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Characterization of primary and secondary wastewater treatment sludge from a pulp and board mill complex to evaluate the feasibility of utilization as a soil amendment agent and a fertilizer product

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ABSTRACT

In this study, we have determined the main important physical and chemical properties as well as the heavy metal concentrations of the primary and secondary wastewater treatment sludge from a pulp and board mill complex located in Finland in order to evaluate the utilization of these by-products as a soil amendment agent or a fertilizer product. Easily soluble Ca, Mg, K, Na, P and S concentrations in the sludges were extracted by ammonium acetate ($\text{CH}_3\text{COONH}_4$) and easily soluble Cu, Mn and Zn concentrations by $\text{CH}_3\text{COONH}_4 + \text{Na}_2\text{EDTA}$. For the determination of total nutrient and total heavy metal concentrations in sludges, they were digested using *aqua regia* (3 mL $\text{HCl} + 9 \text{ mL } \text{HNO}_3$). The total heavy concentrations in the primary sludge were lower than the Finnish heavy metal limit values for fertilizer products. In the secondary sludge, all other total heavy metals than the total Cd concentration (4.8 mg/kg; d.w.) were lower than the heavy metal limit values for fertilizer products. Due to the low total heavy metal concentrations, which were lower than the Finnish limit values for fertilizer products, the primary sludge is a potential fertilizer. Although the total Cd concentration (4.8 mg/kg; d.w.) in the secondary sludge exceed the limit value of 1.5 mg/kg (d.w.) for fertilizer products, this residue may be used as a soil improver, a growing media or as a fertilizer product in landfill sites or in other closed industrial areas, because the Finnish limit values for fertilizer products are not applied at these sites.

Keywords: Activated sludge; Fertilizer; Forest industry; Biosludge; Board mill; Fibre sludge; Pulp mill; Waste; Wastewater treatment

1. INTRODUCTION

Many industrial by-products are treated like wastes, but many of these materials also have the potential to providing extra value, either in the form of material or energy. Globally, many different types of industrial by-products and wastes are produced in general global industrial sectors and in sectors that are locally important. The forest industry (pulp, paper and board mills) is an example of a locally important industry sector in Finland.

Solid residuals generate a continuous disposal problem for the forest industry. The rising cost of landfill is driven by the need to protect the environment and human health. The European Council Waste Framework Directive (WFD) 2006/12/EC has been amended by the new WFD Directive 2008/98/EC, which came into force in December 2010.¹ The aim of this waste policy is to reduce resource usage and recover the wastes in order to promote sustainability. As a result, there is a growing tendency in the Finnish forest industry to look for options for the reuse or recycling of solid residues originating at different production stages of this industry.²

Wastewater treatment plant residuals are the largest volume waste streams generated by the forest industry

because water plays a central role during various stages of this industry.³ Water is needed for example as a medium to carry fibres through production processes. Water is also used for cooling machinery at the mills, for cleaning, and as a carrier of energy in the form of steam. The production of pulp, paper and board is therefore associated with the generation of large quantities of wastewater that have to be purified at wastewater treatment plants before the water is discharged into the environment or reused in the mill.⁴ Due to the effectiveness of wastewater treatment plants, the modern pulp, paper and board mills generate considerable amount of sludge, which is the final solid residue recovered from the wastewater treatment processes.

Three main types of wastewater treatment sludge are generated in different processes stages: primary sludge, secondary sludge and tertiary sludge.⁵ The primary sludge which is also called fibre sludge, is produced at the primary wastewater treatment plant. Primary treatment generally consists of screening, sedimentation, neutralization and flotation. The main purpose of primary treatment plant is to remove large particles such as bark, and sand, suspended and floating solids, fibre, fillers, pigments and coating materials and consequently organic materials.⁶ After this treatment, nutrients such as N and P, dissolved organic

compounds and colloidal particles are still in the wastewater and must be removed using biological treatment. The most usual method for this second treatment is the activated sludge process, generally either of an aerobic or an anaerobic nature or their combination, which is known as a hybrid process.⁵ Allowing micro-organisms to utilize the pollutants as nutrients, the dissolved organic compounds and colloidal particles can be lowered and oxidized into low molecular fractions. The micro-organisms grow and multiply in this process forming a secondary sludge, which is also called a biological sludge or an activated sludge.⁷ If there is a need for further removal of recalcitrant organic compounds, colour, toxicity, micro-organisms, suspended solid or COD (chemical oxygen demand), to render the effluent suitable either for circulate again into the process or to fulfil the discharge limit values set by the environmental authorities before wastewater is discharged to receiving waters, a tertiary wastewater treatment may also be used. Tertiary treatment of high volume wastewaters is expensive and produces a further waste stream, called a tertiary sludge.⁸ The selection of the treatment technologies used in the forest industry depends on the type of the wastewater and the economic and environmental requirements.

