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FERTILISER PROPERTIES OF WASTEWATER SLUDGE AND SLUDGE ASH - A CASE STUDY FROM THE FINNISH FOREST INDUSTRY

Abstract: In this case study we compared the fertiliser properties of an industrial wastewater treatment sludge and a sludge ash to the requirements of the Finnish Fertiliser Product Decree. The sludge was obtained from the activated sludge wastewater treatment plant of a Finnish non-integrated pulp mill. The sludge was furthermore incinerated at a laboratory in a muffle furnace (850 °C) to obtain sludge ash. The total Cd (4.9 mg/kg d.m.) concentration in the pulp sludge exceeded the Finnish limit value (1.5 mg/kg d.m.) for fertiliser products used in agriculture. In the sludge ash, the total concentration of Cd (39 mg/kg; d.m.) exceeded the Finnish limit value (25 mg/kg d.m.) for ash fertilisers used in forestry. These results restrict the potential reuse options of these residues. However, from the utilisation point of view, the enrichment of essential plant macro-nutrients was most notable, resulting to the following total concentrations of these elements in the sludge ash: P (26,000 mg/kg d.m.), S (40,000 mg/kg d.m.), K (11,000 mg/kg d.m.), Ca (83,000 mg/kg d.m.) and Mg (10,000 mg/kg d.m.). Therefore, we conclude that, the converting of sludge into ash may promote the reuse of this wastewater treatment residue to a more value-adding fertiliser by-product to be used as a soil improver and growing medium in landscaping or landfills sites or other closed industrial areas, where heavy metal limit values for fertilisers are not applied in Finland.

Keywords: ash, circular economy, extraction, fertiliser, pulp mill, sludge, waste, wastewater treatment

Introduction

Water is an essential raw material in the manufacturing of pulp that is further processed into various board and paper products. During the processing of pulp, chemicals and fibres that are not recirculated within the mill are concentrated into effluents which are finally treated at the wastewater treatment plant before being discharged into receiving water bodies. The pulp industry wastewater is generated from several sources, such as like washing of raw wood materials before pulping, washing of cooked pulp and bleaching pulp, and finally, chemical recovery system. The amount and type of wastewater sludges generated in the forest industry varies naturally depending on the type of process, raw materials, as well as the grade of products manufactured and wastewater cleaning techniques applied [1].

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The circular economy concept is being promoted worldwide and the European Union (EU) has a dedicated strategy and stakeholder platform for its increased implementation. Important aspects in a circular economy are nutrient recycling [2] and preserving the value of used materials as much as possible for as long as possible by using process side-stream fractions as raw materials for other products instead of regarding them as a waste [3]. The European Waste Framework Directive (2008/98/EC) sets a hierarchy in which the main priority is to prevent waste or to prepare it for reuse, recycling or other forms of recovery [**4**, 5]. There is also a need to seek and implement new sustainable alternatives to replace conventional commercial fertilisers, which price fluctuate unpredictably and for which known supplies are dwindling [6]. Together, these are the factors why industrial operators like the forest industry are increasingly investigating the utilisation potential for all kinds of industrial side-streams.

In the Finnish forest industry wastewater treatment sludges are usually incinerated together with other fuels such as bark, other wood residues and/or peat, in, for example at fluidised-bed boilers. Due to this co-incineration, the ash originating from these power plants is a mixture of all fuels feed into the boiler [7]. Wanting to clarify whether wastewater sludge ash itself is a potential fertiliser product, was what prompted us to carry out this study. If the wastewater sludge is incinerated separately, then its physical and chemical properties are possible to be studied without any contamination from other fuels.

The aim of this study was to determine the fertiliser properties of non-integrated pulp mill wastewater sludge and sludge ash based on the requirements of the Finnish Fertiliser Product Decree. In addition, we have assessed the extraction properties of these residues using a three-stage sequential extraction procedure by the Standard, Measurement and Testing programme (former Community Bureau of References), commonly known as BCR sequential extraction [8]. The solubility index and recovery factor values for elements were calculated based on the results of the total element concentrations and of the BCR sequential extraction procedure in order to assess the potential mobility and bioavailability of elements from the sample matrix.

Materials and methods

Origin of the sludge and sludge ash

The wastewater treatment sludge investigated in this study was sampled from the activated sludge wastewater treatment plant of the non-integrated pulp mill of Stora Enso Sunila Mills located in Kotka, Southern Finland. The mill produces about 375,000 tonnes (1 tonne = 10^6 g = 1 Mg) of bleached softwood pulp annually, in addition to turpentine and tail oil. The mill has an annual lignin production capacity of 50,000 tonnes. Sludge samples were collected after the sludge drying process over a five-day period in May 2021. During sampling, a total of five sub-samples (5 L each) were collected each day. After sampling, a coning and quartering method [9] was applied repeatedly to reduce the sample to a size suitable for conducting laboratory analysis. After sampling, the sample was stored in a polyethylene bottle in a refrigerator (+4 °C) until analysis.

