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Can pyrolysis and composting of sewage sludge reduce the release of traditional and emerging pollutants in agricultural soils? Insights from field and laboratory investigations

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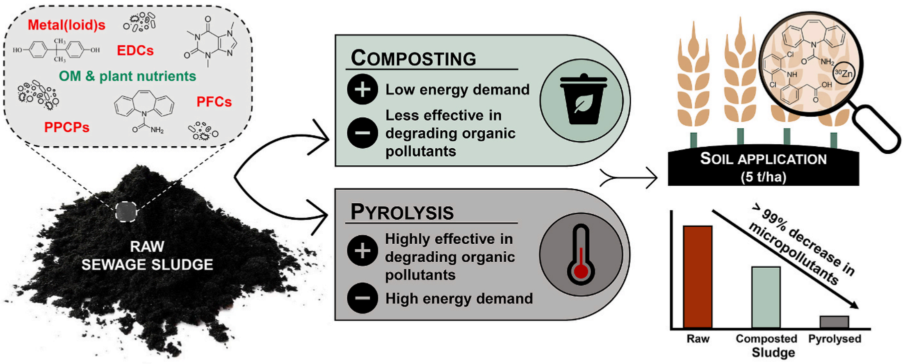
HIGHLIGHTS

- Pyrolysis removed endocrine-disrupting chemicals and PFAS from sludge.
- Leaching of metal(loid)s from sludges was significantly influenced by the treatments.
- Diclofenac and carbamazepine were detected only in wheat seeds after application.
- Telmisartan and triclosan were the most abundant emerging pollutants in sludges.

GRAPHICAL ABSTRACT



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ABSTRACT

The potential extractability, crop uptake, and ecotoxicity of conventional and emerging organic and metal(loid) contaminants after the application of pre-treated (composted and pyrolysed) sewage sludges to two agricultural soils were evaluated at field and laboratory scale. Metal(loid) extractability varied with sludge types and pre-treatments, though As, Cu, and Ni decreased universally. In the field, the equivalent of 5 tons per hectare of both composted and pyrolysed sludges brought winter wheat grain metal(loid) concentrations below statutory limits. Carbamazepine, diclofenac, and telmisartan were the only detected organic pollutants in crops decreasing in order of root > shoot > grains, whilst endocrine-disrupting chemicals, such as bisphenol A and

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Pyrolysed sludge
Metal(loid)s

perfluorochemicals were heavily reduced by composting (up to 71%) or pyrolysis (up to below detection limit) compared to raw sludges. As a consequence, no detectable concentrations were measured in soils 12 months after field application. This study highlights the potential advantages of processing sewage sludge before soil applications, especially in the context of reducing the mobility of emerging contaminants, though further studies are required on a broad range of soils and crops before land application can be considered.

1. Introduction

Sewage sludge is a by-product of the municipal wastewater treatment process that is often repurposed as soil conditioners (Kowalski et al., 2024). Global population increase will result in larger quantities of sludge waste for disposal (Bagheri et al., 2023; Gao et al., 2020; Kowalski et al., 2024; Meng et al., 2021), and untreated or inadequately treated sewage sludges could increase metal(loid)s, polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), pharmaceuticals and personal care products (PPCPs), endocrine disrupting chemicals (EDCs) and poly and perfluorinated alkyl substances (PFAs), and antibiotic resistance genes, prevalence in the environment, and potential entry into the food chain (Chen et al., 2016; Costello and Lee, 2020; Kumar et al., 2023; Wu et al., 2012). Perfluorooctane sulfonic acid (PFOS) and perfluorooctanoic acid (PFOA) are already recognized as persistent organic pollutants (Liu et al., 2019).

The ecological dynamics of metal(loid)s have garnered considerable understanding, evidenced by extant research. Presently, the regulatory parameters governing metals (such as Cd, Cu, Hg, Ni, Pb, and Zn) are predominantly delineated within Council Directive 86/278/EEC, which delineates guidelines for the agricultural application of biosolids within the European Union (CEC, 1986). However, this directive may lack provisions to adequately address emergent hazards to vegetation, animal welfare, and human health arising from the influx of novel contaminants into wastewater and, by extension, sewage sludges. Several EU member states, such as the Czech Republic, have established limits for other potential risk elements, select organic compounds, and microbial contamination (Hudcová et al., 2019). National-level restrictions on sludge utilization in agriculture vary among EU member states, with some countries, including Denmark, France, Spain, and Ireland, employing more than half of their total sewage sludge production in agriculture, while others, such as Romania, Slovakia, Greece, Finland, the Netherlands, and Slovenia, utilize less than 5% of their generated sludges in the agricultural sector (Lamastra et al., 2018). Current legislation in the Czech Republic mandates the use of only pre-treated sewage sludge in the context of mitigating potential risks. Processing, composting, and pyrolysis, for example, can mitigate sewage sludge impacts, converting them into safer products for agriculture (Gao et al., 2020; Magdziarz and Werle, 2014). Composting is a low-energy aerobic process, while pyrolysis involves heating sludges in oxygen-free conditions, reducing contaminants (Moško et al., 2021; O'Laughlin and McElligott, 2009; Zielińska and Oleszczuk, 2016).

While there have been many studies dealing with the risks associated with the application of raw and treated sludges to soils, comprehensive and complex studies simultaneously investigating the behaviour of both conventional and emerging contaminants are lacking, especially those investigating their application and impact in field conditions. Thus, the objectives of this study were to: i) measure the potential extractability of metal(loid)s, PAHs, PCBs and emerging contaminants such as PPCPs, EDCs, PFCs after sludge pre-processing by composting and pyrolysis; ii) assess the medium term fate of contaminants and implications by sampling field amended soils 12-months after amendment and iii) discuss the findings in the context of the judicious application of composted and pyrolysed sludges, and consider the broader environmental risks associated with this practice when applied at a dosage of 5 tons per hectare, as recommended in the Czech Republic.

2. Materials and methods

2.1. Preparations and characterization of sludges

Sewage sludges sourced from five distinct wastewater treatment plants (WWTPs) were chosen from a pool of 30 WWTPs located across the Czech Republic and processed individually, designated as S1–S5. The origins of the input raw sludges, categorized by city population, are depicted in Table S1. Urban greenery materials were used in a three-month composting process at Kobra Údlice, s.r.o., Czech Republic. Anaerobically stabilized dewatered sludges from five WWTPs were mixed with grass and wood chips in 300 L containers for three months. Each sludge batch (50 kg) underwent composting for homogenisation. The mixture comprised 50 kg dewatered sludges (17–27% dry matter), 30 kg grass, and 10 kg wood chips. Temperature monitoring showed a peak of 52 °C over a week, meeting sanitation standards despite a shorter duration compared to larger compost heaps. The resulting samples are denoted as CS1-CS5.

