Occurrence and risk assessment of trace organic contaminants and metals in anaerobically co-digested sludge

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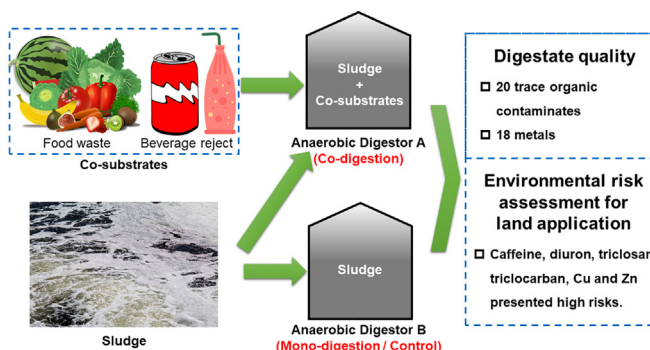[a] School of Agricultural Engineering, Jiangsu University, Zhenjiang 212013, China
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HIGHLIGHTS

- 38 TrOCs and metals quantified in sludges co-digested with beverage and food waste.
- Cola reject resulted in accumulation of caffeine in digestate.
- Bisphenol A significantly increased in food waste co-digestion.
- Six pollutants suggest high environmental risks in sludge-amended soils.
- Inputs to sludge processing should be managed to reduce downstream impacts.

GRAPHICAL ABSTRACT

ARTICLE INFO

ABSTRACT

Anaerobic co-digestion of sludge increases biogas production and maintains anaerobic digestion stability. However, it is unclear whether the addition of co-substrates may increase the concentration of trace organic contaminants (TrOCs) and metals, limiting potential resource recovery opportunities when applied to agricultural land. This study explored the occurrence of 20 TrOCs and 18 metals in wastewater sludge anaerobically co-digested with beverage rejects (cola, beer and juice) and food wastes. TrOCs results showed that cola reject caused an accumulation of caffeine in final digestate. Bisphenol A also significantly increased in food waste co-digestion when compared with the mono-digestion (control). No significant difference in TrOCs was observed in the juice reject co-digestion. Analysis of the metal composition revealed a significant increase in Cr and Al in juice reject co-digested sludge. While restaurant food waste increased concentrations of K and Ca, both of which may be beneficial when applied to land. All metals in this study were below the maximum permissible concentrations specified for agricultural land use in Australia. Environmental risk assessment of sludge when used as soil fertiliser, showed that caffeine, diuron, triclocarban, triclosan, Cu and Zn exhibited high risks, with the largest risk quotient (RQ) posed by caffeine. Estrone and naproxen implied medium risks, and ibuprofen implied a high risk except for the co-digestion using cola reject (RQ = 0.9, medium risk). The results emphasise the importance for wastewater utility operators to understand the impact of co-substrate selection on the quality of sludge to minimise environmental risk from the use of biosolids on agricultural land.

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1. Introduction

Continued global urbanisation and population growth are exerting operational pressure on wastewater treatment plants (WWTPs) management. A large amount of sludge containing residual contaminants is produced during the treatment of municipal wastewater. Hence, it is essential to treat the sludge prior to disposal. Anaerobic digestion (AD) is the process in which microbes decompose organic matter into biogas and digestate in the absence of O_2 (Phan et al., 2018). It is the most widely adopted process for the stabilisation of sludge from WWTPs, enabling simultaneous energy recovery and pollutant removal.

Land application of digested sludge allows the reintroduction of crucial nutrients and add economic value to the sludge that is traditionally considered as a waste product. Wastewater sludge contains major nutrients (N, P, S, K, etc.) and a wide range of trace elements (Cu, Zn, Mn and Mo, etc.). In Australia, 67% of the biosolids produced are directly applied onto agricultural land and 24% are used for landscaping or land rehabilitation (ANZBP, 2019). However, the ubiquitous occurrence of trace organic contaminants (TrOCs) and metal elements has emerged as a considerable risk factor when using sludge and biosolids for agricultural land application (Gonzalez-Gil et al., 2018; Phan et al., 2018).

The removal of contaminants from sludge during wastewater treatment can be limited due to the historical focus on the quality of the liquid stream in wastewater treatment, and the recalcitrant and hydrophobic properties of many contaminants, which favour their partitioning in the solid fractions (Stevens-Garmon et al., 2011). Opportunities for contaminant removal may occur due to microbial transformations in sludge treatment or the removal in centrate when dewatering. However, once applied to land, leaching and/or phytoremediation may aid in the removal and dispersion of contaminants from the biosolids (Muthusaravanan et al., 2018) and may impact the soil ecology. Due to difficulties in contaminant removal from sludge, care should be taken to understand the addition and source of chemicals of concern in wastewater sludge.

Although AD is a versatile biotechnology for the treatment of wastewater sludge, the potential of mono-digestion of waste sludge to generate biogas is usually limited by the imbalanced carbon to nitrogen (C/N) ratio and AD product inhibition (Bong et al., 2018). Anaerobic co-digestion, i.e. simultaneous digestion of two or more organic substrates, is thought to be a feasible strategy to solve these shortcomings. Large amounts of organic wastes from agricultural, municipal and industrial sectors are reported to be appropriate co-substrates since they can balance the substrate nutrient levels to obtain the optimal C/N ratio, adjust pH values, and dilute toxic chemicals to reduce the risk to methanogens, thereby increasing the production of biogas, especially methane (Zhang et al., 2017). A previous study on co-digestion with beverage and food wastes confirmed that methane yield increased proportionally due to the co-substrate addition (Wickham et al., 2019). The authors also reported that the co-substrate did not result in any discernible impact on digestate quality in terms of volatile solids (VS) and total chemical oxygen demand (COD) content (Wickham et al., 2019).

Previous studies on anaerobic co-digestion have mostly focused on the optimisation of operating parameters, such as co-substrate types (Nghiem et al., 2014), mixing ratio (Nghiem et al., 2014), organic loading (Wickham et al., 2018), or pretreatment (Wang et al., 2019; Zhang et al., 2017) to improve the biogas yield and sustain the AD system stability.

While the advantages of co-digestion are clear, challenges exist associated with variability in substrate composition, as well as the handling and sorting of the waste materials (Awe et al., 2018). In addition, as the current research focus for co-digestion has been on digester performance optimisation, the downstream implications and effects on sludge quality and end use opportunities are less well understood. Very few studies have measured the impact of co-digestion processes on sludge reuse on land in terms of TrOC and metal content.

