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Valuable elements in sludge from eight municipal wastewater treatment plants in relation to their recovery potential

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Abstract

Background The management of sludge from municipal wastewater treatment plants (WWTPs) is a global issue, but also an opportunity for circular reuse. Recent data show that sludge reuse in agriculture has the highest share of all utilization routes in the EU. Council Directive 86/278/EEC on the spreading of sludge in agriculture, adopted more than 35 years ago, is still relevant, notwithstanding the discussion on the need to update it. Extracting critical, strategic, and precious metals and metalloids from sludge is an alternative for sludge reuse, which offers several benefits, such as avoiding the high environmental and health risks associated with using sludge directly in agriculture. Additionally, it allows for the recovery of metals, including those listed as Critical Raw Materials by the European Commission. To implement this alternative, it is necessary to first assess the metal content in the sludge and then develop economically and technically viable technologies. In this study, the content of chemical elements in the sludge of eight full-scale WWTPs in Bulgaria is analysed with focus on: (1) assessing the suitability for agricultural application by evaluating the content of macro- and micronutrients and hazardous metals; (2) assessing the possibility of using the sludge as a source of critical and precious metals.

Results For the main nutrients, the following contents as a percentage of the sludge dry weight (DW) were recorded—2.06% to 6% for N, 1.52% to 2.67% for P and 0.47% to 0.81% for K, which are in line with case studies of successful sludge application in agriculture. Only sludge samples from two WWTPs exceeded the permitted limit for hazardous metals and metalloids. On the other hand, of the 21 metal and metalloid constituents listed in the EU Critical and Strategic Material (CRM) list, at least one of the examined samples has a content above 10 mg/kg for 15 elements. The average contents in mg/kgDW of Au (1.1), Al (19,272.9), Mg (6677.6), Ti (1730.9), Ga (20.9) and As (16.6) measured in the investigated WWTPs are among the highest or second highest reported in other countries.

Conclusions The results of the study show prospects for optimising and improving the reuse of sewage sludge in Bulgaria. Sewage sludge from most WWTPs has potential for agricultural application due to its high nutrient content. Large amounts of accumulated critical and strategic metals, gold and silver are trapped in Bulgarian sewage sludge, indicating that sewage sludge could be considered an alternative source with high potential for these valuable elements.

Keywords Sewage sludge utilization, Circular economy, Council directive 86/278/EEC, Critical strategic and precious element utilization, Valuable element recovery

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Introduction

Municipalities generally produce hundreds of tons of waste on an annual basis, great part of which is sludge, generated from wastewater treatment plants (WWTPs) [1]. An estimation for the European Union (27 Member States) reports approximately 10 million tons of sludge dry weight (DW) production per year [2–4]. Furthermore, with the rise in population in urbanized areas, the sludge amounts increase with every year [5]. In Bulgaria (6,45 million population) 45 379 tons DW sludge has been produced from 90 full-scale urban WWTPs for 2023 which treat the wastewater from about 67% of the population [6, 7].

The management of the significant amount of sewage sludge is a major concern for regional water utilities worldwide. This is a global issue that requires effective local solutions with a wide range of possibilities—from conventional to more innovative methods. The most common approaches for sludge management include: reuse as fertilizer in agriculture, recultivation of unused terrains/land reclamation, incineration/thermal disposal and composting (Fig. 1).

Nontraditional emerging sludge utilization methods include the use of sludge as a plant fortifiant via enhanced compost manufacturing or biofuel production [9–12]. However, these technologies are still in their infancy due to the number of limitations. For instance, complications related to sludge pre-treatment and quality control of the product, as well as the extensive use of organic solvents, could be required for biofuel production. [13].

Regardless that on average, at EU level (Fig. 1), sludge utilization in agriculture has the highest share, the preferred option differs significantly from country to country depending on the enforced national legislation and/or regional or cultural specifics [14]. In Bulgaria agriculture utilization is the preferred option, similar to Czech Republic, Denmark, Spain, France and Hungary. Sludge incineration has the highest share in the Netherlands, Belgium, Germany, and Austria [4, 8, 15]. In Finland, about 53% of the sludge is utilized for terrain recultivation/land reclamation [8]. Landfill disposal is still practiced in some European countries such as Greece, Malta, Romania, Lithuania and Bulgaria although it cannot be regarded as a sustainable option for utilizing the potential of the WWTPs sludge [8, 9, 16]. Furthermore, this option will soon be completely forbidden at EU level due to the setting of mandatory targets for the reduction of biodegradable waste to landfills [17–19].

The utilization of the sludge for agricultural purposes at EU level is regulated by the Council Directive 86/278/EEC, which encourages the safe use of sludge and contributes to resource efficiency through nutrient recovery. Many research studies report about positive results for improved physicochemical, microbial, and enzymatic properties of the soil due to sludge application [20–22]. One of the limiting factors concerning the WWTP sludge application as a fertilizer is the presence of hazardous heavy metals accumulation [20]. The Council Directive 86/278/EEC stipulates limiting values for certain metals that may induce metabolic disorders in humans and/or lead to soil toxicity [15]. However, the Council Directive 86/278/EEC was issued more than 35 years ago. Knowledge has been accumulated and a number of legislative and strategic documents have been updated, revised

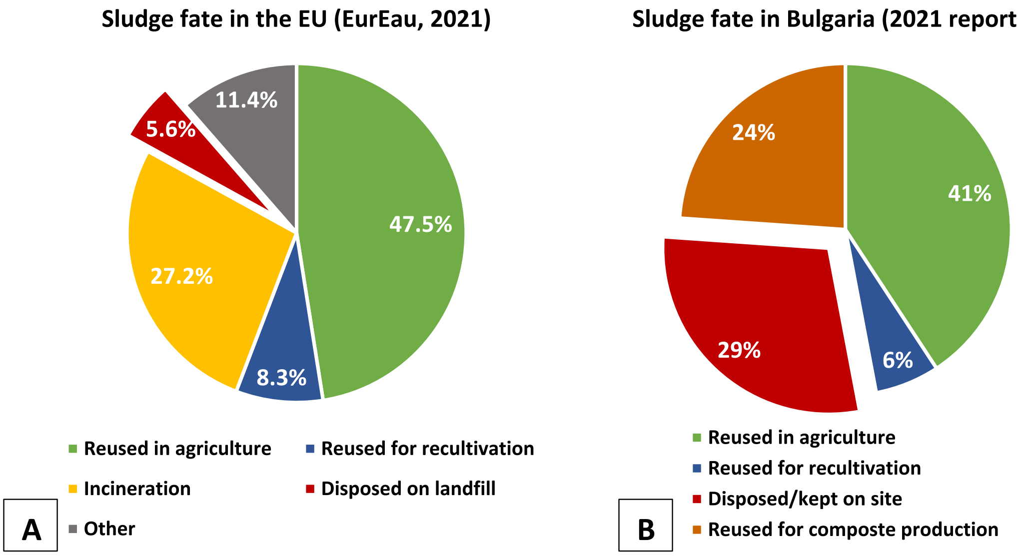


Fig. 1 Sludge disposal routes in the EU **A** and in Bulgaria for 2021 **B** [6, 8]

or issued since then such as the first and second Circular Economy Action Plan, the Bioeconomy Strategy, the new Fertilizing Products Regulation, the Farm to Fork Strategy, the EU Biodiversity Strategy for 2030 and the recently evaluated Urban Wastewater Treatment Directive [23]. The latest evaluation report on the Council Directive 86/278/EEC from 2023 by the European Commission concludes that this Directive is still relevant and it is supported by stakeholders but the list of contaminants which it regulates would need review to limit the risk on agricultural reuse. The suggestion is to aim for applying a mix of techniques, in function of local settings, to maximize the benefits and minimize the negative impacts [24].