Utilization of industrial sludge in soil fertilizer offers a number of advantages over other management alternatives because they (1) may replace and conserve mineral fertilizer that would otherwise be introduced into the biosphere, (2) the application of organic material improves soil structure thus reducing erosion, (3) naturally available but limited supplies of nutrient resources such as rock phosphate are consequently conserved and (4) alternative disposal methods could be environmentally demanding (e.g. burning), expensive or limited by space or by environmental legislation rules (e.g. landfills).⁹

Wastewater treatment sludges from forest industry are typically incinerated in Finland and elsewhere in Europe. However, they do not create any net energy because they are wet, therefore alternatives for the combustion of these residues are keenly searched within the forest industry. In order to promote the forest industry's implementation of the circular economy in which industrial by-products are viewed as valuable raw materials for new products and they are fully utilized or recycled,² we carried out this study. If the wastewater treatment sludges from forest industry are managed via reuse for example as a soil amendment agent or a fertilizer product, this would promote the waste hierarchy of the European Union (EU), in which prevention, minimization, re-use and recycling of wastes are the most desirable options.¹⁰

2. EXPERIMENTAL

2.1 Sampling

The primary and secondary sludge investigated in this study were obtained from a wastewater treatment plant of

Finnish pulp (Kraft) and linerboard mill complex located at the same site. The mill produces about 4000 tonnes of primary sludge and 3000 tonnes of secondary sludge annually. The sampling period for sludges represented normal process operating conditions for the mill. After sampling, the samples were stored in polyethylene bags in a refrigerator (+4 °C) until analysis. Samples should be analysed as soon as possible after sampling. However, if this is not done, according to EPA,¹¹ they should be chemically/physically preserved as soon as possible after sampling to avoid or minimise biological, chemical or physical changes that can occur between the time of collection and analysis. For the above-mentioned reasons we decided to follow the procedure of Stylianou et al.¹² and to store the samples in a refrigerator (+4 °C) until analysis.

2.2 Determination of the mineralogical composition and physical and chemical properties in the sludges

The mineralogical composition of the sludges was determined with a Siemens D 5000 X-ray diffractometer (Siemens AG, Karlsruhe, Germany) using CuK α radiation. The scan was run from 2 to 80° (2-theta-scale), with increments of 0.02° and a counting time of 1.0 seconds per step. The operating conditions were 40 kV and 40 mA. Peak identification was carried out with the DIFFRACplus BASIC Evaluation Package PDFMaint 12 (Bruker axs, Germany) and the software package ICDD PDF-2 Release 2006 (Pennsylvania, USA).

Determination of pH and electrical conductivity (EC) of the sludges were carried out according to European standard SFS-EN 13037 at a solid-to-liquid (ultrapure water) ratio of 1:5. Determination of the dry matter content (DMC) of the sludges was carried out according to European standard SFS-EN 12880. The loss-on-ignition (LOI) of the sludges was carried out according to European standard SFS-EN 12879. The total organic matter content (TOC) of the sludges, which also indicates the total organic carbon (C) content,¹³ was carried out according to European standard SFS-EN 13137. A comprehensive review of the standards, analytical methods and instrumentation is given in our previous publication.¹⁴

2.3 Determination of the easily soluble nutrient concentrations in the sludges

The determination of easily soluble nutrient (Ca, Mg, K, Na, P, S, Cu, Mn and Zn) concentrations in the sludges was carried out according to the procedure of MTT Agrifood Research Finland, in which the easily soluble forms of these metals were extracted with 0.5 M acidic ammonium acetate (pH 4.65). However, in the extraction of Cu, Zn and Mn, the acidic (pH 4.65) ammonium acetate (NH₄Ac) extract contained 0.02 M ethylenediaminetetra-acetic acid disodium salt (Na₂EDTA). In both extraction procedures, one volume part of a dry sample was shaken with ten parts

of extraction solution for 1 h. Before analysis, the extract was separated from the solid residue by filtration through a 12.5 mm diameter Schleicher & Schull 589 blue ribbon filter paper (Schleicher & Schull, Dassel, Germany).

The concentrations of Ca, Mg, Na, K and S were determined by an inductively coupled plasma optical emission spectrometer (ICP-OES, Thermo Elemental Iris Intrepid II XDL, Franklin, USA), and the concentrations of Cu, Zn and Mn by the 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 FIASStar 500 Flow Injection Analyser (Högnäs, Sweden). Before the nutrient determination on the sludges, the sample was dried overnight to constant mass at 105 °C in a drying oven (Termaks) according to the European standard SFS-EN 12880. A comprehensive review of the standards, analytical methods and instrumentation is given in our previous publication.¹⁴

2.4 Determination of total nutrient and heavy metal concentrations in the sludges

To determine the total nutrient (Ca, Mg, K, Na, P, S, Cu, Mn and Zn) and heavy metal concentrations in the sludges, the dried sample was digested with a mixture of HCl (3 mL) and HNO₃ (9 mL) in a CEM Mars 5 microprocessor-controlled microwave oven with CEM HP 500 Teflon vessels (CEM corp., Matthews, USA) using USEPA method 3051A.¹⁵ This digestion method is accepted in Finland legislation for the total element digestion.¹⁶

The cooled solution was transferred to a 100 mL volumetric flask and the solution was diluted to volume with ultrapure water. The ultrapure water was generated by an Elgastat Prima reverse osmosis and Elgastat Maxima ion exchange water purification system (Elga, Ltd., Bucks, United Kingdom). All reagents and acids were suprapure or pro analysis quality. Except for N and Hg, the total nutrient (Ca, Mg, K, Na, P, S, Cu, Mn and Zn) and heavy metal concentrations in the sludges were determined with ICP-OES (Thermo Fisher Scientific iCAP6500 Duo, UK).

