Comparison of Untreated, Lime-Stabilised and Composted Wastewater Sludges from a Pulp, Board and Paper Mill Integrate as a Fertiliser Product

Juha Oksanen[1*], Risto Pöykiö[2], Olli Dahl[3]

[1] Stora Enso International Oy, Imatra Research Centre, Tornansaarenraitti 48, FI-55800 Imatra, Finland

[2] City of Kemi, Department of Environmental Protection, Valtakatu 26, FI-94100 Kemi, Finland

[3] Aalto University, School of Chemical Technology, Department of Bioproducts and Biosystems. PO Box 16300, FI-00076 Aalto, Finland

[*] Corresponding author´s e-mail: juha.oksanen@storaenso.com

ABSTRACT

In this study, the physical and chemical properties of untreated, lime-stabilised and composted wastewater sludges from a Finnish pulp, board and paper mill integrate were compared in order to assess their fertiliser properties based on the requirement of the Finnish Fertilizer Product Decree. Furthermore, the extraction properties of heavy metals in the sludges were assessed by the three-stage sequential extraction procedure of the Community Bureau of Reference (BCR) and the solubility indices for heavy metals were calculated in order to evaluate the release potential of elements from the sample (sludge) matrix. The results of this study indicated that the total heavy metal (As, Cd, Cr, Cu, Hg, Ni, Pb and Zn) concentrations in all sludges were lower than the statutory Finnish limit values for fertiliser products. However, the untreated sludge required either lime-stabilisation or composting in order to fulfil the Finnish maximum concentrations of pathogens (coliforms and *Escherichia coli*) for fertiliser products.

Keywords: pulp and paper mill sludge, fertiliser, forest industry, BCR sequential extraction

INTRODUCTION

In 2020, the European Commission adopted a new circular economy (CE) action plan highlighting the importance of promoting the circularity of industrial processes. The CE is based on the waste hierarchy principles of the European Union (EU) and promotes the reuse and recycling of residues instead of combustion for energy and disposal. In addition, the EU supported a transition towards the CE and circulation of biological streams by prohibiting the landfilling of organic waste beginning in 2016 [Muscio and Sisto, 2020]. However, considerable amounts of organic waste and residues from industrial processes are still underutilised as low-value energy sources, which is not in accordance with the current CE principles. In order to reach the CE policy targets, companies should adopt new sustainable practices in their processes that promote the reuse of sludges instead of their incineration.

Pulp and paper mills generate a wide range of wastes and side streams from various processes. The composition of these mainly depends on the type of pulp and paper manufactured, as well as the origin of cellulose fibres, process conditions and chemicals used [Kinnarinen et al., 2016]. These side streams may be categorised as high-value, medium-value and low-value. They were previously unjustifiably regarded as waste, although, in recent years, the side streams from one stage of production typically are often utilised in a further process step at the mill or as a product where markets and uses exist.

Typical high-value side streams are bark and wood residues produced during the sawmill process, which can be used as a raw material for pulp production. High-volume side streams also

include tall oil and turpentine, which can bring in financial benefit if they are sold outside the mill to other manufacturers for the production of liquid biofuels (green renewable diesel) or black and green liquor, which are both digesters from the causticizing process. Black liquor is mainly used for the mill own energy consumption during kraft pulping, and green liquor is circulated in a causticizing process as a cooking chemical. Typical medium-value side streams are bark, woodchips and sawdust residues, which cannot be used in the cooking process and are therefore incinerated at the mill to generate energy [Watkins et al., 2010].

Low-value side streams, such as biosludge, which is also called activated sludge, as well as primary sludge and secondary sludge, which originate from forest industry wastewater treatment plants, do not have an economical value in the form of fuel. Instead, in Finland, after dewatering, they are mostly incinerated in fluidised-bed boilers to reduce their volume. The paper mill residue "fibre clay", which is also known as fibre sludge, is a secondary sludge originating from the chemical wastewater treatment of papermaking effluent stream. These, along with the causticizing by-products such as green liquor dregs and lime mud, are all low-value side streams and are mostly utilised in landscaping [Watkins et al., 2010].

In 2018, approximately 370,000 dry tons of pulp and paper mill sludges were generated in Finland, of which 83% was incinerated, 12% was used as an earth construction agent and only 5% was used for a more value-added end use, such as agricultural fertiliser. Consequently, investigating the utilisation options for pulp and paper mill sludges other than incineration has become increasingly attractive, and comprehensive research studies that support the circulation of these residues are required. Circulation of waste should not cause any danger or hazard to health or the environment. In order to secure the proper reuse of sludges, limit values are often set in national legislations in the European Union (EU), for example, for heavy metals and for pathogens [Collivignarelli et al., 2019].