Sludge ash was obtained by incinerating the above-mentioned wastewater sludge at a temperature of 850 °C (overnight) in a Nabertherm L24/11 muffle furnace (Nabertherm GmbH, Lilientjal, Germany) until a constant weight was obtained. This temperature was selected because the European Union Industrial Emission Directive (2010/75/EC), known as “The Industrial Emission Directive”, requires this minimum temperature to be used in

the incineration plants where wastes are incinerated [10, 11]. This directive is also applied to forest industry power plants that incinerate wastewater treatment sludges.

Determination of minerals in the sludge and sludge ash

To determine the mineralogical composition of the sludge and sludge ash, an X-ray diffractogram of the sample was obtained with a Siemens D 5000 diffractometer (Siemens AG, Karlsruhe, Germany) using CuKα radiation. The scan was run from 5° to 80° (2-theta scale) in increments of 0.02° with a counting time of 1.0 s per step. The operating conditions were 40 kV and 40 mA. Peak identification was carried out using the DIFFRACplus BASIC Evaluation Package PDFMaint 12 (Bruker AXS, Germany) and ICDD PDF-2 Release 2006 software package (Pennsylvania, USA).

Determination of the physical and chemical properties of the sludge and sludge ash

The pH in the sludge and sludge ash was determined according to the standard ISO 10390:2005 at a solid-to-liquid (ultrapure water) volume ratio of 1:5 [12]. The dry matter content, DMC was determined according to the European standard SFS-EN 15934:2012 [13], in which a sample is dried overnight to a constant mass in an oven at 105 °C. The loss-on-ignition, LOI value was determined according to European standard SFS-EN 15169 at a temperature of 550 °C [14]. The neutralising value, *NV*, also called a liming effect value and the reactivity value, *RV* were determined according to the European standards SFS-EN 12945 [15] and the SFS-EN 13971 [16], respectively.

The total organic carbon (TOC) of the sludge and sludge ash was determined by dry combustion using a LECO CN 828 analyser (Leco Corp; USA). The total nitrogen (Tot-N) of the ash was determined according to the European standard SFS-EN 13654-1 by the Kjeldahl method using a Foss-Tecator Kjeltee 2300 Analyzer (Hoganas, Sweden) equipped with a Foss-Tecator 2020 Degistor (Hoganas, Sweden) [17]. Temperature-resistant coliforms and *Escherichia coli* in the sludge and sludge ash were determined by the NMKL method 125 [18] and *Salmonella* by the standard ISO 6579 [19, 20].

Determination of easily soluble nutrients in the sludge and sludge ash

The easily soluble forms of P, Ca, Na, K, Mg and S were extracted with 0.5 M acidic (pH 4.65) ammonium acetate (CH_3COONH_4), and in the extraction of Mn, Cu and Zn, the acidic (pH 4.65) ammonium acetate extract contained 0.02 M ethylenediaminetetra-acetic acid disodium salt (Na_2EDTA). In both extraction procedures, one part by volume of a dry sample was shaken with 10 parts of the extraction solution for 1 h. Before analysis, the extract was separated from the solid residue by filtration through 12.5 mm-diameter Schleicher & Schuell 589 blue ribbon filter paper.

The concentrations of Ca, Na, K, Mg and S were determined using a Thermo Fisher Scientific iCAP6500 Duo (United Kingdom) inductively coupled plasma optical emission spectrometer (ICP-OES), and the concentrations of Mn, Cu and Zn were determined using a flame atomic absorption spectrometer (FAAS, Perkin Elmer AAnalyst 700, Norwalk, USA). The concentration of P in the extract was determined spectrophotometrically by the molybdenum blue method using an automatic Foss-Tecator FIAStar 500 Flow Injection Analyser (Hoganas, Sweden). The above-mentioned methods were selected for the determination of easily soluble nutrients in the sludge and sludge ash investigated in this study because they are widely used and commonly accepted. Furthermore, Finnish

legislation does not define the digestion method for nutrients [21]. Details of the analytical methods of the standards can be found in a previous publication [19].

Determination of total element concentrations in the sludge and sludge ash

For the determination of the total element concentrations in the sludge and sludge ash, a dried sample was digested with a mixture of HCl (3 mL) and HNO_3 (9 mL) in a CEM Mars 5 microprocessor-controlled microwave oven with CEM HP 500 Teflon vessels (USA) using USEPA method 3051A [21]. This digestion method is accepted in Finnish legislation for the determination of total element concentrations in environmental samples, e.g. in fertiliser products [21]. The cooled solution was transferred to a 100 mL volumetric flask, and the solution was diluted to volume with ultrapure water. Except for Hg, the total element concentrations in the sludge and sludge ash were determined with a Thermo Fisher Scientific iCAP6500 Duo (United Kingdom) ICP-OES. The concentration of Hg in the sludge and sludge ash was determined using a Perkin Elmer AAnalyst 700 cold-vapour atomic absorption spectrometer.