The circular economy concept gives new perspectives for sludge utilization as a source of critical elements and appears alternative to sludge utilization in agriculture [25–27]. The ever growing development of electrical, IT and telecommunication industry, the search for energy storing facilities has raised significantly the demand of metals such as nickel, lithium, copper, cobalt, manganese [28]. The Global Supply Chains of EV Batteries 2022 report suggests a 30-time increase of the mineral demand from 2020 to 2040 [28, 29]. Other studies report a tendency that the increased needs in the electrical sector will lead to future scarcity of copper in the world by 2050 [30, 31]. Both lithium and cobalt are included in the most recent Critical Raw Materials list of the European Commission for 2023 due to the complications with their natural extraction [32]. In March 2023, the EU published a Proposal for establishing a framework for ensuring a secure and sustainable supply of critical raw materials, aiming at finding surrogate and circular pathways for critical materials supply [33].

Municipal sewage sludge has shown potential for being an alternative source for not only critical but also precious metal extraction. This will reduce the amount of the pure metals derived from the natural mine sites, thus providing a "circular" route for their fate [13, 25, 27]. Siddiqui et al. report in their review that copper (Cu), iron (Fe), zinc (Zn), palladium (Pd), titanium (Ti), iridium (Ir), chromium (Cr), gallium (Ga), manganese (Mn), gold (Au), cadmium (Cd), aluminum (Al) and silver (Ag) have the highest potential for economic recovery from sewage sludge. Furthermore, according to Mulchandani et al. 2016—approximately 336,000 tons of Al and 18 tons of Au could be recovered globally from sludge [25]. Another study by Varennes et al. 2023 assessed the techno-economic feasibility of potential recovery of different metals based on the recovery amount and the financial potential. They report that Cu and Cr should be co-recovered with other elements, while iron and aluminum could be reused in-situ for physico-chemical treatment to reduce chemicals consumption on the WWTP. Also, palladium (Pd), platinum (Pt) and rhodium (Rh) are better to be recovered after incineration of sludge as they are more concentrated and no longer bound to the organic matter [27]. The advancements in recent recovery techniques from sewage sludge, reported by Adeeyo et al. suggest that due to increased yield and cost reduction, gold, palladium, platinum, and silver are of the highest interest for recovery from sludge [26].

The aim of this research is to analyze the chemical element content in the sludge of eight full-scale WWTPs in Bulgaria in relation to the current most common sludge utilization route in agriculture, but also in relation to the potential for recovery of critical elements. The study focuses on: (1) assessment of the suitability for agricultural application by evaluation of the macro-, micronutrient and heavy metal content; (2) assessment of the possibility for the use of the sludge as a critical and precious metal source. The two sludge utilization approaches under consideration suggest benefits when used in combination. This will result in the extraction of valuable and critical metals, while also preventing the accumulation of toxins in the soil, plants, animals, and humans during subsequent sludge reuse in agriculture. The study contributes to enhancing of the global knowledge in regard to the content of key elements in sludge generated in municipal WWTPs of different sizes. The recorded information of content of various elements could be utilized by interested parties when discussing legislative and regulatory documents.

Materials and methods

Selection of the municipal WWTPs

Sewage sludge from eight municipal WWTPs in Bulgaria was investigated in this study. WWTPs with different sizes (from 10 332 to 962 682 population equivalents (p.e.)) were selected to enable a comparative analysis. The analyzed sludge was taken after the dewatering installations on-site—either mechanical or natural (sludge drying beds) dewatering processes. Since not all of the information provided to us by the WO is public and not all WOs agree to disclose it, the WWTPs will be presented with numbers only. The information for the capacity (in p.e.) and the generated sludge amount (tDW/year) for 2022 as well as the treatment technologies for wastewater and sludge for each WWTP is summarized in Table 1:

Only one WWTP does not have primary sedimentation (WWTP1). All WWTPs remove nitrogen biologically with preliminary denitrification. Phosphorus removal is either chemical with $FeCl_3$ (majority of the WWTPs except WWTP 4 where the inlet P is much lower than the limit and no P removal is performed) or biological

Table 1 Summarized information for the studied WWTPs (as of 2022)

WWTP	Measured inlet load[a]	Generated sludge	Primary clarifyers	Nitrogen (N) removal	Phosphorus (P) removal	Sludge stabilization	Dewatering	Current sludge utilization
	p.e	t DW/year						
WWTP1	10 332	95	no	DN	$FeCl_3$	AS	centrifuge	no data
WWTP2	109 694	1263	yes	DN	$FeCl_3$ + Bio	MT	belt press	agriculture
WWTP3	142 980	526	yes	DN	FeCl3	OD	centrifuge	recultivation
WWTP4	75 939	no data	yes	DN	not needed	EA and OD	drying beds	kept on site
WWTP5	962 682	16,005	yes	DN	$FeCl_3$ + Bio	MT	belt press	agriculture
WWTP6	28 308	153	yes	DN	$FeCl_3$ + Bio	AS	belt press	agriculture
WWTP7	34 340	203	yes	DN	$FeCl_3$	AS	centrifuge	kept on site
WWTP8	36 634	183	yes	DN	$FeCl_3$	MT	auger press	kept on site

[a] Reported in the Bulgarian National Report 2022 to the European Commission on the compliance with The Urban Waste Water Treatment Directive [34]

DN denitrification/nitrification, *Bio* biological phosphorus removal, *AS* aerobic stabilization, *MT* methane tank, *OD* open digesters, *EA* extended aeration

Table 2 Analyzed chemical elements analyzed and their place in the study

Groups	Elements
Macronutrient	N, P, K, Ca, **Mg**
Micronutrient	B, Fe, Mo, **Mn, Zn**, **Cu**, **Ni**
Heavy (hazardous) metals and metalloids	**Zn, Cu, Ni, Cr, Co**, As, Cd, Hg, Pb
Critical, Strategic and Precious elements	**Cu**, **Ni, Cr, Co**, **Mg**, **Mn, B, As**, Li, Al, Ti, V, Sr, Ga, Sb, Pd, Ag, Au

Elements in bold belong to more than one group

(for three WWTPs). Various sludge stabilization methods are applied: anaerobic digestion in methane tanks (three WWTPs), open digesters (two WWTPs), aerobic stabilization (two WWTPs) and extended aeration in the nitrification section of the bioreactor (one WWTP). The dewatering is mechanical in all WWTPs except one. All WWTPs have sludge drying beds as a reserve sludge storage capacity.