This paper explored the main physical, chemical, and microbiological, as well as extraction properties of the untreated, lime-stabilised, and composted activated sludge from a biological wastewater treatment plant from a Finnish pulp, board, and paper mill integrate, located in southeastern Finland. This study investigated the potential utilisation of these residues as a biofertiliser based on the requirements of Finnish Fertilizer Product Decree.

MATERIAL AND METHODS

Sampling of sludges

This study was carried out at the integrated pulp, paper and board mill of Stora Enso Imatra Mills in southeastern Finland. The mill facility is complex and consists of a pulp mill with a bleached hardwood pulp production line and both bleached and unbleached softwood pulp production lines. In addition, chemi-thermomechanical pulp (CTMP) is produced at the mill. Paperboard is produced on four board machines. The annual capacity of the mill is 1,195,000 tonnes of consumer packaging board and 1,300,000 tonnes of pulp. The board mill effluents are handled at a chemical wastewater treatment plant, whereas the effluents from the pulp production are purified at an activated sludge treatment plant.

The typical composition of the sludge generated at Stora Enso's Imatra mill site is 85% primary sludge and 15% biosludge. Primary sludge, rich in wood-based fibers, is derived mostly from the chemical wastewater treatment process of board mill effluents, but also to some extent from the pre-sedimentation phase of the activated sludge treatment plant. Biosludge is derived from the activated sludge treatment plant.

The biosludge and primary sludge are combined and then dried with screw presses. The total sludge amount generated is 100 tons dry weight per day. Most of this mixed sludge is incinerated in the biomass boiler together with wood bark, but some goes to agricultural end-uses.

In this research, three different kinds of wastewater treatment sludges were investigated: 1) untreated mixed sludge collected from the wastewater treatment plant of the mill, 2) lime-stabilised mixed sludge collected from the stockpile located at the sludge-handling area of the mill site, and 3) composted mixed sludge collected from the composting field located at the mill site. The liming of the sludge was carried out by adding calcium hydroxide ($Ca(OH)_2$) in order to reach a pH value of 12 in the sludge. The sampling of the lime-stabilised sludge was carried out four weeks after the

liming. The composting of the sludge was carried out under normal field conditions without any accelerators or additives. The sampling of the composted sludge was carried out five weeks after the start of composting.

During the sampling of sludges, a total of ten sub-samples (100 mL each) of each kind of sludge were collected. Ten individual sub-samples of each kind of sludge were combined to give one composite sample (1,000 mL) per sludge type. After collection, these samples were stored in polyethylene bottles in a refrigerator (+4°C). Sterilised bottles were used for the sample collection. After sampling, a coning and quartering method was applied repeatedly to reduce the sample to a size suitable for conducting a laboratory analysis.

Determination of the mineralogy of sludges

In order to determine the mineralogical composition of the sludges, an X-ray diffractogram of the sludge 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 sec 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 sludges

The pH of the sludge was determined according to the European standard SFS-EN 13037 at a solid-to-liquid (i.e. ultrapure water) volume ratio of 1:5. The dry matter content (DMC) was determined according to the European standard SFS-EN 12880, 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 the European standard SFS-EN 12879 at a temperature of 550 °C.

The total organic carbon (TOC) of the sludges was determined by dry combustion using a LECO CN828 analyser (Leco Corp; USA). The total nitrogen (Tot-N) of the sludges 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). The details of the analytical methods of the standards can be found in other publications [Pöykiö et al., 2019]. Temperature-resistant coliforms and *Escherichia coli* in the sludges were determined by the NMKL method 125 [Luukkonen et al., 2020] and *Salmonella* by the standard ISO 6579 [Machado et al., 2019].

Determination of easily soluble nutrients in the sludges

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 also 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 with the molybdenum blue method using an automatic Foss-Tecator FIAStar 500 Flow Injection Analyser (Högnes, Sweden). The details of the analytical methods of the standards can be found in other publications [Pöykiö et al., 2019].

Determination of total element concentrations in the sludges

For the determination of the total element concentrations in the sludge, 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. The cooled solution was transferred to a 100 mL volumetric flask, and the solution was diluted to

volume with ultrapure water. The total element concentrations in the sludges except for Hg, were determined with a Thermo Fisher Scientific iCAP6500 Duo (United Kingdom) ICP-OES. The concentration of Hg in the sludges was determined using a Perkin Elmer AAnalyst 700 cold-vapour atomic absorption spectrometer. The details of the analytical methods of the standards can be found in other publications [Pöykiö et al., 2019].