Anaerobically stabilized dewatered sludges from the five WWTPs were air-dried in 50 kg batches for several weeks. The dried samples were subsequently pyrolysed at 600–650 °C under an inert nitrogen atmosphere and the samples are denoted as PS1-PS5. During this process, the primary pyrolysis products, i.e., pyrolysis gas or bio-oil in its vapor form, were forcibly evacuated. As the focus of this study was on the treated sludge rather than the pyrolysis gas, the primary gas was immediately combusted in a separate combustion chamber.

The pH values of raw and treated sludges were measured per EN 15933 protocol. Total concentrations of toxic elements (As, Cd, Cr, Cu, Ni, Pb, Zn) were determined using EPA methods 3051a and 3052, involving acid digestion ($HNO_3 + HCl + HF$) in a microwave system (Anton Paar, Multiwave PRO). Elemental concentrations were analysed via inductively coupled plasma optical emission spectrophotometry (ICP-OES, iCAP 7000 series, Thermo Scientific) or inductively coupled plasma mass spectrometry (ICP-MS, iCAP Q, Thermo Scientific) depending on concentration levels. Mercury content was assessed with a single-purpose atomic absorption spectrophotometer (AMA 254, Altec), involving thermal decomposition of the sample to generate mercury vapor.

The extractability of potentially toxic elements from the sludges was evaluated in accordance with three different standardized waste characterization methodologies. Specifically, i) the compliance test using deionized water at L/S ratio of 10 L/kg for 24h leaching (EN 12457-4, 2003) as employed, proceeding to increasing extractant strengths for ii) the Toxicity Characteristic Leaching Procedure (TCLP) (US EPA, 1992) using acetic acid solution at L/S ratio of 20 for 18 h, and iii) the Synthetic Precipitation Leaching Procedure (SPLP) (US EPA, 1994) with a mixture of H_2SO_4/HNO_3 at a ratio of 60/40 wt% and at L/S ratio of 20 for 18 h.

2.2. Treatments and experimental design

The Department of Environmental Geosciences at the Czech University of Life Sciences Prague maintains agricultural test plots located in Central Bohemia, specifically at coordinates N 50°26′29.25528, E 13°29′9.54672 (referred to as site 1), and 50°36′41.6″N 14°25′09.5″ E (referred to as site 2). These plots serve as the experimental sites for the study. Composted or pyrolysed sludges were applied to randomized 1 m^2 experimental plots' surface layer (~15 cm). The application rate was

0.5 kg dry matter per plot, aligning with the maximum permissible dose of 5 tons of sludge per hectare specified in Decree No. 273/2021 Coll, 2021 on the details of waste management. Before field application, the actual moisture content of composted sludges was not adjusted (to keep the composts fresh), while pyrolysed sludges underwent activation in water for a week (500 g of sludge char in 2 L of tap water), followed by decantation to increase the porosity and surface area of the sludge char. To ensure a uniform blend, the freshly composted (CS1-CS5) or wet pyrolysed sludges (PS1-PS5) were carefully mixed with soil using manual techniques with a trowel. Winter wheat (*Triticum aestivum* L.) was promptly sown in autumn 2021 to germination, followed by harvesting in summer 2022.

Soil sampling occurred one year after treatment application. Five soil samples from each plot were collected at a depth of approximately 20 cm, which represents the arable layer of the soil and combined into one composite sample in a polypropylene plastic bag. The collected soil was thoroughly mixed for homogeneity, air-dried, and sieved through a 2 mm stainless steel sieve. Plants were harvested, and roots were carefully separated from aboveground biomass. Roots were washed with demineralised water and further cleaned using an ultrasonic water bath sonicator to eradicate soil particles. After cleaning, plant materials were air-dried in a glasshouse and individually milled to produce homogenised fine materials for further analysis.

2.3. Analysis of basic soil parameters and potentially toxic elements in soil and plant materials

Soil parameters such as pH, cation exchange capacity (CEC), and organic matter content influence the release, adsorption, and speciation of metal(loid)s in sludges (Shaheen et al., 2013; Silveria et al., 2003). Therefore, the basic soil parameters of the two experimental sites were determined and are depicted in Table S2. Soil pH was measured using demineralised water and a 0.01 M $CaCl_2$ solution in a 1:5 (v/v) ratio. The readily exchangeable fraction of macro and micronutrients was determined with 0.01 M $CaCl_2$ (Houba et al., 2000). Total carbon (TC) and total inorganic carbon (TIC) levels were quantified using a carbon analyzer (TOC-L CPH, Shimadzu-SSM 5000A, Japan), with total organic carbon (TOC) content calculated from TC and TIC values. Exchangeable cations and effective CEC were determined using the $BaCl_2$ extraction method proposed by Schwertfeger and Hendershot (2009).

The pseudo-total concentrations of potentially toxic elements (As, Cd, Cr, Cu, Ni, Pb, and Zn) in soils were determined via digestion with *aqua regia* (HCl and HNO_3 mixture) at 200 °C, and in plant materials (roots, shoots, and grains) via digestion with HNO_3 and H_2O_2 in a microwave reaction system (Anton Paar, Multiwave PRO). All material was analysed by ICP-OES or ICP-MS (similar to sludge materials) and selected based on concentration levels.

2.4. Analysis of organic contaminants in sludges, soils, and plant materials

The PAHs and PCBs were extracted from the sludges and soil samples with acetone, and the resulting extracts were analysed on a liquid chromatograph with an electron capture detector (GC-EDC Agilent 6890). The sludges, soils, and plant materials were extracted for PPCPs, EDCs, and PFCs using an Accelerated Solvent Extractor ASE 200 (Dionex; Plaiseaut, France) with heated methanol as the extraction solvent (80 °C, 10.3 MPa, three extraction cycles with 5 min static periods). The PPCPs and EDCs were analysed using liquid chromatography-mass spectrometry (LC-MS/MS) (Agilent 6470 Triple Quadrupole) (Cimetiere et al., 2013). For PFC analysis by LC-MS, the concentrated methanol extract was acidified with formic acid. Elution was performed with 1% formic acid in methanol from the Solid Phase Extraction Cartridge (SPE Superclean), followed by concentration under nitrogen before analysis. Procedural blanks using uncontaminated sea sand ensured quality control (Semerád et al., 2020).

2.5. Statistical treatment

Statistical analyses were conducted using nonparametric one-way ANOVA for individual samples with IBM SPSS Statistics 28 software, separately for each sludge type. Pairwise comparisons were performed when the null hypothesis was rejected at the significant level ($P = 0.05$). The null hypothesis was tested using the Kruskal-Wallis one-way ANOVA test or Mann-Whitney *U* test, depending on the number of samples. Graphs were generated using software R 4.3 (www.R-project.org).