The current sludge utilization routes are: use in agriculture (3 WWTPs), recultivation (1 WWTP) and no sludge utilization for the remaining WWTPs.

Selection of analyzed elements

A total of 22 out of all 69 measured chemical elements are a subject of this study. The measured element contents are divided into 3 main groups—(1) macro- and micronutrients for the soil, (2) heavy (hazardous) metals which accumulation could cause environmental or health risk and thus are regulated by the Council Directive 86/278/EEC and (3) critical, strategic and precious elements that are included in the Critical and Strategic Raw Material list of the EC and could potentially be worth extracting. The groups are shown in Table 2.

Two legislative documents were used in the current research to assess the risk of potential soil toxicity with respect to heavy metals and metalloids—the Sewage Sludge Directive 86/278/EEC and the Bulgarian National Ordinance 339/2004 for the use of sludge in agriculture. According to them, the content of a total of 8 metals and metalloids should be initially and periodically monitored in the fertilizing product's DW (i.e., the sewage sludge DW) and in the soil after its application—Cr, Ni, Cu, Zn, As, Cd, Hg, and Pb [15, 35].

The metals and metalloids from the Critical and Strategic Raw Material lists (CRM) of the European Commission with a more significant detected content (above 10 mg/kgDW) are analyzed in the study [32]. In addition, the precious and highly valuable metals palladium (Pd), silver (Ag) and gold (Au) were also included in the analysis.

Chemical analysis of the chosen parameters

Dewatered sludge grab sample was taken three times in a half year period from each WWTP and for each sample chemical analyses of the chemical elements content was carried out. The results use in the paper represents an average value of the chemically analyzed content from all dewatered (mechanically and naturally) sludge samples for the respective plant. For some plants either only mechanical or natural dewatering was available, whereas for others both dewatering process were accessible, and thus sampled. The total amount of samples for the average value calculations are presented in Table 3.

The chemical analysis of the chemical elements was done using the following procedure: The sewage sludge samples were dried to constant weight, grinded and well homogenized. For the sample preparation, HNO_3 (67–69%, Fisher Chemicals, Ultra-TraceMetal Grade,

Table 3 Amount of samples taken from each WWTP

WWTP	1	2	3	4	5	6	7	8
Mechanical dewatering	2	3	3	–	3	3	3	3
Natural dewatering (drying beds)	3	3	3	3	3	3	–	3
Total for average content calculation	5	6	6	3	6	6	3	6

Loughborough, UK), H_2O_2 (30% Fisher Chemicals, Ultra-Trace Analysis Grade, Loughborough, UK), HF (47–51%, Fisher Chemicals, Ultra Trace Metal Grade, Loughborough, UK) and double deionized water (Millipore purification system Synergy, Molsheim, France) were used. Samples of 0.20–0.25 g (three parallels of each sample) were accurately weighed using an analytical balance (KERN & Sohn GmbH—Ziegelei 1 72,336 Balingen, Germany, Type ABT 100-M), and transferred in PTFE vessels. Then 5 mL HNO_3, 3 mL H_2O_2 and 2 mL HF were added and acid digestion of the samples was performed in a microwave reaction system (Anton Paar, Multiwave 3000, Graz, Austria) using four steps with the following power: 600 W (10 min), 800 W (20 min), 900 W (10 min) and 0 W (20 min). Afterwards, the solutions were transferred in Teflon vessels and evaporated to about 1 mL on a heating plate. Finally, 5 mL HNO_3 were added and the samples were heated on a heating plate (Stuard CB 500, China) until the volume was reduced to 0.5–1 mL. The digested solutions were then diluted to 50 mL with double deionized water. Prior the ICP-MS measurement, an additional dilution of 1 mL to 10 mL was performed.

The analysis of the samples was carried out using a PerkinElmer SCIEX ELAN DRC- ICP-MS (MDS Inc., Concord, ON, Canada) system with a cross-flow nebulizer. The spectrometer was optimized to provide minimal values of the ratios CeO^+/Ce^+ and Ba^{2+}/Ba^+ and optimal intensity of the analytes. The concentrations of the elements were determined using the isotopes as follows: ^{7}Li, ^{11}B, ^{24,25,26} Mg, ^{27}Al, ^{31}P, ^{39} K, $^{42,44}Ca$, $^{46-49}Ti$, ^{51} V, ^{52}Cr,$^{54,57}Fe$, ^{55}Mn, ^{59}Co, $^{60,62}Ni$, $^{63,65}Cu$, $^{64,66}Zn$, ^{69} Ga,^{75}As, $^{86,88}Sr$, $^{96,\ 98}Mo$, $^{105,\ 108}Pd$, $^{107,109}Ag$, $^{112,\ 114,\ 116}Cd$, $^{121,123}Sb$, ^{197}Au, $^{200,202}Hg$ and $^{206,207,208}Pb$. Due to the presence of spectral polyatomic interferences on the isotopes of As and Pd, their concentrations were determined in DRC mode [36, 37]. The determination of the macroelements P, K, Ca, Mg and Fe was performed in cell-based mode by optimization and application of an individual dynamic bandpass tuning parameter (RPa) for each isotope, as described in Lyubomirova et al. [38].

Multielement standard solutions for calibration were prepared from single-element standard solutions (Fluka, Steinheim, Switzerland) with initial concentrations of 1000 mg/L. The calibration standard solutions were in the concentration range from 0.001 to 10 mg/L for the macroelements and in the range 0.001–100 µg/L for the microelements. External calibration was performed and the calibration coefficients for all calibration curves were at least 0.99.

The accuracy was checked by analysis of two sewage sludge certified reference materials: CRM 029 (Trace Metals—Sewage Sludge 2—Sigma–Aldrich, Laramie, WY 82070, USA) and ERM-CC144 (Sewage Sludge, elements, European Commission—Joint Research Centre Directorate F—Health, Consumers and Reference Materials, Geel, Belgium). The comparison of the results showed a good agreement between the experimental and certified values.

The moisture (MC) and nitrogen (N) content of each sample were also measured.

The moisture content was measured with a classical gravimetric (weight) laboratory method [39]. The samples' weights were measured with a laboratory scale (RADWAG, AS 310/C/2, Kern, Germany) before and after drying to constant weight at 105 °C. The following formula was used to determine the moisture content:

$$MC = \frac{\mathrm{m, n[g]} - \mathrm{m, d[g]}}{\mathrm{m, n[g]}} \times 100, [\%] \tag{1}$$

where m, n is the weight of the sample in a natural state (as it was taken from the WWTP) and m, d is the weight after complete drying to constant weight at 105 °C.