Determination of the extractable element concentrations in the sludge

The three-step sequential extraction scheme for the fractionation of heavy metals in sludges was carried out with the BCR (Community Bureau of References) method, which is fully described in the paper of Devi and Saroha (2014). Briefly, in this procedure the sequential extraction of sludge (1 g) was carried out as follows: (1) acetic acid (40 mL CH_3COOH; 0.11 mol/L; pH 3.0) extraction to recover the heavy metals in the sludge into the acid soluble fraction, (2) hydroxylamine hydrochloride (40 mL $NH_2OH\text{-}HCl$ in nitric acid medium, 0.1 mol/L; pH 1.5) extraction to recover the heavy metals in the sludge 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 sludge into the oxidisable fraction.

In order to avoid the possible chemical and/or microbiological changes in the sludge, the extraction was carried out using the sample in its natural state, rather than using of a dried sample. According to Luo et al., [2016], drying of sludge before sequential extraction can change the form in which the elements occur in the sludge and may alter the bioavailability of elements. 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, it was 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

Mineralogy of sludges

According to X-ray diffraction (XRD) data (Table 1), calcite ($CaCO_3$), which is a carbonate mineral, and cellulose Ibeta (($C_6H_{10}O_5)_n$), were observed in all sludges. The amount of calcite was 15.8% in the untreated sludge and 52.8% and 51.7% in the lime-stabilised and composted sludges, respectively. The amount of cellulose Ibeta in the above-mentioned sludges was 48.8%, 47.2% and 36.9%, respectively. Kaolinite ($Al_4(OH)_8(Si_4O_{10})$), which is a silicate mineral, was observed only in the untreated sludge (35.4%), and quartz (SiO_2), which is also a silicate mineral, only in the composted sludge (11.4%).

The existence of calcite and quartz in the sludges is expected. Woodchips, the main raw material in the manufacturing of pulp, are abundant in calcium. Si is associated with plant tissues, e.g. in cellulose and lignin, as amorphous hydrated opaline silica ($SiO_2 \times nH_2O$) [Guerriero et al., 2020]. The calcite content of 52.8% in the lime-stabilised sludge was about 3.3 times higher than that of the untreated sludge (15.8%) and slightly higher than that of the composted sludge (51.7%). This is due to the fact that lime-stabilised sludge was hygienised by mixing slaked lime ($Ca(OH)_2$), which reacts with carbon dioxide (CO_2) to form calcite ($CaCO_3$). Another reason for this might be

Table 1. Identified minerals in sludges. All values expressed as percentage (%).

Mineral	Formula	Untreated sludge	Lime-stabilised sludge	Composted sludge
Calcite	$CaCO_3$	15.8	52.8	51.7
Cellulose Ibeta	$(C_6H_{10}O_5)_n$	48.8	47.2	36.9
Kaolinite	$Al_4(OH)_8(Si_4O_{10})$	35.4		
Quartz	SiO_2			11.4

that slaked lime contains $CaCO_3$ as an impurity. Furthermore, the reason for high calcite content in the composted sludge might be the degradation of organic matter content, which results in the net loss of dry mass [Fei-Baffoe et al., 2016], as well as the formation of $CaCO_3$ due to the microbial-induced carbonate precipitation ("biomineralization") that occurs as a by-product of metabolic processes such as photosynthesis and urea hydrolysis [Anbu et al., 2016; Chen et al., 2019].

The XRD spectra support the use of sludges as a soil amendment agent, since the $CaCO_3$ content was relatively high especially in the lime-stabilised and composted sludges. The cellulose content was high in all sludges studied. Calcite could be helpful as a soil improver to help neutralise the soils with low pH, which are especially common in the Finnish coastal areas and are usually called "acid sulphate soils". The cellulose fibres in sludge could in turn help enhance the water holding capacity, aeration, aggregating property and microbial community structure of soil, thus improving soil fertility [Rasa et al., 2020].

The amount of cellulose was lower in the composted sludge than in the untreated sludge. According to Bohacz [2019], this suggests that during composting part of the organic matter in sludge is degraded and converted to humic substances. The lower total organic carbon value (TOC) of 17 % in the composted sludge compared to that of the untreated sludge (40 %) supports this phenomenon (see Table 2).

Physical and chemical properties of the sludges

Table 2 presents the results of physical and chemical properties of the sludges. The dry matter content (DMC) of the sludges was relatively low (33.1 – 44.3%), which indicates that the incineration of these residues for energy production is not economically viable. However, the moisture content of the composted sludge (55.7%), did not exceed the recommended moisture value between 40% and 60% for composting materials and is thus capable of maintaining the metabolic activities of microbes [Ayilara et al., 2020].

