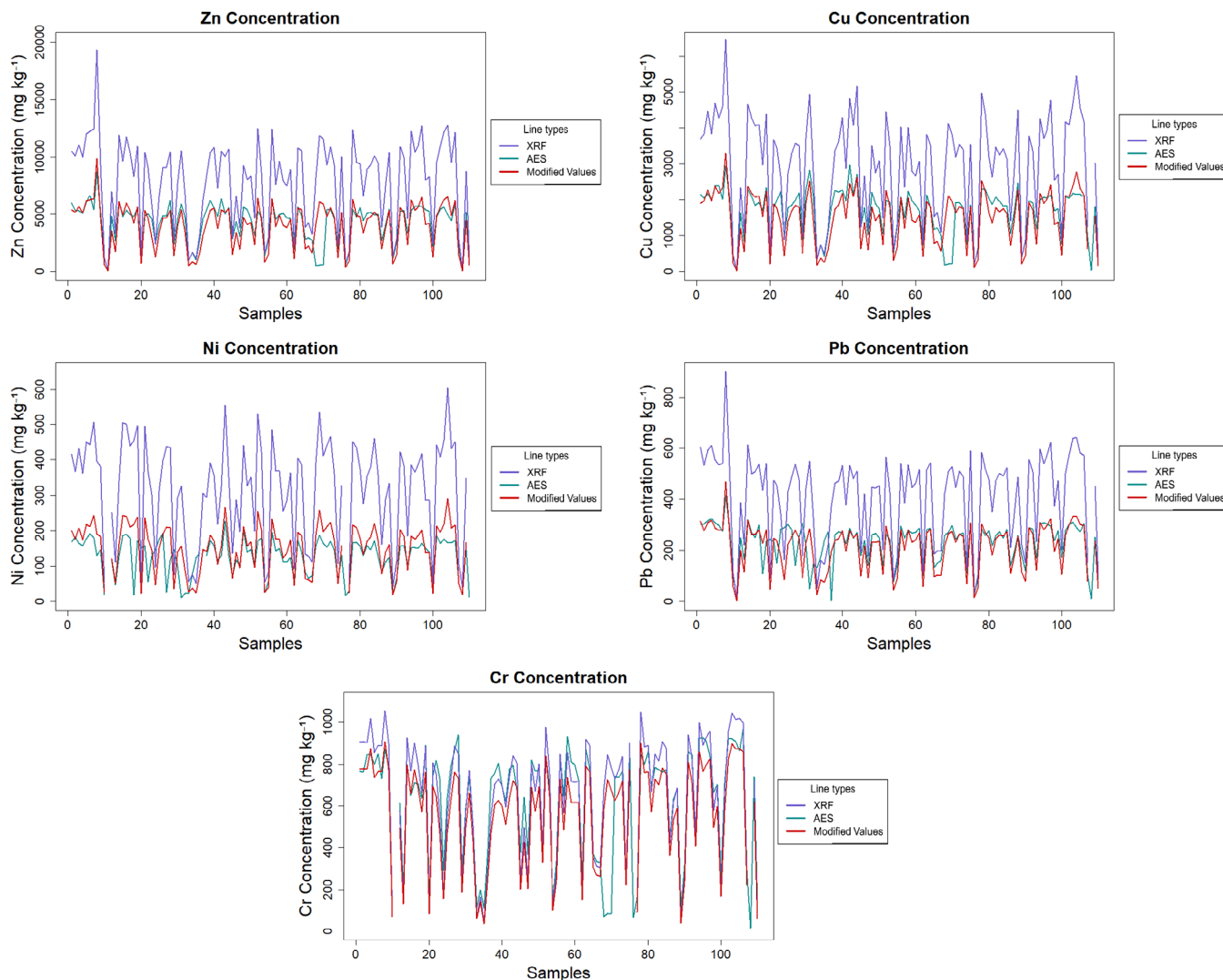


FIGURE 5 Comparison of portable X-ray fluorescence (pXRF) [after loss on ignition (LOI)], atomic emission spectrometry (AES), and modified values using organic matter (OM)-based correction factor [Colour figure can be viewed at wileyonlinelibrary.com]

higher than the AES reference data. In Figure 5, the correlation for the Zn concentrations reveals good correlation of pXRF modified values with slight underestimation of AES values, especially in the higher concentration ranges. Ni indicates good correlation of pXRF-modified values, with an overestimation of AES values especially in higher concentrations. Pb shows good correlation of modified pXRF and AES concentrations, similarly to Cu, where only slight underestimation of AES reference values can be noticed.

