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Heavy metal(loid)s and nutrients in sewage sludge in Portugal – Suitability for use in agricultural soils and assessment of potential risks

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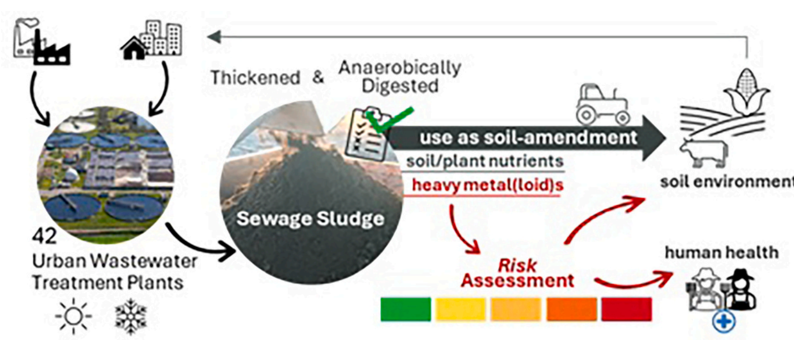
HIGHLIGHTS

- Sum of 7 heavy metals and As in sewage sludge ranged from 398 to 5852 mg kg^{-1} dw.
- Nutrients N (31–97 g kg^{-1} dw) and P (8–54 g kg^{-1} dw) at higher levels in sludge.
- Heavy metal(loid)s and nutrients at higher levels in anaerobically digested sludge.
- Risk characterization ratios (PEC/PNEC) indicate no risk to sludge-amended soils.
- Dermal was the main exposure route of heavy metals in the health risk assessment.

GRAPHICAL ABSTRACT



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ABSTRACT

The presence of heavy metal(loid)s in sewage sludge is a cause of concern and an obstacle to its agricultural valorisation. This study analysed the elemental composition of sewage sludge from 42 Portuguese wastewater treatment plants (WWTPs) during summer and winter, investigating heavy metal(loid) contamination, nutrient content, and potential risks related to sludge application to agricultural soils. Levels of 8 heavy metal(loid)s were investigated, ranging from not detected (Hg) to 5120 mg kg^{-1} dw (Zn), decreasing in the order Zn > Cu > Cr > Ni > Pb > As>Cd > Hg. The legal requirements for agricultural use of sludge were overall met, but elevated levels of Zn and Cu, linked to industrial sources, exceeded the permitted limits in 3 WWTPs. On average, N, P, K, Mg, and Ca comprised 80 % of the sludge nutrient profile. No seasonal variations were found, but sludge composition varied with WWTP size, wastewater origin, and between thickened and digested samples. Environmental hazard indicators showed significant sludge contamination with Zn, Cu, and Cd. However, the geo-accumulation index, potential ecological risk indicators, and risk characterization ratios showed no significant risks to sludge-amended soils, assuming a single application of 5 tons ha^{-1}. Human health risk assessment for workers handling sewage sludge identified dermal contact as the main route of exposure, with non-carcinogenic risk for Cr and carcinogenic risk for Ni and Cr at the highest reported levels. Sewage sludge produced in Portugal

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was considered suitable for agricultural use, provided that it is closely monitored and well-managed to meet the needs of crops and receiving soils, while mitigating environmental risks.

1. Introduction

Effluents reaching wastewater treatment plants (WWTPs) undergo a variety of mechanical, physicochemical, and biological processes to ensure that the treated wastewater meets the requirements for its safe reuse or discharge to the environment (Rorat et al., 2019). The solid residues and contaminants removed from wastewater are concentrated in sewage sludge, a semi-solid waste that requires further treatment and proper disposal.

Sewage sludge composition depends on the type and degree of treatment used at WWTPs but is mainly determined by the origin of the wastewater reaching treatment facilities (Buta et al., 2021; Kanteraki et al., 2022). The final sludge contains a significant amount of water, even after dewatering (Bianchini et al., 2015; Rorat et al., 2019), and its solid fraction has a high load of organic matter, essential soil macronutrients such as nitrogen (N), phosphorus (P), and potassium (K), as well as several other micronutrients that can improve soil fertility (Kanteraki et al., 2022). On the other hand, it also accumulates a wide range of contaminants, including heavy metals, pharmaceuticals, chemicals used in personal care products, microplastics, polycyclic aromatic hydrocarbons, and pathogens (Fijalkowski et al., 2017).

Current approaches to sludge management reflect a paradigm shift in the perception of this by-product of WWTPs. Direct disposal routes such as ocean dumping and landfilling are either banned or being phased out, replaced by strategies more in line with a circular economy model (Bianchini et al., 2015; Di Costanzo et al., 2021; Raheem et al., 2018; Rorat et al., 2019). Sewage sludge is now seen as a widely available and cost-effective source of energy and materials, rather than simply an undesirable waste product. Its agricultural valorisation is often appointed as one of the most appropriate management strategies (D'Imporzano and Adani, 2023; Hoang et al., 2022; Kanteraki et al., 2022; Kowalik et al., 2022; Seleiman et al., 2020).

Sewage sludge use as a soil-amendment has been associated with positive effects on crop yields and improvements in overall soil structure (Hamdi et al., 2019; Kanteraki et al., 2022; Koutroubas et al., 2014; Sharma et al., 2017). Its enriched nutrient profile contributes to soil fertility, while reducing dependence on synthetic fertilizers derived from energy-intensive processes (N) and non-renewable and geographically scarce minerals (P and K) (D'Imporzano and Adani, 2023; Seleiman et al., 2020). However, there is growing concern about the potential risks to soils and crop safety related to the occurrence of numerous contaminants in sewage sludge (Buta et al., 2021; Feng et al., 2023; Fijalkowski et al., 2017; Kanteraki et al., 2022; Liu, 2016). In addition, the sludge nutrient profile can also lead to imbalances of these elements in amended soils, negatively affecting the sustainability of farmland and the quality and safety of food goods (Breda et al., 2020; Seleiman et al., 2020).

In the European Union, sewage sludge production remained relatively stable between 2007 and 2018, at 7 to 8 million tonnes dry weight (dw) per year (European Commission, 2022). Its use on soils has been regulated since 1986 by the Council Directive 86/278/EEC, which establishes rules for its application and sets limits for the concentration of 6 heavy metals in sludge and receiving soils (namely, cadmium, copper, nickel, lead, zinc, and mercury). Almost 40 years after the implementation of this Directive, no major amendments have been adopted. However, most Member States have introduced stricter limits for heavy metals and metalloids, including for chromium (for which the EU Directive never addressed levels) and arsenic, as well as restrictions for some pathogens and organic micropollutants (Collivignarelli et al., 2019; European Commission, 2022).

In terms of sewage sludge management at the EU level, up to 50 % is applied to land, while the remaining fraction is incinerated (31 %), landfilled (12 %), or managed in some other way (European Commission, 2022). Although agricultural valorisation remains the preferred option, there are significant differences in the acceptance of this practice among Member States, ranging from little or no use in some countries to up to 80 % of the produced sludge being applied to soils in others. Several factors contribute to these differences, including the amount of sludge generated and the availability of receiving soils, compliance with national legal limits, the competitiveness of sewage sludge with other fertilizer alternatives, and the overall perception and acceptance by landowners and the public, often driven by precautionary principles.

Sewage sludge stabilization is required prior to land application to prevent fermentation of organic matter in amended soils and to minimize odour emissions (Hoang et al., 2022). Conventional approaches to sludge treatment in WWTPs include thickening and dewatering, often aided by the addition of synthetic polymers or iron salts, and biological stabilization through anaerobic digestion, which produces biogas that can be used for energy recovery (Kanteraki et al., 2022; Raheem et al., 2018; Rorat et al., 2019). By removing water and decomposing biodegradable solids, these processes reduce the amount of generated sludge, facilitating storage and transport. The temperatures achieved during biological stabilization, especially under thermophilic conditions, can also kill pathogens and help reduce the load of some contaminants (Hoang et al., 2022; Kanteraki et al., 2022). However, sludge treatment has little effect on heavy metal(loid)s removal (Feng et al., 2023; Montusiewicz et al., 2020). These constitute a major environmental concern due to their toxicity, persistence, environmental mobility, and potential for bioaccumulation in trophic chains (Buta et al., 2021; Feng et al., 2023; Liu, 2016).

Heavy metal(loid)s in sewage sludge are mainly derived from the wastewater reaching treatment facilities (Feng et al., 2023). In domestic effluents, human excreta are a noteworthy contributor, especially for Zn and Cu (Sörme and Lagerkvist, 2002). Other sources include corrosion and leaching from plumbing systems (Zn, Cu, and Pb in old pipes), use of toiletries, personal care products, laundry detergents and household cleaning goods (Zn, Cu, Cr, Cd, As), colouring agents, paints, and textile pigments (Zn, Cd, As), metal alloys and coatings in kitchenware and sanitation installations (Zn, Cu, Ni, Cr, Pb, Cd) (Buta et al., 2021; Feng et al., 2023; Sörme and Lagerkvist, 2002). Surface runoffs constitute significant sources of Zn (leached from galvanized materials in buildings and traffic infrastructure), Cu (from degradation of roofing materials) and metal-rich dust that builds-up on roads and urban surfaces (Cheng et al., 2022; Feng et al., 2023; Sörme and Lagerkvist, 2002). As for industrial wastewaters, petrochemical refining, power plants, metal casting industries and production of metal alloys are known sources of Zn, Cu, Cd, Cr, Cu, and Ni. Other industrial activities releasing heavy metal-rich discharges include the manufacture of batteries and electronic devices (Cu, Hg, Cd, Ni, Pb, Zn), plastics (Cd, Cu, Zn), tyres (Zn), textiles (Cr, Cu), tanneries (Cr), and intensive livestock farming (Cu, Zn, As) (Buta et al., 2021; Cheng et al., 2022; Feng et al., 2023; Sörme and Lagerkvist, 2002). Although regulatory controls and improved industrial practices have led to a reduction in heavy metal(loid)s entering WWTPs over the years (largely due to pre-treatment of effluents prior to discharge into sewerage systems), industrial activities remain a significant source in municipal sewage sludge (Buta et al., 2021; Fijalkowski et al., 2017).

Monitoring the heavy metal(loid) and nutrient content in sewage sludge is of paramount importance to reap the benefits of its use on farmland without compromising environmental safety and public health. Previous studies have reported levels of metal(loid)s in sewage sludge, but most deal with local or narrow regional scales, and an in-depth characterization of sewage sludge composition in terms of macro- and micronutrients is relatively uncommon in the literature. On the other hand, while some country-level analyses have been carried out on this topic, the contamination status of sewage sludge and the environmental and human health risks associated to its use in agriculture have not been thoroughly assessed. This study fills these gaps by investigating the levels of 23 elements in final dewatered sewage sludge from 42 representative WWTPs across mainland Portugal. Differences in sludge composition were evaluated between seasons and regarding the WWTP size, wastewater origin, and type of sludge produced (thickened or anaerobically digested). The suitability of sewage sludge for agricultural soil-amendment was investigated and the contamination status of sewage sludge was assessed using different ecological and environmental risk indicators. A comprehensive assessment of the environmental and human health risks of metal(loid)s associated with sewage sludge application to soil was proposed.