Addition of co-digestion substrates during anaerobic digestion can affect the degradation of certain TrOCs, due to the presence of trace elements and substrates either enhancing or inhibiting certain microbial pathways (Montecchio et al., 2019; Wei et al., 2021). Additionally, some co-substrates may themselves contain contaminants, making them unsuitable for use when the sludge will be applied to land. Bonetta et al. (2014) revealed that Cu, Ni and Zn contents in some co-digested digestate exceeded the maximum limit for fertiliser based on Italian law. Another study examined the effect of the co-digestion ratio between chicken manure and corn stover and found that the concentrations of eight metals (Mn, Zn, Cu, Ni, As, Cd, Pb and Cr) were elevated after co-digestion (Yan et al., 2018). These studies revealed that despite providing improvements in biogas production, the co-digestion of sludge with different co-substrates may lead to an increased likelihood of TrOC and metal contamination when later applied to land. The impact on sludge quality will depend on the variability in feedstock and sludge as well as digester performance, dilution effects and mixing. While characterisation of input substrate concentrations can provide valuable information on substrate suitability, monitoring the final sludge composition is necessary to determine the overall impact on sludge quality and land application.

In this study, the occurrence of 20 TrOCs and 18 metals in the final wastewater sludge were systematically examined to determine the downstream implications following anaerobic co-digestion with a range of beverage reject and food wastes. Variations in resultant sludge concentrations as well as the potential environmental risk caused by the addition of multiple co-substrates were evaluated and compared with anaerobic mono-digestion control.

2. Materials and methods

2.1. Chemicals

Acetonitrile, methanol, dichloromethane, methyl tert-butyl ether (MTBE) and acetone (all of HPLC grade) were purchased from Honeywell Company (Australia). Milli-Q grade ultrapure water was produced by a Direct-Q purification system from Millipore (Australia). Nitric acid (70%) and hydrochloric acid (Trace Metal grades) were purchased from RCI Labscan Limited (Australia).

2.2. Digester operation

AD sludge was collected from a wastewater treatment plant (WWTP) in New South Wales (NSW), Australia, and used as the inoculum at the beginning of the study (200 L for each digester). Primary sludge (or sludge) was also sampled from this plant for the AD feeding operation. Two types of co-substrates, beverage reject and food waste, were adopted in this study. Beverage reject, namely cola, beer and juice drinks, was obtained from a commercial waste collector in NSW. These drinks were damaged, expired or contaminated and thus had to be disposed. Food waste originated from two locations, one from a cafeteria in NSW (denoted as food waste A) and the second from restaurants in NSW (denoted as food waste B). The wastewater sludge, beverage reject, and food waste were all stored at 4 °C in the dark prior to use. Basic characteristics of the wastewater sludge and co-substrates used are listed in Table 1.

Two identical pilot anaerobic digesters were operated in parallel in this study. Each digester consisted of a conical stainless-steel reactor with working volume of 1000 L, a recirculation pump for mixing and a gas holder. The temperature inside the digester was maintained at 35 ± 1 °C by circulating hot water through a water jacket surrounding the digester bottom. The reactors and pipes were wrapped with insulating foam to reduce heat loss. Further details of the digester system are available elsewhere (Wickham et al., 2019).

Prior to the co-digestion experiment, the two digesters (Digester 1 and Digester 2) had reached steady state conditions in terms of volatile solids (VS) removal and biogas production. Afterwards, Digester 1 was conducted over six stages (Table 2), to evaluate the various co-

Table 1
Properties of co-substrates and sludge ($n \geq 5$).

Index	Co-substrates					Sludge
	Cola reject	Beer reject	Juice reject	Food waste A	Food waste B	
TS %	0.1	5.9	6.5	3.8 ± 0.7	11.8	2.0 ± 0.4
VS %	0.1	5.3	4.7	3.6 ± 0.6	10.7	1.7 ± 0.3
pH	3.1	3.1	3.6	3.4 ± 0.1	3.8 ± 0.1	5.8 ± 0.5
Total COD*g/L	3	151	126	136 ± 89	214 ± 95	30 ± 4

Note: total solids (TS), volatile solids (VS), *total COD is on the fresh weight basis.

substrates with different feeding ratios (10% and 20%, *v*/v of co-substrates to total feeding). Digester 2 was operated in mono-digestion mode (the control). The two digesters were operated under the same conditions, except the feeding for Digester 1 was a mixture of co-substrates and primary sludge, and only primary sludge was fed into Digester 2. Feeding was run semi-continuously, involving four discharging/feeding cycles of 7.5 L/day at the feeding rate of 1 L/min. The peristaltic hose pump was continuously operated to mix the digestate at 60 L/h. The hydraulic retention time (HRT) was set at 20 days.

2.3. Sampling protocol

Digested sludge samples were taken from the well mixed digesters prior to the feeding cycles. The measurement TS, VS, total COD and pH of the sludge feed, co-substrates and digestate have been comprehensively described previously (Wickham et al., 2018; Wickham et al., 2019). Digestate samples were centrifuged at 3750 rpm for 10 min (Allegra X-12R centrifuge, Beckman Coulter, Australia) and stored at −80 °C until TrOC and metal analysis.

2.4. Trace organic contaminants measurement

A total of 20 compounds were selected as representative TrOCs commonly detected in treated effluents and sludge. The selected TrOCs included 7 pharmaceuticals (caffeine, carbamazepine, clozapine, naproxen, diclofenac, ibuprofen and gemfibrozil), 2 personal care products (PCPs, including triclocarban and triclosan), 1 pesticide (diuron), 5 industrial chemicals (benzotriazole, tris(2-chloroethyl) phosphate, sucralose, bisphenol A and phenylphenol), 1 steroid hormone (estrone) and 4 surfactants (perfluorohexanoic acid (PFHxA), perfluorooctanoic acid (PFOA), perfluorooctanesulfonic acid (PFOS) and nonylphenol).

All dewatered digestate samples were freeze dried (ModulyoD, Thermo Electron Corporation) at −45 °C and 0.01 mbar. The freeze-dried samples were ground, then 0.3–0.5 g of the ground sludge powder was weighed for TrOCs extraction in duplicate. Prior to the following two extraction procedures, ground samples were spiked with 50 ng (50 μL of a 1 mg/L solution) isotope-labelled internal standards. In addition, a recovery sample was spiked with 10 ng of the standard to show the extraction efficiency. Blank samples were also prepared for comparison.

2.4.1. Ultrasonication extraction

Methanol (10 mL) was added to sludge powder, mixed thoroughly using a vortex mixer, and ultrasonicated for 10 min (40 °C). After centrifuging at 3000 g for 10 min, the supernatant was collected. The ultrasonication extraction was repeated once with methanol and dichloromethane (1:1, *v*/v, 10 mL). The supernatants from the previous two steps were combined in an acid-washed glass bottle, and then diluted with Milli-Q water (500 mL) in preparation for solid phase extraction (SPE) as reported by Yang et al. (2016).