4 | DISCUSSION

4.1 | Distribution of potentially toxic elements

In the study conducted by Blumenstein et al. (1997), soil samples (0–30 cm) of a former sedimentation basin in the south of Berlin illustrated correlating Ni (1–190), higher Pb (3–977), and lower Cu (8–

1306), Cr (3–425), and Zn (42–2718) concentrations. Schenk (1997) studied potentially toxic metals in the topsoil of the former sewage farm fields in the south of Berlin and revealed maximal concentrations (mg kg^{-1}) reaching 540 for Pb, 750 for Cu, and 3000 for Zn. Our results indicate that the long-term (about 100 years) wastewater irrigation led to the significant accumulation of potentially toxic elements and organic matter (Table 1; Figure 2) in sedimentation basin sites, where even after 30 years of cessation the heavy metals concentrations, except of Pb, are higher than in above mentioned literature. The comparison to more up-to-date study is not possible since no recent evaluation has been conducted to determine the contamination status at the former sedimentation basin. According to Utermann et al. (2006), the European soil background values for Ni and Cr are 3–48 and 5–68 mg kg^{-1} based on parent material, respectively. The common geochemical occurrence of Cu, Zn, and Pb are estimated at 2–50, 10–1000, and about 17 mg kg^{-1} , respectively (Alloway, 2012). The amount of wastewater (2000–6000 mm per year according to Blume

et al., 1980) and the principal of the gravity-treated sludge sedimentation, prior to field flooding with no-sludge wastewater, in the sedimentation basin resulted in long-term significant retention of potentially toxic metals (Figure 2). This proved contents, even after long-term termination of sewage farm activities, still exceed threshold values according to the Federal Soil Protection and Contamination Ordinance for sandy soils (Bodenschutz, 2003). Sewage sludge and manure application are two major Zn- and Cu-input sources of contamination for agricultural lands. Nowadays, concentration of these elements is strongly regulated, and the levels of Cu in European sewage sludge vary between 190 and 641 mg kg⁻¹ dry matter (SCHER, 2008). Considering the values obtained in this investigation, it can be realized that the past wastewater must have had higher potentially toxic elements contents when compared to the present wastewater composition.

Soil organic matter content and pH are two important parameters that influence elements mobility and transformation in soil (Li et al., 2018). pH at the investigation site was very slightly acidic (Table 1), indicating rather low dissolution potential of investigated elements (Rieuwerts et al., 1998). Previous publications report more acidic character (4.4–6.2) of the organic waste affected topsoil (LUA, 1993). According to LUA (2003), remediation of the former sewage farms involved removal of the highly contaminated soil (0–30 cm), but due to vast areas being affected, it became more economically feasible to stabilize the contaminants. In order to reduce the mobility of potentially toxic metals at the investigated former sedimentation basin, calcium carbonate (CaCO₃) was yearly applied, which correlates with almost basic pH values obtained. This phenomenon also relates to low correlation of the pH values and elements concentrations presented in Table 2, since the soil chemistry/acidity has been affected by the neutralizing lime treatment.

In the Brandenburg arable sandy Arenosols, common OM content reaches 0.5%–0.9% (Grimm & Wirth, 1995). Results obtained in this study revealed mean organic matter content equal to 32.2% (Table 1; Figure 2), which indicates strong influence of the long-term sedimentation of municipal soil wastes. Our results correlate with the study conducted by Grunewald et al. (1996), which revealed mean OM content, in sedimentation basins of the former sewage farms in the south of Berlin, equal to 35.5%. According to the analysis conducted in this study, soil at the former sedimentation basin should be characterized as a Technosol. Naturally, soil organic matter (SOM) is a complex, heterogeneous mixture of organic compounds. According to Escalona et al. (2021), humic substances are the principal component of SOM and are formed by the humification process of plant and microbial remain, which make the properties and the structure of organic matter source dependent. Sewage farming activities influenced the composition of SOM in the investigated sedimentation basin, by flooding the site with a mixture of industrial waste and municipal sewage. Therefore, various potentially toxic substances and high amounts of organic pollutants are assumed to be present in the soil. It may also contain insoluble fractions and be enriched with high nitrogen, phosphorous, and resistant organic contents (Alloway, 2012). According to Harrison et al. (2006), the sludge-related organic pollutants have been