2. Materials and method

2.1. Sample collection and characterization

Dewatered sewage sludge was collected from 42 urban WWTPs located throughout mainland Portugal in two monitoring campaigns, carried out in summer (June/July 2019) and winter (January/February 2020). Most of the Portuguese population is concentrated in urban areas served by WWTPs of >2000 population equivalent. Smaller WWTPs produce negligible amounts of sewage sludge, which are often transferred to larger plants for further treatment. For this reason, sampling points were selected from about 450 urban WWTPs serving >2000 population equivalent. The selected 42 WWTPs were chosen in collaboration with national bodies responsible for wastewater management to cover the entire territory of mainland Portugal and to be representative in terms of WWTP size (categorized based on population equivalent), sewage source (domestic wastewater or the mixture of domestic and industrial effluents), and type of sewage sludge produced (thickened only or anaerobic digested). Information on each sampled WWTP is presented in Table S1 of the Supporting information (SI). In each season, a single grab sample of sewage sludge of approximately 0.5 kg was collected from each WWTP. Whenever possible, the sludge was sampled directly at the outlet of the dewatering process. When sampled from a stockpile, sludge was only considered if it had been generated in the previous 24 h, and a polypropylene spoon was used to take a portion from throughout the pile. Samples were stored in a sterile resealable polyethylene bag, and transported in a cooler until proper storage in the laboratory at 0–4 °C. An aliquot of fresh sample was sent to an accredited laboratory for the determination of nitrogen levels (N Kjeldahl), and another portion dried to constant mass at 105 ± 5 °C, finely grinded with a mortar and pestle, and used for the analysis of heavy metal(loid)s and nutrients by inductively coupled plasma optical emission spectrometry (ICP-OES). Water content was determined by oven drying at 105 ± 5 °C to constant mass, and organic matter estimated following a loss on ignition protocol at 550 ± 25 °C. Sample pH and electroconductivity were measured in a suspension of 5 g (fresh sample) in distilled water, at a 1:5 (*w*/*v*) ratio, using a Bante900 multiparameter equipped with a P18 pH probe (Sentek) and a CON-1 conductivity electrode (Bante Instruments). Three replicates were performed for each parameter.

2.2. Chemicals and reagents

For sample digestion, 34 % hydrochloric acid (HCl) and 67 % nitric acid (HNO_3), NORMATOM® for trace metal analysis, were purchased from VWR. A multi-element standard solution for ICP with 21 elements (Al, As, B, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, P, Pb, S, Si, Ti, Zn), 100 mg L^{-1} in 5 % HNO_3, and a mercury ICP standard, 1000 mg L^{-1} in 10 % HNO_3, (ARISTAR®, VWR Chemicals, Leuven/Belgium) were used for calibration. Yttrium standard for ICP (TraceCERT®, Sigma-Aldrich, Buchs/Switzerland), 1 g L^{-1} in 2 % HNO_3, was used as internal standard. Ultrapure water was obtained from an Elix® reverse osmosis system combined with a Synergy® UV purification unit (Merck Millipore, Germany). Argon (99.9999 %), for plasma generation, was supplied by Air Liquide (Maia, Portugal).

2.3. Sample analysis

Heavy metal(loid)s and nutrients in sewage sludge were determined by microwave-assisted digestion with *aqua regia*, followed by ICP-OES analysis. Samples were digested in closed 100 mL modified polytetrafluoroethylene vessels in a Milestone START D Microwave Digestion System (Sorisole, Italy), equipped with an HPR-1000/10S high pressure rotor (holding up to 10 vessels) and an ATC-400 CE temperature sensor. Three replicates were performed for each sample, and a procedural blank was prepared for each microwave-assisted digestion run. A previously described protocol was used (Rocha et al., 2022). In short, 0.4 g of dried and finely grinded sample were mixed with 9 mL of 37 % HCl and 3 mL of 67 % HNO_3 in a digestion vessel. The vessels were sealed, and the microwave-assisted digestion was performed with the following temperature programme: 20 min ramp to 210 °C, followed by 15 min at 210 °C, and allowed to cool for 25 min with ventilation. The digested samples were then filtered through Grade 542 hardened ashless paper (Whatman® GE Healthcare) and their volume made up to 50 mL with ultrapure water prior to ICP-OES analysis. Additional dilutions were performed when required. Yttrium was added as an internal standard at a concentration of 1 mg L^{-1} prior to the instrumental reading. Analysis was performed in a Thermo Scientific® iCAP 7400 ICP-OES Duo, coupled with a CETAC® ASX-520 Autosampler. Argon was used as plasma source. Instrumental specifications and acquisition parameters (plasma observation view and spectral emission lines for each element) are detailed, respectively, in Tables S2 and S3 (SI).

2.4. Quality assurance and quality control

To minimize contamination during sample preparation and analysis, ultrapure water and reagents suitable for trace level analysis were used. Glassware was kept for 24 h in a bath of 10 % (*v*/v) HNO_3 solution and rinsed with ultrapure water. Digestion vessels were cleaned in a microwave cycle (20 min ramp to 200 °C, held for 15 min) with 12 mL of 30 % (v/v) HNO_3 solution, then rinsed with ultrapure water.

The method validation was performed considering the linearity ranges, coefficients of determination, limits of detection and quantification, precision, and accuracy (Rocha et al., 2022). Instrumental detection limits (IDL) ranged from 0.05 μg L^{-1} (Cd) to 32 μg L^{-1} (K), while method detection limits (MDL) ranged from 0.03 mg kg^{-1} dw (Cd) to 22 mg kg^{-1} dw (Ca). Accuracy, assessed by the recovery percentage in a certified reference material, varied between 92 and 133 %, while precision (intra- and inter-day), evaluated by the relative standard deviation (RSD), was lower than 10 % for most elements (Table S3, SI).

2.5. Sewage sludge contamination status and ecological risk assessment

Considering the potential use of sewage sludge in agricultural soils, the geoaccumulation index (I_{geo}) (Eq. (1)) was used to evaluate the degree of contamination of all target elements in sewage sludge in relation to a reference concentration in the soil (Tytła and Widziewicz-Rzońca, 2023).

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

C_i is the concentration of a given element (i) in sewage sludge (mg kg^{-1}_{dw}), B_i is its background concentration in a reference soil (mg kg^{-1}_{dw}), and the factor 1.5 is used to account for variability in the soil levels. I_{geo}

values were ranked into 7 classes (Table S4, SI), ranging from “not contaminated” ($I_{geo} \leq 0$) to “extremely contaminated” ($I_{geo} > 5$).

The degree of ecological risk was assessed for each heavy metal(loid) using the potential ecological risk factor (*Er*) (Eq. (2)) (Håkanson, 1980).

$$Er_i = Tr_i \times \frac{C_i}{B_i} \tag{2}$$

C_i is the concentration of the heavy metal(loid) (*i*) in sewage sludge (mg kg_{dw}^{-1}), B_i is its background concentration in a reference soil (mg kg_{dw}^{-1}), and Tr_i is the respective toxic-response factor. *Tr* values used were 40 for Hg; 30 for Cd; 10 for As; 5 for Cu, Ni, and Pb; 2 for Cr; 1 for Zn (Espinoza-Guillen et al., 2024; Håkanson, 1980). *Er* values were calculated for 8 heavy metal(loid)s and then summed to determine the potential ecological risk index (*PERI*). *PERI* assesses the degree of ecological risk resulting from the occurrence of multi heavy metal(loid)s in the same matrix (Eq. (3)) (Håkanson, 1980).

$$PERI = \sum Er_i \tag{3}$$

The classification of the potential ecological risk level for both indicators is shown in Table S5 (SI), ranging from “low” ($Er < 40$; $PERI < 150$) to “very high” ($Er \geq 320$; $PERI \geq 600$). The background concentrations in a reference soil (B_i values) considered for the calculation of these indicators were the median values of the target elements in European agricultural soils (Matschullat et al., 2018; Reimann et al., 2018), presented in Table S6, SI.

2.6. Environmental risk assessment in sewage sludge-amended soils

The environmental risk assessment (ERA) of heavy metal(loid)s in agricultural soil after a single application of sewage sludge was carried out using the methodology and assumptions proposed in the EU Technical Guidance Document on Risk Assessment (European Commission, 2003). This approach was chosen because it is widely adopted for numerous contaminants and provides a standard for comparison with other studies in the literature.

The concentrations of heavy metal(loid)s in sewage sludge were used to estimate their predicted environmental concentrations in soil (PEC_{soil}). For the heavy metal(loid)s investigated, their occurrence in soil prior to sludge addition should also be considered (ECHA, 2008). Therefore, the predicted total concentration in sludge-amended soil ($PEC_{soil,total}$, mg kg_{dw}^{-1}) was calculated by summing the predicted environmental concentration added by sewage sludge application ($PEC_{soil,added}$, mg kg_{dw}^{-1}) with the background concentration in a reference soil (B_i, mg kg^{-1}dw) (Eq. (4)).

$$PEC_{soil,total} = PEC_{soil,added} + Bi = \frac{MEC_{sludge} \times APPL_{sludge}}{DEPTH_{soil} \times RHO_{soil}} + Bi \tag{4}$$

MEC_{sludge} is the measured concentration of the target heavy metal (loid) in the sewage sludge (mg kg^{-1} dw), $APPL_{sludge}$ is the sewage sludge application rate (0.5 kg m^{-2} yr^{-1}), $DEPTH_{soil}$ is the soil mixing depth (0.20 m) and RHO_{soil} is the bulk density of dry soil (1500 kg m^{-3}).

PEC_{soil} values were then compared to the predicted no-effect concentrations of heavy metal(loid)s in terrestrial organisms ($PNEC_{soil}$) for the determination of risk characterization ratios (*RCRs*) (Eq. (5)). PNEC values were surveyed in literature and are presented in Table S7, SI. A *RCR* higher than 1 indicates a potential environmental risk.

$$RCR = \frac{PEC_{soil}}{PNEC_{soil}} \tag{5}$$

Two approaches were considered for the calculation of the *RCR* (ECHA, 2008). If the background concentrations in soil were not significant compared to the PNEC values, the Total Risk Approach was used and the *RCR* was determined using the $PEC_{soil,total}$. If the background concentration of a given heavy metal(loid) in soil was significant compared to the PNEC value, the Added Risk Approach was used. In this case, given the availability of $PNEC_{added}$ values for some heavy metal (loid)s (estimated based on the added concentrations in toxicological studies), the *RCR* was determined using the ratio of PEC_{added} and $PNEC_{added}$. This takes into account that species are fully adapted to the ambient background concentration, and therefore only the added fraction is considered for the ERA (ECETOC, 2003; ECHA, 2008).

In addition to the *RCR*, the degree of contamination and the potential ecological risk in agricultural soils following a single sewage sludge application was also assessed using the I_{geo}, *Er*, and *PERI* indicators. The values of $PEC_{soil,total}$ were used instead of the concentration in sewage sludge in the respective equations.

2.7. Human health risk assessment

The potential non-carcinogenic and carcinogenic effects of heavy metal(loid)s exposure on the health of workers (adults) in contact with sewage sludge were assessed using the methodology proposed by the U. S. EPA, considering three routes of exposure – accidental ingestion, dermal contact, and inhalation (Varol et al., 2021; Yakamercan et al., 2021). The parameters and input assumptions used in the risk models are summarized in Table S8, SI.