The total N concentration in the sludges was carried out according to European standard SFS-EN 13654-1 by the Kjeldahl method using a Foss-Tecator Kjeltree 2300 Analyser (Höganäs, Sweden) equipped with a Foss-Tecator 2020 Digestor. The concentration of Hg in the sludges was determined with a Perkin Elmer AAnalyst 700 cold-vapour atomic absorption spectrometer (Norwalk, USA) equipped with a Perkin Elmer FIAS 400 and AS 90 plus autosampler. A comprehensive review of the standards, analytical methods and instrumentation is given in our previous publication.¹⁴

3. RESULTS AND DISCUSSION

3.1 Primary and secondary sludge characterization

According to the XRD spectra, only cellulose ([C₆H₁₀O₅]_n; 42.6%), its derivatives such as cellulose I alpha (44.8%) and cellulose nitrate glycerinformal (8.1%) as well as quartz (SiO₂; 4.5%) could be identified in the primary sludge. Furthermore, cellulose (32.6%) was also identified in the secondary sludge, as well as aragonite [CaCO₃; 17.3%], calcite [CaCO₃; 15.7%] and talc [Mg₃Si₄O₁₀(OH)₂; 34.4%]. Our spectra are consistent with the findings of Jackson and Line,¹⁷ who also observed cellulose and calcite in the pulp and paper sludge.

According to Lawrence and Scheske,¹⁸ carbonate minerals such as calcite are the most effective neutralizing minerals because they have relatively high reactivity. In this context it is worth to note, that an XRD spectrometer is unable to identify the amorphous (glass) phase (non-crystallised matter), and its detection limit is normally 1-2% (w/w).¹⁸ This is probably why crystalline compounds containing all the heavy metals in sludge were not identified by XRD, despite the fact, that the concentrations of these elements could be quantitatively measured by ICP-OES.

Table 1. Physical and chemical properties of primary sludge (PS) and secondary sludge (SS) investigated in this study

Property	Unit	PS	SS
pH		5.8	7.4
DMC	%	32.3	2.9
LOI	% (d.w.)	95.4	73.0
TOC	g/kg (d.w.)	473	450
EC	mS/m	7.8	600
NV	% (Ca; d.w.)	2.9	5.1
RV	% (Ca; d.w.)	2.5	5.0
(RV/NV) × 100	%	86.2	98.0

d.w. = dry weight

According to the results in Table 1, the primary sludge was slightly more acidic (pH 5.8) than the secondary sludge (pH 7.4). This is reasonable because the activated sludge treatment plant, where the secondary sludge is generated, is a biological treatment and can be suitably applied to wastewater only if pH value is near neutral, about 6.5 - 7.5.¹⁹ Both sludges are proper for land application since the limit set in several manuals and codes of good practice is 5.²⁰ According Abdullah et al.²¹ the CaCO₃, which was observed in the XRD spectra of our secondary sludge, could be helpful for the soil improver if this residue is utilized for land applications. The dry matter content (DMC) in the primary sludge was 32.3%. In the secondary sludge it was 2.9%, which agrees well with the value of 2.0% reported by Forsell-Tattari²² for Finnish pulp mill sludge. The low dry matter content in the primary and secondary sludges indicates that the incineration of these residues as such does not create any net energy. Therefore, prior any utilization or incineration, the dry matter content of these residues needs to be to increase.

The higher moisture content of the secondary sludge investigated in this study compared to that in the primary sludge agrees with the findings of Mahmood and Elliott,²³ who reported that the secondary sludge is far more difficult to dewater than the primary sludge. Water in sludge can be in the following forms, namely: (1) free water (bulk water) - water not associated with solid particles including void water not associated with capillary forces, (2) intestinal water - water trapped in crevices and interstitial spaces of flocs and microbes, (3) vicinal water - water held to particle surfaces by adsorption and adhesion, for instance by hydrogen bonding and (4) water of hydration - water chemically bound within the particle structure.²⁴ Although conventional mechanical sludge dewatering methods such as centrifuge and filter press can only remove free water and an insignificant amount of intestinal water resulting in high water content sludge,²⁵ they are commonly used in medium and in large scale wastewater treatment plants at the forest industry,²⁶ as too in the case of our mill in this study.