categorized into 15 main groups, including 516 different chemicals, including polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCB), dibenzofurans (PCDF), or polychlorinated dibenzo-p-dioxins (PCDD). Furthermore, the continuous sewage application may cause organic matter mineralization and pH reduction, where the buffer capacity is low (Roig et al., 2012). The behaviour of heavy metals can be strongly altered by the municipal waste input. Naturally, metals can be found as dissolved species, exchangeable, adsorbed on organic and inorganic matter, precipitated solid, and trapped in primary and secondary minerals (Shuman, 1991). In the municipal sewage sludge, the predominated forms of heavy metals are associated with organic compounds and sesquioxides (Kabata-Pendias, 2010). Figure 3 illustrates the presence of municipal solid waste artefact anthropogenically deposited in the topsoil (0–30 cm), which correlates with the study conducted by Grunewald et al. (1996). This layer is characterized by increased OM and metals contents. Generally, high OM content stabilizes the potentially toxic elements in soil, due to organic ligands formation, alteration of cation exchange capacity, and increase in buffer capacity, which prevents soil acidification and decreases metals solubility (Olaniran et al., 2013).

In Table 2, listed determination coefficients illustrate various response of the selected potentially toxic metals to OM content. According to Alloway (2012), sewage farming and industrial activities are two main anthropogenic sources responsible for the high concentration of Cr in soil. A high level of Cr was found in organic matter of a sewage sludge sample from a wastewater treatment plant in China (Zhang & Zhu, 2012). This result correlates with the high coefficient obtained in our study. According to Alloway (2012), anthropogenic sources including sewage sludge or fertilizers containing phosphates lead to Ni accumulation in agricultural soil. In our study, high correlation of Ni concentration and OM content was found. Our results are contradictory to the study published by Kim & McBride (2006), indicating that in the sludge amended soil Ni is more likely to be associated with minerals (particularly with Fe and Mn oxides) than organic matter. Unexpectedly low correlations have been found for Zn and Cu concentrations in the investigated soil influenced by the municipal waste irrigation. Both elements occur naturally in soils; however, their elevated concentrations can be induced by the sewage sludge, manure, fertilizers, and soil amendments applications (Alloway, 2012). Cu and Zn strongly associates with soil organic matter, and corresponding results for the sewage amended soils were published by Kim & McBride (2006). Our next study relates to the sequential extraction of the potentially toxic metals at the former sewage farm in Ragow and will hopefully bring more insight into the accumulation of Cu and Zn in the municipal waste influenced soil. Comparably low correlations were found for the lead. Pb elevated concentrations can be a result of atmospheric dispositions but also disposal of sewage containing industrial (petrol) waste (Alloway, 2012). According to Khadhar et al. (2020), in the waste influenced soils, the highest amount of Pb was held in the residual fraction, which corresponds to our low correlation with OM. Ramos et al. (1994) stated that also in soils not affected by municipal waste irrigation, Pb is reported to be associated with metal oxides or other soil minerals rather than organic matter.

4.2 | Plasma atomic emission spectrometry

For the purposes of this study, to evaluate the pseudo total element concentration, AES measurement was performed using 8 ml of 65% HNO₃ acid, which is not a standard procedure. However, since the soil samples investigated in this study are not the standard matrixes, but soil very strongly influenced by municipal waste irrigation, it was decided, due to high OM content (up to 45%, Table 1) to apply the above-mentioned procedure. A study published by Melaku et al. (2005) reveals the aqua regia extraction has a recovery span within the range of 90%–110% for eight trace elements in soil (Cd, Co, Cr, Cu, Mn, Ni, Pb, and Zn). According to Caporale et al. (2018), total element content can only be obtained by using hydrofluoric acid (HF) because of dissolving metals bound to silicates. On the other hand, the usage of HF is highly restricted due to high corrosivity, overestimation, and potential damages to the flame absorption technique (Atgin et al., 2000; Caporale et al., 2018; Marin et al., 2008). To evaluate the feasibility of our approach, 30 random samples were chosen and analyzed using aqua regia extraction, which demonstrated the recovery rates within the range published by Melaku et al. (2005) (data not shown). Additionally, sequential Tessier extraction performed on this samples, for the purposes of different study, indicated high correlation of the analyzed potentially toxic metals to OM content (article in preparation).

4.3 | pXRF applicability for soil highly influenced by municipal wastewater

To evaluate the applicability of pXRF to define elements content in technosols highly influenced by long-term municipal waste disposal, the measurement was conducted prior and after the removal of organic material.