The non-carcinogenic risk was estimated according to Eq. (6), by calculating hazard quotients (*HQs*) comparing the average daily dose (*ADD*; mg kg_{bw}^{-1} day^{-1}) of each heavy metal(loid) (*i*) for each exposure route (*j*) with the respective risk reference dose (*RfD*; mg kg_{bw}^{-1} day^{-1}).

$$HQ_{i,j} = \frac{ADD_{i,j}}{RfD_{i,j}} \tag{6}$$

Risk reference doses for ingestion ($RfD_{ingestion}$) were adopted from literature (El Fadili et al., 2022; U.S. EPA, 1996; Varol et al., 2021). Risk reference doses for inhalation ($RfD_{inhalation}$) were estimated according to Eq. (7), where *InhR* is the inhalation rate (m^3 day^{-1}), *BW* the body weight (kg_{bw}), and RFC_i is each heavy metal(loid)’s inhalation reference concentration (mg m^{-3}). Risk reference doses for dermal contact (RfD_{dermal}) were estimated based on the $RfD_{ingestion}$ and the gastrointestinal absorption factor (*GIABS*), according to Eq. (8).

$$RfD_{i,inhalation} = RFC_i \times \frac{InhR}{BW} \tag{7}$$

$$RfD_{i,dermal} = RfD_{i,ingestion} \times GIABS \tag{8}$$

The average daily doses were estimated as follows (Eqs. (9) to (11)):

$$ADD_{i,ingestion} = \frac{C_{sludge,i} \times IngR \times 10^{-6} \times RBA_i \times EF \times ED}{BW \times AT} \tag{9}$$

$$ADD_{i,dermal} = \frac{C_{sludge,i} \times SA \times SL \times 10^{-6} \times ABS_i \times EF \times ED}{BW \times AT} \tag{10}$$

$$ADD_{i,inhalation} = \frac{C_{sludge,i} \times InhR \times EF \times ED}{PEF \times BW \times AT} \tag{11}$$

where C_{sludge} is the concentration of heavy metal(loid)s in fresh sewage sludge (mg kg^{-1}), *IngR* the ingestion rate of sewage (mg day^{-1}), *InhR* the inhalation rate (m^3 day^{-1}), *SA* the exposed skin area (cm^2), *SL* the skin adherence factor (mg cm^{-2} day^{-1}), 10^{-6} is a conversion factor (kg mg^{-1}), RBA_i the relative bioavailability factor, *ABS* the dermal absorption factor, *EF* the exposure frequency (day $year^{-1}$), *ED* the exposure duration (year), *BW* the body weight (kg_{bw}), *AT* the averaging time (day) and *PEF* the sewage sludge-air particulate emission factor (m^3 kg^{-1}).

Along with the hazard quotients (*HQs*), the hazard index of each heavy metal(loid) (HI_i), defined as the sum of *HQs* of all exposure routes for a given metal (Eq. (12)), and the total hazard index (*THI*), as the sum of the *HQs* of all metal(loid)s for a given exposure route (Eq. (13)), were also calculated.

$$HI_i = HQ_{i,ingestion} + HQ_{i,dermal} + HQ_{i,inhalation} \quad (12)$$

$$THI_j = \sum_i HQ_{i,j} \quad (13)$$

If HQ or HI or THI is >1, it reflects the possibility of non-carcinogenic health effects in workers exposed to heavy metal(loid)-contaminated sewage sludge.

The carcinogenic risk (CR) of each heavy metal(loid) (i) was calculated for each exposure route (j) based on Eq. (14), multiplying the lifetime average daily dose ($LADD$; mg kg_{bw}^{-1} day^{-1}) by the respective cancer slope factor (CSF; kg_{bw} day mg^{-1}).

$$CR_{i,j} = LADD_{i,j} \times CSF_{i,j} \quad (14)$$

The lifetime average daily doses were estimated similarly to the average daily doses in the non-carcinogenic risk model (Eqs. (9) to (11)) but using a different AT. The AT_{cancer} was determined based on an average life expectancy of 70 years. $CSF_{i,ingestion}$ values were obtained from literature (Karimian et al., 2021; U.S. EPA, 1996; Varol et al., 2021), while the dermal and inhalation cancer slope factors were estimated from Eqs. (15) and (16):

$$CSF_{i,dermal} = \frac{CSF_{i,ingestion}}{GIABS_i} \quad (15)$$

$$CSF_{i,inhalation} = \frac{IUR_i \times BW}{InhR} \quad (16)$$

where $GIABS$ is the gastrointestinal absorption factor, IUR the inhalation unit risk (m^3 mg^{-1}), and BW the body weight (kg_{bw}).

The total cancer risk (TCR) for a given heavy metal(loid) was obtained from the sum of the CRs for the three exposure routes (Eq. (17)), and the cumulative cancer risk (CCR) as the sum of the CRs of all metal (loid)s for a given exposure route, according to Eq. (18).

$$TCR_i = CR_{i,ingestion} + CR_{i,dermal} + CR_{i,inhalation} \quad (17)$$

$$CCR_j = \sum_i CR_{i,j} \quad (18)$$

If CR, TCR or $CCR < 10^{-6}$, the carcinogenic risk to human health can be considered negligible; from 1×10^{-6} to 1×10^{-4} it could be considered an acceptable risk, and if $>1 \times 10^{-4}$ it represents a high risk of cancer development in humans.

2.8. Statistical analysis

Statistical analyses were performed using the IBM® SPSS® Statistics software, Version 27. Normality tests were performed using the Kolmogorov-Smirnov and Shapiro-Wilk statistics. Since normality was not found for most cases, non-parametric Mann-Whitney U tests and Kruskal-Wallis tests were used to compare the distribution of the concentration of the studied elements across sample groups. Spearman's correlation analysis was used to assess correlations between target elements. In all tests, significance was set at a 0.05 probability level (p-value). For these statistical analyses, the non-detected values were replaced by half of the method detection limit of the corresponding element.

3. Results and discussion

3.1. Physicochemical parameters and elemental composition of sewage sludge

Dewatered sewage sludge was collected from 42 WWTPs in summer and winter seasons, resulting in a total of 78 samples (42 in summer and 36 in winter). The range and mean values of the elemental composition and the physicochemical parameters of the investigated samples are presented in Table 1. The moisture content ranged from 58.2 to 88.6 % (mean: 80 ± 5 %), and the volatile solids varied between 49.0 and 91.4 % of dw (mean: 76 ± 9 % of dw). Overall, sludge pH was close to neutral in most samples (mean of 6.9 ± 0.7), varying between 4.7 and 8.2. Electroconductivity ranged from 0.2 to 4.3 mS cm^{-1} (mean: 1.5 ± 0.7 mS cm^{-1}).

The concentrations of 23 elements in the different sewage sludge samples are summarized in Fig. 1. These include 8 potentially toxic metal(loid)s (Cd, Cr, Cu, Hg, Ni, Pb, Zn, As) (Fig. 1A), typically regulated in sludge to be used in soils, and 11 soil macro and micronutrients (N, P, K, Mg, Ca, S, Fe, Mn, B, Mo, Co), plus 4 other elements (Na, Al, Si, Ti) that integrate this matrix composition (Fig. 1B). With the exception of the metalloid As, the Portuguese Decree-Law No. 276/2009 establishes limits for their concentration in sewage sludge (Table 2). It should be noted that some of these heavy metal(loid)s, namely Cu, Zn, and Ni, are also considered essential plant micronutrients at trace levels (Molaey et al., 2024). However, in the context of this study, the significance of Cu, Zn, and Ni as potentially toxic metals in sewage sludge was emphasized over their classification as micronutrients, and these were therefore grouped alongside the other targeted heavy metal(loid)s. The values determined in this study are the *pseudo*-total concentrations (*aqua regia* soluble). For N, total Kjeldahl nitrogen was measured, i.e. the organic N plus ammonia (NH_3) and ammonium (NH_4^+).

Regarding the 8 heavy metal(loid)s, Hg was detected in only 19 % of the samples, up to 1.4 ± 0.2 mg kg^{-1} dw. The others were quantified in all sewage sludges and ranged from 0.46 ± 0.02 mg kg^{-1} dw (Cd) to 5120 ± 49 mg kg^{-1} dw (Zn). The sum of the heavy metal(loid)s concentrations in individual samples differed by >10-fold, varying from 398 mg kg^{-1} dw (WWTP#28, winter) to 5852 mg kg^{-1} dw (WWTP#18, summer), with a mean of 1378 ± 1034 mg kg^{-1} dw. Zn and Cu were consistently found at higher concentrations, accounting for an average of 67 % and 21 %, respectively, of the total heavy metal(loid)s in the studied samples, while Cd (0.2 %) and Hg (< 0.02 %) were consistently at the lowest levels. Overall, the concentrations decreased in the following order: Zn (mean of 885 mg kg^{-1} dw), Cu (332 mg kg^{-1} dw), Cr (76 mg kg^{-1} dw), Ni (37 mg kg^{-1} dw), Pb (36 mg kg^{-1} dw), As (10 mg kg^{-1} dw), Cd (2.2 mg kg^{-1} dw), and Hg (0.7 mg kg^{-1} dw). In fact, this profile can be explained by the widespread presence of heavy metal (loid)s such as Zn and Cu in domestic and industrial waste, whereas heavy metal(loid)s such as Cd and Hg tend to be more toxic and therefore their use is usually more restricted and subjected to stricter regulatory controls. Similar trends have been reported in the literature (Chen et al., 2021; Yakamercan et al., 2021). Feng et al. (2023) reviewed the average concentration of heavy metals in sewage sludge from different countries and identified the order Zn > Cu > Cr ≈ Pb ≈ Ni > Cd in most cases. Fewer studies include Hg and As, but their levels in sewage sludge are usually lower than those of most heavy metal(loid)s (Zhang et al., 2017). The concentration ranges reported in this work are also in the same order of magnitude as those reported in sewage sludge from other countries (Abreu et al., 2017; Chen et al., 2021; Cheng et al., 2022; Espinoza-Guillen et al., 2024; García-Delgado et al., 2007; Sichler et al., 2022; Singh et al., 2021; Vriens et al., 2017; Yakamercan et al., 2021), as shown in Table S9, SI.

Concerning the occurrence of nutrients, all elements were quantified in all samples. The sum of 11 nutrients ranged from 73 g kg^{-1} dw (WWTP#8, winter) to 297 g kg^{-1} dw (WWTP#12, winter), with an overall mean of 145 ± 38 g kg^{-1} dw. N was found in higher concentrations in most samples (mean of 63 g kg^{-1} dw), followed by P (22 g kg^{-1} dw), Ca (21 g kg^{-1} dw), Fe (17 g kg^{-1} dw), and S (13 g kg^{-1} dw). On average, these macronutrients accounted for up to 93 % of the total nutrient content of sewage sludge (44 % N, 14 % P, 14 % Ca, 12 % Fe, and 9 % S). The prevalence of these elements was expected as all samples were collected from urban WWTPs, which predominantly treat sewage generated in households, public and commercial facilities. In addition, regardless of the different treatment processes employed, all WWTPs increased the solid content of sludge by thickening processes and used

Table 1
Physicochemical parameters and elemental composition of sewage sludge. Concentrations in mg kg^{-1} dw.