The pH values between 8.0 and 9.1 of the sludges indicate that these residues may act as a pH buffer and neutralising agent in acidic soils. The pH value of 8.0 of the untreated sludge is consistent with the pH values of the wastewater effluents originating at the process, since paper and board manufacturing processes of the mill investigated in this research operate at a the neutral pH range. The pH value of 9.1 of the lime-stabilised sludge sample was slightly more alkaline than the pH values of untreated (pH 8.0) and composted (pH 8.3) sludges. This is due to the use of slaked lime ($CaCO_3$), which was used for hygienisation of this residue. Although the composted sludge had pH value only slightly higher than the untreated sludge, this confirms the finding of Nafees et al. [2018] that generally, composted sludge is more alkaline in nature. According to Thyagarajan et al. [2010], this phenomenon is

Table 2. Physical and chemical properties, as well as easily soluble nutrient concentrations (mg/kg; d.w.) in sludges and in arable soil in the Pirkanmaa region in southern Finland (Mäkelä-Kurtto et al., 2007).

Property	Unit	Untreated sludge	Lime-stabilised sludge	Composted sludge	Finnish arable soil
DMC	%	33.1	39.8	44.3	
pH		8.0	9.1	8.3	
LOI	% (d.w.)	80.9	73.7	77.4	
TOC	%	40.0	17.0	17.0	
Tot-N	mg/kg (d.w.)	8,760	8,000	13,500	
TOC/N		45.6	21.3	12.6	
Ca	mg/kg (d.w.)	32,800	52,900	17,400	799 – 3,828
Mg	mg/kg (d.w.)	570	1,000	470	62.0 – 455
K	mg/kg (d.w.)	250	370	370	58.0 – 349
Na	mg/kg (d.w.)	1,580	2,310	2,070	
P	mg/kg (d.w.)	27.0	320	61.0	4.1 – 97.0
S	mg/kg (d.w.)	1,360	1,530	1,300	6.7 – 35.0
Mn	mg/kg (d.w.)	620	770	760	44 – 231
Cu	mg/kg (d.w.)	3.8	7.2	3.2	1.6 – 7.7
Zn	mg/kg (d.w.)	26.0	50.0	25.0	0.9 – 4.9

due to the degradation of short-chained fatty acids and ammonification of organic N.

The elevated total nitrogen (Tot-N) concentration in the composted sludge reveals the outcome of the ammonification process during composting. Another reason for the high total nitrogen concentrations in all sludges is the use of urea ($CO(NH_2)_2$) at the mill to enhance the microbial activity during the aerobic purification process at wastewater treatment plants. The obvious disadvantage of denitrification during the combustion process is the loss of nitrogen in the form of volatile ammonia (NH_3) gas, although nitrous oxide (N_2O) emissions can also occur [Barthod et al., 2018].

According to Hazarika et al.[2018], the optimum pH for the sustainability and degradation efficiency of the micro-organisms in composting is between 5.5 and 8.0. However according to Thyagarajan et al. [2010], pH between 5.5 and 9.0 indicates good quality compost. Although the pH in the considered composted sludge (8.3), falls slightly outside of the optimum ranges, it is still well within the preferential limits for agricultural use. Furthermore, it can be concluded that the relatively mild pH values of the investigated sludges are not likely to cause an unexpected pH shock-effect to biota if these residues are applied as a soil conditioning agent.

The lower total organic carbon (TOC) value of the composted sludge (17%) compared to that (40%) of the untreated sludge is reasonable indicating the degradation (mineralisation) of organic matter, thus releasing the carbon dioxide (CO_2) emissions into the atmosphere [Bohacz, 2019]. However, the very high loss-on-ignition (LOI) values between 73.7 % and 80.9 % and TOC values between 17.0% and 40.0% indicate that the organic matter content in these residues is high, which aligns with the high cellulose content observed by XRD (see Table 1). The high TOC values in the investigated sludges indicate that these residues may act as a source of organic carbon for soils if they are used as a fertiliser. Furthermore, calcite ($CaCO_3$) may act as a source of inorganic carbon in the form of carbonate ion (CO_3^{2-}). Organic matter with a high carbon content helps stimulate microbial population of the soil, especially if it is degraded. The addition of organic material to soil, that has low organic matter content may also improve soil porosity and structure, as well as the ability to store water and nutrients.