2.4.2. Solid phase extraction

Oasis® HLB SPE cartridges (6 cc, 500 mg, Waters Australia) were preconditioned with methanol (5 mL) and Milli-Q water (5 mL). The aqueous samples were loaded onto the SPE cartridges through Teflon lines, maintaining the flow rate of less than 15 mL/min. The cartridges were rinsed with Milli-Q grade water (5 mL) prior to drying under nitrogen gas until visibly dry (approx. 30 min). TrOCs were eluted from the dried cartridges under gravity using methanol (2 × 3 mL) and 1/9 (*v*/v) methanol/MTBE (5 mL). The combined eluants were evaporated to approximately 1 mL under nitrogen gas using a Turbo-Vap (Caliper Life Sciences, Waltham, MA. USA), and transferred to a 2 mL amber autosampler vial for quantification (Terechovs et al., 2019).

2.4.3. Quantification of trace organic contaminants

Three different analytical methods were employed to identify and measure TrOCs in this study. Except for estrone, PFOS, PFOA and PFHxA, all TrOCs were determined using high-performance liquid chromatography/tandem mass spectrometry (HPLC-MS-MS). Target analytes were separated using an Agilent 1200 series HPLC system (Agilent, Santa Clara, CA, USA) equipped with a 150×4.6 mm, 5 μm particle size, Luna C18(2) column (Phenomenex, Torrance, CA, USA). The target analytes and their isotope labelled internal standards were identified using an API 4000 triple quadrupole mass spectrometer (Applied Biosystems, USA) with electrospray ionization (ESI) in both positive and negative electro-spray modes. Two precursor ion-product ion transitions were monitored for each analyte and one for the internal standard (Supplementary Material – Table S1-a and S1-b). An injection volume of 10 μL was used and a binary gradient consisting of 5 mM ammonium acetate in water (A) and 100% methanol (B) at a flow rate of 800 μL/min was used. For ESI positive analyses, the gradient was as follows: 10% B held for 0.50 min, stepped to 50% B at 0.51 min and increased linearly to 100% B at 8 min, then held at 100% B for 2 min.

Table 2
Operational conditions of the two digesters.

Stage	Operating period	No. of sampling events	Feed streams[a]	
			Digester 1 (co-digestion)	Digester 2 (control)
1	Aug. 21–Sept. 14, 2017	5	Sludge + cola reject (10%)	Sludge
2	Sept. 15–Oct. 12, 2017	8	Sludge + beer reject (10%)	
3	Oct. 13–Nov. 10, 2017	4	Sludge + juice reject (10%)	
4	Jan. 22–Mar. 4, 2018	10	Sludge + food waste A (10%)	
5	Mar. 5–Apr. 7, 2018	6	Sludge + food waste A (20%)	
6	Apr. 23–Jul. 1, 2018	14	Sludge + food waste B (10%)	

[a] Sludge: primary sludge.

For ESI negative analyses, the gradient was as follows: 10% B held for 0.50 min, stepped to 60% B at 0.51 min and increased linearly to 100% B at 8 min, then held at 100% B for 3 min. A 5 min equilibration step at 10% B was used at the beginning of each run. A 3 min equilibrium step preceded injection. Except for sucralose and phenylphenol which used external calibration, analytes were quantified by isotope dilution, in which a relative response curve was generated by plotting analyte/internal standard peak area ratio against analyte/internal standard concentration ratio. The calibration range was 0.5–500 ng/mL with correlation coefficients of 0.99. Limits of Detection (LODs) were defined as the concentration of an extracted analyte giving a signal to noise (s/n) ratio greater than 3. The Limits of Quantification (LOQ) were defined as the concentration of an extracted analyte giving a signal to noise (s/n) ratio greater than 10. LOQ values of all TrOCs of interest are available in Supplementary Material (Table S3).

Identification and measurement of estrone followed that described by Trinh et al. (2011). A brief method description is given in Supplementary Material (Tables S1-c and S2).

PFOS, PFOA and PFHxA were determined using ultra-high performance liquid chromatography and identification-tandem mass spectrometry (UHPLC-MSMS). Analyte separation was performed using a Shimadzu (Rydalmere, NSW, Australia) Nexera X2 Liquid Chromatograph equipped with a XR-ODS-III (1.6 μm) 2 mm × 50 mm column. A binary mobile phase system of a solution of 5 mM ammonium acetate in 10% acetic acid/water (v/v) (A) and methanol (B) was used in the following gradient: initial 40% B held for 0.2 min increased to 100% B by 5 min and held to 8.5 min at a total flow of 0.5 mL/min. Column temperature was maintained at 40 °C and a 1 μL injection volume was used for all analysis. Mass Spectrometry (MS) was performed using a Shimadzu (Rydalmere, NSW, Australia) LCMS-8050 tandem mass spectrometer with ESI in negative mode. Ion source conditions as follows: interface temperature: 290 °C, nebulizing gas flow: 2 L/min, heating gas flow: 10 L/min, desorption line temperature: 200 °C, heat block temperature 400 °C, drying gas flow 10 L/min. Total run time of 10 min. Two precursor and product ion transitions were monitored for each target analyte and one for each internal standard, the most abundant used for quantitation (Table S1-d). Isotope dilution was used to quantify the target analytes. A 7 point (0.1, 0.5, 1, 5, 10, 50, 100 ng/mL) calibration standard curve was generated for each batch run. In this study, isotopically labelled standards (50 ng for each compound) for 18 of the 20 selected TrOCs were introduced into all samples for method recovery confirmation and quantification (Phan et al., 2018).

2.5. Metals quantification

In order to determine metal contents, the freeze-dried sludge samples were digested according to the US-EPA 3052 method using a microwave digestion system (Anton Paar, Multiwave PRO) in duplicate, and then analysed by an inductively coupled plasma mass spectrometry (ICP-MS) (Agilent 7700×, Japan). Between 0.1 and 0.3 g of dried sludge was weighed into HP-500 plus Teflon vessels with 9 mL of 70% nitric acid and 3 mL of 32% hydrochloric acid. The temperature during digestion remained at 180 ± 5 °C for at least 10 min. After cooling down, the vessels were rinsed three times with Milli-Q water, and the total volume was set to 250 mL for analysis of B, Cr, Co, Ni, Cd, Tl and Pb; to 1250 mL for analysis of Na, Mn, Cu, Zn, Sr and Ba; and to 7500 mL for analysis of Mg, Al, K, Ca and Fe, respectively, adjusted to fall within the dynamic range of the ICP-MS instrument. ICP-MS analyses of filtered samples (0.22 μm) were performed under standard operating conditions in helium mode (3.5 mL/min) to remove potential polyatomic interferences. A judicious selection of isotopes analysed prevented major overlaps in mass interferences. In addition to frequent recalibration, matrix interferences and instrument drift were monitored through the recovery of an inline-added internal standard (Agilent Internal Standard #5183-4681) containing ^{45}Sc, ^{72}Ge, ^{89}Y and ^{159}Tb. Samples for which the internal standard recoveries fell beyond the 80–120% range were

diluted and re-analysed. A 7- to 10-point (1 to 2000 μg/L) external calibration procedure was performed using the multi-element standard solution IV (Merck, Germany), with standards matrix-matched in terms of HNO$_3$ and HCl concentrations based on the different dilution ratios identified above. The detection limit and LOQ values represent concentrations obtained when the measured intensity differed significantly from the background intensity (Table S4). Sample variations, expressed as percent errors, were calculated for duplicate experimental replicates and averaged for each individual isotope analysed (Table S4).