3. Results and discussion

3.1. Characterization of selected sewage sludges

3.1.1. Leaching of potentially toxic elements

The basic characteristics and the concentrations of major alkali elements of the individual raw and treated sludge samples are shown in Table S3. A significant increase in pH of pyrolysed sludges was observed, attributed to the thermal destruction of acidic functional groups and the release of alkali elements (Ca, Mg, K, Na) from organic constituents during the pyrolysis process (Al-Wabel et al., 2013; Weber and Quicker, 2018). Table 1 delineates the concentrations of As, Cd, Cr, Cu, Hg, Ni, Pb, and Zn in raw and treated sludges, alongside regulatory limits outlined in Directive 86/278 EEC and the prescribed limits established within the Czech Republic (Decree No. 273/2021 Coll, 2021) for sludge management. Specific criteria by the Czech Ministry of Agriculture (Decree No. 474/2000 Coll, 2000) apply to composted sludges and pyrolysis-derived products for agricultural use. Total risk element concentrations were approximately similar across raw sludges, except for Cu and Ni in S3. All metals fall within Directive 86/278/EEC limits for S1, S2, S4, and S5, with Cu and Ni in S3 decreasing after composting due to dilution by biomass. Composting can either concentrate or dilute metal concentrations due to leaching or organic matter decomposition (Ciavatta et al., 1993; Zorpas et al., 2003). Similar to prior research (Walter et al., 2006; Zheng et al., 2007), our study found composting to elevate Cd, Ni, and Pb concentrations. The biomass mixture used for composting exceeded limits for Cd and Zn under Decree No. 474/2000 Coll., 2000 (Table S4). Previous studies (Garcia et al., 1995) similarly noted increased metal concentrations post-composting due to mineralization. Mercury levels were significantly reduced after pyrolysis treatment via volatilization, while metals (Cu, Ni, Zn) were enriched due to organic compound decomposition and volatile loss at pyrolysing temperatures (de Souza Souza et al., 2021; Devi and Saroha, 2014).

Leachate pH values from the EN 12457-4 test ranged from 6.2 to 7.0, 6.4–7.3, and 9.6–11.9 for raw, composted, and pyrolysed sludges, respectively. Composting resulted in increased extractability compared to raw sludges, particularly evident for Cd, Cr, and Pb both for water and TCLP extracts (Fig. 1) due to changes in total concentrations (Table 1) and chemical speciation with bulking biomass. Conversely, composting and pyrolysis significantly reduced As, Cu, and Ni extractability in water extracts (Fig. 1a–j, m), with no significant change observed for Zn in water extracts (Fig. 1s). The reduced extractability following pyrolysis is attributed to the rather strong bonding of risk elements in the pyrolysed material compared to the raw sludge material, which limits their availability in aqueous solutions (Mitzia et al., 2024).

The TCLP test exhibited significant variability across elements, individual sludge samples, and their respective treatments (Fig. 1b–e, h, k, n, q, t). Notably, pyrolysis led to a significant reduction in potential extractability only for As (Fig. 1b), while pyrolysis led to a significant increase in the extractability of Cd and Pb (Fig. 1e and q). Leachates from all samples, including pyrolysed sludges, displayed a slightly acidic to neutral pH range. Specifically, pH values ranged from 4.7 to 5.7 for raw sludges, 5.3–5.5 for composted sludges, and 5.3–6.8 for pyrolysed sludges. Such low pH values can explain the increased metal(loid) extractability in acetic acid solution for the treated sludges compared to

Table 1

Total concentration of metal/metalloids in raw and treated sludge materials as mean ± standard deviation ($n = 3$) (RS - Raw Sludge, CS - Composted Sludge, PS - Pyrolysed sludge) Values exceeding the limits for raw sludges[a], composted sludges[b] and pyrolysed sludges[c] to be used in the Czech Republic are highlighted in bold.

Sludge No.	Treatment	As (mg/kg)	Cd (mg/kg)	Cr (mg/kg)	Cu (mg/kg)	Hg (mg/kg)	Ni (mg/kg)	Pb (mg/kg)	Zn (mg/kg)
Directive 86/278/EEC Sludge		**N/A**	**20–40**	**N/A**	**1000–1750**	**16–25**	**300–400**	**750–1200**	**2500–4000**
Limit – RS[a]		**30**	**5**	**200**	**500**	**4**	**100**	**200**	**2500**
Limit – CS[b]		**30**	**2**	**100**	**100**	**1**	**50**	**100**	**300**
Limit – PS[c]		**30**	**5**	**100**	**N/A**	**0.5**	N/A	**100**	**N/A**
1	**RS**	3.37 ± 0.39	1.05 ± 0.03	37.9 ± 2.54	229 ± 4.35	1.51 ± 0.21	23.3 ± 0.70	31.1 ± 6.81	736 ± 23.6
	CS	3.03 ± 0.03	**2.63 ± 0.16**	77.8 ± 3.79	66.2 ± 0.31	0.13 ± 0.01	38.9 ± 1.57	53.9 ± 0.55	290 ± 9.03
	PS	6.51 ± 0.12	1.66 ± 0.28	15.5 ± 3.84	332 ± 28.2	0.002 ± 0.001	49.6 ± 1.53	27.9 ± 3.46	1428 ± 9.78
2	**RS**	2.46 ± 0.01	0.75 ± 0.01	30.9 ± 0.73	144 ± 2.17	0.68 ± 0.04	18.8 ± 0.16	11.8 ± 0.25	803 ± 11.5
	CS	1.38 ± 0.23	1.38 ± 0.30	32.5 ± 7.43	**133 ± 6.11**	0.37 ± 0.03	34.3 ± 0.60	84.9 ± 15.0	**454 ± 13.6**
	PS	7.58 ± 3.36	1.58 ± 0.14	39.4 ± 4.85	190 ± 36.7	<0.001	46.8 ± 2.17	22.3 ± 3.10	2155 ± 70.2
3	**RS**	6.12 ± 0.19	1.04 ± 0.09	49.2 ± 4.34	**1263 ± 117**	1.41 ± 0.32	**422 ± 31.3**	39.8 ± 5.26	905 ± 47.2
	CS	1.24 ± 0.02	1.22 ± 0.08	33.7 ± 3.87	**635 ± 23.4**	0.70 ± 0.03	**216 ± 4.16**	21.8 ± 4.32	**553 ± 13.3**
	PS	8.65 ± 5.21	3.19 ± 0.19	25.1 ± 4.36	1776 ± 229	0.005 ± 0.001	692 ± 50.3	20.1 ± 0.57	1717 ± 114
4	**RS**	5.36 ± 0.10	0.92 ± 0.01	48.7 ± 1.62	261 ± 9.56	1.87 ± 0.16	49.9 ± 1.64	31.6 ± 9.19	930 ± 72.3
	CS	2.43 ± 0.03	**2.23 ± 0.03**	55.4 ± 1.32	**101 ± 2.17**	0.46 ± 0.08	35.0 ± 0.85	45.2 ± 4.70	**395 ± 1.62**
	PS	12.5 ± 4.13	3.06 ± 1.36	47.2 ± 20.9	410 ± 45.5	<0.001	115 ± 2.70	28.8 ± 12.1	1732 ± 17.0
5	**RS**	12.1 ± 0.44	1.37 ± 0.01	50.7 ± 4.12	209 ± 3.20	1.76 ± 0.19	24.7 ± 0.41	22.8 ± 3.63	843 ± 12.9
	CS	2.95 ± 0.43	**2.36 ± 0.33**	55.7 ± 17.4	78.7 ± 4.45	0.18 ± 0.01	31.9 ± 0.37	51.4 ± 11.9	**378 ± 3.10**
	PS	10.7 ± 2.32	2.03 ± 0.18	27.2 ± 5.23	268 ± 29.2	<0.001	53.8 ± 2.80	36.2 ± 8.87	1593 ± 48.9