The higher Tot-N concentration in the composted sludge (13,500 mg/kg; dry weight, abbr. d.w.) compared to in the untreated sludge (8,760 mg/kg; d.w.) may, according to Fei-Baffoe et al. [2016] be attributed to a release of CO_2 into the atmosphere during the composting process due to the decomposition of organic matter chemically bound with nitrogen. The lower TOC in the composted sludge (17%) compared to that in the untreated sludge (40%) supports this phenomenon.

The carbon to nitrogen ratio (C/N), which is calculated traditionally in Table 2 as the ratio of total organic carbon (TOC) to total nitrogen (N) using method of Puyuelo et al. [2011], is an index of maturity of the compost and is one of the most important indicators of the composting process and compost quality. In general, the optimal C/N ratio in the composting of most materials is between 25 and 30 [Azim et al., 2018]. A C/N ratio between 20–30 results in an equilibrium state between mineralisation and immobilisation [Biswass and Micallef, 2019], whereas fast N mineralisation and availability is expected for organic fertilisers with the C/N ratio lower than 15 [N`Dayegamiye et al., 2013].

A C/N value of 45.6 was observed in the untreated sludge, whereas in the lime-stabilised sludge it was 21.3 and in the composted sludge it was 12.6. The lowest C/N ratio in the composted sludge, can be explained by the loss of organic carbon in the form of CO_2 due to the decomposition of organic matter into CO_2 and H_2O [Thyagarajan et al., 2010]. The relatively low C/N ratio in the composted sludge means that rapid mineralisation and release of N will occur if this residue is utilised as a fertiliser. Due to this property the composted sludge is not likely to keep its effect as an N reserve on the soil for a long time. Furthermore, the relatively low C/N ratio in the composted sludge means, according to Wiater [2020], that ammonia gas (NH_3), which is toxic to micro-organisms, may be formed when C/N is below 25:1.

The Tot-N concentration in sludges is the sum of organic and inorganic nitrogen present in the sludge [Nafees et al., 2018]. According to Ribeiro et al. [2010], it is possible that during land application, the organic N is converted (mineralises) into ammonia nitrogen (NH_4-N) and released into the air as NH_3 (volatilisation). Furthermore, during land application of these sludges, it is also possible that methane (CH_4) and N_2O, both greenhouse gases, are formed and released into the atmosphere [Barthod et al., 2018].

Easily soluble nutrient concentrations in the sludge

Table 2 shows that in particular the easily soluble Ca, but also Mg, S, Mn and Zn concentrations in all sludges were markedly higher than the maximum concentrations of these elements observed in arable soils in the Pirkanmaa region in southern Finland [Mäkelä-Kurtto et al., 2007]. Additionally, the concentration of the easily soluble P in the lime-stabilised sludge was clearly higher than in the arable soil. These results indicate that all sludges are rich in many nutrients which are essential for plants. These residues could, therefore, be utilised as a fertiliser, assuming the total concentrations of elements do not exceed the limit values for fertiliser products as regulated by the Finnish Fertilizer Product Decree [Collivignarelli et al., 2019].

All easily soluble nutrient concentrations in the lime-stabilised sludge were significantly higher than those in untreated sludge. Furthermore, the easily soluble nutrient concentrations of K, Na, P and Mn in the composted sludge were significantly higher than those in the untreated sludge. These results suggest that both liming and composting can improve certain nutritional values in pulp sludge, which is beneficial if these sludges are utilised as a fertiliser. However, the easily soluble Ca concentration (17,400 mg/kg; d.w.) of the composted sludge was clearly lower than that of the untreated sludge (32,800 mg/kg; d.w.) and that of the lime-stabilised sludge (52,900 mg/kg; d.w.). Due to relatively low easily soluble Cu concentrations, which were lower than those observed in the soils in southern Finland, these residues may not be used as a Cu supplementation fertiliser.

Total element concentrations in the sludge

Table 3 shows the total concentrations of elements in the sludges obtained after the microwave oven digestion using *aqua regia* (3 mL HCl + 9 mL HNO_3). This commonly used digestion method is accepted by Finnish legislation for element total digestion [Kaakinen et al., 2014]. Although total concentrations of certain heavy metals in sludges were very high (e.g. Al) or highly elevated (e.g. Na and S), from the utilisation point of view, the total concentrations of As, Cd, Cr, Cu, Hg, Ni, Pb and Zn in all sludges are the most important, because the Finnish Fertilizer Product

Decree sets limit values only for these elements in fertiliser products [Collivignarelli et al., 2019]. According to Table 3, total concentrations of As, Cd, Cr, Cu, Hg, Ni, Pb and Zn in all sludges were significantly lower than the statutory Finnish limit values for these elements for fertiliser products. This means that according to Finnish legislation, the heavy metal concentrations in our sludges do not restrict the utilisation of these residues as a fertiliser product. These limit values are not applicable if the sludges are to be used during the landscaping of a landfill or in industrial or other areas that are closed to the public. However, an environmental permit for this kind of application may be needed.