The organic matter content measured as loss-on-ignition (LOI) and total organic carbon (TOC) was higher in the primary sludge compared to those in the secondary sludge. According to Ribeiro et al.,²⁰ this phenomenon is due to the fact, that primary sludge is less mineralized than the secondary sludge. According to Zbytniewski and Buszewski,²⁷ the very high LOI values in these sludges are reasonable, because both sludge and especially the primary sludge is rich in biomass, comprising wood-based fibrous material such as lignin, hemicellulose and cellulose fibres, as well as organic binders originating from the pulping process. The higher TOC value in the primary sludge compared to that in the secondary sludge results from the higher fibrous content in this residue.²⁸

When the treatment options for primary and secondary sludge investigated in this study are considered, it is worth to notice that the Finnish government Decree on Landfills,²⁹ which came into force on 1.1.2016 and is based on the EU Landfill Directive (1999/31/EC) and on the EU Waste Framework Directive (2008/98/EC),¹ prohibits the disposal of organic wastes to landfills if the organic matter content expressed as LOI or TOC is 10% or more. Therefore, due to the very high LOI and TOC values in the primary sludge (95.4% and 47.3%, respectively) and in the secondary sludge (73.0% and 45.0%, respectively), these materials are not allowed to be landfill at conventional landfills in Finland anymore and other advanced treatment methods than landfilling for these residues have to be found.

From the utilization point of view, the high TOC values in both sludge indicates that these residues may act as a source of carbon (C) if they are used as a fertilizer. According to Abdullah et al.²¹ the high organic matter content is an extra benefit for the soils that will improve soil fertility and enhance the soils' physical properties. Organic matter with high C content helps also stimulate microbial population of the soil, especially if it is degraded.²² The

addition of organic material in soil, which has low organic matter content, may also improve soil porosity and structure, as well as the ability to store water and nutrients.³⁰ However, according to Rios et al.³¹ in some cases, the utilization of sludge from forest industry may be limited by the phytotoxic properties due to inadequate decomposition.

The electrical conductivity value (EC), which is an index of the total dissolved electrolyte concentrations, was 7.8 mS/m in the primary sludge and 600 mS/m in the secondary sludge indicating that part of dissolved metals occurs in both sludges as dissolved basic metal salts. The capacity of a liming agent to neutralize soil acidity depends in its content of soluble and hydrolysable bases such as oxides, hydroxides, carbonates and silicates. Cations such as calcium, magnesium and potassium are the interactive counter-ions.³² The neutralizing value (NV) of secondary sludge was 5.1 expressed as Ca equivalents (d.w.) indicating that about 7.5 tonnes of this residue would be required to replace 1 tonne of a commercial limestone produced by SMA Mineral Ltd (Finland), the neutralizing value of which is 38% (Ca equivalents, d.w.). The NV value of primary sludge was 2.9% (Ca; d.w.) indicating that about 13.1 tonnes of this residue would be required to replace 1 tonne of a limestone produced by SMA Mineral Ltd (Finland). The reactivity value (RV) was determined in order to assess the speed and effectiveness of the neutralizing potential of sludges as a liming material. The RV/NV ratio indicates that the so called "fast acting" capacity is ca. 86.2% for the primary sludge and ca. 98.0% for the secondary sludge. This means, that both sludges are potential soil conditioning agents and pH buffers.

Table 2. The easily soluble plant nutrient concentrations in the primary sludge (PS) and secondary sludge (SS) investigated in this study and in mineral soil at Northern Finland.³⁴ All concentrations expressed as mg/kg (d.w.)

Nutrient	PS	SS	Soil
Ca (NH ₄ Ac)	3800	16900	960
Mg (NH ₄ Ac)	210	1090	135
K (NH ₄ Ac)	< 200	1820	77
Na (NH ₄ Ac)	510	10800	14
P (NH ₄ Ac)	48	260	11.7
S (NH ₄ Ac)	79	2900	23
Cu (NH ₄ Ac+Na ₂ EDTA)	< 1.0	1.6	3.3
Mn (NH ₄ Ac+Na ₂ EDTA)	61	5300	28
Zn (NH ₄ Ac+Na ₂ EDTA)	47	120	3.8

3.2 Easily soluble nutrient concentrations in the sludges

According to Miller,³³ nitrogen (N), phosphorous (P) and potassium (K) are the primary nutrients in fertilizers, whereas magnesium (Mg), sulphur (S) and calcium (Ca) are secondary nutrients. Copper (Cu), manganese (Mn), zinc (Zn), iron (Fe), molybdenum (Mo) and boron (B) are micronutrients, which are also called trace elements, and

are equally important substances for plant growth, even though they are only needed in minute amounts.