[a] Decree 273/2021 coll., limit values in sludge for usage in agricultural lands, set by the Ministry of Agriculture in the Czech Republic.

[b] Decree 474/2000 coll., limit values for substrates, set by the Ministry of Agriculture in the Czech Republic.

[c] Decree 474/2000 coll., limit values for products obtained by pyrolysis, set by the Ministry of Agriculture in the Czech Republic.

water leachates. This decrease in pH reduces the number of negatively charged sites available for metal cation sorption. However, these concentrations are under the maximum concentration of contaminants for toxicity characteristics stipulated in the TCLP test, which are 0.5, 1.0, 5.0, and 5.0 mg L-1 for As, Cd, Cr, and Pb, respectively (US EPA, 1992).

The synthetic precipitation leaching procedure (SPLP) aimed to elucidate the mobility of monitored toxic elements within the sludge under acidic precipitation, simulating an additional plausible environmental scenario. Results from the SPLP leaching tests, depicted in Fig. 1c,f, i, l, o, r, u, exhibited different trends compared to demineralised water leachates (EN 12457-4). The pH values of the leachates of raw, composted, and pyrolysed sludges ranged from 6.3 to 7.1, 6.5–7.2, and 10.7–12.4, respectively, for all samples. While the pH of raw and composted sludges was similar to demineralised water leachates, the potential extractability of monitored metal(loid)s of composted sludges was higher for As, Pb, and Zn (Fig. 1c–r, and u). Pyrolysis notably decreased the potential extractability of As and Cu (Fig. 1c–l) compared to composted counter part. However, for Cd, Cr, Pb, and Zn, potential extractability from pyrolysed sludges increased compared to raw. This phenomenon is attributed to the amphoteric characteristics of these elements, leading to the formation of hydroxyl complexes under alkaline conditions. A similar trend in Pb release under alkaline conditions was previously observed by Król et al. (2020), who suggested that the formation of soluble anionic species, as explained by Cappuyns et al. (2014), also influences increased metal mobility in highly alkaline environments. However, in a soil system, the situation differs due to short contact times in artificial material-solution systems. Application of pyrolysed sludges into soil did not significantly affect alkalinity at either location (Table 2). Nevertheless, potential leachability trends were examined to assess material risks upon application. Considering the benefits and potential drawbacks of treated sludges across all three leaching experiments (Table S5), it is worth noting that pyrolysis notably influences the potential extractability of As, Cu, and Ni, while neither composting nor pyrolysis of sewage sludge can be considered successful treatment strategies for immobilisation of Cd, Cr, and Pb.

3.1.2. *Organic contaminants in selected sewage sludge*

The total concentrations of PAHs in the five selected raw sludges remained below the limit value of 10 mg kg^{-1}. The highest concentrations were observed in sludge samples 4 and 5, at 8.83 and 9.50 mg kg^{-1}, respectively (Table S6). Following composting, a significant reduction in total PAH concentrations was evident, with reductions of 61.5% and 27.6% observed, respectively. Composting had a minor influence on samples with low PAH concentrations (e.g., samples 1 and 3), while the PAH concentration in sample 2 slightly increased after composting. Subsequent pyrolysis significantly decreased total PAHs, exceeding a 90% reduction across all selected raw sludges.

While Directive 86/278/EEC (CEC, 1986) lacks specific limit values for PCB in sludges used in agriculture, various national regulations exist (Urbaniak and Wyrwicka, 2017; Abad et al., 2005). In our study, the sum of seven PCB congeners in all raw and treated samples was below both EU and national limit values (Table S6). However, the impact of composting on PCB concentrations remains inconclusive.

The untreated sewage sludge samples were analysed for emerging micropollutants, encompassing 37 PPCPs, 14 EDCs, and 33 PFCs compounds. Detected micropollutants are listed in Table S7. Telmisartan and triclosan emerged as the most abundant PPCPs across all untreated sludges, constituting 62% of the total PPCPs. Triclosan, a widely utilised antimicrobial agent with a European consumption of 350 tons annually (Singer et al., 2002), has been found in German and US sludges at concentrations ranging from 0.4 to 12.0 and 0.53–15.6 mg kg^{-1}, respectively (Bester, 2003; Mcavoy et al., 2002). In our study, selected sludges contained from 0.11 to 0.83 mg kg^{-1}, comparatively lower than previous reports (Singer et al., 2002; Yang and Metcalfe, 2006). Bisphenol A (BPA) emerged as the most abundant EDC in untreated sludges, with an average concentration of 632 μg kg^{-1}, consistent with ranges reported by Ye et al. (2012) for EDC occurrence in WWTPs. Stasinakis et al. (2008) also noted BPA concentrations ranging from 560 to 1750 μg kg^{-1} in 27 sludge samples collected from five treatment plants in Greece.