For the N content, an internal laboratory method was developed. A certain weight (approx. 1 g) of the respective sample was taken from the sludge in a natural state. After that it was put into a becher glass filled with 100 mL of distilled water. The glass content was homogenized with MICCRA, Model D-9, Homogenizer-Disperser (Buggingen, Germany). The obtained liquid was analyzed for the total nitrogen concentration (TN) using HACH Lange cuvette tests (approved by ISO 15705) and spectrophotometric method analysis (spectrophotometer HACH Lange, DR3900, Germany) [39]. For the determination of the N content of the sludge sample, the following analytical formulas were used:

$$TW = 100[\mathrm{mL}] + \frac{(\mathrm{MC}[\%] \times \mathrm{m, n[g]})}{100}, [\mathrm{mL}] \tag{2}$$

$$DW = \mathrm{m,n[g]} - \frac{\left(\mathrm{MC[\%]} \times \mathrm{m,n[g]}\right)}{100}, \mathrm{[g]} \tag{3}$$

$$N\ content = \frac{\mathrm{TN}\left[\frac{\mathrm{mg}}{\mathrm{L}}\right] \times \frac{\mathrm{TW}}{1000}\mathrm{[mL]}}{\frac{\mathrm{DW}}{1000}\mathrm{[g]}}, \left[\frac{\mathrm{mgN}}{\mathrm{kgDW}}\right] \tag{4}$$

where MC, N content, TN and *m*, *n* are as the mentioned above, the TW is the total water content of the homogenized sample and the DW is the total dry weight of the sludge sample.

The determination of the annual accumulated mass (AM) of the measured elements was done with the following formula:

$$AM = \frac{\text{Element content}\left[\frac{\mathrm{mg}}{\mathrm{kgDW}}\right] \times \textbf{Generated sludge}\left[\frac{\mathrm{kgDW}}{\mathrm{year}}\right]}{1{,}000{,}000\left[\frac{\mathrm{mg}}{\mathrm{kg}}\right]}, \left[\frac{\mathrm{kg}}{\mathrm{year}}\right] \tag{6}$$

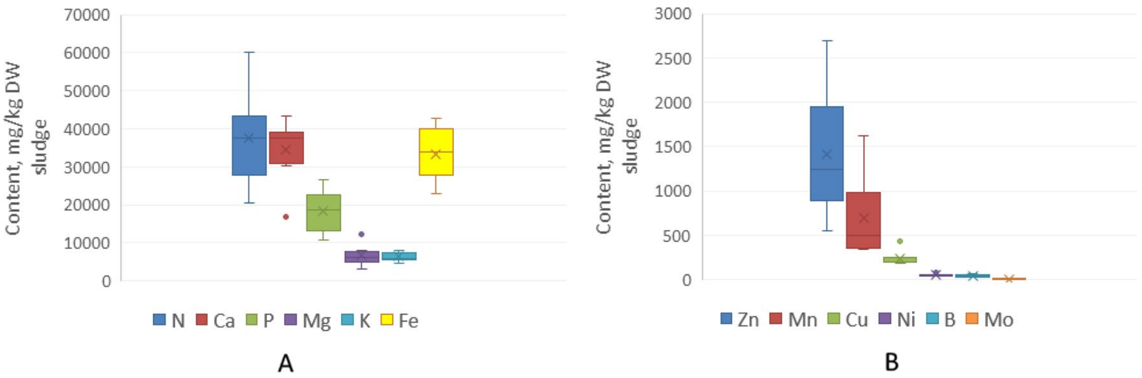


Fig. 2 Macro- and microelement content in mg per kg of sludge DW from all studied WWTP. **A** Macroelement plus Fe from microelements. **B** Microelements (without Fe)

Table 4 Average, minimum and maximum values of the macro- and microelement content in mg per kg of sludge DW from all studied WWTP

mg/kg	**N**	**P**	**Mg**	**K**	**Ca**
Macroelements					
Average	37,408 ± 4115	18,268 ± 5419	6678 ± 2741	6323 ± 1130	34,583 ± 8274
Min	20,593 ± 2265	10,663 ± 521	3147 ± 126	4730 ± 198	16,693 ± 801
Max	60,031 ± 6603	26,726 ± 1098	12,407 ± 606	8102 ± 315	43,310 ± 2122
Median	37,564	18,811	6176	5958	37,606
% DW	2.1% to 6%	1.5% to 2.7%		0.5% to 0.8%	
Range in literature[a]	3.40% to 9.76%	1.06% to 3.8%		0.2% to 0.5%	

mg/kg	**B**	**Mn**	**Fe**	**Ni**	**Cu**	**Zn**	**Mo**
Microelements							
Average	47 ± 15	690 ± 451	33,386 ± 6780	51 ± 12	239 ± 82	1419 ± 699	9.2 ± 1.4
Min	28 ± 1	346 ± 22	22,792 ± 915	42 ± 2	188 ± 9	546 ± 35	7.6 ± 0.2
Max	69 ± 3	1625 ± 103	42,633 ± 1833	79 ± 5	434 ± 21	2688 ± 116	11.7 ± 0.5
Median	45.5	505	33,909	47	201.5	1241	9.0

[a] [16, 20–22, 40–43]

Table 5 Hazardous heavy metal and metalloid content in mg per kg of sludge DW from the studied WWTPs

	WWTP 1	WWTP 2	WWTP 3	WWTP 4	WWTP 5	WWTP 6	WWTP 7	WWTP 8	Sewage Sludge Directive 86/278/EEC	National Ordinance 339/2004 for the Use of Sludge in Agriculture
Cr	127 ± 4	105 ± 4	67 ± 2	87 ± 4	63 ± 4	86 ± 4	165 ± 5	98 ± 5	–	**500**
Ni	52.9 ± 0.6	48.2 ± 0.9	41.8 ± 0.7	54 ± 1	43.1 ± 0.9	45.7 ± 0.8	79 ± 2	43.5 ± 0.9	**300**	**350**
Cu	201 ± 6	249 ± 9	195 ± 4	188 ± 7	435 ± 9	240 ± 7	201 ± 6	202 ± 7	**1000**	**1600**
Zn	546 ± 8	1393 ± 30	1089 ± 20	833 ± 18	1058 ± 31	1712 ± 56	2036 ± 51	2688 ± 78	**2500**	**3000**
As	7.9 ± 0.6	9.6 ± 0.5	9.5 ± 0.5	15.7 ± 0.8	6.5 ± 0.3	7.2 ± 0.4	71 ± 4	5.3 ± 6 ± 0.3	–	**25**
Cd	0.77 ± 0.02	0.97 ± 0.03	1.88 ± 0.07	1.23 ± 0.05	1.56 ± 0.04	2.34 ± 0.08	11.3 ± 0.4	1.1 ± 0.1	**20**	**30**
Hg	0.51 ± 0.03	1.15 ± 0.06	0.72 ± 0.04	0.43 ± 0.02	0.39 ± 0.02	0.30 ± 0.02	0.23 ± 0.01	0.40 ± 0.02	**16**	**16**
Pb	27 ± 1	41 ± 1	54 ± 1	59 ± 2	59 ± 2	54 ± 2	3268 ± 162	42 ± 2	**750**	**800**

[a] The number of the decimal places in all values is related to the precision of the measurements; [b] The numbers in bold represent the limiting values from the legislative documents

where the Generated sludge [kg/year] value for each of the investigated WWTPs is taken from Table 1.

Results and discussion

Macro- and micronutrient content

There is no best content of macro- and micronutrients in the sludge, since the application of the specific product and the selected soil on which it is applied should both be taken into consideration. The measured macro- and microelements for soil fertilization in the investigated WWTPs are presented in Fig. 2 with their displayed values in Table 4.