Although there are significant differences in required quantities of different nutrients, none of these macronutrients or micronutrients can be substituted for another without negative impact on plant growth. The easily soluble nutrient concentrations (Table 2) are lower than the total nutrient concentrations (Table 3), because the acidic ammonium acetate (NH_4Ac) as well as the ethylenediaminetetra-acetic acid disodium salt (Na_2EDTA) extraction give only the nutrients in easily soluble (exchangeable) and readily soluble form, thus simulating the easily available (bioavailable) fraction.³⁵ Therefore both the above mentioned extractions are widely used as an indicator of plant nutrient availability whereas,³⁶ the *aqua regia* (3 mL HCl + 9 mL HNO_3) digestion, which was used to the total digestion of nutrients and heavy metals in this study, is capable to release most of the components bound in the silicate matrix, dissolves carbonates, most sulphide minerals, clay minerals and primary and secondary salts and hydroxides.³⁷

3.3 Total nutrient concentrations in the sludges

According to results in Table 3, the total nutrient concentrations of Ca, Mg, K, Na, P, S, Cu, Mn and Zn in the secondary sludge were clearly higher than those in the primary sludge. Except of magnesium (Mg), all other nutrient concentrations in the secondary sludge were also higher than those observed in the mineral soil at Northern Finland.^{34,38} Furthermore, the total Ca (4970 mg/kg; d.w.), S (2730 mg/kg; d.w.) and Zn (110 mg/kg; d.w.) concentrations in the primary sludge were clearly higher than those in the mineral soil, whereas the total Na concentration (550 mg/kg; d.w.) in this sludge was almost equal to that observed in mineral soil (547 mg/kg; d.w.). However, the use of primary sludge as a fertilizer would not increase the mineral soil concentrations of Mg, K, P, Cu and Mn in Northern Finland, because the concentrations of these nutrients in this residue were lower than those in the mineral soil.

The total concentrations of nitrogen (42600 mg/kg; d.w.) and phosphorous (5660 mg/kg; d.w.) in the secondary sludge were correspondingly ca. 10.6 and 17.7 times higher than those in the primary sludge (4000 mg/kg; d.w. and 320 mg/kg; d.w; respectively). Furthermore, the C/N ratio of 10.6 in the secondary sludge was clearly lower than the C/N ratio of 118 in the primary sludge. This is reasonable because N and P are added to the secondary wastewater treatment at the activated sludge plant since they are the nutrients necessary for microbial metabolism in the biological process.³⁹ In consequence of this, there is a significant rise in N and P concentrations in the secondary sludge, resulting in higher contents of these nutrients compared to those in primary sludge. The high C/N ratio in

the primary sludge reflects the high elements of wood fibre profile being captured during the primary treatment.⁴⁰

The total nitrogen concentration in the primary sludge (4000 mg/kg; d.w.) and secondary sludge (42600 mg/kg; d.w.) were correspondingly ca. 1.3 and 14.2 times higher than that (3000 mg/kg; d.w.) in the mineral soil at Northern Finland.^{34,38} Although dependent on decomposition time, a C/N ratio lower than about 25 usually means that the organic matter has a surplus of N relative to the N demand of the soil microbial community, which then can be mineralized to NH_4^+ , a plant-available mineral form of N.³⁰ Because the C/N ration of 118 in our primary sludge was higher than the ration of 20:1, this means that if this residue is utilized as a fertilizer, in some period, the nitrogen can be immobilized in the soil preventing N from being accessible by plants and the plants can suffer from nitrogen deficiency.³¹ Conversely, the high total concentration of N in the secondary sludge could potentially cause nitrate leaching if this residue is to be utilized as a soil amendment agent or a fertilizer product.³²

Table 3. Total metal, nitrogen (N) and plant nutrient (Ca, Mg, K, Na, P, S, Cu, Mn, Zn) concentrations in the primary sludge (PS) and secondary sludge (SS) investigated in this study, in mineral soil at Northern Finland,^{34,38} and the Finnish limit values for maximum concentrations of metals in fertilizer products.^{43,44} All concentrations expressed as mg/kg (d.w.)

Metal	PS	SS	Soil	Limit
Al	1910	8940	7400	
As	< 3.0	4.6	1.25	25
B	< 4.0	68	2.5	
Ba	23	340	64	
Be	< 1.0	< 1.0	0.3	
Cd	0.5	4.8	0.04	1.5
Co	< 1.0	2.8	5.4	
Cr	19	49	28	300
Fe	1930	6280	24800	
Mo	< 1.0	4.7	0.6	
Ni	8.6	32	12	100
Hg	< 0.04	< 0.04	0.01	1.0
Pb	< 3.0	6.0	4.0	100
Sb	< 3.0	< 3.0	0.6	
Se	< 3.0	< 3.0	0.4	
Ti	53	90	564	
N	4000	42600	3000	
Ca	4970	34900	3000	
Mg	540	3830	4900	
K	< 200	2490	1500	
Na	550	13500	547	
P	320	5660	500	
S	2730	20100	156	
Cu	6.3	20	17.5	600
Mn	79.0	6330	273	
Zn	110	490	24	1500