2.6. Environmental risk assessment

Environmental risk assessment was conducted by calculating the risk quotient (RQ_{soil}) value in digested-sludge amended soil. RQ_{soil} values are usually expressed as the ratio between the predicted environmental concentrations (PEC_{soil}), or the measured environmental concentration when available, and the predicted no-effect concentration ($PNEC_{soil}$), shown as Eq. (1). In this study, PEC_{soil} was used for the calculation of RQ_{soil} as sludge amended soil trials were not conducted. PEC_{soil} was calculated applying Eq. (2) from the European Commission Technical Guidance Document on Risk Assessment EUR 20418 EN/2 (ECB-TGD, 2003):

$$RQ_{soil} = \frac{PEC_{soil}}{PNEC_{soil}} \tag{1}$$

$$PEC_{soil} = \frac{C_{sludge} \times APPL_{sludge}}{DEPTH_{soil} \times RHO_{soil}} \tag{2}$$

where: C_{sludge} was the measured concentration of the pollutant in dry AD sludge (see Tables 3 and 4); $APPL_{sludge}$ was the dry-sludge application rate: 0.5 kg/m^2 year; $DEPTH_{soil}$ was the mixing depth of soil: 0.20 m; and RHO_{soil} was the bulk density of wet soil: 1700 kg/m^3. The above values were based on agricultural soils. The estimation methodology of $PNEC_{soil}$ values is summarised in the Supplementary Material (Table S5), in which the terrestrial or aquatic toxicity data for the worst-case scenario was adopted.

2.7. Statistical analyses

Data were analysed with ANOVA (Analysis of Variance) using SPSS (version 22.0). A P-value less than 0.05 was set as the level of statistically significant. Results were expressed as mean ± standard deviation.

3. Results and discussion

3.1. TrOCs in AD sludge

The 20 TrOCs in this study were targeted as they had one or more of the following characteristics: bioaccumulation, toxicity, environmental persistence or endocrine disrupting effects. Fig. 1 shows that the concentrations of the 20 monitored TrOCs in AD sludge varied greatly, indicating differences in their physicochemical properties and use frequencies. The detailed results are presented in Fig. S1-a. Among the 20 TrOCs, the personal care product triclocarban exhibited the highest accumulation, with the mean concentration of 12,470 ± 2742 ng/g and 12,910 ± 2597 ng/g for the co-digestion and the control, respectively. The concentrations of triclocarban were within the reported range in the literature. Yang et al. (2016) found that the triclocarban concentration was between 10,000 and 20,000 ng/g dry weight (dw) in digested sludge for all sludge retention time of 15 d, 20 d and 30 d. Another study reported that triclocarban accumulated in municipal sludge anaerobically digested for 19 days was up to 51,000 ± 15,000 ng/g dw (Heidler et al., 2006).

Another two TrOCs that occurred at notable concentrations were triclosan and bisphenol A. The occurrence of TrOCs in sludge is governed

Table 3
Impacts of various co-digestion substrates on TrOC concentrations in AD sludge (ng/g dw)[*].

Compound	Co-digestion						Control	Values in published literature
	Cola reject (10%)	Beer reject (10%)	Juice reject (10%)	Food waste A (10%)	Food waste A (20%)	Food waste B (10%)		
PFHxA	19 ± 11 a	17 ± 5 a	/	/	/	/	16 ± 8 a	<LOD–19.4 [1]
PFOA	30 ± 1 ab	59 ± 44 a	22	6 ± 0 b	/	24 ± 12 ab	14 ± 8 ab	<LOD–19.4 [1]
PFOS	24 ± 0 b	75 ± 7 a	41	17 ± 5 b	14 ± 2 b	36 ± 12 b	22 ± 12 b	1.8–160 [1], [2]
Estrone	/	4	/	9	/	/	10 ± 6	<LOQ–137 [3]
Caffeine	656 ± 78 a	146 ± 132 b	75 ± 16 b	76 ± 16 b	43 ± 13 b	733 ± 679 a	68 ± 20 b	<LOQ–102 [3], [4]
Benzotriazole	/	/	/	48 ± 18 a	49 ± 1 a	80 ± 11 a	74 ± 24 a	12–129 [5]
TCEP	41	15 ± 4 b	41 ± 3 a	25 ± 6 ab	20 ± 2 b	28 ± 8 ab	28 ± 15 ab	<100 [6]
Carbamazepine	256 ± 100 a	262 ± 23 a	255 ± 7 a	174 ± 8 b	189 ± 17 ab	176 ± 18 b	211 ± 47 ab	3–84.1 [3], [4], [7]
Clozapine	210 ± 68 c	262 ± 7 b	290 ± 7 ab	317 ± 11 a	282 ± 14 ab	297 ± 13 ab	306 ± 32 ab	45.3–250 [7], [8]
Sucralose	/	/	/	410 ± 28 a	395 ± 119 a	655	422 ± 132 a	21.1–122 [9]
Naproxen	20	17	/	/	/	/	6	<LOQ–57 [3]
Bisphenol A	365 ± 8 d	356 ± 24 d	397 ± 25 d	1289 ± 479 c	2372 ± 428 a	1873 ± 423 b	508 ± 157 d	<LOQ–3910 [10]
Diclofenac	66 ± 11 a	70 ± 6 a	57 ± 7 ab	56 ± 1 ab	47 ± 2 b	60 ± 4 ab	59 ± 11 ab	<LOQ–87 [3], [4]
Diuron	32 ± 12 d	40 ± 3 cd	51 ± 0 ab	55 ± 2 a	46 ± 2 abc	41 ± 3 bcd	50 ± 7 abc	50–100 [11]
Ibuprofen	146 ± 60 b	203 ± 15 a	218 ± 17 a	228 ± 18 a	200 ± 13 a	203 ± 19 a	210 ± 18 a	24–1170 [3], [12]
Phenylphenol	27 ± 8 b	35 ± 12 b	28 ± 1 b	38 ± 25 b	70 ± 12 a	30 ± 17 b	35 ± 19 b	–
Gemfibrozil	36 ± 12 b	27 ± 9 b	35 ± 7 b	85 ± 43 ab	108 ± 3 a	47 ± 38 ab	63 ± 39 ab	25–75 [11]
Triclocarban	11,660 ± 3290 bc	15,900 ± 886 a	15,710 ± 716 a	12,450 ± 1890 ab	8623 ± 580 c	11,600 ± 866 bc	12,910 ± 2597 ab	1540–66,000 [4], [13], [14]
Triclosan	2038 ± 334 a	1998 ± 351 a	2086 ± 507 a	1649 ± 132 a	1504 ± 10 a	1689 ± 366 a	1838 ± 604 a	410–46,000 [4], [13], [15]
Nonylphenol	23	38 ± 4 b	29 ± 2 b	107 ± 80 ab	174 ± 29 a	58 ± 60 b	78 ± 55 b	<LOD–358200 [16]