All of the measured micro- and macronutrients are present in the studied WWTPs. According to the Sewage Sludge Directive 86/278/EEC the three main elements that should be regularly monitored are N, P and potassium (K). The ranges, in which their contents varied in the sewage sludge, are also presented in Table 4. The obtained values from the experimental data are compared to the values from review and original research papers on the topic from the scientific literature.

The case studies in the reference literature (Table 4) have successfully applied the WWTP sludge for increasing the soil fertility with periodic monitoring of the soil itself [16, 20–22]. In addition, the highest measured amounts of the other macronutrients are 12,407 mg/kgDW for Mg (WWTP 4), 8102 mg/kgDW for K (WWTP 4), and 43,309 mg/kgDW for Ca (WWTP 2). The amount of the most essential elements (nitrogen, phosphorus and potassium) in our study are within the range of the reported content in the literature as shown in Table 4. Thus, from this perspective the investigated sludge is suitable for agricultural application.

From the microelements, the highest content from all WWTPs was registered for Fe. This is probably due to the fact that all of the studied WWTPs have a chemical P removal step in their treatment process with $FeCl_3$ which leads to the accumulation of the metal as chemical part of the sludge. Furthermore, WWTP 4 does not remove P in their technological scheme but the plant is serving the settlement with the largest steel production company in the country and the settlement has some other iron processing industries nearby. This explains the increased Fe content in their generated sludge without a step for chemical P removal in the plant. Also, the highest amounts of B and Zn were found in WWTP 8, the maximum value of Ni was obtained in WWTP 7 and the maximum value of Cu—in WWTP 5. In this regard, even though Fe, Zn, Ni and Cu are essential for plant and crop life, excessive amounts of these metals could lead to soil toxicity and hinder plant production. An analysis on the presence of potentially hazardous metals and metalloids that could affect the application of the sludge as an agricultural additive and the currently active regulations on the topic is presented in the next subsection of the paper.

Hazardous heavy metal and metalloid content

All of the regulated elements in the two legislative documents (Sewage Sludge Directive 86/278/EEC and the Bulgarian National Ordinance 339/2004) were measured and analyzed. The results are presented in Table 5 [15, 35].

Each regulated hazardous metal or metalloid was measurable in most of the examined sludge samples from all WWTPs. None of WWTPs 1 to 6 exceed the permitted values. Furthermore, the content of these sludge samples for As, Cd, Hg and Pb are at least ten times lower than the limiting value.

However, the sewage sludge DW from WWTP 7 has higher As and Pb packing than the allowed content. Each of the two elements are present with values of approximately 3 times the limiting amount. Another WWTP that provokes the attention with its Zn content is WWTP 8. The average value is lower than the permit in the Bulgarian National Ordinance but higher than the Sewage Sludge Directive. Both WWTP 7 and WWTP 8 are located in settlements that have large industries such as galvanized pipes and fittings production, zinc extraction, thermal power plants with their landfills, etc. that could be the cause of the generated heavy metals and metalloids in the sludge [44]. In this case WWTP7 and WWTP 8 are not recommended to utilize the sludge as a fertilizer in agriculture since it will cause soil toxicity and hinder the quality of the crops. For the other WWTPs there is no regulatory problem for their use in agriculture, at least from the heavy metal and metalloid perspective, registered and analyzed during our sampling campaign.

The transportation of heavy metals in soil and plants depends on the pH value. Therefore, it is important to consider the pH value both in the sewage sludge that may be used as fertilizer and in the soil itself. According to Article 8 of the Sewage Sludge Council Directive 86/278/EEC, Member States must consider the increased mobility and availability of heavy metals to crops when sludge is used on soils with a pH below 6. If necessary, they must reduce the limit values they have established [15]. In our study of the investigated WWTPs, the pH values of the sludge ranged from 6.5 to 8.1. This range is positive as it shows potential for maximum effectiveness while minimizing the risk of transporting hazardous substances and metals to crops.

Critical, strategic and precious element content

The content of each element from this group in the sewage sludge DW from the respective WWTPs are presented in.

Out of all 21 metal and metalloid elements suggested in the EU CRM list, 15 have more significant content (> 10 mg/kg) in the sewage sludge DW in at least one WWTP. The data from Fig. 3 indicate that in terms of absolute values—the elements Al, Mg, Mn, Ti, Cu and Sr were present with the largest amount. The maximum values for Co, Al, Mg, Mn, Ti, V, and Pd were registered in WWTP 4, whereas the WWTP 7 has the highest Li, Cr, Ni, As, and Sb content. WWTP 8's sludge encompassed the most Sr and B. For the precious metals—the paramount Au content was observed in WWTP2 and Ag was the highest in WWTP 6. The exact amounts of each element are presented in Table 6.

Table 7 presents the accumulated mass (AM) of each element in kg per year when the generated amount of sludge on an annual basis is taken into consideration. The AM was based on a rough estimate and does not include analysis of what exact amount of the elements could be extracted and what will be the losses due to the extraction process itself. Taking this into consideration, WWTPs 2 and 5 generate the highest amounts of all critical, strategic and precious elements—WWTP 2 due to its high content in the sewage sludge DW and WWTP 5 due to the largest amount of generated sludge per year. Also high AM of Ti, Cu, Pd, Ag, and Au were registered in WWTP 2 and WWTP 3, and high AM of As and Sb—in WWTP 7. WWTPs 2, 3, 4 and 7 have industries nearby that use different metals in their production processes and this could be the reason for the higher contents of these elements in wastewater, and respectively, in sludge. It is visible that in terms of total AM, a maximum of hundreds to hundreds of thousands of kg of critical and strategic metals could be potentially extracted from sewage sludge DW. Furthermore tens of kg of precious Au and hundreds of kg of Ag are locked into the sludge of Bulgaria on an annual basis. The fields for temporary storage of the dewatered sludge and the sludge landfills could be an alternative "gold mine" and a possible solution for critical, strategic and precious element deprivation.

Since the further extraction and purification of those elements are expensive and time-consuming steps for the production of raw element materials, more extensive research is needed to verify this potential and prove its practical application for wastewater critical, strategic and precious elements utilization.

The pattern between the critical element content and the size (capacity in p.e.) of the WWTPs was also investigated Fig. 4.

No direct correlation between inlet load and content of elements was established. Only 3 elements were chosen in Fig. 4 to represent the dependency (WWTP 5 was excluded since it is too large for the chosen graph and it does not change the identified pattern). Also, as mentioned above, the maximum content of elements (mg/kgDW) was registered in different WWTPs, not just in the largest ones. Furthermore, the greatest amount of critical and strategic elements were present in the WWTP 4 sludge that has the biggest number of local industries near the served settlement. Hence, regional production potentially impacts the amount of elements in the sludge to the highest degree, regardless of the size of the served settlement and the inlet capacity of the WWTP. This correlation should be an object of future research to better understand the origins and fate of the elements in sewage sludge.