	All samples (n = 78)		Thickened (n = 29)		Digested (n = 49)	
Parameter	Min–Max	Mean ± SD	Min–Max	Mean ± SD	Min–Max	Mean ± SD
Moisture (%)	58.2–88.6	80 ± 5	73.3–88.4	82 ± 4	58.2–88.6	79 ± 6
TS (%)	11.4–41.8	20 ± 5	11.6–26.7	18 ± 4	11.4–41.8	21 ± 6
VS (% dw)	49.0–91.4	76 ± 9	66.6–91.4	83 ± 6	49.0–90.0	72 ± 9
pH	4.7–8.2	6.9 ± 0.7	4.7–7.5	6.5 ± 0.7	5.3–8.2	7.2 ± 0.6
EC (μS cm^{-1})	230–4347	1452 ± 727	230–3180	1202 ± 629	315–4347	1599 ± 746
∑ 8 heavy metal(loid)s	398–5852	1378 ± 1034	398–1221	791 ± 238	620–5852	1725 ± 1162
Cd	0.6–11.1	2.2 ± 1.9	0.5–3.1	1.1 ± 0.5	0.7–11.1	3 ± 2
Cu	78–4429	332 ± 601	78–407	175 ± 73	107–4429	424 ± 743
Ni	8.2–206	37 ± 43	8.2–115	23 ± 24	8.3–206	45 ± 49
Pb	11.1–204	36 ± 28	11.1–52.3	22 ± 10	16.4–204	44 ± 32
Zn	271–5120	885 ± 678	271–870	532 ± 177	381–5120	1095 ± 773
Hg[a]	0.4–1.4	0.7 ± 0.3	0.4–0.8	0.6 ± 0.1	0.4–1.4	0.7 ± 0.3
Cr	10.3–919	76 ± 133	10.3–100	30 ± 19	15–919	103 ± 161
As	2.6–31	10 ± 7	2.6–25.7	8 ± 5	2.8–31	11 ± 8
∑ 11 nutrients	73,171–297,142	144,706 ± 38,059	73,171–175,654	130,147 ± 23,971	87,046–297,142	153,323 ± 42,244
N	30,700–97,000	63,442 ± 13,168	42,200–97,000	69,806 ± 13,544	30,700–82,000	59,676 ± 11,499
P	7819–53,461	21,776 ± 10,218	7819–42,065	20,123 ± 9072	9343–53,461	22,754 ± 10,809
K	1380–11,895	4289 ± 2541	1847–11,895	5436 ± 2941	1380–9709	3610 ± 2012
Mg	1470–14,284	3862 ± 2114	1841–8306	3647 ± 1532	1470–14,284	3989 ± 2399
Ca	5585–51,922	20,726 ± 11,994	5585–28,446	12,830 ± 6211	8502–51,922	25,400 ± 12,177
S	4970–37,883	12,897 ± 5265	4970–37,883	11,076 ± 6246	7362–26,366	13,974 ± 4304
Fe	1581–132,307	17,359 ± 22,291	1581–35,608	6760 ± 6621	2476–132,307	23,632 ± 25,758
Mn	37–895	209 ± 184	37–895	143 ± 183	52–848	249 ± 175
B	5.0–96.4	24 ± 19	5–96.4	23 ± 25	5.0–57.3	25 ± 14
Mo	2.1–83	7 ± 11	2.1–20.8	5 ± 5	2.8–83	8 ± 14
Co	1.2–5514	114 ± 712	1.2–5514	299 ± 1156	1.3–16.9	5 ± 3
∑ 4 minerals	6089–85,380	23,463 ± 14,507	6089–85,380	20,854 ± 16,544	6856–63,406	25,008 ± 13,091
Na	236–6773	1296 ± 1217	236–6773	1459 ± 1571	385–4446	1199 ± 953
Al	3273–77,188	20,069 ± 14,425	3273–77,188	17,223 ± 16,097	3784–60,556	21,754 ± 13,224
Si	806–2721	1629 ± 453	875–2721	1792 ± 475	806–2484	1533 ± 414
Ti	158–1781	469 ± 259	158–831	380 ± 120	203–1781	522 ± 303

Min – minimum; Max – maximum; SD – standard deviation; TS – Total solids; VS – Volatile solids; EC – Electrical conductivity.
[a] Hg was only detected in 15 samples (thickened, n = 7; digested, n = 8).

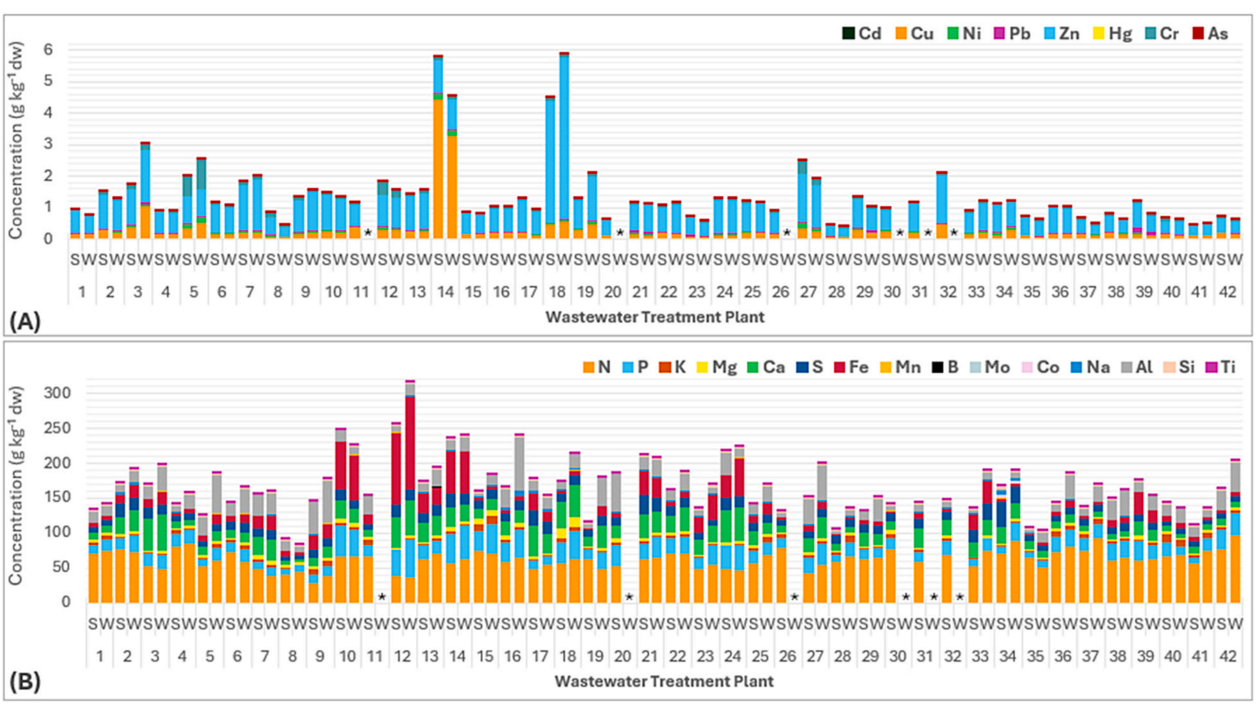

Fig. 1. Concentrations of 8 heavy metal(loid)s (A) and 11 nutrients and other elements (Na, Al, Si, Ti) (B) in sewage sludge from the different WWTPs. S (summer); W (winter). **Due to technical problems, these samples could not be collected.*

Table 2
Overview of the concentrations of heavy metal(loid)s reported in sewage sludge and comparison with regulated limits in Portuguese and EU legislation.

	Legal limit in sewage sludge (mg kg^{-1} dw)		Concentration in sewage sludge (mg kg^{-1} dw)		Amount of heavy metal(loid) added annually to agricultural soil (kg ha^{-1} yr^{-1})	
	Portugal[a]	EU[b]	Mean (*n* = 78)	Maximum (*n* = 78)	Regulated limit[c] in Portugal[a]/EU[b]	Estimated from maximum concentration in sludge
Cd	20	20–40	2.2	11.08	0.15	0.05
Cu	1000	1000–1750	332	4429	12	22
Ni	300	300–400	37	206	3	1
Pb	750	750–1200	36	204	15	1
Zn	2500	2500–4000	885	5120	30	26
Hg	16	16–25	0.7	1.4	0.1	0.01
Cr	1000	nd	76	919	4.5[d]	4.6
As	nd	nd	10	31	nd	0.16

nd – not defined.
[a] Decree-Law No. 276/2009.
[b] Council Directive 86/278/EEC.
[c] Maximum amounts that can be added yearly, based on a 10-year average.
[d] Value for Cr not defined in the EU legislation.

mechanical dewatering to improve water removal from the final sludge, often aided by the addition of polymers or salts. N, P, and Ca are mostly derived from human waste and the use of certain soaps and detergents (U.S. EPA, 2023), while a significant fraction of Fe is related to the use of iron salts in wastewater and sludge treatment (Bratby, 2016; Wei et al., 2018). S is also mainly derived from domestic wastewater, but additional sources include industrial emissions and the use of sulphate salts in WWTPs (Fisher et al., 2017; Wei et al., 2018). The use of coagulants in WWTPs is also a source of Al (Bratby, 2016), which was found in sewage sludge with a mean of 20 g kg^{-1} dw. Lower levels of other nutrients were found in the following order: K (mean of 4.3 g kg^{-1} dw), Mg (3.9 g kg^{-1} dw), Mn (209 mg kg^{-1} dw), Co (1114 ± 81 mg kg^{-1} dw), B (24 mg kg^{-1} dw), and Mo (7 mg kg^{-1} dw). The magnitude of the concentrations found is consistent with previous studies in other countries (Abreu et al., 2017; Chen et al., 2021; Cheng et al., 2022; Sichler et al., 2022; Singh et al., 2021; Vriens et al., 2017), as shown in Table S10, SI.

3.1.1. *Seasonal variation and correlations between elements*

The elemental composition of samples collected in summer and winter (Table S11) was compared to assess possible seasonal variations. Analysing the distribution of the combined concentrations of 8 heavy metal(loid)s and 11 nutrients in summer and winter (Fig. 2), no statistically significant differences were found between seasons ($p > 0.05$). When analysing each element individually, although in some cases the mean concentrations were slightly higher in winter (e.g. As, N, P, K, Fe), no significant differences were found either ($p > 0.05$). The only exception was Al ($p = 0.003$), with winter samples ranging from 7 to 77 g kg^{-1} dw (mean of 25 g kg^{-1} dw), and summer samples ranging from 3 to 53 g kg^{-1} dw (mean of 16 g kg^{-1} dw). Al is commonly introduced into WWTPs through the use of aluminium-based coagulants, which are frequently used to enhance the removal of suspended solids and phosphorus. In winter, increased rainfall and runoff in urban areas can lead to higher loads of suspended particles, requiring greater use of coagulants to maintain treatment efficiency, potentially resulting in higher

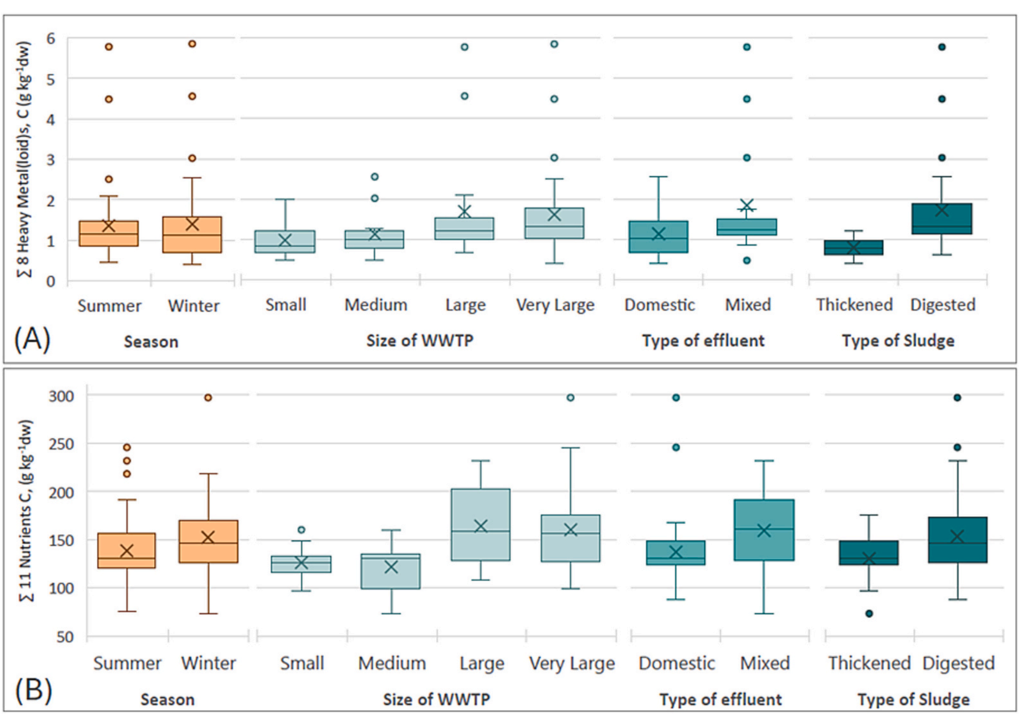

Fig. 2. Distributions of the combined concentrations of 8 heavy metal(loid)s (A) and 11 nutrients (B) in sewage sludge samples grouped according to sampled season, WWTP size, source of treated effluent, and type of sludge treatment.