Abbreviations: Perfluorohexanoic acid (PFHxA), Perfluorooctanoic acid (PFOA), Perfluorooctane sulphonate (PFOS), Tris(2-chloroethyl) phosphate (TCEP).
Data from: 1. (Arvaniti et al., 2012); 2. (Schultz et al., 2006); 3. (Nieto et al., 2010); 4. (Narumiya et al., 2013); 5. (Liu et al., 2012); 6. (Yang et al., 2017); 7. (Thomaidi et al., 2016); 8. (Song et al., 2018); 9. (Subedi et al., 2014); 10. (Samaras et al., 2013); 11. (Yang et al., 2016); 12. (Martin et al., 2012); 13. (Heidler and Halden, 2009); 14. (Heidler et al., 2006); 15. (Armstrong et al., 2017); 16. (Gonzalez et al., 2010)
  [*] Different lowercase letters indicate significant difference between the samples for the same compound. The detailed sample distributions for each compound are shown in Appendix Fig. S1.

by their hydrophobicity and biodegradability. Hydrophobic TrOCs with Log Kow > 2 partitioned mainly into sludge (Stevens-Garmon et al., 2011), and the high hydrophobicity of triclocarban, triclosan and bisphenol A (log Kow > 3.3) were in accordance with their abundance in this study. Triclocarban and triclosan are also known to resist biodegradation due to the chloro functional group in their molecular structures. Negligible removal of these three most abundant contaminants was previously reported during AD processing (Phan et al., 2018; Stasinakis, 2012; Yang et al., 2017), and Armstrong et al. (2017) reported that triclosan levels may increase during microbial anaerobic respiration due to the reduced digestion sludge volume. The abundance of these three chemicals was mainly attributed to their wide range of

use. For example, triclocarban and triclosan are antimicrobial agents widely applied in personal care products added in an amount from 0.1% to 0.3% (w/w), including cosmetics, shampoos, soaps and toothpastes (Clarke and Smith, 2011).

Among the 20 TrOCs, most were relatively comparable in average concentrations regardless of the co-digestion substrates added, with a few exceptions (Fig. 1). A greater removal of clozapine and diuron was observed in the co-digestion than in the control ($P < 0.05$). No removal of clozapine and limited removal of diuron (22–53%) have been previously reported during AD (Phan et al., 2018). In this study, the added co-substrates were equivalent to diluting the sludge feed by 1.11 (addition ratio of 10%) or 1.25 times (addition ratio of 20%), which probably

Table 4
Impacts of various co-digestion substrates on metal concentrations in AD sludge (mg/kg dw). C_2 upper limits indicate the maximum concentration threshold in sludge for land application according to EPA 943 Guidelines (EPA, 2004).

Metals	Co-digestion[*]						Control	Grade C_2 upper limit
	Cola reject (10%)	Beer reject (10%)	Juice reject (10%)	Food waste A (10%)	Food waste A (20%)	Food waste B (10%)		
B	44.0 ± 8.2 b	60.2 ± 8.4 a	49.0 ± 2.2 b	44.1 ± 2.2 b	51.3 ± 7.9 ab	42.9 ± 3.9 b	47.2 ± 7.0 b	–
Cr	93.7 ± 3.1 c	103 ± 11 bc	120 ± 0 a	113 ± 14 ab	101 ± 5 bc	93.6 ± 8.2 c	98.8 ± 8.1 bc	3000
Co	18.1 ± 0.0 b	17.6 ± 0.3 b	18.1 ± 0.1 b	22.7 ± 5.7 a	19.9 ± 0.9 ab	17.5 ± 2.1 b	19.7 ± 1.3 ab	–
Ni	33.9 ± 2.2 b	30.9 ± 3.6 b	35.1 ± 4.2 b	41.4 ± 9.2 ab	53.1 ± 2.2 a	53.6 ± 3.8 a	43.7 ± 12.1 ab	270
Cd	5.1 ± 0.3 a	5.4 ± 0.4 a	5.2 ± 0.1 a	7.6 ± 5.0 a	5.3 ± 0.2 a	5.8 ± 0.4 a	5.8 ± 0.6 a	10
Tl	0.8 ± 0.0 a	0.7 ± 0.0 a	0.8 ± 0.1 a	0.7 ± 0.0 a	0.7 ± 0.1 a	0.6 ± 0.0 a	0.7 ± 0.1 a	–
Pb	30.0 ± 3.7 a	30.6 ± 0.9 a	33.5 ± 4.5 a	36.8 ± 7.0 a	38.9 ± 1.7 a	41.7 ± 21.7 a	35.0 ± 3.8 a	500
Na	1674 ± 154 bc	2115 ± 54 abc	2056 ± 237 abc	2261 ± 136 a	2155 ± 165 ab	1648 ± 206 c	2047 ± 366 abc	–
Mn	143 ± 7 a	155 ± 2 a	158 ± 4 a	123 ± 7 b	123 ± 3 b	125 ± 7 b	139 ± 15 ab	–
Cu	602 ± 9 b	636 ± 19 ab	643 ± 33 ab	648 ± 41 ab	689 ± 24 a	624 ± 48 ab	682 ± 44 a	2000
Zn	662 ± 27 b	714 ± 18 ab	719 ± 24 ab	791 ± 43 a	790 ± 27 a	776 ± 57 a	810 ± 70 a	2500
Sr	110 ± 3 ab	117 ± 4 a	114 ± 3 a	89.4 ± 5.0 d	93.7 ± 1.5 cd	103 ± 6 bc	108 ± 8 ab	–
Ba	171 ± 12 a	167 ± 7 a	162 ± 10 a	131 ± 5 b	162 ± 36 a	136 ± 9 b	152 ± 13 ab	–
Mg	2274 ± 222 b	2598 ± 120 a	2693 ± 30 a	2548 ± 112 a	2598 ± 45 a	2732 ± 202 a	2764 ± 178 a	–
Al	20,610 ± 14,450 b	31,340 ± 11,250 b	74,000 ± 37,200 b	32,660 ± 12,130 b	24,850 ± 3220 b	14,380 ± 7190 b	27,000 ± 14,060 b	–
K	553 ± 54 c	634 ± 85 c	798 ± 78 bc	1121 ± 58 bc	1281 ± 210 ab	1766 ± 490 a	856 ± 381 bc	–
Ca	18,060 ± 1244 c	18,070 ± 1301 c	20,060 ± 912 ab	17,820 ± 689 c	18,610 ± 750 bc	21,450 ± 1527 a	19,110 ± 1104 bc	–
Fe	7785 ± 316 a	7754 ± 495 a	7798 ± 512 a	7812 ± 747 a	8662 ± 193 a	8164 ± 846 a	8447 ± 688 a	–