The average value for each critical and valuable element from all investigated WWTPs in Bulgaria was compared with the mean value from other countries. The results are presented in Fig. 5 using a logarithmic ordinate scale. The data for the other countries are taken from the review paper of Mulchandani and Westerhoff, [25].

The cited study [25] and Fig. 5 demonstrate that the accumulation of metals in municipal sludge is a global issue, rather than a local one. Developing technologies to recover metals from sludge appears worthwhile due to its potential economic and environmental benefits.

It is noted that Bulgaria has the highest mean value of Au content in sludge out of all presented countries. In terms of Al, Mg, Ti, Ga, and As the contents are the second highest.

It could be concluded that such significant accumulation of those valuable elements in the sewage sludge draws attention to the sludge in Bulgaria. The high potential for deprivation of those critical, strategic and precious elements from sludge is a positive step forward towards natural raw material extraction reduction and circular economy's future development.

Environmental and health risks and mitigation opportunities

The use of sludge as fertilizer carries a risk to the environment and human health due to its heavy metal content. Heavy metal accumulation can increase soil toxicity, hinder plant growth, alter the natural food chain, and ultimately lead to health problems in animals and humans who consume food produced in such soil [45]. Exposure to soil toxins, such as heavy metals, can directly affect plant development and physiological cycles. This includes reducing seed germination, limiting plant growth, disrupting nutrient uptake, stifling photosynthesis, and

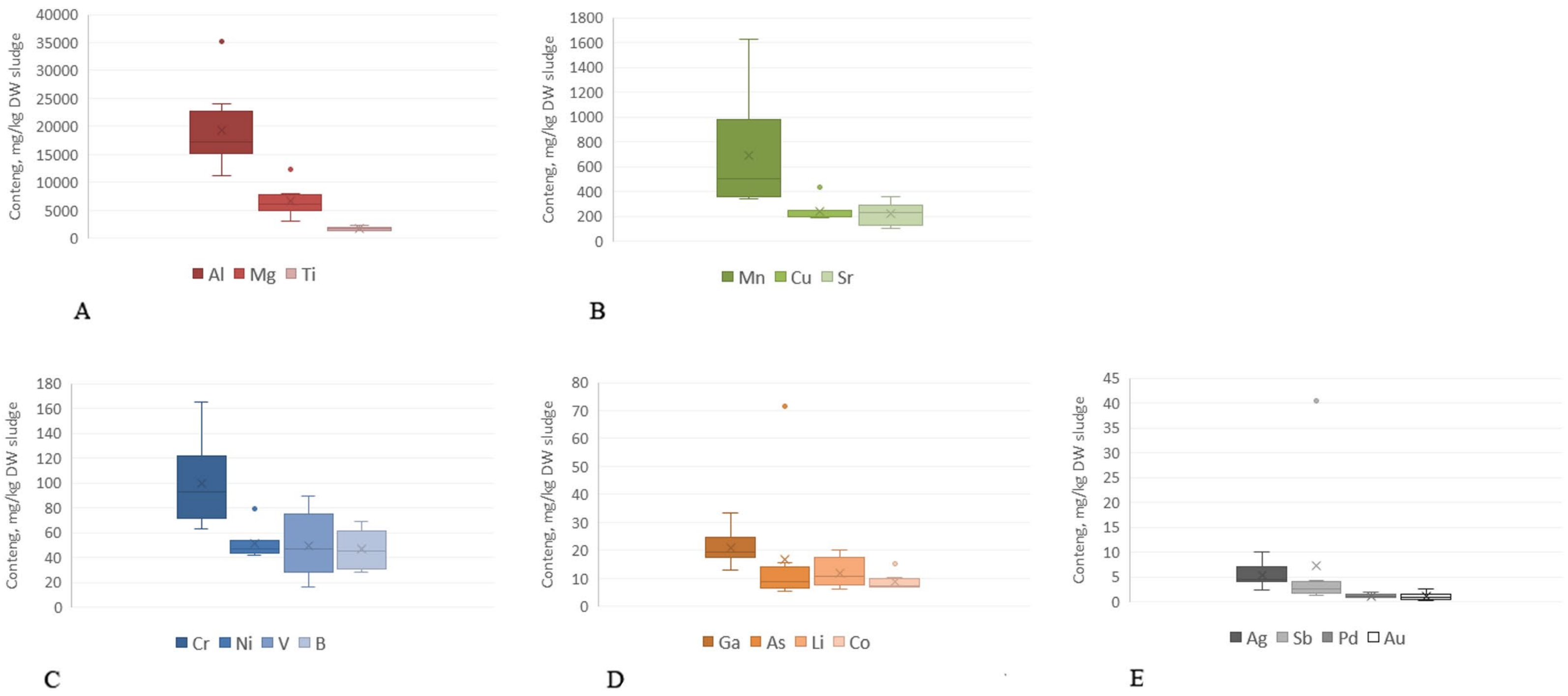


Fig. 3 Critical, strategic and precious element content (in mg per kg of sludge DW) of the studied WWTPs distributed in groups according to their minimum content. **A** Min content above 1000 mg/kg DW sludge. **B** Min content in the range 100 to 1000 mg/kg DW sludge. **C** Min content in the range 20 to 100 mg/kg DW sludge. **D** Min content in the range 5 to 20 mg/kg DW sludge. **E** Min content in the range 1 to 5 mg/kg DW sludge

Table 6 Average, minimum and maximum values of the critical, strategic and precious element content in mg per kg of sludge DW from the studied WWTPs. The different ranges of the ordinate axes are presented in separate panels (A to E) in order to better visualize the results

Element	Unit	Average	Minimum	Maximum	Median	WWTP with maximum content
Li	mg/kgDW	11.9 ± 5.1	6.2 ± 0.3	20.0 ± 1	10.8	WWTP7
Cr	mg/kgDW	99.8 ± 33.3	63 ± 3	165 ± 5	92.5	WWTP7
Ni	mg/kgDW	51.1 ± 12.1	42 ± 1	79 ± 3	47	WWTP7
As	mg/kgDW	16.6 ± 2.2	5.3 ± 0.3	71 ± 2	8.7	WWTP7
Sb	mg/kgDW	7.4 ± 1.4	1.4 ± 0.1	41 ± 2	2.65	WWTP7
Co	mg/kgDW	8.6 ± 2.8	6.7 ± 0.3	15.0 ± 0.4	7.4	WWTP4
Al	mg/kgDW	19,273 ± 741	11,166 ± 390	35,246 ± 1445	17,177	WWTP4
Mg	mg/kgDW	6678 ± 2741	3147 ± 120	12,407 ± 510	6176	WWTP4
Mn	mg/kgDW	690 ± 45	346 ± 10	1625 ± 66	505	WWTP4
Ti	mg/kgDW	1731 ± 367	1293 ± 50	2366 ± 85	1661	WWTP4
V	mg/kgDW	49.8 ± 25.6	16.8 ± 0.7	90 ± 2	46.6	WWTP4
Cu	mg/kgDW	239 ± 82	188 ± 4	434 ± 13	202	WWTP4
Pd	mg/kgDW	1.2 ± 0.4	0.82 ± 0.05	1.9 ± 0.2	1.2	WWTP4
Sr	mg/kgDW	220 ± 88	102 ± 5	358 ± 11	228	WWTP8
B	mg/kgDW	46.5 ± 15.4	28.0 ± 0.8	69 ± 3	45.5	WWTP8
Ga	mg/kgDW	20.9 ± 6.1	12.9 ± 0.4	33 ± 1	19.3	WWTP6
Ag	mg/kgDW	5.4 ± 2.4	2.3 ± 0.1	10.0 ± 0.6	4.5	WWTP6
Au	mg/kgDW	1.1 ± 0.8	0.36 ± 0.02	2.7 ± 0.2	0.86	WWTP2