Al concentrations in the sewage sludge. Yakamercan et al. (2021) also analysed potential seasonal differences in sewage sludge from 22 Turkish cities, collected in the summer and winter, and found no significant variability. Similarly, Chen et al. (2021) investigated factors influencing the elemental composition of dewatered sludge from 32 WWTPs in Japan, sampled in four seasons over 1 year, and concluded that season had minimal influence. However, García-Delgado et al. (2007) reached different conclusions while monitoring Cd, Cr, Cu, Ni, Pb and Zn in samples collected in Salamanca (Spain) during summer and winter months over 3 years. Significantly higher concentrations of Cr, Cu, Ni and Zn were reported in summer, which was explained by a faster decomposition of organic solids during this season, resulting in an increased proportion of inorganic matter (and heavy metal(loid)s) in final samples. However, in our study, no significant variations in total solids (mean of 20 ± 4 % in summer and 20 ± 6 % in winter) or organic matter content (volatile solids of 77 ± 9 % of dw in summer and 76 ± 9 % of dw in winter) were found between seasons ($p > 0.05$), which could explain the different results.

Correlation analysis was carried out to look for relationships between the different elements measured in the sewage sludge. Spearman's correlation coefficients between the concentrations of heavy metal(loid)s and nutrients in samples collected in summer and winter are presented in Tables S12 and S13, SI, respectively. In general, similar correlation patterns were found in both seasons. Very high and highly significant positive correlations were observed between thirteen pairs of elements: Cd—Pb ($r_s > 0.71$), Cd—Ca ($r_s > 0.70$), Cd—Fe ($r_s > 0.90$), Cu—Zn ($r_s > 0.71$), Ni—Cr ($r_s > 0.78$), Ni—Co ($r_s > 0.75$), Pb—Fe ($r_s > 0.76$), Zn—Ca ($r_s > 0.77$), Zn—Mn ($r_s > 0.70$), Zn—Co ($r_s > 0.77$), Ca—S ($r_s > 0.73$), S—Mo ($r_s > 0.78$) and Mn—Co ($r_s > 0.75$). This may indicate common sources, identical behaviour in WWTPs, or even interdependence. For example, Cu—Zn, which are used together in alloy production and galvanization processes, Ni—Cr, which are also used together in alloy production and metal plating due to their corrosion resistance, or even Ca—S, which are both used in fertilizers and in various industrial processes (e.g., in steel production, calcium oxide (lime) and sulphur compounds used as fluxes to remove impurities). In previous studies, some of these positive correlations have been observed (Chen et al., 2021; Espinoza-Guillen et al., 2024; Tytła and Widziewicz-Rzońca, 2023; Yakamercan et al., 2021), especially between heavy metal(loid)s, as few works include the study of nutrients. Chen et al. (2021) also included some nutrients in their work, with no significant correlations reported for N and K, while P was strongly correlated with Mg (a moderate correlation in our study) and moderately correlated with Fe, Ca, and S.

3.1.2. Differences in the heavy metal(loid)s and nutrients content

Significant differences were found in the distribution of concentrations of most elements among the sampled WWTPs ($p < 0.017$). The only exceptions were Hg ($p = 0.310$), Al ($p = 0.053$), and Si ($p = 0.125$). For instance, analysing Fig. 1A, higher total concentrations of heavy metal(loid)s were found in WWTP#14 (mean of both seasons of 5167 ± 863 mg kg^{-1} dw) and WWTP#18 (mean of both seasons of 5166 ± 969 mg kg^{-1} dw). Both WWTPs receive domestic and industrial inputs and sewage sludge is anaerobically digested. In WWTP#14, these high concentrations are mainly explained by the unusually high levels of Cu (4429 ± 46 mg kg^{-1} dw in summer and 3295 ± 21 mg kg^{-1} dw in winter), which accounted for 75 % of the total heavy metal(loid) load in these samples, but on average only 20 % in sludge from other WWTPs. The sewage sludge from this WWTP also has a higher Ni content (179 ± 1 mg kg^{-1} dw in summer and 151 ± 7 mg kg^{-1} dw in winter) compared to the total average concentration for this metal (38 mg kg^{-1} dw). WWTP#14 receives wastewater from an important industrial area where several foundries and metallurgical companies are located, with relevant production of alloys and copper castings, which may explain these values. In the case of WWTP#18, the predominant heavy metal (loid) is Zn (3842 ± 46 mg kg^{-1} dw in summer and 5120 ± 49 mg kg^{-1} dw in winter), with a concentration 4 to almost 6 times higher than the overall average of Zn in other samples. This WWTP receives effluents from intensive pig farming as well as slurry that is treated together with the sewage sludge. The slurry is characterized by high levels of Zn, which is used as an additive in swine feed formulations and is inevitably excreted by the animals as it is not fully absorbed (Sonne et al., 2019). Considering the levels of nutrients and other elements in the different WWTPs (Fig. 1B), the reported concentrations were higher in samples from WWTP#12 (mean of both seasons of 286 ± 42 g kg^{-1} dw), with Fe (117 ± 21 g kg^{-1} dw) accounting for about 41 % of this total, followed by Ca (47 ± 6 g kg^{-1} dw, 16 %), P (45 ± 12 g kg^{-1} dw, 16 %) and N (39 ± 1 g kg^{-1} dw, 14 %). This WWTP receives mainly domestic effluents and serves a population equivalent of 230,000. The sewage sludge is anaerobically digested, suggesting that the high levels of Fe are due to the use of iron salts in the wastewater and sludge treatment lines. On the other hand, samples from WWTP#8 show the lowest combined concentration of nutrients and other elements (mean of both seasons of 88 ± 6 g kg^{-1} dw), with N (44 ± 3 g kg^{-1} dw) representing about 50 % of total, followed by Al (11 ± 4 g kg^{-1} dw, 12 %), P (8.4 ± 0.8 g kg^{-1} dw, 10 %), Ca (6 ± 1 g kg^{-1} dw, 7 %), S (5.4 ± 0.6 g kg^{-1} dw, 7 %), and only 6 % Fe (5 ± 3 g kg^{-1} dw, 14 %). This WWTP receives both domestic and industrial inputs, serves a population equivalent of 42,000, and sewage sludge is not digested.

The previous examples highlight the wide variability in the elemental composition of the studied samples. To identify possible patterns of variation in the sludge composition, some factors related to the characteristics of sampled WWTPs were investigated, namely the size of treatment facility, source of wastewater, and degree of treatment of final sewage sludge. Fig. 2 compares the distribution of the combined concentration of 8 commonly regulated heavy metal(loid)s and the sum of 11 nutrients between selected groups of samples.

To assess differences in sewage sludge composition related to the size and design capacity of WWTPs, samples were grouped into 4 categories based on the population equivalent (PE) of the respective treatment facility – Small (PE < 20,000); Medium (20,000 ≥ PE > 50,000); Large (50,000 ≥ PE > 100,000); Very Large (PE ≥ 100,000) (Table S14, SI). The results showed that the sum of heavy metal(loid)s concentrations was not the same across these categories ($p = 0.017$), being higher in samples from large to very large WWTPs (mean values of 1690 ± 1368 and 1614 ± 1209 mg kg^{-1} dw, respectively), compared to small (974 ± 458 mg kg^{-1} dw) and medium ones (1132 ± 567 mg kg^{-1} dw). Larger WWTPs typically serve more diverse and densely populated areas, often in the vicinity of industrial clusters, which may result in a greater influx of wastewater with higher loads of heavy metal(loid)s. In addition, 77 % of larger WWTPs in this study treat sewage sludge by anaerobic digestion, compared to 42 % of small and 50 % of medium-sized WWTPs, which may also contribute to these findings. Looking at heavy metal (loid)s individually, the contents of Cd, Ni, Zn, and As varied significantly with WWTP size ($p < 0.028$), while Cu ($p = 0.079$), Pb ($p = 0.193$), Hg ($p = 0.314$) and Cr ($p = 0.070$) did not show any significant variation. Significant differences were also found in the distribution of the sum of 11 nutrients between most pairwise comparisons based on WWTP size ($p < 0.001$), except for similar levels between large/very large (means of 164 ± 39 and 160 ± 42 g kg^{-1} dw, respectively) and small/medium WWTPs (means of 126 ± 16 and 122 ± 25 g kg^{-1} dw, respectively). A more detailed analysis showed no significant differences for the contents of N ($p = 0.112$), Mg ($p = 0.663$), B ($p = 0.114$), and Co ($p = 0.155$) or for the elements Al ($p = 0.257$), Si ($p = 0.112$) and Ti ($p = 0.881$). For P, Ca, S, Fe, Mn, Mo, and Na, higher concentrations were typically found in samples from larger WWTPs. While serving areas with higher demographic pressure, larger WWTPs treat larger volumes of wastewater from more diverse sources, often using more efficient treatment processes to remove organic loads and contaminants from the wastewater. These elements can accumulate and concentrate in the sewage sludge, especially when it is further stabilized by anaerobic digestion, a treatment process more commonly used in larger WWTPs. In contrast, K levels in small WWTPs (mean of 7 ± 2 g kg^{-1} dw) were higher than in medium/larger ones (mean concentrations between 3 and 4 g kg^{-1} dw). This may be related to the type of wastewater entering smaller WWTPs (of the 10 small WWTPs assessed, 9 treated only domestic sewage), as well as their lower design capacity and sewage flow rate. Assuming that K levels in wastewater are mainly derived from human metabolic wastes, domestic effluents are expected to be the main source of this nutrient in sewage sludge. Moreover, K is easily leached into the water phase during sludge treatment (Johansson, 2018). Due to the smaller volumes of wastewater reaching smaller WWTPs, there may be less dilution of K, contributing to higher concentrations in sewage sludge. In addition, significant losses of K solubilized in the water phase may also occur during mechanical dewatering of sewage sludge. In the samples analysed, the moisture content of sludge from small WWTPs (mean of 84 ± 3 %) was significantly higher ($p < 0.024$) than that of samples collected from larger treatment plants (mean varying between 77 % in very large WWTPs and 81 % in medium-sized WWTPs). Therefore, the less effective water removal in small WWTPs may also have contributed to the higher K content in the sludge produced.

To analyse the influence of the type of effluent treated by WWTPs on the elemental composition of sewage sludge, the samples were grouped into two categories – Domestic (from WWTPs treating predominantly wastewater from households and public infrastructure) and Mixed (from WWTPs treating urban sewage with industrial effluents, or directly collecting industrial discharges) (Table S15, SI). Significant differences in the total heavy metal(loid) content were found ($p = 0.012$), with higher mean concentrations in sludge from WWTPs treating mixed effluents (Mixed: 1840 ± 1499 mg kg^{-1} dw; Domestic: 1133 ± 548 mg kg^{-1} dw). This is consistent with information in the literature indicating a strong dependence on the origin of the sewage that reaches the WWTPs and the heavy metal(loid) content, which is commonly associated with industrial activities (Feng et al., 2023; Zhang et al., 2017). When analysing heavy metal(loid)s individually, Cd, Ni, Zn, and Cr were found in higher concentrations in samples from WWTPs receiving industrial inputs ($p < 0.034$). No significant differences were found for Cu ($p = 0.105$), Pb ($p = 0.121$), Hg ($p = 0.951$), and As ($p = 0.854$), suggesting that their occurrence in the sludge is likely less related to the industrial contribution. For the total nutrient content of the studied samples, significant differences were also found between sludge originating from domestic and mixed effluents ($p = 0.004$). The sum of 11 nutrients was, on average, higher in samples from WWTPs treating also industrial inputs (mean of 159 ± 41 g kg^{-1} dw vs 137 ± 34 g kg^{-1} dw in sludge from WWTPs receiving only domestic sewage). Looking at individual nutrients, concentrations of Ca, S, Mn, Mo, and Co were significantly higher ($p < 0.033$) in sludges from WWTPs treating mixed effluents. Industrial effluents reaching these WWTPs may contain higher amounts of these elements, which were found to be strongly or moderately correlated with Cd, Ni, Zn, and Cr (Tables S12 and S13, SI), heavy metals also found in higher concentrations in sludge from WWTPs treating mixed effluents. On the other hand, K concentrations were higher ($p = 0.003$) in samples from WWTPs treating domestic sewage (mean of 5 ± 3 g kg^{-1} dw vs 3 ± 1 g kg^{-1} dw in the "mixed" category). No correlations were found between K and heavy metal(loid) content (Tables S12 and S13, SI), suggesting that its source is less related to industrial inputs. This is consistent with the reported higher concentrations of K in WWTPs treating only domestic effluents. No significant differences were found for N ($p = 0.950$), P ($p = 0.686$), Mg ($p = 0.364$), Fe ($p = 0.102$), and B ($p = 0.217$), nor for the elements Na ($p = 0.296$), Al ($p = 0.065$), Si ($p = 0.871$), and Ti ($p = 0.904$).