The compound 5:3 fluorinated telomer acid (5:3 FTA) emerged as the most abundant PFC compound in selected untreated sludges. Pyrolysis treatment proved highly effective for removing PPCPs, EDCs, and PFCs, achieving reductions from 99.9% to below the detection limit for the compound (Fig. 2). Moško et al. (2021) demonstrated that pyrolysis at 600 °C efficiently removes organic micropollutants from stabilised sludges. Composting, as expected, had a less significant impact on micropollutant degradation than pyrolysis. On average, composting

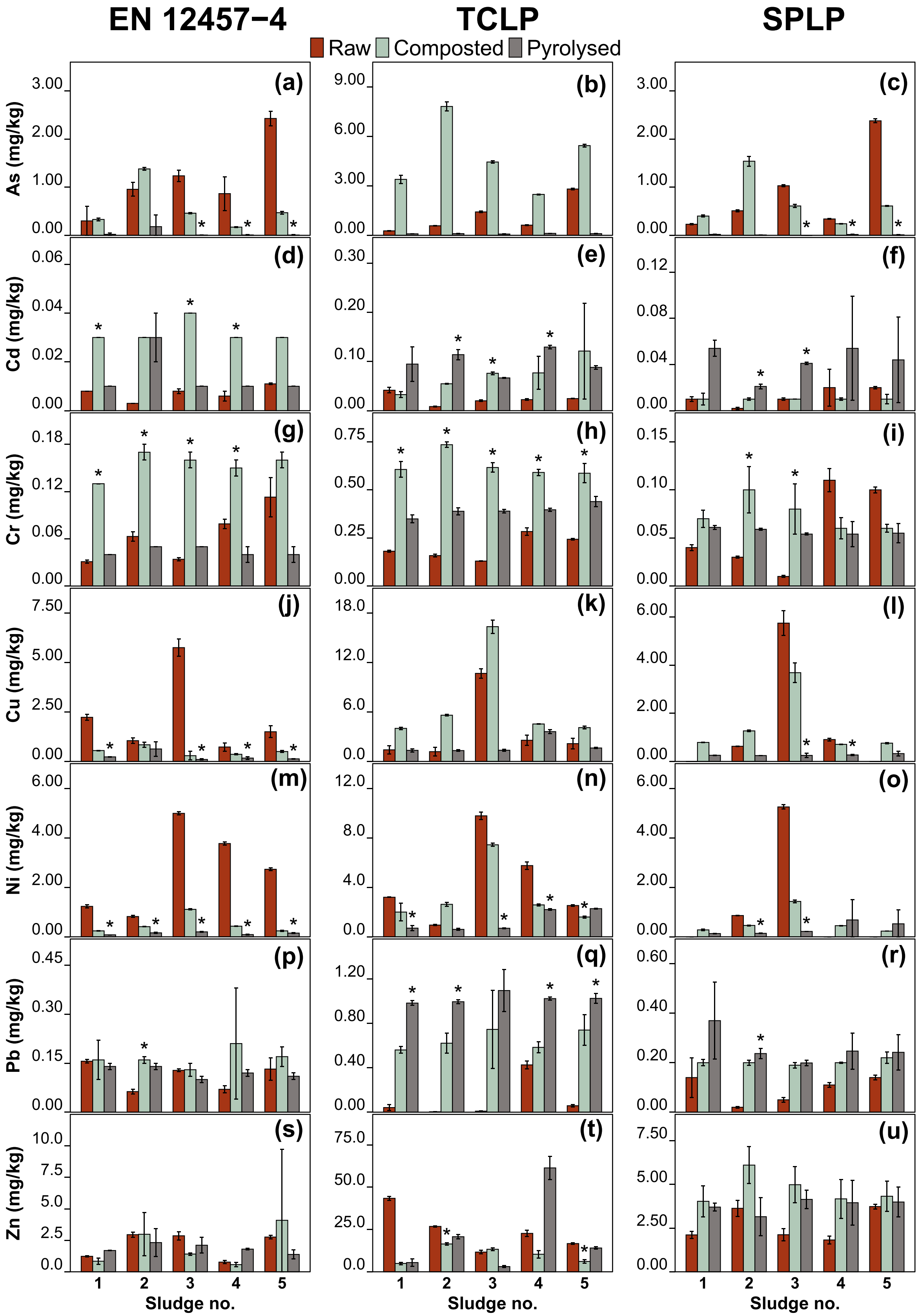

Fig. 1. Leaching characteristics of risk elements (As, Cd, Cr, Cu, Ni, Pb and Zn) for raw, composted, and pyrolysed sludges according to EN 12457-4, TCLP and SPLP leaching tests as mean ± standard deviation. Statistical analysis was performed separately for every sludge type; data with * represent statistically different values compared to the raw sludge ($P < 0.05$) ($n = 3$).

reduced PPCPs by 63.4% across all sludge samples, while EDCs decreased by 75%–87% in S1, S3, S4, and S5 samples. However, there was a significant 26.4% increase in EDCs (Daidzein, Genistein, and Estriol) in composted sludge 2 compared to untreated counterpart (Fig. 2), likely due to the bulking biomass (Table S4). BPA reduction percentages ranged from 28% to 88% through composting, consistent with findings by Abril et al. (2020) showing decreased or stable BPA concentrations after composting. In the case of PFCs, composting reduced total concentrations by 77%–99%. Estrone, a female hormone, was undetected in raw sludge samples but found in composted samples 2, 3, and 4 at 20.9, 14.9, and 15.1 μg kg-1 concentrations, respectively. Similar results were reported by Shafrir and Avisar (2012), indicating estrone presence in composted biosolid but not in the original material, possibly originating from the initial compost mix.

Table 2

Effects of altered SS on selected soil quality indicators measured for the surface (0–15 cm) soil of site 1 and 2 (mean ± standard deviation, (*n* = 3). Data with * represent statistically different values compared to the control, and data with ** represent statistically different values between treatments within the specific sludge type ($P < 0.05$) ($n = 3$).

SS No.	Treatment	Site 1			Site 2		
		pH (H_2O)	pH ($CaCl_2$)	TOC (%)	pH (H_2O)	pH ($CaCl_2$)	TOC (%)
Control		7.78 ± 0.01	7.23 ± 0.01	3.48 ± 0.04	6.34 ± 0.02	5.78 ± 0.01	1.63 ± 0.02
1	**CS**	7.40 ± 0.02	6.85 ± 0.02	3.63 ± 0.12	6.47 ± 0.05	5.96 ± 0.01	1.77 ± 0.04
	PS	7.50 ± 0.05	7.00 ± 0.01	3.40 ± 0.07	5.99 ± 0.03	5.45 ± 0.01	1.99 ± 0.06
2	**CS**	7.70 ± 0.03	7.14 ± 0.01	3.27 ± 0.08	6.36 ± 0.01	5.91 ± 0.01	1.91 ± 0.01
	PS	7.63 ± 0.01	7.20 ± 0.02	3.68 ± 0.22	6.12 ± 0.01	5.61 ± 0.02	1.96 ± 0.05
3	**CS**	7.78 ± 0.02	7.22 ± 0.01	3.40 ± 0.04	6.34 ± 0.01	5.89 ± 0.02	1.89 ± 0.00
	PS	7.30 ± 0.03	6.90 ± 0.03	3.33 ± 0.04	6.19 ± 0.03	5.68 ± 0.03	1.94 ± 0.04
4	**CS**	7.73 ± 0.01	7.18 ± 0.01	3.36 ± 0.04	6.32 ± 0.02	5.82 ± 0.00	1.85 ± 0.01
	PS	7.45 ± 0.01	7.01 ± 0.00	3.24 ± 0.04	6.19 ± 0.03	5.77 ± 0.01	1.90 ± 0.05
5	**CS**	7.81 ± 0.00	7.28 ± 0.04	3.21 ± 0.03	6.36 ± 0.03	5.87 ± 0.01	1.81 ± 0.01
	PS	7.60 ± 0.02	7.19 ± 0.02	3.54 ± 0.06	6.45 ± 0.03	5.90 ± 0.00	1.66 ± 0.04