[a] The number of the decimal places in all values is related to the precision of the measurements

Table 7 Estimated potential annual accumulated mass (AM) of critical, strategic and precious elements in the sludge from the investigated WWTPs

	Unit	WWTP 1	WWTP 2	WWTP 3	WWTP 4	WWTP 5	WWTP 6	WWTP 7	WWTP 8
Li	kg/year	1.2	15.0	3.8	–	149.3	1.5	4.1	1.1
Cr	kg/year	12.1	132.7	35.2	–	1006.5	13.2	33.6	17.9
Co	kg/year	0.7	9.3	4.4	–	120.7	1.0	2.1	1.2
Al	kg/year	1499.8	21,708.5	9034.1	–	299,038.0	2289.9	4885.2	2043.9
Mg	kg/year	588.8	7551.4	3625.3	–	128,927.2	705.8	638.7	1128.0
Mn	kg/year	32.9	455.0	186.4	–	8349.0	74.9	213.8	140.4
Ti	kg/year	136.4	2610.2	770.5	–	30,469.9	234.6	364.3	236.6
V	kg/year	4.5	53.7	43.7	–	736.6	3.6	10.2	3.1
Ni	kg/year	5.0	61.0	22.0	–	689.0	7.0	16.1	8.0
Cu	kg/year	19.1	314.5	102.4	–	6953.5	36.8	40.8	37.0
Sr	kg/year	29.1	249.8	120.0	–	3626.3	16.5	20.7	65.6
B	kg/year	6.0	52.2	14.7	–	476.0	8.7	10.1	12.6
Ga	kg/year	1.7	16.3	9.7	–	283.7	5.1	4.1	4.6
As	kg/year	0.8	12.1	5.0	–	104.5	1.1	14.5	1.0
Sb	kg/year	0.1	4.0	1.1	–	70.0	0.3	8.2	0.3
Pd	kg/year	0.1	1.2	0.6	–	14.6	0.2	0.3	0.2
Ag	kg/year	0.2	7.3	2.3	–	120.4	1.5	0.9	0.7
Au	kg/year	0.1	3.4	0.7	–	12.0	0.1	0.1	0.3

[a] The number of the decimal places in all values is related to the precision of the measurements

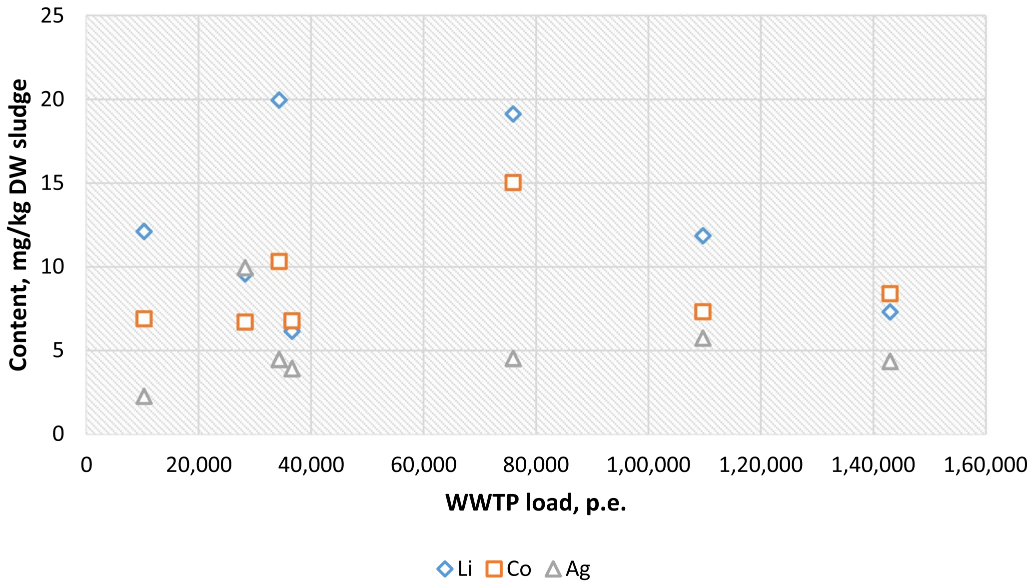
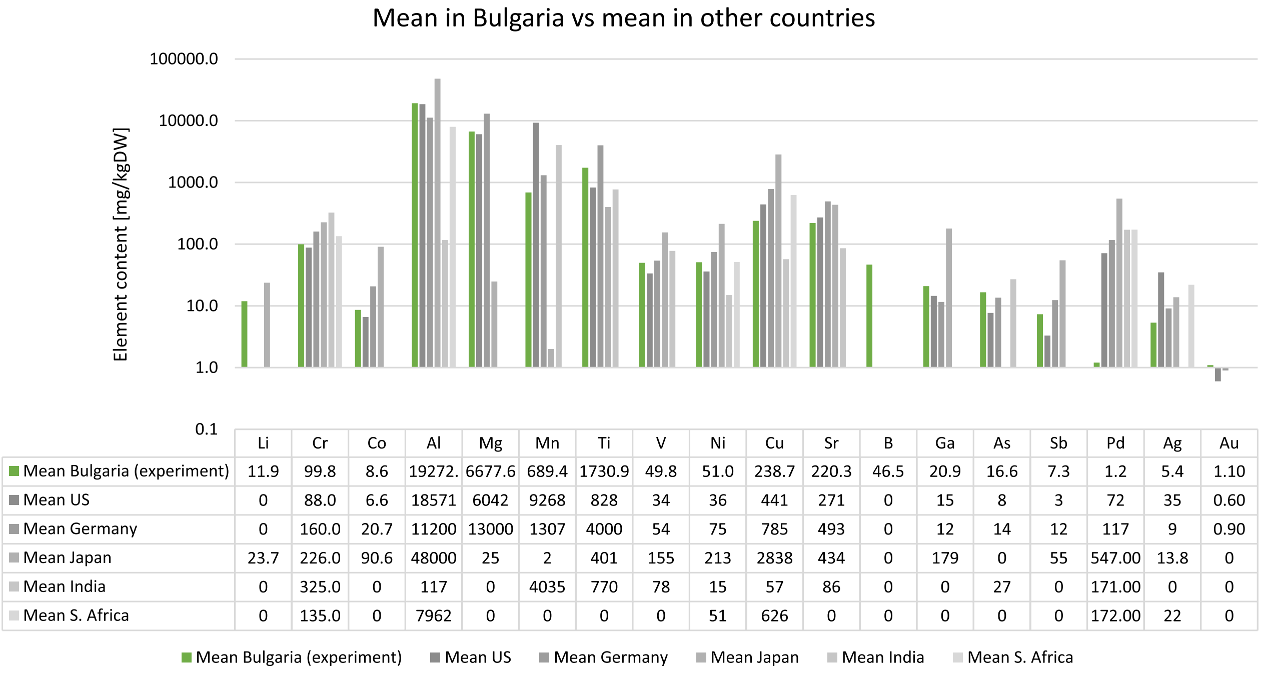