The elevated total concentrations of macronutrients (Ca, Mg, K, P and Mn) in Table 3 as well as the Tot-N concentrations (see Table 2), all of which are essential for plants, also support the utilisation of these residues as a fertiliser. The elevated total Na concentrations (1,850 – 2,710 mg/kg) were significantly higher than those in Finnish humus [Minolfi et a., 2017], so these residues would provide additional benefits for soils if they were used as a fertiliser product and a soil conditioning agent. Although Na is not considered an essential nutrient for plants its concentration effects soil structure [Nafees et al., 2018]. However, during land applications of these sludges, nitrate (NO_3^-) leaching may occur, since the Tot-N concentrations (see Table 2) in sludges were high [Gallardo et al., 2016].

While comparing the untreated sludge and the composted sludge, it can be observed that that the composting process increased the total concentrations of certain elements. For example, the total concentrations of Ni and Cr were correspondingly 131% and 110% higher in the composted sludge than in the untreated sludge. The total concentration of K in the composted sludge was 69% higher than that in the untreated sludge. This phenomenon may be attributed to a reduction in volume of the compost mass and to mineralization of elements. Although the exact reason for the reduction in the concentration of certain metal (e.g. Al, Fe, Mg, Pb and Zn) when comparing composted sludge to untreated sludge are not known, Fei-Baffoe et al. [2016] suggested that this phenomenon results from the complexing actions of newly formed humic compounds in compost.

The very high Al and elevated Fe concentrations in the sludges are due to the use of Al- and Fe-based chemicals in wastewater treatment

Table 3. Total element concentrations in the sludges and in humus from southern Finland (Minolfi et al., 2017), as well as Finnish limit values for maximum concentrations of elements in fertilizer products (Collivignarelli et al., 2019). All concentration expressed as mg/kg (d.w.).

Element	Untreated sludge	Lime-stabilised sludge	Composted sludge	Finnish humus	Finnish limit value
Al	18,500	17,200	17,900	664 – 17,100	
As	< 3.0	< 3.0	< 3.0	0.47 – 23.0	25
B	8.9	11.0	13.0	< 2.0 – 11.0	
Ba	78.0	160	110	17.7 – 460	
Ca	36,000	72,900	27,000	596 – 12,900	
Cd	0.5	0.6	0.5	< 0.01 – 2.22	1.5
Cr	10.0	14.0	21.0	< 0.2 – 43.5	300
Cu	14.0	16.0	19.0	0.85 – 1,310	600
Fe	3,500	3,730	3,230	809 – 31,100	
Hg	< 0.04	< 0.04	< 0.04	0.04 – 0.62	1.0
K	360	1,450	610	413 – 4,560	
Mg	970	1,860	910	302 – 7,310	
Mn	760	1,030	1,100	25.8 – 5,160	
Na	1,850	2,710	2,410	< 20 – 309	
Ni	3.5	4.6	8.1	1.8 – 435	100
P	1,140	1,610	1,560	< 30 – 2,190	
Pb	5.1	5.7	4.5	5.0 – 657	100
S	4,340	4,550	5,090	329 – 37,100	
Zn	56.0	130	53.0	18.5 – 595	1,500

plants, although Fe is also a result of corrosion and erosion processes. The very high Ca and elevated Mg, Na and S concentrations in the sludges are also excepted because these elements are the most abundant mineral nutrients in wood. Mg based chemicals are used during the oxygen delignification process. Na based chemicals are used in cooking of pulp and Ca is used as a filler material in the production of board. The total concentrations of Be, Co, Sb, Se and V in the sludges were negligible (< 3.0 mg/kg; d.w) and are therefore not presented in Table 3.

The chemical fractionation of elements in the sludges

The total concentration of elements in the sludges is a very reliable overall pollution indicator, but it cannot provide the information about the potential release of elements from the sample matrix or about the potential bioavailability of the metals [Devi and Saroha, 2014]. Therefore, in this context the chemical fractionation and potential bioavailability of elements in sludge were assessed using the three-stage sequential extraction procedure developed by the Community Bureau of Reference (BCR) and calculated the solubility index (SI) for every element following the

procedure of Jamroz et al. [2020], because the mobility and bioavailability of heavy metals depend on their chemical forms in sludge.