3.4 Total heavy metal concentrations in the sludges

The Finnish Fertilizer Product Act⁴³ and Fertilizer Product Decree⁴⁴ ensure that all fertilizer products placed

on the market in Finland are safe, of good quality, and suitable for plant production. The Finnish Fertilizer Product Act⁴³ and Decree⁴⁴ also promote the utilization of by-products as fertilizers, if they have proved to have a positive impact on plant growth and cause no damage or danger to humans, animals, plants or the environment. According to the Fertilizer Product Act⁴³ and Decree,⁴⁴ fertilizer products include for example the following type designation groups: (1) fertilizers, (2) liming materials, and (3) soil conditioners. In Finland, the Ministry of Agriculture and Forestry has set limit values for maximum concentrations for As, Cd, Cr, Ni, Hg, Pb, Cu and Zn in fertilizer products.^{43,44}

According to results in Table 3, the heavy concentrations (As, Cd, Cr, Ni, Hg, Pb, Cu and Zn) in the primary sludge were lower than the Finnish heavy metal limit values for fertilizer products. This indicates that the primary sludge investigated in this study is a potential fertilizer. Except for Cd (4.8 mg/kg; d.w.) in the secondary sludge, all other heavy metals (As, Cr, Ni, Hg, Pb, Cu and Zn) in this residue were lower than the heavy metal limit values for fertilizer products. Although the Cd concentration of 4.8 mg/kg (d.w.) in the secondary sludge exceeded the Cd limit value of 1.5 mg/kg (d.w.) for fertilizer products, the secondary sludge may be utilized as a soil improver, a growing media or as a fertilizer product in landfill sites (e.g. surface structures) or in other closed industrial areas, because the above mentioned Finnish limit values are not applied at these sites. However, if the secondary sludge is to be utilized in these kinds of areas, an environmental permit may be needed.

The highly elevated total Al (8940 mg/kg; d.w.) and Na (13500 mg/kg; d.w.) concentrations in the secondary sludge agree with the finding of Abdullah et al.,²¹ who reported that the concentrations of these metals in sludges can be at levels higher than would typically be found in non-amended soil. This is reasonable due to the fact that Al based chemicals are used in the wastewater treatment process and as a filler material in the production of board to improve optical properties, printability and other physical properties of the products, whereas Na based chemicals are used in the pulping process.

The highly elevated total Ca (34900 mg/kg; d.w.) and total S (20100 mg/kg; d.w.) concentrations as well as total Mg (3830 mg/kg; d.w.) concentration in the secondary sludge are reasonable since calcium is the most abundant mineral in wood and is also used as a filler material in the production of board at the mill investigated in this study. Sulphur in different forms is used as a cooking chemical and magnesium compounds are used during the oxygen delignification process at the mill investigated in this study.

Due to the fact that the characteristics of wastewater treatment sludges from forest industry depends on several things, such as, raw materials, chemicals, the type and grade of produced products, the types and efficiency of equipment used both in the main process and in wastewater treatment

processes and specific operating conditions such as internal wastewater recycling,^{3,19} a more comprehensive reasons for the possible factors effecting the composition of primary and secondary sludges investigated in this study is not possible to discuss further in this context. A good example from this is that in our secondary sludge, the total nutrient and total heavy metal concentrations were higher than those in the primary sludge (see Table 3). This result agrees with the findings of Alakangas et al.⁴⁵ but is contrary to the findings of Ribeiro et al.²⁰ who reported that the total concentrations of Cd, Cu, Ni, Pb, Zn and Cr were higher in the primary sludge than those in the secondary sludge (i.e. a Portuguese pulp mill).

4. CONCLUSIONS

The total heavy metal concentrations in the primary sludge were lower than the Finnish maximum allowable heavy metal concentrations for fertilizer products, which together with high total nutrient concentrations and a high TOC value of 473 g/kg (d.w.) indicates that this residue is a potential fertilizer product. Except for total Cd concentration (4.8 mg/kg; d.w.) in the secondary sludge, all other total heavy metals (As, Cr, Ni, Hg, Pb, Cu and Zn) in this residue were lower than the heavy metal limit values for fertilizer products. Although the total Cd concentration of 4.8 mg/kg (d.w.) in the secondary sludge exceeded the Cd limit value of 1.5 mg/kg (d.w.) for fertilizer products, the secondary sludge may be utilized as a soil improver, a growing media or as a fertilizer product in landfill sites (e.g. surface structures) or in other closed industrial areas, because the above mentioned Finnish limit values are not applied at these sites. However, if the secondary sludge is to be utilized in these kinds of areas, an environmental permit may be needed.

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REFERENCES

1. Bratina B., Šorgo A., Kramberger J., Ajdnik U., Zemljč L.F., Ekart J., Šafarič R. From municipal/industrial wastewater sludge and FOG to fertilizer: A proposal for economic sustainable sludge management. *Journal of Environmental Management*, 2016, 183: 1009-1025.
2. Husgafvel R., Karjalainen E., Linkosalmi L., Dahl O.