  [*] Different lowercase letters indicate significant difference between the samples for the same metal analyte. The detailed sample distributions for each element are shown in Appendix Fig. S1.
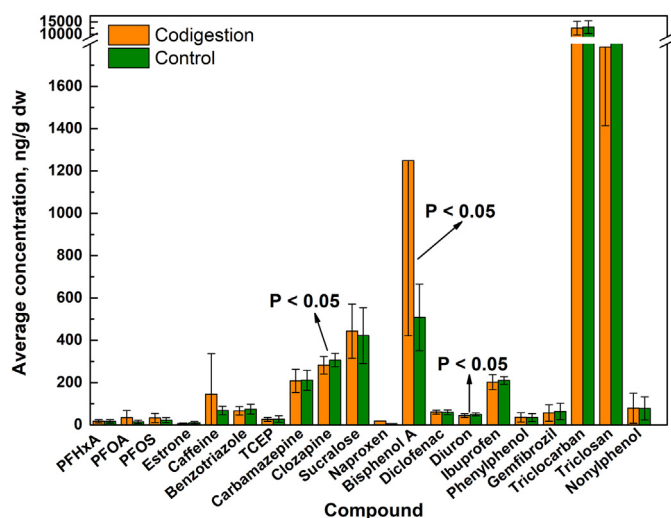
Fig. 1. Average TrOC concentrations in AD sludge. The number of samples is given in Table 2, and each sample was conducted in duplicate. Significant differences between the co-digested and control samples are indicated. Trends between the group are shown in Table 3 and Fig. S1.

resulted in the decreasing concentration of these two chemicals in co-digested sludge. In contrast, bisphenol A was increased in co-digestion compared with the control ($P < 0.05$). This indicates that some co-substrates in this study might contain a large amount of bisphenol A, thereby increasing the pollution potential of the co-digested sludge. Bisphenol A is a mass-produced plasticiser, used to produce polycarbonate, epoxy resins, flame retardants and unsaturated polyester styrene resins. The final products are used as coatings on cans, thermal paper additives, and antioxidants in plastics (Staples et al., 1998).

Table 3 shows the impact of different co-digestion substrates on TrOC concentrations. For most TrOCs, the concentrations detected in this study were similar or lower than those reported in the literature (Table 3). Higher concentrations than those in literature were observed for few contaminants (Narumiya et al., 2013; Nieto et al., 2010; Subedi et al., 2014; Thomaidi et al., 2016), namely caffeine (43–733 ng/g dw), carbamazepine (174–262 ng/g dw) and sucralose (395–655 ng/g dw), suggesting their higher usage in NSW, Australia.

When using cola reject as the co-digestion substrate, it was found that clozapine, diuron and ibuprofen decreased compared with the control. Noticeably, regarding the caffeine concentration, sludge co-digested with cola reject and food waste B (10%) were 656 ± 78 ng/g and 733 ± 679 ng/g, respectively, both much higher than the control (68 ± 20 ng/g, $P < 0.05$). Caffeine is the key constituent as the stimulant in coffee (~95 mg for 1 cup), tea (~45 mg for 1 cup), and energy drinks (Voskoboinik et al., 2019). Thus, cola reject as the co-substrate for digestion would easily cause the accumulation of caffeine in final digestate. By contrast, no significant increase of the 20 monitored TrOCs was observed when using juice reject as the co-substrate, suggesting that juice reject would be a more prudent alternative co-substrate considering the absolute concentrations of TrOCs.

PFOS concentrations of 75 ± 7 ng/g measured in the sludge co-digested with beer reject, were significantly higher than the control, 22 ± 12 ng/g ($P < 0.05$, Table 3). PFOS is an anthropogenic compound consisting of fluorinated carbon backbones and different functional groups, both of which can cause toxicity and further affect environmental behaviour (Semerád et al., 2020). Importantly, it was reported that the PFOS concentration in 50% of the 93 tested beer samples exceeded the quantification limit, with the highest concentration being 18.4 ng/L (Stahl et al., 2014). Thus, the significantly higher PFOS concentrations in samples using beer reject may be attributed to the abundance of PFOS in beer.

For all co-digestion treatments using food waste (food waste A 10%, food waste A 20%, food waste B 10%), bisphenol A was significantly increased compared with the control. Also, bisphenol A concentrations increased from 1289 ± 479 ng/g to 2372 ± 428 ng/g when the food waste A ratio was increased from 10% to 20% ($P < 0.05$). Bisphenol A is widely used in the production of polycarbonate for food packaging (Abraham and Chakraborty, 2020; Vilarinho et al., 2019). This pollutant exhibits toxicity due to its endocrine disrupting effects. It was noted that bisphenol A could partially migrate from food packaging materials into food (Vilarinho et al., 2019). Thus, the potential residues of bisphenol A could be an environmental risk factor when adopting food waste as a co-digestion substrate.

Phenylphenol content was comparable between the control and the co-digestion using food waste A (10%). In contrast, when the ratio of food waste A was increased to 20%, the phenylphenol content was found to be significantly higher than the control ($P < 0.05$). This may be attributed to the wide occurrence of phenylphenol in food paper packages (Votavova et al., 2014). Alternatively, it is also used as a preservative and broad-spectrum fungicide, being widely adopted for fruit storage (Hou et al., 2018).

The nonylphenol concentration (174 ± 29 ng/g) measured in food waste A (20%) co-digested sludge was significantly higher than the other beverage co-digestions and the control ($P < 0.05$). Though nonylphenol has estrogenic activity and can cause reproductive effects on animals, it is ubiquitous in food-contact materials such as rubber, paper and polyvinylchloride wraps and when present at high concentrations can be detected in food products (Fernandes et al., 2008).