3.2. Risks associated with the application of sewage sludge to agricultural soils

3.2.1. Soil and plant accumulation of metal(loid)s

Table S2 presents the major soil parameters of the two experimental plots, while Fig. S1 displays the concentrations of metal(loid)s (As, Cd, Cr, Cu, Ni, Pb, Zn) and their significant variations between the sites. The elemental concentrations of the control soil sample reflect the background values of each element. Site 1 exhibited higher concentrations of elements (As, Cd, Cr, Cu, Ni, Pb, Zn) compared to site 2, regardless of sludge application. On site 1, no negative impact of sludge application on total metal(loid) concentrations was observed due to the higher background concentrations of the original soils. However, the PS5 plot showed elevated Zn concentration (Fig. S1a). Assessing the effect of sludge application at site 2, a significant increase in total risk elemental concentrations (As, Cd, Cr, Cu, Ni, Pb, Zn) was observed in all composted sludge-treated plots (CS1-CS5) (Fig. S1b) compared to the control. Notably, there was a significant increase (p = 0.007) in Zn concentrations in all plots at site 2 treated with composted sludges, while Cd concentrations did not show a significant difference compared to the control. Chromium exhibited a significant increase in total concentrations in all composted sludge-amended soils except for CS1, whereas As showed a significant increase of total concentration only in soils treated with composted sludges CS1, CS3, and CS4. Zn was the only element showing a significant increase in total concentration in all selected five sludges in the composted treatment strategy. However, in general, there

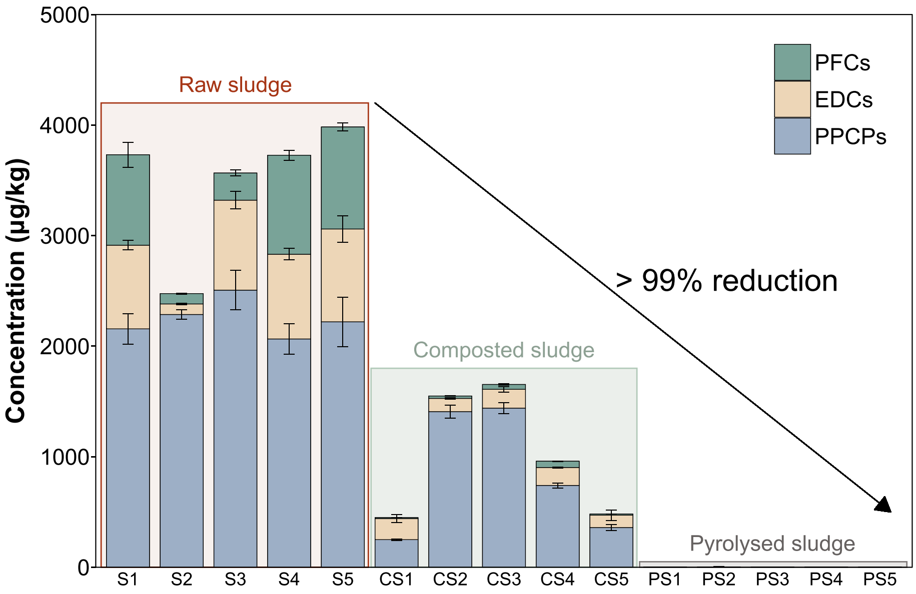

Fig. 2. Effect of sludge treatment strategy on the total concentration of PPCPs, EDCs, and PFCs (raw sludges; S1–S5, composted sludges; CS1-CS5, pyrolyzed sludges; PS1-PS5).

was no significant difference in Zn extractability with 0.01 M $CaCl_2$ in soils treated with sludge compared to control on site 1 (Table S8). The applied composted variant of sludge 2 showed a significant decrease in Cu and Ni concentration compared to the control soil (Table S8). Previous studies reported higher Zn leaching in soils treated with biosolids than in untreated soils, for example, Sukkariyah et al. (2005), where ~5–40 times higher application rates of biosolids were used than in our study.

At site 2, a significant decrease in Ni extractability was observed in the pyrolysed sludge-amended soil of sludge 5 compared to the control (Table S8). Several authors have reported the immobilisation of metals in pyrolysed sludges through various mechanisms, and Mitzia et al. (2024) recently evaluated the immobilisation potential for a wide range of metal(loid)s using the same set of pyrolysed sludges as used in the present study. Biochar stabilises risk metal content in soil due to its surface heterogeneity, diverse functional groups, and large surface area, facilitating heavy metal adsorption onto soil particles. Another mechanism involves the micro-porous structure of biochar, promoting the physical encapsulation of toxic elements (Irfan et al., 2021; Sun et al., 2018).

In summary, the immobilisation of metal(loid)s depends on the origin of sewage sludges, treatment strategy, and soil type. At site 1, both composted and pyrolysed amendments positively affected the immobilisation of Cu in all five sludges, whereas at site 2, it varied among the sludge number and treatment. Composted amendments showed greater success in immobilising Ni, Pb, and Zn in either location than pyrolysed ones. This is attributed to the concentrating effect on metal(loid)s after pyrolysis, as discussed in section 3.1.1 (Table 1).