Determination of the extractable element concentrations in the sludge and sludge ash

The three-step sequential extraction for the fractionation of heavy metals in sludge and sludge ash was carried out using the method of Standard, Measurement and Testing programme (former Community Bureau of References), which is fully described in Table 1 [8]. In this procedure, which is widely known as the BCR extraction procedure, the sequential extraction of sludge (1 g) and sludge ash (1 g) was carried out as follows: (1) acetic acid (40 mL CH_3COOH; 0.11 mol/L; pH = 2.9) extraction to recover the heavy metals in the sample into the exchangeable fraction, (2) hydroxylamine hydrochloride (40 mL NH_2OH-HCl in nitric acid medium, 0.1 mol/L; pH = 2.0) extraction to recover the heavy metals in the sample into the reducible fraction, and (3) hydrogen peroxide digestion (10 mL H_2O_2; 30 %; twice) followed by ammonium acetate (50 mL CH_3COONH_4; 1.0 mol/L; pH = 2.0) extraction to recover the heavy metals in the sample into the oxidisable fraction.

Table 1

Three-step BCR sequential extraction procedure for sludge and sludge ash

Step	Fraction	Reagent (1 g sample)	Time and temperature
1	Exchangeable	40 mL 0.11 M CH_3COOH (pH = 2.9)	16 h at 25 °C
2	Reducible	40 mL 0.1 M NH_2OH-HCl (pH = 2.0)	16 h at 25 °C
3	Oxidisable	10 mL 30 % H_2O_2 (evaporation; twice) + 50 mL 1.0 M CH_3COONH_4 (pH = 2.0)	1 h at 85 °C (twice) 16 h at 25 °C

In order to avoid possible chemical and/or microbiological changes in the samples, the extraction was carried out using the samples in their original form as such without further processing, since drying a sample before sequential extraction may change the form in which the elements occur in the sample and may change the bioavailability of elements [22]. After each extraction step, the extracts were separated from the solid residue by filtration through a 0.45 µm membrane filter (47 mm diameter; Schleicher & Schuell, Dassel, Germany). In order to avoid losses between the extraction stages, the filters and adhering residue particles from the previous extraction stage were also included in the next stage. After the addition of 200 µL of 65 % HNO_3 to the supernatant phase, the extracts

were stored in a refrigerator (+4 °C) until the extraction test was performed and trace element concentrations were determined. The element concentrations in the extracts (extraction stages 1-3) were determined with a Thermo Fisher Scientific iCAP6500 Duo (United Kingdom) inductively coupled plasma optical emission spectrometer (ICP-OES).

Results and discussion

Minerals in the sludge and sludge ash

According to results in Table 2, only small amounts of quartz (1.3 %), which is a silicate mineral was observed in the sludge. This is reasonable because wastewater sludge from the forest industry is rich in fibrous material and an XRD spectrometer is unable to identify amorphous (i.e. non-crystalline) matter. This together with the fact that the detection limit of XRD spectrometry is normally between 1 % - 2 % [23] and only the crystalline forms of cellulose fibres are able to be identified by XRD were reasons why the presence of cellulose was not observed in our sludge, although it is a common material in pulp and paper mill sludges [24].

The most prevalent minerals occurring in the sludge ash were albite (32.1 %), hematite (25.1 %) and bobdownsite (14.7 %) followed by smaller amounts of quartz (8.3 %), microcline (7.9 %), oldhamite (5.0 %), hauyne (4.3 %) and cristobalite (2.5 %). The amount of anhydrite was negligible (0.1 %) with the exception of quartz (SiO_2), which also existed in the sludge (1.3 %), the occurrence of the above-mentioned minerals in the sludge ash is according to Vassilev et al. [25] mainly due to new phases generated by solid, liquid and gas reactions among pre-existing and newly formed compounds during the combustion process.

Table 2

Minerals in the sludge and sludge ash

Mineral	Formula	Sludge [%]	Sludge ash [%]
Albite	$NaAlSi_3O_8$	n.d.	32.1
Anhydrite	$CaSO_4$	n.d.	0.1
Bobdownsite	$Ca_9Mg(PO_4)_6PO_3F$	n.d.	14.7
Cristobalite	SiO_2	n.d.	2.5
Hauyne	$KNa_5Ca_2Al_6Si$	n.d.	4.3
Hematite	Fe_2O_3	n.d.	25.1
Microcline	$KAlSi_3O_8$	n.d.	7.9
Oldhamite	(Ca,Mg)S	n.d.	5.0
Quartz	SiO_2	1.3	8.3

n.d. - not detected

Physical and chemical properties of the sludge and sludge ash

According to the results in Table 3, the dry matter content of the sludge when it was purged out of the wastewater treatment plant was only 31.6 %. The poor drying characteristic of the sludge is due to its the gel-like structure consisting largely of extra-cellular polymeric substances and high interstitial water, i.e. water stored within the sludge flocs by capillary forces and chemically bound intracellular water [24]. This indicates that the incineration of this residue as such will lead to an uneconomical energy balance when combusted in biomass boilers. Although processes and wastewater treatment

plants among different pulp and paper mills are not identical, the DMC for sludge investigated in this study agrees relatively well with the findings reported in another study [26], in which the dry matter content of the pulp/paper mill sludge was 29.4 %.