The results indicated in Table 1 reveal strong metal concentration increase after the LOI was performed. It can be also observed that with increasing elements content, the difference between measurement conducted after and prior LOI rises. The findings of this study are relatable to results published by Ravansari and Lemke (2018), where the pXRF measurement of the chosen elements in soil was affected by addition of various organic matter types and the increase in OM was negatively proportional to analyzed concentrations. Since pXRF analysis is based on dispersive spectrometry, in soil science, the reflection of the radiation wavelength is strongly influenced by soil heterogeneity and geometry (Tjallingii et al., 2007; Löwemark et al., 2011). However, even though a natural soil can contain up to 90% of organic matter, the influence of this parameter on pXRF measurement is still very poorly understood (Troeh, 2005; Ravansari & Lemke, 2018). According to Ravansari et al. (2020), organic matter causes scattering and attenuation of X-ray radiation, having analogous behavior as water content that influences sample density and effective volume. Since pXRF algorithms and calibrations are developed on the organic-free silica metrics, which do not apply divergence factor arising from high OM content, the applicability of this methods for

wetland, agricultural, or contaminated soils can be limited. In this study, the great advantage of pXRF, which is its field application was not reflected, since the investigation of elements concentration in soils highly affected by organic waste needs first a proper laboratory set up and comparison to the reference values (AES). Therefore, we strongly believe that this preliminary investigation in laboratory setup serves as a proper base for the application on waste irrigated agricultural soils, which is already undertaken.

4.4 | Correlation between pXRF and AES results

The correlation reveals that the degree of deviations from the reference lines is element dependent (Figure 4). The underestimation of the low metals concentration observed in Figure 4 clearly shows the superior of AES sensitivity over pXRF method, which underlines its application for the hotspots determination.

In the Table 1, it can be clearly seen that the lack of organic matter (pXRF after LOI) leads to strong overestimation of the pXRF to the AES references values for each element except of Cr.

As already mentioned, the lack of organic matter should reduce the scattering and attenuation of X-ray radiation. According to our results, the main influence on the measurement had the reduction of sample density and effective volume, which correlates with the study published by Ravansari et al. (2020).

Based on the observed deviations in the results of AES and pXRF, correction factors were applied to modify the pXRF results for each element by considering the amount of eliminated OM [Equation (4)] since the observed increase in elemental concentrations was proportional to the OM loss. According to Conklin (2013), two important cation exchange sites exist in soil organic constituents such as humus; the negatively charged oxygens resulted from ionization of phenolic and acidic functional groups that can attach to the metal cations as ligands. Therefore, ligand formation and high buffer capacity lead to strong metal sorption. Consequently, in contaminated soil with sludge, the excessive OM can hinder metals from vertical movement and cause accumulation in the topsoil. The effects of high OM can be also long-lasting as the municipal sewage contains nonbiodegradable organic compounds.

In Figure 5, considerable differences among the elements are visible, which indicates element-specific response. Both elements, Pb and Cu, but also Zn, are known to be very accurately detectable by pXRF (Kalnicky & Singhvi, 2001). The most interesting and unique results are obtained for Cr. Figure 5 indicates only slight overestimation of pXRF (after LOI) data over AES, whereas the applied correction factor led to slight underestimation of reference values. We assume that reduction of OM in soil sample has an influence on the sample density and effective volume, that interferes with elemental concentration determination using pXRF. However, taking soil organic matter content into account corrects its influence on the pXRF measurement. Our results indicate that data correction as a function of organic matter, for some elements, can reduce the matrix influence on pXRF measurements.

5 | CONCLUSION

Horizontal and vertical site screening of a sewage farm abandoned for decades revealed heterogenous distribution of potentially toxic elements. An existing waste layer at 20 cm depth is characterized by elevated metal concentrations ($Zn > Cu > Cr > Pb > Ni$) and exhibits high OM contents. The spatial pattern of the waste layer coincides with the topography of the sedimentation basin suggesting that the original dispersal of sewage during discharge is the primary cause of the determined element distribution. Our study indicates that the OM elimination leads to strong overestimation of the pXRF values for each element, except for Cr. Removal of OM in soil sample influences its density and effective volume interfering with pXRF elemental analysis. Data correction as a function of organic matter, for some elements, can reduce the matrix influence on pXRF measurements. Additionally, our study demonstrates element-dependent correlation of pXRF and AES analysis in soil samples highly influenced by sewage waste disposal. The results validate a usage of pXRF as an alternative method for the conventional wet-chemical based AES analysis for soil samples highly influenced by sewage wastes. The observed pXRF underestimation of the low metals' concentration underlines its application for the hotspot's determination. Future study will include field application of XRF technique at the sewage-influenced agricultural soils.

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CONFLICT OF INTEREST

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this article.

DATA AVAILABILITY STATEMENT

Research data are not shared.

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