Finally, regarding the degree of sewage sludge stabilization, the elemental composition of the samples studied was compared between two groups of samples – Thickened (thickened and dewatered sludge) and Digested (thickened, anaerobically digested, and dewatered sludge) (Table 1). The total heavy metal(loid) content in digested samples was significantly higher ($p < 0.001$), with a mean of 1725 ± 1662 mg kg^{-1} dw, almost twice the mean in undigested samples (791 ± 238 mg kg^{-1} dw). This parameter clearly influenced the results obtained for the individual heavy metal(loid)s ($p < 0.013$), except for Hg ($p = 0.452$). The average concentrations in the digested samples were about 1.4 times higher for As, around 2 times higher for Cu, Ni, Pb, and Zn, and up to 3 times higher for Cd and Cr than in the thickened samples. Other studies in the literature also indicate that anaerobic digestion can result in an increase of heavy metal(loid)s concentrations in sewage sludge (Chen et al., 2021; Feng et al., 2023). Assuming that heavy metal(loid)s are not removed from the solid fraction in the sludge treatment line, this could be related to the loss of volatile solids during digestion, resulting in an increase in the concentration of these elements in the solid medium (Feng et al., 2023). In fact, volatile solids were significantly lower in digested samples than in thickened sludge (mean of 72 ± 9 % of dw vs 83 ± 6 % of dw, respectively) ($p < 0.001$). Dry matter content also differed between these groups of samples ($p = 0.019$), with a mean of 21 ± 6 % in digested sludge and 18 ± 4 % in thickened samples.

Significant differences were also found between thickened and digested samples in terms of total nutrient content ($p = 0.021$), with the sum of 11 nutrients registering higher values in digested samples (mean of 153 ± 42 g kg^{-1} dw vs 130 ± 24 g kg^{-1} dw in thickened sludge). However, a more detailed analysis revealed that the concentrations of N and K were significantly higher in thickened samples ($p < 0.002$), with a mean for N of 70 ± 14 g kg^{-1} dw vs 60 ± 11 g kg^{-1} dw in digested sludge, and a mean for K of 5 ± 3 g kg^{-1} dw vs 4 ± 2 g kg^{-1} dw in digested samples. This could be explained by the decomposition of the biomass-bounded nitrogen during anaerobic digestion, resulting in significant N losses by volatilization, as well as N re-solubilisation into the water phase, which is later removed during the final sludge dewatering process (Hoang et al., 2022). The lower K concentrations in digested sludge are also most likely related to leaching to the liquid fraction during digestion (Johansson, 2018). In the case of P and Mg, no statistically significant differences were found, although the mean concentrations were 13 % and 9 % higher in digested sludge, respectively. In the case of these elements, the effect of the concentration increase due to the decomposition of organic matter during anaerobic digestion may have been partially offset by possible losses of P and Mg from the solid fraction of the sludge. Volatilization of P and Mg is not expected to occur as in the case of N, but several P species are released to the water phase during anaerobic digestion, including Mg-bound P (Yu et al., 2021). However, these P complexes are only partially removed during dewatering, mainly due to their limited water solubility. Precipitation can occur in the digestor, with part of P and Mg tending to remain in the solid fraction of the sludge (Marti et al., 2008; Yu et al., 2021), so there were no significant differences between thickened and digested samples. As for the other nutrients, Fe, S, Ca, Mn, Mo, and B were significantly higher in digested samples ($p < 0.015$). As mentioned above, the loss of volatile solids during the anaerobic digestion of sewage sludge may help to explain these results. Moreover, the higher Fe and S concentrations may also be related to the use of $FeCl_3$ prior to the digestion process to reduce the release of odour-causing compounds, generally volatile organic sulphur gases (Park and Novak, 2013). As less S is released in the form of gas during the decomposition of organic matter, it eventually accumulates in the sewage sludge (Dewil et al., 2009; Zhang et al., 2023). In the case of Co, the highest recorded values for this element are both from the WWTP#34 (average of both seasons of 4306 ± 1708 mg kg^{-1} dw), a treatment facility generating thickened sewage sludge. These values are clearly outside the typical range observed for this element (1.2–17 mg kg^{-1} dw without accounting for this WWTP) and are most likely related to industrial inputs. Comparing the distribution of Co concentrations without these outliers between digested and thickened samples, a statistical difference is still found ($p < 0.001$), with higher average concentrations in digested sludge (mean of 5 ± 3 mg kg^{-1} dw vs 2.5 ± 0.8 mg kg^{-1} dw in thickened sludges). As for the other elements, Al, Si, and Ti varied significantly between digested and undigested sludge ($p < 0.021$), while no differences were found for Na content ($p = 0.873$).

3.2. Compliance with legislation and suitability of sewage sludge for its use in soils

Concerning the heavy metal(loid) content of sewage sludge, most of the samples in this study were suitable for their use in soil, considering national and EU regulations (Table 2). However, a total of 5 samples were deemed unsuitable for agricultural use due to high concentrations of Zn and Cu. The limit concentration in sewage sludge to be used in soils in the Portuguese legislation for Zn (2500 mg kg^{-1} dw) was exceeded in 2 samples, both from WWTP#18 (3841 mg kg^{-1} dw in summer and 5120 mg kg^{-1} dw in winter), and for Cu (limit of 1000 mg kg^{-1} dw) in the 2 samples from WWTP#4 (4429 mg kg^{-1} dw in summer and 3295 mg kg^{-1} dw in winter) and in 1 sample from WWTP#3 (1072 mg kg^{-1} dw in winter). These unusually high values were attributed to industrial effluents entering these WWTPs, and to pig slurry treated with sludge in WWTP#18. No limit values are set for As in sewage sludge in the EU or Portuguese legislation. However, as a reference, the limit value for inorganic As was set at 40 mg kg^{-1} dw in different classes of fertilizers (including organic and organo-mineral fertilizers, soil improvers, and growing medium) by the Regulation (EU) 2019/1009 on fertilising products. In this study, total As was below this value in all sewage sludge samples, up to a maximum of 31 mg kg^{-1} dw.

The maximum amounts of heavy metals that can be added annually to the soil are also established in EU and Portuguese legislation (except for the metalloid As) (Table 2). These limits are based on a 10-year average and aim to prevent the accumulation of these contaminants in the soil. Assuming a standard application rate of sewage sludge of 5 tons ha^{-1} (dry weight), the added amount of each heavy metal(loid) was estimated for the sludge samples collected in this study. All but 3 samples could be applied to agricultural soils on an annual basis (assuming a single application per year). The exceptions are the two samples from WWTP#18 because of the high Cu content (16 and 22 kg of Cu per ha would be added yearly, whereas the limit is set at 12 kg ha^{-1} $year^{-1}$), and the sludge from WWTP#5 in winter due to the Cr levels (4.6 kg of Cr per ha would be added yearly to soil, limit of 4.5 kg ha^{-1} $year^{-1}$).

In terms of agronomic parameters, the Portuguese regulation also requires the characterization of sewage sludge in terms of total solids, organic matter, pH, and the content of macronutrients such as N, P, K, Mg and Ca. Although no specific levels are mentioned for these parameters in sewage sludge legislation, its use in agriculture must meet the requirements of the receiving soils and the cultivated crops, while avoiding impairment of soil quality. For instance, in Portugal, the Decree-Law No. 235/97 implements the European Union Nitrates Directive. In this regard limits were established for the amount of total N to be applied to nitrate-vulnerable zones, i.e., areas of land that drain into waters that are or may be polluted by nitrates and where agricultural practices may exacerbate the problem. In these areas, the amount of N from organic fertilizers (including sewage sludge) must not exceed 250 kg ha^{-1} per year, of which no >170 kg ha^{-1} per year from manure. Considering that concentrations of N in the studied samples ranged from 31 to 97 g kg^{-1} dw (mean of 63 g kg^{-1} dw), the application rate of sewage sludge to agricultural soils in nitrate vulnerable zones would be limited to 2.6 to 8.1 tons ha^{-1} dw per year (4.1 tons ha^{-1} dw per year, considering the mean of N in all samples). In other areas of the territory, these limits do not apply, but the amounts of sewage sludge to be used as soil-amendment must be in accordance with the requirements of the soil and the crops grown. Within the framework of these regulations, a code of good agricultural practices provides information and measures to be implemented by farmers on a voluntary basis.

Regarding other agronomic parameters, the agricultural use of sewage sludge has been reported to increase soil electrical conductivity, a measure of soil salinity conditions (Sharma et al., 2017). Soil salinisation is currently a major threat to European soils, critically reducing fertility and leading to land degradation, which can occur at electrical conductivity values above 4 mS cm^{-1} (Daliakopoulos et al., 2016; Dhanker et al., 2021). In the sludge studied, a single value above this threshold was found (4.1 mS cm^{-1}), and electrical conductivity was below 2 mS cm^{-1} in 80 % of the samples. Depending on the dose of sludge application, these values do not seem to pose a risk to receiving soils and are lower than the electrical conductivity of other organic wastes used for soil improvement, namely composted organic matter (Alvarenga et al., 2015).

Changes in soil pH have also been attributed to the use of sewage sludge (Dhanker et al., 2021; Sharma et al., 2017). The availability of plant nutrients is pH dependent, and the mobility and bioavailability of heavy metals tend to increase at lower soil pH (Dhanker et al., 2021; Feng et al., 2023). For this reason, sludge pH should also be monitored to avoid unwanted changes in this parameter in the soil. In the samples studied, thickened sludge had on average a slightly more acidic pH (6.5 $\pm$ 0.7) than digested sludge (7.2 $\pm$ 0.6) ($p < 0.001$), but overall, these values are suitable for sludge use in farmland. The decrease in soil pH following sludge application may also be related to the release of organic acids from the decomposition of organic matter (Dhanker et al., 2021). As noted above, the organic matter content of the samples studied was significantly higher in the thickened undigested sludge, which in addition to its lower pH value suggests that these sludges are more likely to reduce soil pH than digested sludges. Anaerobic digestion not only reduces the organic matter content, but also contributes to its biological stabilization, thus preventing its rapid deterioration after application to soils (Hoang et al., 2022). Despite some losses of key macronutrients during digestion (mean concentrations of N and K in digested samples were, respectively, 15 % and 34 % lower than those in thickened sludge), both types of sewage sludge showed an interesting nutrient profile with potential to suppress soil deficiencies. In fact, the nutrient content of all the samples analysed was significantly higher than the median concentrations reported for European agricultural soils. For instance, comparing the concentrations of the three main soil macronutrients in the studied samples to the median levels in European agricultural soils, sewage sludge contained 18 to 57 times more N, 12 to 82 times more P, and similar amounts to up 10 times more K. On the other hand, these large variations in the nutrient profile highlight the need for routine analysis of sludge before choosing this valorisation route, as well as regular monitoring of the receiving soils after application.