3.2. Metals in AD sludge

Among the 18 metals monitored, most had comparable concentrations between the co-digestion and the control treatments (Fig. 2). Detailed results are shown in Fig. S1-b. Average concentrations of Cu, Zn, Sr, Mg and Fe were lower in co-digestions than the control ($P < 0.05$). Among these five elements, the metals Cu and Zn could be considered toxic and persistent, thus posing potential toxicity for land application. Lower concentrations may be related to dilution effects and the absence of these elements in co-substrates. The co-digestion substrates resulted in a significant increase in the average concentration of K compared to the control, where much of the effect was due to high K in food waste amended samples (Table 4). In general, the addition of co-substrates did not result in an increase of toxic metals in AD sludge. Conversely,
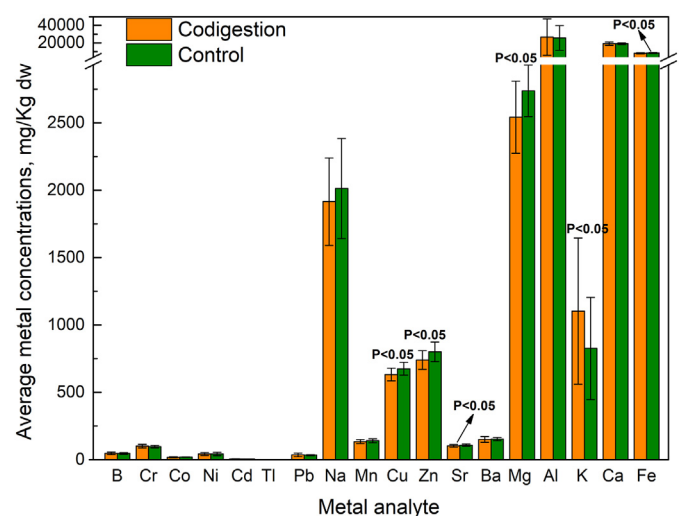

Fig. 2. Average metal concentrations in AD sludge. The number of samples is given in Table 2, and each sample was conducted in duplicate. Significant differences between the co-digested and control samples are indicated. Trends between the group are shown in Table 4 and Fig. S1.

the co-digestion processing may in fact reduce the toxicity of AD sludge constituents (Cu and Zn) and increase the content of fertiliser source (K). Thus, from the aspect of the average concentration of metals, it is encouraging to adopt the co-substrates for AD processing.

According to the EPA 943 Guidelines for biosolids land application (EPA, 2004), Grade C_2 upper limits of 6 metal elements (Table 4) indicate concentrations above which land application should not be allowed. All regulated elements (Cr, Ni, Cd, Pb, Cu and Zn) in both the co-digestion and the control were lower than the set limits, indicating the applicability of the sludge for land use.

Table 4 shows the metal profiles relating to individual co-substrate amendments. When adding cola reject as the co-digestion substrate, Cu, Zn and Mg concentrations were much lower than those of the control ($P < 0.05$). Concentrations of B in the sludge co-digested with beer reject was 60.2 ± 8.4 mg/kg dw, significantly higher than that of the control, 47.2 ± 7.0 mg/kg dw ($P < 0.05$). Conversely, Cr and Al concentrations were higher in juice reject co-digested sludge than those of the control ($P < 0.05$). The increased abundance of Cr and Al was likely due to the addition of flavours and other ingredients during beverage processing, with elevated concentrations reported in these components (Barroso et al., 2009). For elements displaying significant changes (Cu, Zn, Mg, B, Cr and Al) caused by beverage additions, three of them (Cu, Zn and Cr) were potentially toxic elements. From this perspective, our study suggests that the use of cola and beer rejects as co-digestion substrates has greater application potential when compared to juice reject. However, this needs to be balanced against substrate variability and importance of the overall effect.

While Ba significantly increased from 131 ± 5 mg/kg dw to 162 ± 36 mg/kg dw when the ratio of food waste A increased from 10% to 20% ($P < 0.05$), this was not significantly different to the control ($P > 0.05$). Additionally, when using food waste B (10%) as the co-digestion substrate, K and Ca were as high as 1766 ± 490 mg/kg dw and $21,450 \pm 1527$ mg/kg dw, respectively, both significantly higher than the control and the co-digestion using food waste A (10%). K and Ca can maintain the growth and development of plants and are indispensable components of plant inorganic nutrition. This indicates that food waste B likely contains K- and Ca-rich food types, such as bananas, fish and meat. These observations also suggest that metal elements are source-dependent and can potentially vary greatly between different sources of food waste.

From the perspective of metals for land application, beer reject as well as food waste (A and B) as the anaerobically co-digested substrates would have potentially less impact compared to cola reject and juice reject. The results also show that the potential threat of harmful metals in co-digested sludge for land use was not worsened, and for some co-substrates, the content of major (K, Ca) or trace (B) elements increased, which could be regarded as a source of nutrients. However, an estimation of the individual environmental risk needs to be conducted to determine the overall implications of sludge application to agricultural soils.

3.3. Environmental risk assessment

The RQ value has been widely adopted for the evaluation of ecotoxicological risk of digested sludge-amended soils (Martin et al., 2012; Terechovs et al., 2019; Verlicchi and Zambello, 2015). The ecological risk can be divided into three levels: low risk if RQ < 0.1; medium risk if $0.1 \leq RQ < 1$; and high risk if $RQ \geq 1$ (Hernando et al., 2006). It should be noted that $PNEC_{soil}$ of TrOCs was based on the worst-case scenario of terrestrial or aquatic (i.e., equilibrium partitioning) data. However, considering the ionic charge and various factors (pH, Eh, etc.) that affect the speciation and equilibrium of metals, terrestrial data was adopted directly for metals rather than using the equilibrium partitioning method which was used for TrOCs. In addition, the concentration of metals in wastewater and waste streams has been steadily declining over the past 20 years as a result of pollution control measures. Therefore, attention to TrOCs is considered more important from a risk assessment perspective.

Table 5 shows the highest environmental risk in sludge-amended soil stemmed from caffeine, with an RQ value exceeding 3000. The extremely high RQ value indicates that caffeine will likely have a significant effect on the ecology when applying AD sludge onto agricultural land. This aligns with previous research reporting that caffeine is the only individual emerging contaminant that may pose a significant risk for Mediterranean coastal wetlands (Sadutto et al., 2021). A high RQ value for caffeine (i.e. 47) has also been documented in literature (Thomaidi et al., 2016). However, an RQ value of the magnitude found in our study has yet to be reported. Importantly, there is conclusive evidence that environmental-related caffeine concentrations exhibit adverse effects on aquatic and terrestrial species, including lethality,

Table 5
Risk quotient (RQ) of the investigated contaminant in AD sludge-amended soil.