Table 3

Physical and chemical properties, as well as easily soluble plant nutrient concentrations and pathogens in sludge, sludge ash and in arable soil in the Pirkanmaa region in southern Finland [35] and Finnish limit values for pathogens in fertiliser products

Property	Sludge	Sludge ash	Limit value	Finnish arable soil
DMC [%]	31.6	99.8		
pH [-]	6.4	9.5		5.7-7.3
EC [mS/cm]	0.2	6.9		0.06-0.13
NV [% Ca d.m.]	3.0	7.1		
RV [% Ca d.m.]	1.4	7.0		
LOI [%]	90.3	< 0.2		
TOC [%]	47	< 0.5		1.4-4.1
Tot-N [g/kg d.m.]	19	0.8		
TOC/Tot-N	24.7	6.7		
Ca [mg/kg d.m.]	1,500	21,000		799-3,828
Mg [mg/kg d.m.]	230	400		62.0-455
K [mg/kg d.m.]	130	6,000		58.0-349
Na [mg/kg d.m.]	720	26,000		
P [mg/kg d.m.]	32	830		4.1-97.0
S [mg/kg d.m.]	68	18,000		6.7-35.0
Mn [mg/kg d.m.]	150	140		44-231
Cu [mg/kg d.m.]	1.7	7		1.6-7.7
Zn [mg/kg d.m.]	34	77		0.9-4.9
Salmonella [CFU/25 g]	not detected		not detected	
Escherichia coli [CFU/g]	< 10	0	1000	

d.m. - dry matter, CFU - colony forming unit

The pH of the sludge and sludge ash is an important factor when these residues are applied as a fertiliser or soil amendment since it affects the pH of soil, which in turn may change the availability of elements and the soil microbial community [27]. According to Khater [28], the optimal pH value for a growing medium is between 5.2 and 7.3, whereas Neina [29] reported that it is between 5.5 and 8.8. Therefore, we conclude that if the pulp sludge investigated in this study is used as a fertiliser or soil amelioration agent, it is not likely to cause an unexpected pH shock-effect to biota, due to its pH value of 6.4. If the sludge ash is utilised as a fertiliser product or as a soil amendment, it would not cause a pH shock-effect to biota as easily as ash from the incineration of conventional Finnish biomass-based fuels (bark, woodchip and sawdust), which are strongly alkaline in nature (pH = 12). Such ash is by volume one of the main side-stream from municipal district heating plants and industrial-scale power plants, e.g. forest industry plants in Finland [7, 18].

The electrical conductivity, *EC* value, which does not identify the type of salt present in the sample but only the total cumulative concentration of the soluble salts [30], was 0.2 mS/cm in the sludge and 6.9 mS/cm in the sludge ash. The electrical conductivity value in our sludge is similar to the *EC* value of 0.5 mS/cm found in another paper mill sludge, although *EC* values up to 3.1 mS/cm have been observed [31]. From the utilisation point of

view, the *EC* values in our sludge and sludge ash were significantly below the threshold value of 180 mS/cm, which causes salt stress for most plant seedlings [32].

The neutralising value, *NV* and reactivity value, *RV* are important indicators when evaluating the fertiliser potential of samples as a liming agent in acidic soil. The capacity of liming agent to neutralise soil acidity depends on its content of soluble and hydrolysable bases (oxides, hydroxides, carbonates and silicates), which is measured as a *NV*-value. The *NV*-values of sludge and sludge ash were 3.0 % and 7.1 % expressed as Ca in dry matter, respectively.

According to Rasa et al. [33], the relatively high organic matter content in pulp sludge measured as LOI and TOC is an advantage, because it may increase the organic matter of soil if this residue is used as a fertiliser or soil improvement product. A decline in soil organic carbon (C) increases the risk of erosion and nutrient leaching. For example, in Finland the average annual decline in mineral soils in recent decades has been 0.4 % or 220 kg/10,000 m^2 [34]. If the decomposition of pulp sludge in soil is slow, as one may expect due to containing relatively slowly degrading organic compounds like cellulose and lignin, this residue would potentially provide a platform for microbial substances to form an organo-mineral association with clay-sized soil particles, which in turn reduces erosion, surface runoff and improves water- and nutrient retention [35].

Carbon and nitrogen are important nutrients in fertilisers. In soil, microbes use carbon for energy and growth, and nitrogen for protein and reproduction [36]. In this study, the total organic carbon content in the sludge measured as TOC was 47 %, loss in ignition LOI (90.3 %) and total nitrogen 19 g/kg d.m. The ratio of carbon to nitrogen (C/N) is an important parameter that influences the biochemical conversion of biomass in soil. In general, microbial decomposition slowed when the C/N ratio of any biomass is greater than 25. According to Li et al. [37], commercial organic amendments must have the C/N ratio less than 30 in order to make nitrogen available to crops. As the TOC/N ratio in the sludge we studied was 24.7, we conclude that this residue has the potential to act as a slow-release nitrogen fertiliser in soil.