3.3. Contamination status and ecological risk assessment of heavy metal(loid)s in sewage sludge

3.3.1. Geoaccumulation index

The geoaccumulation index (I_{geo}) essentially compares the concentration of a given element in the matrix under investigation with that in a reference medium. It was initially proposed for the assessment of metal contamination in sediments (Müller, 1969), but has since been applied to other environmental samples, including sewage sludge (Espinoza-Guillen et al., 2024; Suanon et al., 2017; Sundha et al., 2023; Tytła and Widziewicz-Rzońca, 2023). In this context, background elemental concentrations in the upper continental crust, or regional or local topsoil concentrations, have been used as a reference. In this study, I_{geo} was used to assess the degree of accumulation of the target elements in sewage sludge to be used on farmland, hence the median concentrations in European agricultural soils were used as reference (Table S6, SI). The I_{geo} of all 23 elements studied was determined for the sewage sludge produced by each sampled WWTP, using the mean concentration of samples collected in summer and winter. The results and the classification of the I_{geo} values are summarized in Fig. 3. For the typically regulated heavy metal(loid)s, most sewage samples appear to be heavily contaminated with Zn and Cu, moderately to heavily contaminated with Cd, and not contaminated to moderately contaminated with Ni, Pb, Cr, and As. The I_{geo} values for Hg, found in sludge from 13 WWTPs indicate mainly heavy contamination with this metal. Regarding the I_{geo} values for nutrients and other elements, the sewage sludge was generally classified as extremely contaminated with S, and heavily to extremely contaminated with N and P. The degree of contamination for Na and Mo varied from

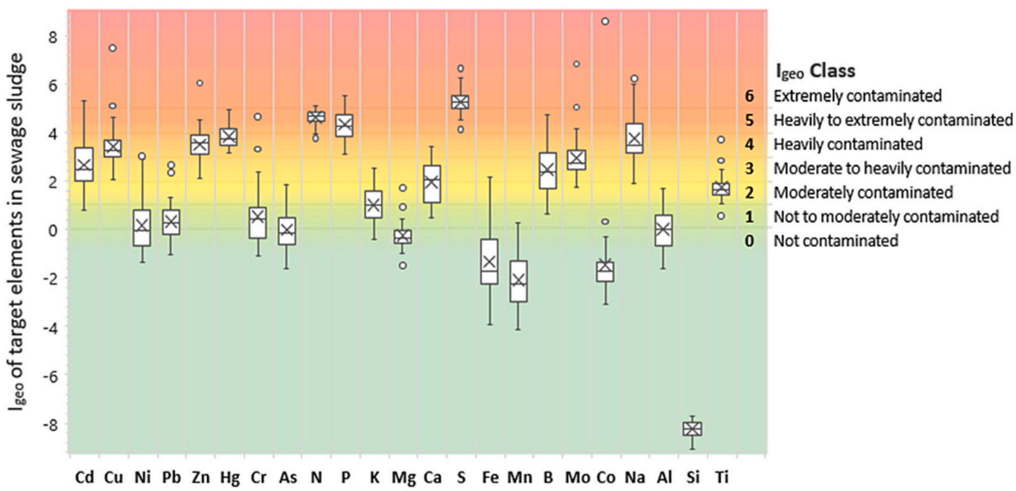

Fig. 3. Distribution of the geoaccumulation index (I_{geo}) for 23 elements in sewage sludge from 42 WWTPs.

moderately to extremely contaminated, with mean I_{geo} values of 3.8 for Na and 3.0 for Mo, while most samples were moderately to heavily contaminated with B and not contaminated or only moderately contaminated with K. I_{geo} values were generally below 0 for Mg, Fe, Mn, Co, and Si, indicating that concentrations of these elements in the sludge are similar to or lower than the median levels in agricultural soils. The lowest I_{geo} was determined for Si, an abundant element in soils, primarily in the form of silicate minerals. Although Si is not expected to be a major constituent of sewage sludge, it may have been undetermined in the samples studied, as *aqua regia* digestion is not the most appropriate method for its determination (Sichler et al., 2022). The accumulation of some of the elements studied in sewage sludge was remarkably high compared to typical levels in agricultural soils. However, when sludge is applied to soils, the amounts of these elements transferred to farmland will largely depend on the frequency and rate of application. As mentioned before, the concentration of the target elements was estimated in sludge-amended soil after a single application of sewage sludge at 5 tons ha^{-1} (dry weight). The I_{geo} values determined using these estimated concentrations indicate no contamination in the sludge-amended soils ($I_{geo} \leq 0$ in all but one case). The only exception was due to the high levels of cobalt in the sludge from WWTP#34, which resulted in an I_{geo} of 0.4 (class 1 – not contaminated to moderately contaminated).

3.3.2. Potential ecological risk factor and potential ecological risk index

Although the reported concentrations of heavy metal(loid)s in sewage sludge are typically higher than the background levels in agricultural soils, their potential ecological risk is also influenced by their toxicity. The potential ecological risk factor (*Er*) and the potential ecological risk index (*PERI*) are indicators that include a toxicity-response factor (*Tr*) to weight in each metal(loid)'s toxicity along with its contamination degree (Håkanson, 1980). *Er* and *PERI* have been used to assess the potential ecological risk of heavy metal(loid)s in different environmental matrices, including sewage sludge (Espinoza-Guillen et al., 2024; Sundha et al., 2023; Tytła and Widziewicz-Rzońca, 2023).

Er and PERI were determined considering the content of 8 heavy metal(loid)s in sewage sludge produced by each sampled WWTP. Results are detailed in Table S16, SI. In general, *Er* for Ni, Pb, Zn, Cr, and As was below 40 in most samples, indicating a low potential ecological risk. The few exceptions, related to unusually high levels in sewage sludge, were mainly from WWTPs that also treat industrial effluents. On the other hand, Cu presented a moderate to high potential ecological risk in most samples (*Er* between 40 and 160 in sludge from 35 WWTPs). A very high potential ecological risk was reported for Hg, with *Er* for this metal varying between 533 and 1867, mainly due to its high toxicity-response factor (*Tr* of 40). Similarly, Cd presented a high or very high potential ecological risk in most samples, despite the low levels found compared to other heavy metals, also due to its high toxicity (*Tr* of 30). *PERI* values were higher than 150 in all samples. A moderate potential ecological risk ($150 \leq PERI < 300$) was reported for sewage sludge from 19 % of WWTPs, a considerable potential ecological risk ($300 \leq PERI < 600$) for 24 %, and a very high potential ecological risk ($PERI \geq 600$) for 57 % of the samples (Table S16, SI). *PERI* values in sewage sludge from WWTPs treating domestic effluents ranged from 206 to 2022, with an average of 722. These values were generally lower than those found in samples from WWTPs treating also industrial effluents, which ranged from 193 to 2352, with an average *PERI* of 1007.

Assuming a typical sewage sludge application rate of 5 tons ha^{-1} (dry weight), the resulting concentrations of heavy metal(loid)s in a reference agricultural soil were estimated, and the potential ecological risk in sludge-amended soils was also assessed. In this scenario, Er values in sludge-amended soil indicate a low potential ecological risk for all heavy metal(loid)s, except for Hg (for which *Er* ranged from 40.9 to 43.1, indicating a moderate potential ecological risk). Similarly, *PERI* values ranged from 98.3 to 101.9, indicating a low ecological risk. Despite the low ecological risk estimated in sludge-amended soils after a single application of sewage sludge, the significant risk due to the heavy metal (loid) content assessed by these indicators in the sewage sludge samples underlines the need to regulate and monitor its use in agriculture. Especially bearing in mind that successive sludge applications may lead to an accumulation of heavy metal(loid)s in the soil over time, with potential cumulative effects on the terrestrial environment.

3.3.3. Environmental risk characterization ratios of heavy metal(loid)s in sludge-amended soil

The environmental risk assessment of heavy metal(loid)s is a challenging task. In addition to the natural occurrence of heavy metal(loid)s in soils and the conditioning of plants and soil-dwelling organisms to ambient background concentrations, changes in their chemical speciation and bioavailability depend on abiotic and environmental conditions, making it difficult to establish fixed thresholds (ECETOC, 2003; Zhang et al., 2017).

In this study, risk characterization ratios were determined for the 8 typically regulated heavy metal(loid)s in sewage sludge intended for soil application. Potential risks for the soil compartment were assessed following a worst-case scenario approach, in which no corrections were made for the bioavailability fraction of heavy metal(loid)s in sewage sludge, i.e., using the total concentrations measured in sewage sludge for the estimation of PEC_{soil}. The concentration of heavy metal(loids) in soil resulting from a single application of sewage sludge at 5 tons ha^{-1} (dry weight) was estimated from the reported concentrations in the investigated samples and then added to the median values for European agricultural soils. These values ($PEC_{soil,total}$) were then compared with predicted no-effect concentrations (*PNEC*) derived from the literature. For most metal(loid)s, the toxicity to terrestrial organisms is well described and *PNEC* values are typically derived from species sensitivity distributions with low assessment factors (Table S7, SI). The lowest *PNEC* values were chosen for a more conservative determination of *RCRs*. In the case of As and Cr, *PNECs* based on the added concentration in toxicological studies ($PNEC_{added}$) were collected from the literature and the *RCR* was determined based on the added approach. Table 3 summarizes the input parameters used to calculate the *RCRs* and the respective results. These *RCRs* were <1 for all heavy metal(loid)s in all samples, indicating a low environmental risk for terrestrial organisms in sludge-amended soil. Urbaniak et al. (2024) also used the *PEC/PNEC* approach to assess the environmental risk of heavy metal(loid)s in soil, after a single application of sewage sludge at 5 tons ha^{-1} (dry weight), and found a low level of risk, although they did not consider pre-existing levels in the soil. It should be noted that this assessment was based on a single sludge application, as in our study, and did not address the potential accumulation of heavy metal(loid)s in the soil with repeated sludge use.

The increase in soil concentration of heavy metal(loid)s due to a single sludge application was very small compared to the median concentrations in agricultural soils (Table 3). On average, it varied from a 0.3 % increase for As, to a 3.8 % increase for Cu. However, the continuous and long-term application of sewage sludge to agricultural land may pose an increased risk to the soil compartment, as the concentration of potentially toxic metal(loid)s may build up over time, which was not assessed in this study. The fate and distribution of heavy metal(loid)s in the soil is influenced by numerous factors, including sorption processes between the solid and water phases of the soil, leaching, surface runoff, volatilization, and uptake by crops. These are influenced by the physicochemical properties of the metal(loid)s, soil characteristics, climatic conditions, and environmental biotic factors (ECHA, 2008; Eggen et al., 2022). For these reasons, and in the absence of specific data, risk assessment modelling of heavy metal(loid)s in long-term sludge application scenarios is a very challenging task. On this matter, a Norwegian report (Eggen et al., 2022) assessed the environmental risk of the use of fertilizer products, including sewage sludge, by modelling the potential accumulation of heavy metal(loid)s in soils after repeated use. Although soil concentrations of most heavy metal(loid)s were expected to increase to undesirable levels, these were not expected to exceed the *PNEC* values in most regions. Similarly, a Danish report (Pedersen et al., 2019) on the risk assessment of soils considering repeated sewage sludge application concluded that heavy metal(loid)s posed a medium to low risk to the soil environment. Concentrations in sludge-amended soils were estimated to increase by <1 % per year in relation to continuous sludge application and were only expected to reach levels close to or above the *PNECs* only within 100 years.

Another aspect that significantly affects the potential risks to agricultural soils is related to the transformation of heavy metal(loid)s speciation over time. They can occur in different valence and oxidation states, depending on the pH of the medium, the redox potential, the presence of reductants/oxidants (related to the organic matter content and mineral constituents), and the reaction kinetics. Interactions between certain heavy metal(loid)s species and essential soil and plant nutrients can disrupt plant nutrient uptake, leading to deficiencies in crops and reducing agricultural productivity (Angon et al., 2024).