Chemical	Co-digestion						Control
	Cola reject (10%)	Beer reject (10%)	Juice reject (10%)	Food waste A (10%)	Food waste A (20%)	Food waste B (10%)	
PFHxA	<0.001	<0.001	–	–	–	–	<0.001
PFOA	0.017	0.033	0.013	0.003	–	0.013	0.008
PFOS	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001
Estrone	–	0.16*	–	0.39*	–	–	0.44*
Caffeine	48250**	10710**	5507**	5566**	3169**	53860**	4985**
Benzotriazole	–	–	–	<0.01	<0.01	<0.01	<0.01
TCEP	<0.01	<0.001	<0.01	<0.01	<0.01	<0.01	<0.01
Carbamazepine	0.07	0.07	0.07	0.04	0.05	0.05	0.05
Clozapine	0.05	0.06	0.07	0.07	0.06	0.07	0.07
Sucralose	–	–	–	–	–	–	–
Naproxen	0.15*	0.13*	–	–	–	–	0.05
Bisphenol A	0.01	0.01	0.01	0.03	0.05	0.04	0.01
Diclofenac	<0.01	<0.01	<0.01	<0.01	<0.001	<0.01	<0.01
Diuron	29.5**	37.1**	46.4**	50.9**	42.4**	37.7**	46.0**
Ibuprofen	0.90*	1.24**	1.34**	1.40**	1.22**	1.24**	1.29**
Phenylphenol	<0.001	<0.001	<0.001	<0.001	0.001	<0.001	<0.001
Gemfibrozil	0.015	0.011	0.014	0.035	0.044	0.019	0.026
Triclocarban	77.9**	106.3**	105.0**	83.2**	57.6**	77.5**	86.3**
Triclosan	10.3**	10.1**	10.6**	8.4**	7.6**	8.6**	9.3**
Nonylphenol	0.01	0.02	0.01	0.05	0.08	0.03	0.04
Cu	521.0**	549.9**	556.1**	560.8**	596.3**	540.1**	589.7**
Zn	42.3**	45.6**	46.0**	50.6**	50.5**	49.6**	51.8**

** indicates high risk (RQ ≥ 1); * indicates medium risk (0.1 ≤ RQ < 1); and values without * or ** indicate low risk.

neurotoxic effects, and reproductive interference, etc. (Li et al., 2020). Implications of the caffeine dose on agricultural land should be investigated using field studies to understand the potential adverse effects and minimise its loading in the environment when necessary.

Diuron, triclocarban, triclosan, Cu and Zn were another five contaminants found to result in high risks for both application of the co-digestion and the control sludge. Among these, triclocarban and triclosan have often been reported to show high risks in digested sludge-amended soils (Clarke and Smith, 2011; McClellan and Halden, 2010; Mejías et al., 2021). Additionally, it was identified that triclosan can be dispersed as well as remain persistent to a greater degree in the environment than expected (von der Ohe et al., 2012). In contrast, there are currently few reports that show diuron poses a critical risk due to sludge land application. Verlicchi and Zambello (2015) reviewed 59 papers and concluded that based on a risk assessment approach the most critical compounds in sludge-amended soils include caffeine, triclosan and triclocarban, which was in accordance with the results in our study. The above results reinforced the argument that caffeine, diuron, triclocarban, triclosan, Cu and Zn should be considered as candidates for regulatory monitoring and prioritisation regarding the land application of wastewater sludge. Further monitoring and control of the contaminants in AD sludge may be needed prior to land application to prevent accumulation within the environment.

Ibuprofen, with RQ values ranging from 1.2 to 1.4, implied a high risk to soil environments except when co-digested using cola reject (RQ = 0.9). A previous study revealed that ibuprofen posed a high risk (RQ = 4.4) for digested sludge, while the risk drastically decreased to less than 1 due to the dilution effect when applying the sludge onto land (Martin et al., 2012). The longer-term impact of any contaminant is highly dependent on its subsequent behaviour in soils. For example, Ibuprofen has a short half-life in soil (Shu et al., 2021), so the risk is likely to decrease rapidly over time as well as with incorporation into soils.

Estrone and naproxen represented medium risk for some sludge-amended soil scenarios. For the remaining 13 substances included in Table 5, RQ values were less than 0.1, so environmental risks were considered low (i.e., PFHxA, PFOA, PFOS, benzotriazole, TCEP, carbamazepine, clozapine, sucralose, bisphenol A, diclofenac, phenylphenol, gemfibrozil and nonylphenol).

Notably, assumptions associated with the RQ method rely on the incorporation of a set amount of sludge into a fixed volume of soil. Naturally, significant variations to the amounts applied to land or the incorporation into soil may cause changes to the RQ value and impacts on the environment. It is also with noting that the environmental risk assessment based on RQ values was evaluated separately for each substance in this study. This ignores the effects associated with multiple contaminants existing in the soil or that due to their continuous land application, which may cause complex synergistic and chronic toxicity (Verlicchi et al., 2012). Future work in this area should include measurement of samples before after repeated land application. In addition, a refined future assessment should focus on the risks to humans through consuming agricultural products, i.e. the food chain pathway (Clarke and Smith, 2011).

4. Conclusion

Land application of wastewater sludge is widely practiced and has many benefits including nutrient addition to soils. However, due to challenges in contaminant removal and control, sludge quality and suitability should be considered in the wastewater treatment processing. Co-digestion is being increasingly used by wastewater utilities to provide additional organic matter to anaerobic digestors, increasing biogas yields. This study assessed the potential chemical contamination caused by the addition of various co-substrates to pilot scale anaerobic digestors. TrOCs and metal elements in the resultant co-digested and control sludges were measured and evaluated using environmental

risk assessment. It was found that co-digestion with cola reject increased the caffeine content, while reducing the metal contents of Cu, Zn and Mg. Micropollutant PFOS and element B increased in beer reject co-digested sludge, whereas for food waste co-digestion, concentrations of bisphenol A, phenylphenol, nonylphenol and caffeine were noticeably increased. Metals K and Ca increased in sludge co-digested with certain food wastes, which could provide beneficial inorganic plant nutrients for agricultural application. Among the contaminants, six (caffeine, diuron, triclocarban, triclosan, Cu and Zn) presented high risks of applying the digested sludge to soils. The highest toxicity was mainly driven by caffeine. The results emphasise the need to better understand and control the inputs to wastewater treatments processes, such as anaerobic digestion, in order to protect and fully realise the benefits of sludge application to agricultural land.

CRediT authorship contribution statement

Changwei Li: Investigation, Formal analysis, Writing – original draft, Visualization. **Nhat Le-Minh:** Conceptualization, Methodology. **James A. McDonald:** Methodology, Investigation. **Andrew S. Kinsela:** Methodology, Investigation. **Ruth M. Fisher:** Conceptualization, Methodology, Writing – review & editing. **Dezhao Liu:** Writing – review & editing, Supervision. **Richard M. Stuetz:** Conceptualization, Methodology, Writing – review & editing, Supervision.

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.2021.151533.

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