Easily soluble nutrient concentrations in the sludge and sludge ash

The easily soluble plant nutrient concentrations in Table 3 are expressed on a dry matter basis. The easily soluble nutrient concentrations for Ca, Mg, K and P in the sludge are comparable by those in typical Finnish arable soil. This means that the nutrification effect of the sludge is limited. However, the results show that these elements concentrate after the sludge has been incinerated into ash. Relatively low nutrient concentrations may be beneficial, as the main purpose to use sludges in agriculture is to increase the carbon content of the soil. The low concentration of phosphorus in sludge, (32 mg/kg d.m.) might also be beneficial from a leaching perspective. The concentration of sulphur in the ash (68 mg/kg d.m.) is somewhat higher than typical Finnish arable soil values.

Total element concentrations in the sludge and sludge ash

According to the Finnish Fertiliser Product Act, the term “fertiliser product” refers to fertilisers, liming materials, soil conditioners, substrates, microbe products and by-products used as fertiliser products [38]. All fertiliser products on the market need to be safe, of good quality, and suitable for plant growth. The Finnish Fertiliser Product Decree sets maximum limit values for certain heavy metal (As, Hg, Cd, Cr, Cu, Pb, Ni and Zn) concentrations for sludge used as a fertiliser product [39] and for ash fertiliser used in forestry [21] (Table 4).

These limit values, as well as the total metal concentrations in the sludge and sludge ash are expressed on a dry matter basis in Table 4.

Table 4
Total concentrations of elements in the sludge and sludge ash, the enrichment factors, *EF* as well as the EU [43] and Finnish limit values for elements [21]

Element	Sludge [mg/kg d.m.]	Sludge ash [mg/kg d.m.]	*EF*[a]	Limit values [mg/kg d.m.]			
				EU1	EU2	FP	AF
Al	1,500	14,000	9.3				
As	< 3.0	10	> 3.3	40	40	25	40
B	31	150	4.8				
Ba	130	1,000	7.7				
Ca	7,400	83,000	11.2				
Cd	4.9	39	7.9	1.5	2.0	1.5	25
Cr	17	160	9.4	2.0[b]	2.0[b]	300	300
Cu	14	180	12.9	300	300	600	700
Fe	13,000	140,000	10.8				
Hg	< 0.04	< 0.04	n.d.	1.0	1.0	1.0	1.0
K	750	11,000	14.7				
Mg	1,100	10,000	9.1				
Mn	570	7,000	12.3				
Na	3,100	30,000	9.7				
Ni	13	99	7.6	50	50	100	150
P	2,200	26,000	11.8				
Pb	6.9	84	12.2	120	120	100	150
S	6,500	40,000	6.2				
Zn	190	2200	11.6	800	800	1,500	4,500

[a]*EF* - [(Total concentration in sludge ash) / (Total concentration in sludge)], [b] - Hexavalent chromium Cr^{VI}, EU1 - EU limit values for elements in organic fertiliser, EU2 - EU limit values for elements in organic soil improvers, FP - Finnish limit value for elements in fertiliser products used in agriculture, AF = Finnish limit values for elements in ash fertiliser used in forestry

The limit values in Table 4 are not applied to soil improvers, growing media or other fertiliser products used in landscaping, landfill sites or other closed areas such as closed industrial areas and airports; however, an environmental permit from the national statutory authority is needed for these kinds of applications, because in this kind of utilisation sludge and sludge ash are legally not any more regarded as a fertiliser, but a waste.

Although the efficiency of chemical recovery unit in modern pulp mills can be very high (> 97 %), traces of chemicals nevertheless pass through this recovery unit and the pulp washing process, after which they accumulate in wastewaters and in wastewater treatment sludge. The highly elevated total Ca concentration in the sludge (7,400 mg/kg d.m.) and sludge ash (83,000 mg/kg d.m.), therefore is reasonable given that calcium is the most abundant mineral in wood and it plays an important role in the chemical recovery cycle of pulp mill, especially in the causticising process [40]. The elevated total Na concentrations in sludge (3,100 mg/kg d.m.) and sludge ash (30,000 mg/kg d.m.) is also reasonable, given that white liquor is the main active cooking chemical in the sulphate (Kraft) pulping process, in which sulphur exists e.g. in the form of NaOH and Na_2S [41]. Furthermore, the total sulphur concentration in the sludge (6,500 mg/kg d.m.) and sludge ash (40,000 mg/kg d.m.) are reasonable, given that sulphur in black liquor takes many forms, for instance sulphide, thiosulphate, sulphite, sulphate, and organic sulphur [42].