The variation in metal(loid) accumulation in different plant parts across treatments is detailed in Tables S9 and S10. Across root, shoot, and grain samples, metal(loid) concentrations follow the order of Cu > Ni > Zn > Cr > Pb > As > Cd > Hg in roots; Cu > Ni > Zn > Cr > Pb > As > Cd > Hg in shoots; and Zn > Cu > Ni > Cr > Pb=Cd > As > Hg in grains. Zn concentrations were consistently higher in grains than in roots and shoots, indicating greater translocation of Zn towards aerial parts of winter wheat (Fig. 3). This aligns with previous findings by Dang et al. (2010), demonstrating the highest Zn accumulation in wheat grains at maturity. However, Zn accumulation in grains did not differ significantly between treatments. Notably, a significant decrease in Zn concentrations in root samples of pyrolysed sludge-amended soils at site 1 confirmed Zn immobilisation by pyrolysed sludges, reducing its bioavailability. Arsenic and Ni concentrations in plant parts showed no significant differences compared to control soils in both locations. Despite Cu concentrations being higher in roots than Zn, Cu concentrations in grains were much lower than Zn, indicating comparatively lower mobility of Cu compared to Zn. These results are consistent with previous studies (Planquart et al., 1999; Zheljazkov and Warman, 2004). Significant differences ($p < 0.05$) in Cd bioaccumulation in roots were observed between composting and pyrolysis treatments for biosolids 1, 2, 3, and 4 at site 1 (Table S9 and Fig. 3). Similarly, increased Cd bioaccumulation in plant roots after composted sludge application to soil was reported by (Vítková et al., 2024). Arsenic, Cd, Pb, Ni, and Cu concentrations in grains did not exceed WHO/FAO safe limits for food (Tables S9 and S10) at both locations, except for composted sludge 3 at site 1, where As and Cd concentrations exceeded permissible limits. Zinc concentration in grains from site 1 exceeded permissible limits, while metal(loid) concentrations in grains from site 2 were below permissible limits, including Zn. Metal(loid)s exhibit differential mobility within plants due to their distinct chemical properties and physiological responses. As an essential micronutrient, Zinc is actively transported to upper plant parts, where it is utilised in metabolic processes. Conversely, Cd, a non-essential and toxic element, tends to accumulate in roots to minimise its translocation to aboveground tissues (Haider et al., 2021; Khanna et al., 2022). This phenomenon is clearly visible in our study (Fig. 3). Guidelines for safe limits for food/cereals by WHO/FAO are provided in the second row of Tables S9 and S10 for reference.

3.2.2. *Soil and plant accumulation of micropollutants*

Following 12 months of sludge application, no PFCs or EDCs were detected in soils from sites 1 and 2. Only the antimicrobial substance triclosan and cardiovascular substance telmisartan were found at site 1, with telmisartan showing the highest concentration. However, the total concentration of PPCPs was below 10 μg kg^{-1} in all sludge treatments except for composted treatment in S2, which measured 14.7 ± 0.58 μg kg^{-1}. A previous field study by Lozano et al. (2010) in northern Virginia, USA, found triclosan concentrations ranging from 23.6 to 66.6 μg kg^{-1} dry weight in soil one year after a single sludge application. At site 1, triclosan reduction rates in composted sludge-amended soils ranged from 30% to 60%, while in pyrolysed sludge-amended soils, the reduction was 30%–74%. Triclosan concentrations at site 2 were below the detection limit. These results are consistent with other studies reporting up to an 80% decrease in triclosan concentration after one year of sludge

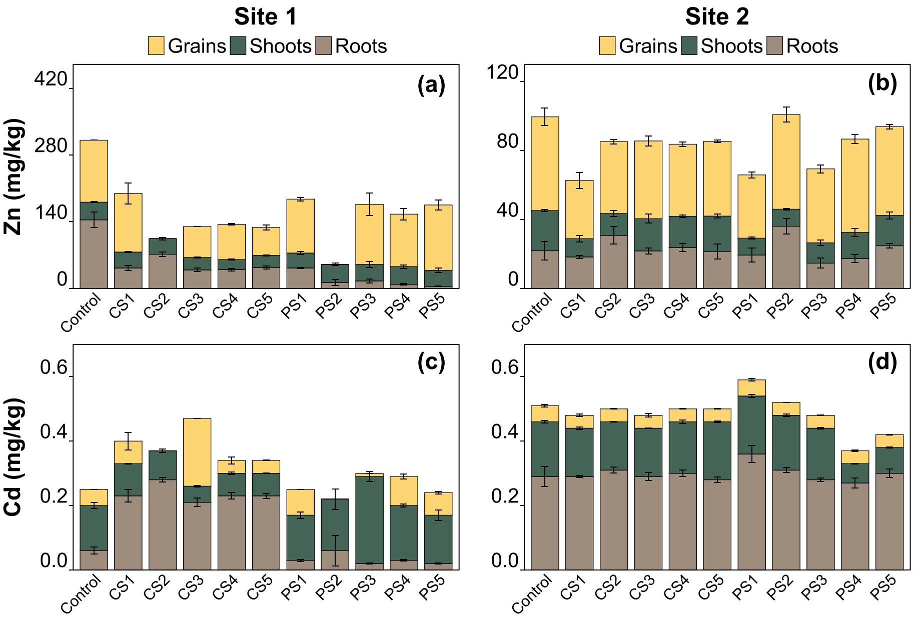

Fig. 3. Concentrations of Zn and Cd in different plant parts of winter wheat in site 1 and site 2; composted sludge (CS1-CS5), pyrolysed sludge (PS1-PS5).

application (Butler et al., 2011; Marti et al., 2013).

No PFCs or EDCs were detected in any plant materials (root, shoot, grains) at either site. When treated sludge was applied to the field, it was mixed with the soil, leading to the dilution of all contaminants present in the sludge. Environmental factors such as temperature fluctuations, natural degradation, and leaching of residual PFCs and EDCs further reduced their concentrations (Masinga et al., 2024). Consequently, the bioavailability of PFCs and EDCs was significantly decreased. A field experiment conducted with an application rate of 4.5 tons per hectare demonstrated that the land application of biosolids could lead to the contamination of PFAS in soils and crops under field conditions (Wen et al., 2014). However, it is important to note that the mentioned study used air-dried biosolids directly from a sludge disposal plant without employing pyrolysis or composting treatment methods. Although 22 compounds of PPCPs were found in untreated sludges (Table S7), only four were found in plants from both locations: caffeine, carbamazepine, diclofenac, and telmisartan. Caffeine, naturally synthesised in many plants, is commonly consumed as a stimulator of the central nervous system (Ashihara and Suzuki, 2004). The highest accumulation in vegetative plant parts was observed in the following decreasing order: roots > shoots > grains. Diclofenac and carbamazepine were detected only in the grains from both locations. According to Fent et al. (2006) and Shenker et al. (2011), carbamazepine and diclofenac are primarily recovered from above-ground parts of the plant, with slow passage from roots to aerial tissues due to high hydrophobicity. Despite significantly lower concentrations of PPCPs detected in pyrolysed sludges (Fig. 2),