Heavy metal(loid)s mobility and bioavailability in sewage sludge and sludge-amended soils can also be significantly affected by adsorption, ion exchange, and precipitation mechanisms, as well as by the formation of complexes with organic and inorganic complexing agents and reactions with humic substances acting as chelating agents. Depending on the specific interactions involved, these processes can increase or decrease the heavy metal(loid)s mobility and bioavailability in the soil (Li et al., 2022; Lwin et al., 2018). In the case of increased solubility, leaching to deeper soil layers may occur, with serious implications for groundwater contamination. Furthermore, increased metal(loid)s bioavailability affects soil microbial diversity and function, and promotes translocation to plants, leading to bioaccumulation in the food chain with enhanced impacts at higher trophic levels, including human health (Angon et al., 2024; Zhang et al., 2017). Chronic exposure to heavy metal(loid)s through contaminated food can lead to serious health effects, including neurotoxicity, kidney damage and carcinogenic risks (Angon et al., 2024). On the other hand, these binding reactions can result in less soluble chemical species that contribute to the immobilisation of metal(loid)s, limiting their bioavailability (Li et al., 2019; Lwin et al., 2018). However, this can lead to long-term accumulation in the soil. Over time, the decomposition of organic matter and changes in soil physical, chemical, and microbiological parameters may gradually release immobilised heavy metal(loid)s back into soluble and bioavailable forms (Li et al., 2022; Molaey et al., 2024; Zhang et al., 2017).

Several approaches can be used to mitigate the potential risks posed by heavy metal(loid)s in sewage sludge for soil application. Improved sludge stabilization, such as co-composting with bulking agents, can help reduce their concentration prior to land application (Zhang et al., 2017). Alternatively, specific nutrients can be recovered from sewage sludge, such as N by ammonia stripping or simultaneous recovery of N, P, and K by struvite precipitation (Di Costanzo et al., 2021). Emerging demetallization techniques for the removal of heavy metal(loid)s from the solid fraction of sewage sludge are also gaining importance, including bioleaching (relying on the activity of microorganisms to mobilize and remove heavy metal(loid)s from sludge), chemical leaching (using acids or chelating agents as extractants), or electrokinetic treatments (using electric fields to mobilize and transport charged ions

Table 3
Summary of estimated PECs, PNEC values, and environmental risk characterization ratios (RCRs).

	Median concentration in European agricultural soils[a] (mg kg^{-1} dw)	$PEC_{soil\text{-}added}$ Min–Max (mg kg^{-1} dw)	$PEC_{soil\text{-}total}$ Min–Max (mg kg^{-1} dw)	$PNEC_{soil}$ (mg kg^{-1} dw)	RCR Mean	RCR Max
Cd	0.181	0.001–0.018	0.182–0.199	0.9[b]	0.21	0.22
Cu	14.5	0.15–6.44	14.65–20.94	65[b]	0.23	0.32
Ni	14.7	0.01–0.30	14.71–15.00	29.9[c]	0.49	0.50
Pb	15.8	0.02–0.25	15.82–16.05	166[d]	0.10	0.10
Zn	45	0.5–7.5	45.5–52.5	83.1[b]	0.56	0.63
Hg	0.03	0.001–0.002	0.031–0.032	0.07	0.43	0.46
Cr	20.2	0.02–1.27	20.22–21.47	3.2[d,*]	0.04	0.40
As	5.48	0.005–0.05	5.485–5.53	2.9[b,*]	0.006	0.02

[a] Reimann et al. (2018).
[b] ECHA CHEM.
[c] European Commission (2008).
[d] Eggen et al. (2022).
[*] $PNEC_{add}$.

through the aqueous phase of sewage sludge for subsequent removal) (Molaey et al., 2024). The use of soil amendments, such as liming materials, biochar, manure and composted organic materials, can also help to the immobilisation of heavy metal(loids)s in the case of ongoing soil contamination (Lwin et al., 2018), but these only serve as a temporary solution as heavy metal(loid)s are not effectively removed from the soil. Remediation techniques using hyperaccumulator plants to effectively remove of heavy metal(loid)s from contaminated soils (phytoextraction) appear to be a promising approach to address this issue but currently lack efficiency and require further development (Liu et al., 2018).

3.4. Human health risk assessment for farm workers

Undoubtedly, workers involved in sewage sludge handling are the most exposed to this matrix and its contaminants. Therefore, a human health risk assessment was performed to estimate the potential health risks (non-carcinogenic and carcinogenic) resulting from the exposure of adults (workers) to heavy metal(loid)s present in sewage sludge, considering three exposure routes – inhalation, dermal contact, and accidental ingestion. The average daily exposure (*ADD*) to heavy metal (loid)s from sewage sludge was estimated from the mean and maximum concentrations reported for each heavy metal(loid) in this study (Table S17, SI). The results of this human health risk assessment are presented in Table S18, SI. The main route of exposure for farmers was dermal contact, followed by ingestion and inhalation. For inhalation, the *ADD* values were 3 to 4 orders of magnitude lower than for the other routes and could therefore be neglected. For the dermal contact, the mean *ADD* values can be ranked as Zn > Cu > Cr > Ni > Hg > As > Pb > Cd. For ingestion and inhalation, the order is similar, except for the last four heavy metal(loid)s, which are substituted by Pb > As > Cd > Hg. Previous studies usually point to ingestion as the main pathway for heavy metal(loid)s from sewage sludge (Espinoza-Guillen et al., 2024; Tytła and Widziewicz-Rzońca, 2023; Yakamercan et al., 2021), but the ingestion rate of sewage sludge used in these studies is also higher (typically 100 mg day^{-1} for adults) than the value used in our model (50 mg day^{-1}).

Considering the *HQs* values used for the assessment of the non-carcinogenic health risks, the highest mean values were found for Cr and As for the ingestion route, Cr and Zn for the inhalation, and Cr and Hg for the dermal contact pathway. In general, most of the *HQs* were below the acceptable non-cancer risk level ($HQ < 1$), except for the HQ_{dermal} for Cr considering the maximum concentration (1.4). Consequently, the highest *HI* was found for this metal (0.12 and 1.5, for the mean and the maximum concentration in sewage sludge). Considering the combination of exposure routes, the *THI* was 0.17 or 1.6, based on the mean and maximum concentrations of all heavy metals, respectively, revealing a non-carcinogenic health risk only when considering the maximum concentrations in sludge.

The carcinogenic risk (*CR*) was calculated considering exposure to Cd, Ni, Pb, Cr and As, the investigated heavy metal(loid)s identified as potentially carcinogenic by the International Agency for Research on Cancer (IARC). The results are also detailed in Table S18, SI. The *CRs* for Ni and Cr for dermal contact were higher than 10^{-4}, indicating a significant cancer risk, but only for the maximum concentrations reported in sewage sludge. However, when adding together the *CR* values for all heavy metal(loid)s considering the mean values in sewage sludge, the resulting CCR_{dermal} also indicates a significant cancer risk (1.8×10^{-4}), but one order of magnitude lower than the same value based on the maximum concentrations in sewage sludge (1.6×10^{-3}). The dermal route contributes >96 % of the total cancer risk (*TCR*) values for Ni and Cr. For the remaining exposure routes and metal(loid)s, the *CRs* are considered negligible or tolerable. No studies were found that applied the health risk assessment approach to farmers or workers involved in sewage sludge handling, but Tytła and Widziewicz-Rzońca (2023) reported a *TCR* value for Ni indicative of cancer risk for adults, which derived mainly from a high *CR* due to ingestion exposure. In that study, $CR_{ingestion}$ for Cr and Cd also indicated a risk for children.

4. Conclusion

This study provided a snapshot of the elemental composition of final dewatered sewage sludge from 42 urban WWTPs in mainland Portugal, collected in summer and winter. The suitability of the sewage sludge for agricultural use was assessed and potential risks associated with its application to soils were investigated.

No seasonal differences in the elemental composition of sewage sludge were found, and significant strong correlations ($r_s > 0.700$) for thirteen pairs of elements were similar in both summer and winter, suggesting possible common sources, interdependence, or identical physicochemical behaviour during wastewater transport and treatment. The combined concentrations of 8 potentially toxic heavy metal(loid)s in individual samples varied >10-fold, ranging from 398 mg kg^{-1} dw to 5852 mg kg^{-1} dw. Overall, Zn and Cu accounted for almost 90 % of the heavy metal(loid)s content in the samples investigated and exceeded regulatory limits in samples from 3 WWTPs receiving industrial effluents. Furthermore, the results showed significantly higher concentrations of some heavy metal(loid)s, namely Cd, Ni, Zn, and Cr, in WWTPs also receiving industrial effluents. This highlights the need for more responsible management of industrial discharges to urban WWTPs and reinforces the importance of routine analysis to monitor the levels of heavy metal(loid)s in the sludge produced. Concentrations of heavy metal(loid)s were also generally higher in larger WWTPs, and average concentrations in anaerobic digested sludge were about 1.4 times higher for As, 2 times higher for Cu, Ni, Pb, and Zn, and up to 3 times higher for Cd and Cr than in thickened sludge alone. Regarding the nutrient profile of the investigated samples, N and P (mean 63 and 22 g kg^{-1} dw, respectively) were the predominant macronutrients, followed by Ca, Fe, and S. The K content was consistently lower than the other macronutrients in sewage sludge (mean of 4.3 g kg^{-1} dw), which may be related to losses to the water phase during dewatering in the final sludge treatment stages. The nutrient composition and other agronomic properties such as organic matter content, pH and electrical conductivity were compatible with its use as a soil-amendment. The combined macro- and micronutrient content of sewage sludge was generally higher in samples from larger WWTPs, in those receiving industrial effluents, and in anaerobically digested samples. However, more detailed analysis revealed that some of the individual nutrients deviated from these trends. For instance, N, Mg, B, and Co did not vary with WWTP size, thickened sludge showed considerably higher levels of N and K than digested samples, N, P, Mg, Fe, and B did not vary with the source of effluent, and K was at significantly higher levels in small WWTPs and in sludge from WWTPs treating exclusively domestic sewage. The significant differences in the nutrient profiles of the sludge samples highlight the need to monitor these parameters to ensure that the fertilization needs of sludge-receiving soils are adequately addressed.

The I_{geo} and the potential ecological risk indicators reported critical concentrations for some heavy metal(loid)s in sewage sludge compared to typical levels in agricultural soils, namely Zn, Cu, Cd, and Hg. However, when modelling a single sewage sludge application of 5 tons ha^{-1} (dw), the level of contamination and potential risks in sludge-amended soil were hampered by the relatively small amounts added compared to ambient background levels. Similarly, the determination of risk characterization ratios based on the *PEC* and *PNEC* values of the target heavy metal(loid)s also indicated no risk to the soil compartment, after a single sludge application. However, the persistence of metal(loid)s in the soil along with repeated sludge applications may lead to long-term accumulation of heavy metals, with potential impacts on the soil environment and ultimately on human health due to contamination of food chains.

Dermal contact was the main route of exposure to heavy metal(loid)s for workers handling sewage sludge, followed by accidental ingestion and inhalation. The human health risk assessment identified a non-carcinogenic risk for Cr and a carcinogenic risk for Ni and Cr via dermal exposure, at the maximum modelled concentrations in sewage sludge (919 mg kg^{-1} dw for Cr and 206 mg kg^{-1} dw for Ni). These results underline the importance of wearing adequate personal protective equipment that covers the skin and exposed parts of the body, when workers handle sewage sludge. No health risks were identified for other heavy metal(loid)s or exposure routes.

Sewage sludge produced in urban WWTPs in Portugal was generally considered suitable for agricultural use in terms of heavy metal(loid)s content and agronomic parameters. However, the periodicity and rate of application, as well as the background concentrations in the sludge-receiving soils, must be taken into account to ensure that fertilization requirements are met while avoiding soil contamination and bio-accumulation in the food chain.

CRediT authorship contribution statement

Filipe Rocha: Writing – original draft, Validation, Methodology, Investigation, Formal analysis. **Nuno Ratola:** Writing – review & editing, Methodology, Investigation, Conceptualization. **Vera Homem:** Writing – review & editing, Validation, Supervision, Resources, Project administration, Methodology, Funding acquisition, Conceptualization.

Declaration of competing 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 paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2025.178595.

Data availability

Data will be made available on request.

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