The sequential extraction procedure of the Community Bureau of Reference (BCR) is a standardised method developed by a group of experts working under the auspices of the Commission of the European Communities and it assess whether the elements in sludges are loosely or tightly bound to the sample matrix. In this procedure, which is also called a BCR procedure, the elements that are loosely bound to the sample matrix are extracted first in the BCR1 fraction (CH_3COOH extractable fraction), and the more tightly bound elements are extracted in the BCR2 fraction (NH_2OH-HCl extraction in nitric acid medium) and in the BCR3 fraction (H_2O_2 digestion following CH_3COONH_4 extraction). The BCR1 fraction corresponds to the elements, which represent water and acid soluble as well as exchangeable fraction. The BCR2 fraction corresponds to the elements, which represent the reducible fraction associated with hydrated Fe and Mn oxides. The BCR3 fraction corresponds to the elements that are associated with organic matter and sulphides [Devi and Saroha, 2014].

The bioavailability of elements for biota is connected to their solubility and decreases in the

Table 4. Chemical fractionation of elements in sludges between BCR1 (acid soluble), BCR2 (reducible,) and BCR3 (oxidizable) fractions, as well as their solubility index (SI) values. All concentrations expressed as mg/kg (d.w.).

Element	Untreated sludge				Lime-stabilized sludge				Composted sludge			
	BCR1	BCR2	BCR3	SI	BCR1	BCR2	BCR3	SI	BCR1	BCR2	BCR3	SI
Al	1,280	8,090	1,480	6.9	1,060	7,300	1,420	6.0	508	7,460	2,310	2.8
Ba	34	29	7.4	44	8.4	47	8.2	5.0	28	53	17	25
Ca	32,000	3,790	570	89	60,500	6,800	570	83	21,500	4,600	800	80
Cd	0.3	0.2	0.1	60	0.2	0.3	0.1	33	0.1	0.3	0.1	20
Cr	0.4	1.9	3.4	4.0	0.5	1.1	3.2	3.6	(< 0.4)	0.7	4.9	(< 1.9)
Cu	0.8	1.7	6.4	5.7	0.6	0.8	11	3.8	(< 0.4)	0.7	17	(< 2.1)
Fe	59	2,200	650	1.7	72	1,700	950	1.9	33	1,530	1,120	1.0
K	260	41	(< 50)	72	370	46	(< 50)	26	433	62	(< 50)	71
Mn	470	240	34	62	722	137	31	70	826	200	51	75
Ni	0.5	0.8	0.9	14	0.4	1.0	0.8	9.0	(< 0.2)	0.3	1.8	(< 2.5)
P	17	430	570	1.5	85	970	350	5.3	37	860	518	2.4
Pb	(< 0.6)	1.7	1.3	(< 12)	(< 0.6)	2.2	1.0	(< 11)	(< 0.6)	1.3	1.7	(< 13)
S	1,090	660	1,870	25	1,370	340	2,200	39	1,350	410	2,690	27
Zn	25	18	13	45	24	30	7.4	18	11	28	7.0	21

following order: BCR1 fraction > BCR2 fraction > BCR3 fraction [Damasceno et al., 2015]. The elements extracted in the first step (i.e. BCR1 fraction) are considered the most sensitive to the changes in environmental conditions such as acidity and the ionic composition of water. The elements extracted in the second step (i.e. BCR2 fraction) are considered to be thermodynamically unstable under anoxic conditions, whereas the elements extracted in the third step (BCR3 fraction) are considered to dissolve only if the organic material decompose and release elements under oxidation conditions [Elmaslar-Özbaş and Balkaya, 2012].

The solubility index of elements in sludges

The solubility index (SI) in Table 4 for each element was determined as the ratio of the extractable element concentration (BCR1 fraction in Table 4) to the total element concentration (see Table 3) in the sludge [Jamroz et al., 2020]. The presence of certain elements fell below detectable levels in some stages; for these values, an estimated concentration is noted in brackets. The high index value indicates that the element releases easily, whereas the low value indicates that the element is poorly released from the sludge matric. The index value can only reach the total value of 100, if an element is completely soluble in the extraction solvent.

If we disregard the elements with the concentrations lower than the detection limits, the

solubility index (SI) value for Ba, Cd, K, S and Zn in the lime-stabilised sludge was significantly lower and for Al, Ca, Cr and Ni slightly lower than those in the untreated sludge. This indicates that the liming reduced the leachability of these elements. However, the solubility indices for Cu, Mn and P in the lime-stabilised sludge were significantly or slightly higher than those in the untreated sludge. This indicates that liming increased the solubility of these elements, whereas it had no effect on the leachability of Fe. According to Singh and Kalamdhad [2014], the reduction of leachability is possible due to the formation of soluble carbonates and the formation of organo-metallic complexes when calcium hydroxide $(Ca(OH)_2)$ is used for liming, which produces calcium ion (Ca^{2+}) and hydroxide ion (OH^-) in the presence of water. The hydroxide ion combines with the metal ion (M^{2+}) to form metal hydroxides. These metal hydroxides can be adsorbed onto charged colloids, such as degraded organic matter, consequently reducing the metal solubility.