The total concentration of Cr (17 mg/kg d.m. in sludge and 160 mg/kg d.m. in the sludge ash) were low and not limiting factors according to current Finnish national legislation for the use of these residues as fertiliser products in agriculture and forestry. In this context it is worth noting, that the European Union regulation 2019/1009 has not yet been implemented in Finland. This regulation has a limit value of 2.0 mg/kg d.m. for Cr^{VI} in solid organic fertiliser and organic soil improvers, and may in the future be a factor that restricts the reuse options of industrial residues as a fertiliser e.g. in agriculture [43].

The enrichment factors of elements in the sludge ash

In order to determine the volatility of elements during the incineration of the sludge, the enrichment factor values for elements in the sludge ash were defined by the concentration of the compound in the sludge ash divided by the concentration of this compound in the sludge (Table 4). The volatility of heavy metals depends on factors such as their form of occurrence, properties of the sludge, and the conditions of combustion [44]. A high *EF*-value indicates that the element is mainly transferred to the sludge ash. A low *EF*-value indicates that the element is relatively volatile during incineration and any vaporised material will not recondense on the surface of ash particles. The enrichment factor value of about 1 indicates that no vaporisation will occur and the element concentration in the sludge and sludge ash are principally equal [45].

The total-N concentration (800 mg/kg d.w.) in the sludge ash was clearly lower than that in the sludge (19,000 mg/kg d.w.), which indicates that nitrogen has vaporised during incineration. With the exception of Hg, all elements studied showed a clear enrichment during the incineration of the sludge to the sludge ash. This result indicates that, while the converting of pulp sludge into pulp sludge ash increased the concentration of heavy metals, the incineration of the pulp sludge may promote the reuse of this industrial side-stream as value-adding by-products by increasing the concentration of certain essential plant nutrients (P, K, S, Ca and Mg).

Extractable element concentrations in sludge and sludge ash

Weathering is a naturally occurring process that change the composition of waste materials (e.g. sludge and ash) and leachability of heavy metals during outdoor storage or utilisation [46]. Weathering is a series of geochemical processes caused by atmospheric gases (e.g. CO_2) and acid rain that change the pH and thus the stability of waste material. During storage or utilisation, the pH of a waste material may also be changed due to natural acid formation during anaerobic microbial degradation and sulphide oxidation [47].

Measuring the total concentrations of elements in a solid sample provide little indication of the environmental and ecological effects of a waste material if it is utilised in a soil environment. Although the total concentration of elements in sludge and related materials can give important information if it is compared to the national statutory permissible threshold values, the mobility, bioavailability and geochemical processes of elements in the different environmental conditions depend strongly on their geochemical fractions [48] and binding capacity [23]. Therefore, the potential mobility and bioavailability of elements in the solid waste materials are typically also investigated, a step now required by Finnish environmental authorities [49].

During the three-step BCR sequential extraction (Table 1), the extraction process is carried out using solutions (extractants), of increasing strength [50]. In the three-step BCR extraction, the most bioavailable category includes the elements extractable in the BCR1

fraction (exchangeable fraction). Therefore, the mobility and bioavailability of element fractions decrease in the following sequence: BCR1 > BCR2 > BCR3 [51].

In the BCR1 fraction (exchangeable fraction), in which acetic acid (CH_3COOH) is used as extractant, elements are adsorbed and retained on the solid surface by relatively weak electrostatic force, metals bonded with weak covalent bonds, or metals bonded to carbonates [52]. Elements in this fraction could be released by ion-exchange processes, or by the influence of adsorption-desorption reactions, lowering of pH or if the ionic composition changes (e.g. acid rain) [48]. The highest extractable concentrations in this fraction were observed for Ca (4,930 mg/kg d.m.) and Na (3,020 mg/kg d.m.) in the sludge, whereas in the sludge ash the highest extractable concentrations were observed for S (32,100 mg/kg d.m.), Ca (31,700 mg/kg d.m.), Na (25,900 mg/kg d.m.), and K (8,190 mg/kg d.m.).

In the BCR2 fraction (reducible fraction), in which hydroxylamine hydrochloride (NH_2OH-HCl) is used as extractant, elements extracted are principally Fe-Mn oxides bound elements. These are not usually easy to release from the sample matrix under normal conditions because of relatively strong ionic bonding [53]. However, with the effect of time, they can be transformed into less mobile, easily adsorbed forms [48]. The highest extractable concentrations in this fraction were observed for Fe (7,170 mg/kg d.m.) and Ca (2,180 mg/kg d.m.) in the sludge, whereas in the sludge ash the highest extractable concentrations were observed for Ca (37,000 mg/kg d.m.), P (22,000 mg/kg d.m.), Al (7,800 mg/kg d.m.), and S (4,800 mg/kg d.m.).