- Recycling industrial residue streams into a potential new symbiosis product - The case of soil amelioration granules. *Journal of Cleaner Production*, 2016, 135: 90-96.
3. Monte M.C., Fuente E., Blanco A., Negro C. Waste management from pulp and paper production in the European Union. *Waste Management*, 2009, 29: 293-308.
 4. Akbary N., Kalamdhad A., Koch M. Anaerobic digestion of dewatered primary sludge (DPMS) from the Nagaon paper mill Morigaon Assam. *Pollution Research*, 2017, 36: 159-167.
 5. Ashrafi O., Yerushalmi L., Haghighat F. Wastewater treatment in the pulp-and paper industry: A review of treatment processes and the associated greenhouse gas emission. *Journal of Environmental Management*, 2017, 158: 146-157.
 6. Aycan, N., Turan, N.G., Ozgonenel, O. Optimization of process parameters for composting of pulp/paper mill sludge with hazelnut kernel using a statistical method. *Environmental Protection Engineering*, 2014, 40: 127-138.
 7. Kinnunen, V., Ylä-Outinen, A., Rintala, J. Mesophilic anaerobic digestion of pulp and paper industry biosludge - long-term reactor performance and effects of thermal pretreatment. *Water Research*, 2015, 87: 105-111.
 8. Slade A.H., Ellis R.J., vanden Heuvel M., Stuthridge T.R. Nutrient minimisation in the pulp and paper industry: an overview. *Water Science Technology*, 2004, 50: 111-122.
 9. Lopes C., Herva M., Franco-Uría A., Roca E. Inventory of heavy metal content in organic waste applied as fertilizer in agriculture: evaluating the risk of transfer into the food chain. *Environmental Science and Pollution Research*, 2011, 18: 918-939.
 10. Keskiääri, A., Kärki T. (2017) Raw material potential of recyclable materials for fiber composites: a review study. *Journal of Material Cycles and Waste Management*, 2017, 19: 1136-1143.
 11. EPA: Industrial waste resources guidelines-sampling and analysis of waters, wastewaters, soils and wastes. 2009. <http://epanote2.epa.vic.gov.au>. Accessed 5 February 2018.
 12. Stylianou M.A., Kollia D., Haralambous K.J., Inglezakis V.J., Moustakas K.G., Loizidou M.D. Effect of acid treatment on the removal of heavy metals from sewage sludge. *Desalination*, 2007, 215: 73-81.
 13. Khaliq S.J.A., Al-Busaidi A., Ahmed M., Al-Wardy M., Agrama H., Choudri B.S. The effect of municipal sewage sludge on the quality of soil and crops. *International Journal of Recycling of Organic Waste in Agriculture*, 2017, 6: 289-299.
 14. Pöykiö R., Mänskinen K., Oksanen J., Nurmesniemi H., Dahl O. Chemical characterisation of biosludge from a wastewater treatment plant in a neutral sulphite semi-chemical pulp mill by single and sequential extraction of heavy metals and micro-/macronutrients - a case study. *Chemical Papers*, 2014, 68: 1546-1554.
 15. Yafa C., Farmer J.G. A comparative study of acid-extractable and total digestion methods for the determination of inorganic elements in peat material by inductively coupled plasma-optical emission spectrometry. *Analytica Chimica Acta*, 2006, 557: 296-303.
 16. Kaakinen J., Kuokkanen T., Pesonen J., Välimäki I. Comparison of different standard methods to evaluate the total concentrations of heavy metals in waste rock. *Soil and Sediment Contamination*, 2014, 23: 437-451.
 17. Jackson M.J., Line M.A. Organic composition of a pulp and paper mill sludge determined by FTIR, ¹³C CP MAS NMR, and chemical extraction techniques. *Journal of Agricultural and Food Chemistry*, 1997, 45: 2354-2358.
 18. Lawrence R.W., Scheske M. A method to calculate the neutralization potential of mining wastes. *Environmental Geology*, 1997, 32: 100-106.
 19. Rajkumar K. An evaluation of biological approach for the effluent treatment of paper boards industry - An economic perspective. *Journal of Bioremediation and Biodegradation*, 2016, 7: 366.
 20. Ribeiro P., Albuquerque A., Quinta-Nova L., Cavaleiro V. Recycling pulp mill sludge to improve soil fertility using GIS tools. *Resources, Conservation and Recycling*, 2010, 54: 1303-131.
 21. Abdullah R., Ishak C.F., Kadir W.R., Bakar R.A. Characterization and feasibility assessment of recycled paper mill sludges for land application in relation to the environment. *International Journal of Environmental Research and Public Health*, 2015, 12: 9314-9329.
 22. Forssell-Tattari I. Biosludge and its ash content in a wastewater treatment plant of a pulp mill. Master Thesis, 2009. University of Tampere, Finland.
 23. Mahmood T., Elliott A. A review of secondary sludge reduction technologies for the pulp and paper industry. *Water Research*, 2006, 40: 2093-2112.
 24. Yang G.C.C., Chen M.C., Yeh C.F. Dewatering of a biological industrial sludge by electrokinetics-assisted filter press. *Separation and Purification Technology*, 2011, 79: 177-182.
 25. Tuan P.A., Sillanpää M. Fractionation of macro and trace metals due to off-time interrupted electrodewatering. *Drying Technology*, 2010, 28: 762-772.
 26. Pham A.T., Sillanpää M., Virkutyte J. Sludge dewatering by sand-drying bed coupled with electro-dewatering at various potentials. *International Journal of Mining, Reclamation and Environment*, 2010, 24: 151-162.
 27. Zbytynski, R., Buszewski, B. Characterization of natural organic matter (NOM) derived from sewage sludge compost. Part 1: chemical and spectroscopic properties. *Bioresource Technology*, 2005, 96: 471-478.
 28. Catricala C.E., Bowden W.B., Smith C.T., McDowell W.H. Chemical characteristics of leachate from pulp and paper mill residuals used to reclaim a sandy soil. *Water, Air & Soil Pollution*, 1996, 89: 167-187.
 29. Finnish Government Decree on Landfills (331/2013; amendments up to 960/2016 included). Ministry of the Environment, Finland, 2013. <https://www.finlex.fi>. Accessed on 8 February 2018.
 30. Sogn T.A., Dragicevic I., Linjordet R., Krogstad T., Eijsink V.G.H., Eich-Greatorex S. Recycling of biogas digestates in plant production: NPK fertilizer value and risk of leaching. *International Journal of Recycling of Organic Wastes in Agriculture*, 2018, 7: 49-58.
 31. Rios D., Pérez C., Sandoval M. Phytotoxic effect of paper pulp sludge on Alfisol soil. *Journal of Soil Science and Plant Nutrition*, 2012, 12: 315-327.
 32. Van Herck P., Vandecasteele C. Evaluation of the use of a sequential extraction procedure for the characterization and treatment of metal containing solid waste. *Waste Management*, 2001, 21: 685-694.
 33. Miller T. Comparative environmental assessment of organic