Fig. 4 Element content compared to the measured WWTP inlet load in p.e

adjusting enzymatic activities [45]. Accumulation of these toxins can also lead to oxidative damage by producing excess reactive oxygen species [45]. Moreover, heavy metals and metalloids such as Hg, As, Pb, Cd, and Cr can disrupt human metabolomics, leading to morbidity and even mortality [46]. This increased risk has been detected in the Chengdu Plain in China, not only in mining areas but also among people who have consumed crops, such as rice, grown in soil with high heavy metal content. It should be noted that not all heavy metals were transferred from the soil to the crops. According to Liu et al. the daily intake of all metals, except for Pb, exceeded the



	Li	Cr	Co	Al	Mg	Mn	Ti	V	Ni	Cu	Sr	B	Ga	As	Sb	Pd	Ag	Au
🟩 Mean Bulgaria (experiment)	11.9	99.8	8.6	19272.	6677.6	689.4	1730.9	49.8	51.0	238.7	220.3	46.5	20.9	16.6	7.3	1.2	5.4	1.10
■ Mean US	0	88.0	6.6	18571	6042	9268	828	34	36	441	271	0	15	8	3	72	35	0.60
■ Mean Germany	0	160.0	20.7	11200	13000	1307	4000	54	75	785	493	0	12	14	12	117	9	0.90
■ Mean Japan	23.7	226.0	90.6	48000	25	2	401	155	213	2838	434	0	179	0	55	547.00	13.8	0
■ Mean India	0	325.0	0	117	0	4035	770	78	15	57	86	0	0	27	0	171.00	0	0
■ Mean S. Africa	0	135.0	0	7962	0	0	0	0	51	626	0	0	0	0	0	172.00	22	0

Fig. 5 Mean value of each of the investigated critical, strategic and precious elements in the experiment from Bulgaria in comparison with other countries around the world (data for other countries from Mulchandani and Westerhoff, 2016) [25]

oral reference dose or minimal risk levels recommended by the United States Environmental Protection Agency [47].

The extraction of hazardous and critical/strategic metals from sludge has the potential to reduce the negative effects and risks associated with direct application of sludge in agriculture, while also decreasing the depletion of natural mineral metal ore sources. Metal extraction from sludge is an area of interest, and technologies for this purpose are currently being developed. According to Siddiqui et al. 2023, Cu, Fe, Zn, Pd, Ti, Ir, Cr, Ga, Mn, Au, Cd, Al and Ag have the highest potential for economic recovery [13]. These elements in the sludge were valued at 480 USD/dry ton sludge [48]. Promising techniques for metal extraction from municipal sewage sludge include bioleaching with certain microorganisms, improved anaerobic bioleaching processes, precipitation, acidification, and sorption [13, 49, 50]. Some methods, such as bioleaching, require a pre-treatment phase, which could involve thermal hydrolysis or ultrasonication [13]. This phase complicates the extraction process. It is important to note that a fully developed method for economically viable metal extraction on a full-scale level has not yet been established. Further research in this direction is necessary for the optimal utilization of this valuable resource.

Conclusions

The findings of the study demonstrate prospects for optimizing and enhancing circular usage of sludge in Bulgaria. The sludge presents potential for agricultural application due to its high nutrient concentration. Furthermore, it is worth noting that the sludge also contains a significant amount of critical and strategic elements that could be extracted.

The percentages of macro nutrients present in the dry mass are between 2.06% and 6% for N, 1.52% and 2.67% for P, and 0.47% and 0.81% for K. These outcomes are consistent with the published scientific literature that demonstrates the successful application of sludge in agriculture. Among the eight WWTPs examined, only two exceeded the permitted limit for hazardous metal and metalloid content.

Considering the demand for a circular economy, an attractive approach to utilize sludge is to extract critical and strategic elements. Among the 21 metal and metalloid components listed in the EU CRM, at least one of the evaluated WWTPs displays content greater than 10 mg/kg for 15 elements. Notably, two WWTPs show an enormous presence of Au and Ag, as they are precious metals. A significant potential yield of critical, strategic, and precious elements was observed in two of the investigated WWTPs. No relation between the capacity of the WWTP and the content of critical and strategic elements was found. It should be a subject of future research to examine the origins and sustainability of content of the elements in sewage sludge. The comparison with previous studies indicates that the average levels of Au (1.1 mg/kgDW), Al (19,272.9 mg/kgDW), Mg (6677.6 mg/kgDW), Ti (1730.9 mg/kgDW), Ga (20.9 mg/kgDW), and As (16.6 mg/kgDW) are among the highest or second highest recorded in other countries. Hundreds of thousands of critical and strategic metals, tens of kilograms of precious gold, and hundreds of kilograms of silver are trapped within Bulgarian sewage sludge DW every year, indicating that the fields reserved for temporary storage of the dewatered sludge and the sludge landfills could potentially be a valuable alternative source for critical, strategic, and precious elements.

Technologies for extracting hazardous and critical/strategic metals from sludge are being developed. They could reduce the negative effects and risks of direct application in agriculture and decrease depletion of natural mineral metal ore sources. This is particularly relevant in the coming years, as the depletion of critical and strategic elements from conventional natural sources will occur slowly but inevitably. Further advancements in such technologies are crucial to achieving full circularity in the sludge reuse realm, with economically optimal resource utilization and reduced environmental stress. The determination of existing metal amounts in municipal sludge, as presented in this paper, is a good starting point.

Abbreviations

AM	Accumulated mass
CRM	Critical raw materials list
DW	Dry weight
EU	European Union
ExEA	Executive environment agency
i.e.,	That is
ICP-MS	Inductively coupled plasma mass spectrometry
NSI	National Statistics Institute of Bulgaria
MC	Moisture content
p.e.	People equivalent
WWTP	Wastewater treatment plant

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Author contributions

Conceptualization, IR, GD and DV; methodology, IR. and VL; validation, VL; formal analysis, IR, DV, VL; investigation, IR, DV; resources, IR, DV, IK, GD, BB, VR, OK, SL; data curation, IR, DV; writing—original draft preparation, IR, DV, VL, GD;

writing—review and editing, IR, VL, GD; visualization, IR, DV VL; supervision, IR; project administration, IR, IK, GD; funding acquisition, IR All authors have read and agreed to the published version of the manuscript.

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Declarations
Ethics approval and consent to participate
All authors have read, understood, and have complied as applicable with the statement on "Ethical responsibilities of Authors" as found in the Instructions for Authors.

Consent for publication
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Competing interests
The authors declare that they have no competing interests.

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