Table 5

The BCR sequential extractable concentrations of element in sludge and sludge ash between exchangeable (BCR1), reducible (BCR2) and oxidisable (BCR3) fractions as well as their solubility index, *SI* and recovery factor, *RF* values

Element	Sludge					Sludge ash				
	[mg/kg d.m.]			[%]		[mg/kg d.m.]			[%]	
	BCR1	BCR2	BCR3	*SI*[a]	*RF*[b]	BCR1	BCR2	BCR3	*SI*[a]	*RF*[b]
Al	47	347	695	3.13	72.6	130	7800	460	0.93	59.9
As	< 0.6	< 0.6	< 0.7	< 20	< 0.2	1.3	5.0	< 0.7	< 0.1	0.7
B	17	7.1	1.9	55	17	55	31	9.5	37	64
Ba	30	73	15	23.1	90.8	2.9	47	890	0.29	94.0
Ca	4930	2,180	321	66.6	100.4	31,700	37,000	960	38.2	83.9
Cd	1.3	3.1	0.35	26.5	96.9	8.4	8.8	4.5	21.5	55.6
Cr	< 0.4	1.3	7.3	< 2.4	50.6	7.1	1.5	1.6	4.4	6.4
Cu	< 0.4	1.7	12	< 2.8	97.9	4.4	10	< 0.5	2.4	8.3
Fe	802	7,170	2,950	6.17	84.0	37	570	280	0.03	0.63
K	524	60	149	69.9	97.7	8,190	990	140	74.4	84.7
Mn	422	152	27	74.0	105	164	330	163	2.34	9.39
Mg	808	174	206	73	108	1,770	2,400	277	18	44
Na	3020	241	73	97	108	25,900	3,400	190	86	98
Ni	1.5	2.1	5.8	11.5	72.3	1.5	2.3	2.1	1.52	5.96
P	104	977	903	4.73	90.2	1950	22,000	560	7.5	94.2
Pb	< 0.6	< 0.6	< 0.75	< 8.70	< 28.2	0.65	36	23	0.77	71.0
S	178	226	4,830	2.74	80.5	32,100	4,800	140	80.25	92.6
Zn	94	83	19	49.5	103.2	60	79	42	2.73	8.23

[a]*SI* - [(BCR1 concentration in Table 5) / (Total concentration in Table 4) · 100 %], [b]*RF* - [(BCR1+BCR2+BCR3 concentration in Table 5) / (Total concentration in Table 4) · 100%]

In the BCR3 fraction (oxidisable fraction), in which the mineral structure of the sample is destroyed using a hydrogen peroxide (H_2O_2) digestion following the extraction using ammonium acetate (CH_3COONH_4), elements are bonded to organic matter or to different sulphides and oxides [50].

Although elements in the BCR3 fraction are not considered very mobile or available, they can be released from the sample matrix slowly [53]. The highest extractable concentrations in this fraction were observed for S (4,830 mg/kg d.m.) and Fe (2,950 mg/kg d.m.) in the sludge, whereas in the sludge ash the highest extractable concentrations were observed for Ca (960 mg/kg d.m.), Ba (890 mg/kg d.m.), P (560 mg/kg d.m.) and Al (460 mg/kg d.m.)

The solubility index values of elements in the sludge and sludge ash

The solubility index, *SI*-values for elements released from the sample matrix during the BCR sequential extraction procedure were determined following the procedure of Jamroz et al. [54]. In this context, the *SI*-value for every element is the percentage ratio of the extractable element concentration in the BCR1 fraction to the total element concentration in the sludge and sludge ash (Table 5). A low *SI*-value indicates that element releases poorly from the sample matrix, whereas a high *SI* value indicates that the element releases more easily from the sample matrix. An *SI*-value of 100 % indicates that the element is completely soluble in the extraction solvent. From an environmental point of view, high *SI*-values mean that elements are potentially bioavailable if the residue is applied as a fertiliser product. The highest *SI*-values in the sludge were observed for Ca, K and Mn, which is positive as they are valuable from a fertilisation perspective. In sludge ash the highest *SI*-values were observed for K and S. The *SI*-values for Ca and Mn differed significantly from the values measured in the sludge. For Cd approximately 25 % cadmium was soluble in the sludge and 21.5 % in sludge ash. This is a positive finding that indicates a relatively poor solubility of Cd. It is notable that for Cu and Cr, the *SI*-values were very low both for the sludge and sludge ash.

The recovery factory values of elements in the sludge and sludge ash

The recovery factor values for elements released from the sample matrix during the BCR sequential extraction procedure were determined following the procedure of Wuana et al. [55]. In this context, the *RF*-value for each element is the percentage ratio of the sum of three extractable fractions to the total element concentration in the sludge and sludge ash (see Table 5). According to Pesonen et al. [52], this ratio corresponds to the potential total bioavailability of elements, although the sum of sequential extraction does not necessarily mean total decomposition and cumulative extractable recovery is usually markedly lower than the total concentration.

From an environmental point of view, an *RF*-value of 100 % corresponds to the “worst case scenario”, in which the components of the sample matrix become totally soluble and mobile. In nature, this is likely only if elements retained within the crystal lattice of minerals and inside crystallised oxides are mineralised e.g. as a result of weathering [51]. The presupposition for a high *RF*-value is that during the BCR sequential extraction, elements are released not only from the sample matrix associated with the exchangeable fraction (BCR1) but also from the reducible (BCR2) and the oxidisable (BCR3) fractions, in which elements are more tightly bound to the sample matrix than in BCR1 fraction.