- and mineral fertilizers - Case study of BioA fertilizer produced from industrial waste. Master Thesis, 2013. Aalto University, Finland.
34. Valkama M. Rovaniemen taajama-alueiden maaperän taustapitoisuudet. Master Thesis, 2017. University of Oulu, Finland. www.jultika.oulu.fi. Accessed 20 February.
35. Fälmarsch R. Biogeochemistry in acid sulphate soil landscapes and small urban centres in Western Finland. Doctoral Thesis, 2010. Åbo Akademi University, Finland. <https://www.doria.fi>. Accessed 23 January 2018.
36. Demeyer A., Voundi Nkana J.C., Verloo M.G. Characteristics of wood ash and influence on soil properties and nutrient uptake: an overview. *Bioresource Technology*, 2001, 77: 287-295.
37. Albanese S. Evaluation of the bioavailability of potentially harmful elements in urban soils through ammonium acetate-EDTA extraction: a case study in southern Italy. *Geochemistry: Exploration, Environment, Analysis*, 2008, 8: 49-57.
38. Lumme I. Early effects of peat ash on growth and mineral nutrition of the silver birch (*Betula pendula*) on a mined peatland. *Silva Fennica*, 1988, 22: 99-112.
39. Rashid M.T., Barry D., Goss M. Paper mill biosolids application to agricultural lands: benefits and environmental concerns with special reference to situation in Canada. *Soil & Environment*, 2006, 25: 85-98.
40. Utanun P. Feasibility of the use of recycled nutrients in fast growing pulpwood production. Master Thesis, 2015. LUT School of Technology, Lappeenranta University of Technology. <https://www.doria.fi>. Accessed 11 January 2018.
41. Camberato J.J., Gagnon B., Angers D.A., Chantigny M.H., Pan W.L. Pulp and paper mill by-products as soil amendments and plant nutrient sources. *Canadian Journal of Soil Science*, 2006, 86: 641-653.
42. Rato Nunes J., Cabral F., López-Piñeiro A. Short-term effects on soil properties and wheat production from secondary paper sludge application on two Mediterranean agricultural soils. *Bioresource Technology*, 2008, 99: 4935-4942.
43. Lannoitevalmistelaki (539/2006) (Finnish Fertilizer Product Act 539/2006, amendments up to 340/2010 included). (2006). <https://www.finlex.fi>. Accessed 14 March 2018.
44. Lannoitevalmistasetus (24/11) Maa- ja metsätalousministeriön asetus lannoitevalmisteista (Finnish Decree on Fertilizer Products). (2011). <https://www.finlex.fi>. Accessed 14 March 2018.
45. Alakangas E., Hurskainen M., Laatikainen-Luntama J., Korhonen J. Properties of indigenous fuels in Finland. 2016. VTT Technical Research Centre of Finland Ltd. <http://vtt.fi>. Accessed 4 January 2018.