If the elements with concentrations lower than the detection limits are disregarded and the untreated and composted sludge are compared, it can be noticed, that the composting process reduced mostly the leachability of Ba, Cd and Zn, where it reduced only slightly the leachability of Al, Ca and Fe (see table 4). However, composting increased the leachability of Mn and P and had no effect on the leachability of K and S. Thus, our results agree with the findings of Bożym and Siemiątkowski [2018]; the composting process

reduces the leachability of certain elements. According to Hazarika et al. [2018], this is due to degraded organic matter, being converted to humic substance in compost. According to Bożym and Siemiątkowski [2018], the increasing solubility of certain elements after the composting process might also be due to suboptimal humification (enhanced decomposition of organic matter and missing re-binding of mobile forms to the structure of humus).

Pathogens in the sludges

According to results in Table 5, *Salmonella* was not detected in any sludges, so this pathogen does not restrict the utilisation of these residues as a fertiliser product. This finding was expected, because sanitary waters originating at the mill are treated at the municipal wastewater treatment plant outside the facility and are thus not mixed with the process waters.

The untreated sludge contained both coliforms and *Escherichia coli* at a concentration of 1,900 colony forming units per gram (CFU/g). The total concentration of *Escherichia coli* in the untreated sludge thus exceeded the limit value of 1,000 CFU/g for this pathogen as regulated by the Finnish Fertilizer Product Decree [Collivignarelli et al., 2019] and this residue is not suitable to be used as a fertiliser without further treatment. However, both liming and composting were able to reduce the *Escherichia coli* concentrations in sludges, to concentrations lower than 10.0 CFU/g, which falls well within the limit value of 1,000 CFU/g. There is no limit value for coliforms in Finland.

The pathogen reducing effect of liming is due to the highly alkaline pH of sludges [Barthod et al., 2018]. According to Fatunla et al. [2017], the pathogen reducing effect of composting could be attributed to heat. On the basis of the results in Table 5, the pathogen levels in lime-stabilised and composted sludges do not restrict the utilisation of these residues as a fertiliser product in Finland.

CONCLUSIONS

The conclusions drawn from this study can be summarised as follows:

1. Heavy metal concentrations (As, Cd, Cr, Cu, Hg, Ni, Pb and Zn) in the untreated, lime-stabilised and composted sludges were significantly lower than the statutory limit values as regulated by the Finnish Fertilizer Degree. Therefore, the heavy metal concentrations do not restrict the utilisation of these residues as a fertiliser product.

2. The use of untreated sludge as a fertiliser product is not possible without additional processing, because the *Escherichia coli* content (1,900 CFU/g) exceeds the Finnish limit values of 1,000 CFU/g for fertiliser products. A hygienic treatment is needed if this residue is to be used as a fertiliser.

3. Both lime-stabilisation and composting treatments reduced the *Escherichia coli* concentrations in sludges to a level lower than 10.0 CFU/g, fulfilling the Finnish limit values for this pathogen for fertiliser products.

4. The large volume of wastewater treatment sludges with high carbon (C) and nutrients contents generated at the investigated mill integrate suggest that the fertiliser use of these residues could represent an important alternative to soil carbon sequestration and provide a potential substitute for synthetic fertilisers. This would reduce the amount of virgin aggregates that need to be obtained, leading to the reduced extraction of natural resources needed to produce synthetic fertilisers.

5. In general, both lime-stabilisation and composting deceased the extractability of elements in sludges indicating a reduced solubility and thus a reduced bioavailability of these elements.

6. However, during land application, the potential emissions of methane (CH_4), carbon dioxide (CO_2) and nitrous oxide (N_2O), all of which are greenhouse gases, may partly decrease the benefits of using these residues as a fertiliser product.

Table 5. Total concentration of pathogens in the sludges, as well as Finnish limit values for pathogens in fertilizer products (Collivignarelli et al., 2019). All concentrations expressed as colony forming units (CFU).

Pathogen	Unit	Untreated sludge	Lime-stabilised sludge	Composted sludge	Finnish limit value
Salmonella	CFU/25g	0	0	0	not detected
Coliforms	CFU/g	1,900	< 10.0	< 10.0	
Escherichia coli	CFU/g	1,900	< 10.0	< 10.0	1,000

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