Generally, the *RF* values of the elements in the sludge approach 100 %. Exceptions include Cr, with an *RF*-value near 50 % and Pb with an *RF*-value falling just above the detectible limits. For sludge ashes we can observe three separate element groups.

Quality control of the BCR extraction procedure

Quality control of the three step BCR sequential procedure used in this study was carried out by the certified reference material BCR 701 (Table 6), which was extracted in a similar fashion to the wastewater sludge and sludge ash in our study (Table 1). The use of this reference material during BCR sequential extraction is reasonable as this material is standardised, developed and certified by the Community Bureau of References (BCR), which also created and named the sequential extraction procedure in 1993. In addition, the BCR 701 reference material (sediment, Lake Orta Piemonte, Italy) is the only currently available reference material for the sequential extraction procedure. However, only Cd, Cr, Cu, Ni, Pb and Zn concentrations are certified for this reference material [56].

The measured values as compared to the certified values for elements varied between 96.5 % and 119 %. These percentages suggested that our three step BCR sequential extraction procedure was accurate. Thus, our results agree well with the values of between 87 % and 121 % for this reference material as observed by other researchers [50]. The precision (repeatability) of the BCR sequential extraction procedure for elements in the certified reference material as calculated by the relative standard deviations varied between 1.0 % and 7.4 %, which is relatively good.

Table 6

Quality control results of the BCR sequential extraction procedure (n = 3)

Step	Value	Cd	Cr	Cu	Ni	Pb	Zn
		[mg/kg d.m.]					
BCR1	Certified	7.34 ±0.35	2.26 ±0.16	49.3 ±1.7	15.4 ±0.9	3.18 ±0.21	205 ±6
	Measured	7.5 ±0.2	2.7 ±0.2	53.0 ±0.0	16.0 ±0.0	3.3 ±0.1	196 ±2
BCR2	Certified	3.77 ±0.28	45.7 ±2.0	124 ±3	26.6 ±1.3	126 ±3	114 ±5
	Measured	3.9 ±0.2	49.7 ±2.1	124 ±2	30.0 ±1.0	137 ±7	118 ±7
BCR3	Certified	0.27 ±0.06	143 ±7	55.2 ±4.0	15.3 ±0.9	9.30 ±2.00	45.7 ±4.0
	Measured	0.3 ±0.0	155 ±9	59.3 ±3.2	15.3 ±0.6	8.1 ±0.4	45.3 ±3.2

The values in our study fall between 96.5 % and 119 % of those in the certified reference material, indicating that our three step BCR sequential extraction procedure was accurate. Our results fall between 87 and 121 % of the values for this reference material observed by other researchers [57]. The precision (repeatability) of the BCR sequential extraction procedure for elements in the certified reference material as calculated by the relative standard deviations varied between 1.0 % and 7.4 %, which is relatively good.

Conclusion

Based on the total element concentrations in the wastewater sludge investigated in this study, the utilisation of this residue as such as a fertiliser or soil improvement material may be troublesome, as the Cd concentration (4.9 mg/kg d.m.) in our sludge exceeded both the statutory Finnish limit value (1.5 mg/kg d.m.) and the European Union limit values (1.5 and 2.0 mg/kg d.m.) or this element for fertilisers and soil improvers. Because the

concentrations of other heavy metals in this sludge were well below the above-mentioned limits set in the legislation, the elevated Cd concentration may be considered the major drawback for the utilisation of this residue as such in agriculture. The Cd concentration in sludge ash (39 mg/kg d.m.) exceeded the Finnish limit for ash fertilisers used in forestry (25 mg/kg d.m.), which restricts the potential reuse options of this residue.

It is worth noting that although the incineration of pulp sludge enriched the concentration of heavy metals in the ash, the converting of sludge into ash may promote the reuse of this wastewater treatment residue as a more value-added fertiliser by-product to be used as a soil improver and growing medium in landscaping or landfill sites, or in other areas such as closed industrial areas, where the heavy metal limit values for fertiliser products are not applied. However separate environmental permits need to be granted for these applications. The enrichment of essential plant macro-nutrients was most notable, resulting to the following total concentrations of these elements in the sludge ash: P (26,000 mg/kg d.m.), S (40,000 mg/kg d.m.), K (11,000 mg/kg d.m.), Ca (83,000 mg/kg d.m.) and Mg (10,000 mg/kg d.m.). Therefore, we conclude that the converting of the sludge into ash may promote the reuse of this wastewater treatment residue, although incineration might be uneconomical.

The solubility index values calculated after BCR sequential extraction show low solubility for Cd as well as for Cr, Cu, Ni and Zn in the sludge ash. Therefore, we conclude that this is beneficial if an environmental permit for the utilisation of this residue is applied for closed industrial areas. One important factor which is worth noting and will in the future regulate the reuse options of all industrial residues is the European Union regulation 2019/1009, as soon as it is implemented in different EU countries.

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