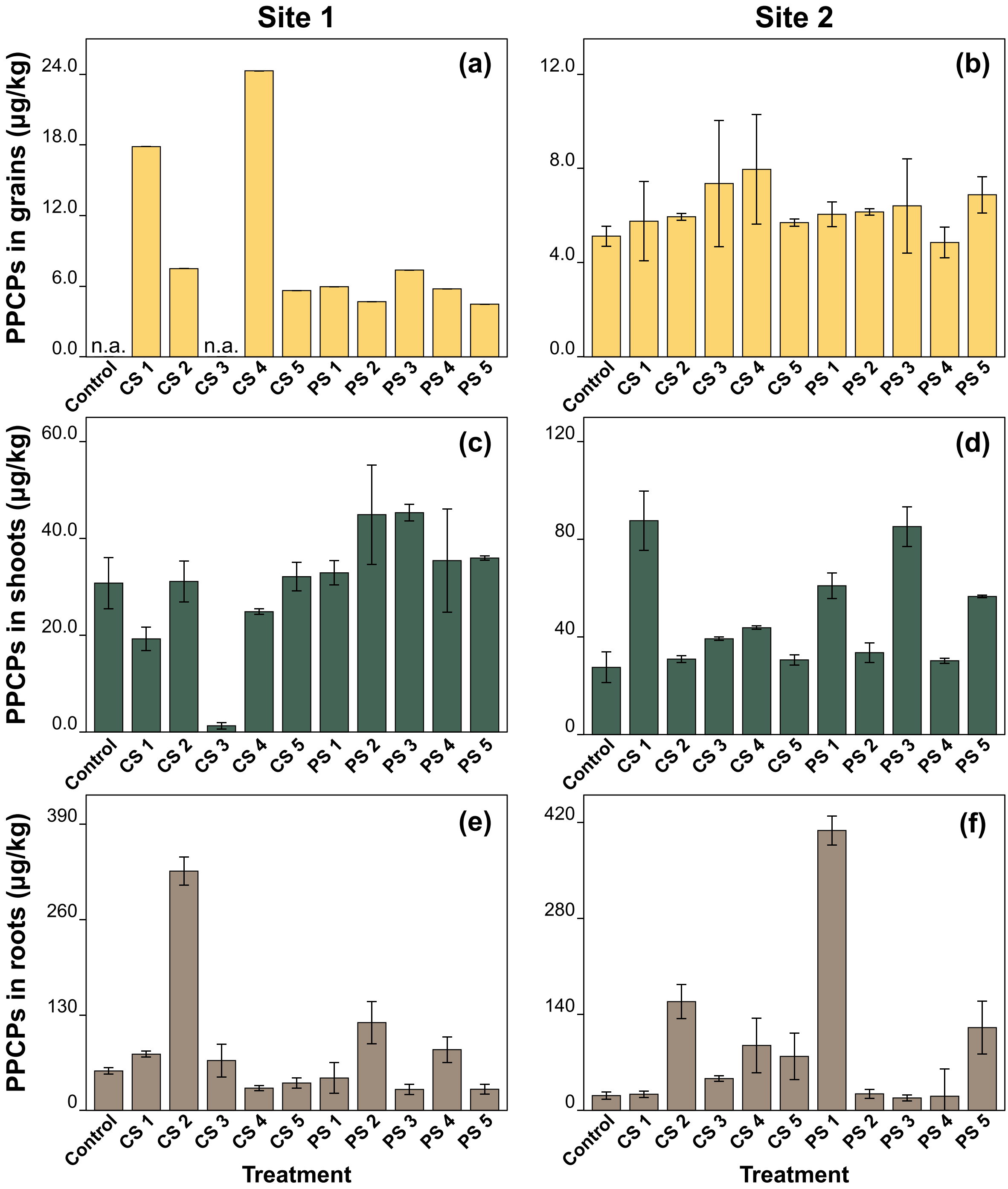

Fig. 4. Total concentrations of PPCPs in different plant parts with treated sludges at site 1 (a) site 2 (b); composted sludge (CS1-CS5), pyrolyzed sludge (PS1-PS5).

considerable concentrations were found in plant materials, especially in root samples at both sites (Fig. 4). This increase was attributed primarily to naturally occurring caffeine rather than other PPCPs. Caffeine is regarded as an emerging contaminant in many ecosystems, including marine organisms (Vieira et al., 2022). In summary, PPCPs were the only detectable organic contaminants in site 1 soil after one year of sludge application, while no organic contaminants were detected in site 2 soil. Therefore, applying pre-treated sewage sludges according to the current recommended dosage (5 tons of sludge/dry weight basis per hectare) has no considerable drawbacks in terms of organic contaminants.

In addition to the potentially toxic elements and emerging organic contaminants, in another experiment conducted on the same localities using the same materials, the application of treated sludges appears to have improved soil health indicators such as glomalin, effective CEC, and permanganate oxidizable carbon periodically, though the impact is site-specific (Wickramasinghe et al., 2024).

4. Conclusions

This study applied composted and pyrolysed sewage sludges to two agricultural field soils to investigate inorganic and organic contaminant fate in the soil environment. Pre-processing of sludges, a necessary precursor to land application in most countries (including the Czech Republic), affected their basic properties. This included reducing bioaccumulation of metal(loid)s in wheat grains to below the limit values set by FAO/WHO. Composting and pyrolysis heavily reduced micropollutants (PPCPs, EDCs, PFCs), though many effects on the fate of organic contaminants were soil-specific. The findings of this study underscore the intricate and context-dependent nature of contaminant dynamics within soil ecosystems, highlighting the necessity for further investigation across diverse soil types and crop varieties to develop a comprehensive understanding. Nevertheless, the study provides suggestive evidence that composting or pyrolysis of sewage sludges could serve as a viable strategy to preserve the advantageous effects of sludge application on soils while concurrently mitigating the hazards posed by entrained contaminants. Also, long-term field experiments evaluating the fate and behavior of the contaminants are inevitably needed.

CRediT authorship contribution statement

Niluka Wickramasinghe: Writing – original draft, Investigation, Formal analysis. **Martina Vítková:** Writing – review & editing, Supervision. **Szimona Zarzsevszkij:** Investigation, Formal analysis. **Petr Ouředníček:** Investigation. **Hana Šillerová:** Investigation. **Omolola Elizabeth Ojo:** Investigation. **Luke Beesley:** Writing – review & editing. **Alena Grasserová:** Investigation, Formal analysis. **Tomáš Cajthaml:** Supervision, Project administration, Methodology, Funding acquisition. **Jaroslav Moško:** Investigation, Formal analysis. **Matěj Hušek:** Investigation, Formal analysis. **Michael Pohořelý:** Methodology, Investigation, Funding acquisition, Formal analysis. **Jarmila Čechmánková:** Investigation, Formal analysis. **Radim Vácha:** Supervision, Methodology, Funding acquisition. **Martin Kulhánek:** Investigation, Formal analysis. **Alena Máslová:** Investigation, Formal analysis. **Michael Komárek:** Writing – review & editing, Supervision, 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.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.chemosphere.2024.143289.

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