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Chapter

Basic Morphological, Thermal and Physicochemical Properties of Sewage Sludge for Its Sustainable Energy and Material Use in the Circular Economy

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Abstract

The treated sewage sludge is a smart material that provides sustainable use of energy and material that can be adapted to the needs of modern human life. Pyrolysis is one of the waste recovery operation that enables the generation of various useful groups of substances from treated sludge, which can then be utilized separately by final energy and material recovery processes: (i) solid residue (pyrogenic material), (ii) liquid fraction (bio-oil), and (iii) non-condensable gas. Those fractions are the basis for fertilizers and alternative fuel or new chemicals production. The chapter combines data on the quality of treated sludge as a case study of an urban wastewater treatment plant (UWWTP) with the capacity of 360,000 population equivalents (PE). The analytical results of dried anaerobically treated sludge over a 10-year period (from 2010 to 2020) are evaluated with respect to the limit values from directives, resolutions, guidelines, and national legislation related to specific processing procedures and quality of the final product. The data provide a comprehensive insight into the basic properties of treated sludge and allow thoughtful use of this smart material for WtE processes, organic matter material conversion, and agricultural use in terms of protecting the environment and human health.

Keywords: circular economy, fertilizer, incineration, pyrogenic material, pyrolysis, sewage sludge, solid residue, urban wastewater treatment plant, waste to energy

1. Introduction

The trend for continual improvement in the collection and treatment of wastewater in Europe's cities and towns is evident, but full compliance with the Urban waste water Directive (UWWTD) [1] has not been achieved yet [2]. The level and intensity of wastewater treatment depend on the sensitivity of the receiving surface waters according to the UWWTD [1]. In Europe, 3.1% of the load is treated at the primary level, 28.5% at the secondary level, and 68.4% at the tertiary level [3]. The EU Commission has also launched an impact assessment to

evaluate different policy options with the aim of modernizing the UWWTD [2]. Among others, specifically, the UWWTD requires controls of sludge disposal and reuse [4]. Article 14 of the UWWTD specifies [1]: (i) sludge arising from wastewater treatment shall be reused whenever appropriate, and (ii) disposal routes shall minimize the adverse effects on the environment. While approximately 20–25 kg of sludge dry matter (DM) are continuously produced annually per person per year all across Europe as a result of the wastewater treatment process, the wastewater operators render the valuable resources found in sewage sludge to be reusable [5].

The term "sewage sludge" does not clearly define the status of its quality. In the literature and regulations, the term "sewage sludge" refers to untreated excess sludge, partially treated sludge, digestate, and pelletized sludge. By Sewage Sludge Framework Directive (SSD) [6], the term "sludge" refers to untreated sludge (residual sludge from sewage plants treating domestic or urban waste waters and from other sewage plants treating waste waters of a composition similar to domestic and urban waste waters, and residual sludge from septic tanks and other similar installations for the treatment of sewage), while the term "treated sludge" refers to sludge which has undergone biological, chemical or heat treatment, long-term storage or any other appropriate process so as significantly to reduce its fermentability and the health hazards resulting from its use. Using the appropriate term in the professional literature helps us to distinguish between the quality of sludge obtained at different levels of processing.

On the European scale, the most common recovery procedures are agriculture and incineration [3]. In the latter procedure, it is not clear whether it is incineration for the purpose of waste to energy (WtE) processes (R 1 recovery operation), or it is just a matter of reducing the amount of sewage sludge (D 10 disposal operation). According to the Waste Framework Directive (WFD) the recovery procedure R 1 takes precedence over the disposal operation D 10 [7].

Quality of municipal infrastructure of urban agglomerations and appropriate pre-treated industrial wastewater has high importance on the stable operation of municipal wastewater treatment plants, and properties of treated sludge. Continuous quality control of treated sludge is the starting point for its efficient recovery processing as a source of raw materials to follow the strategy in the new Circular Economy Action Plan [8]. Some technical solutions enable the recovery of materials from treated sludge like phosphorus, nitrogen, biopolymers, biogas, biochar, biofuel, struvite, and even recovered products from ashes [9]. A market is not always available for these innovative materials because the recovery costs are often high compared to primary raw materials. This is because fossil oil based material or extraction techniques and transportation are cheaper [9]. The chapter will address three main areas of sludge recovery operations [7], namely the use of treated sludge for: (i) energy production—waste to energy (WtE), recovery operation R 1, (ii): the organic matter recovery with pyrolysis, recovery operation R 3, and (iii) agricultural use, recovery operation R 10. All end-use utilizations have advantages and disadvantages and are suitable for recovery processes from a different points of view and engineering approaches, depending on the UWWTP organic load capacity, level of raw wastewater treatment, and excess sludge pre-treatment stage (e.g. aerobic or anaerobic stabilization, dehydration, hygienization, and pelletization). Important are also others conditions such as the UWWTP geographical site, transport infrastructure, and available facilities for sewage sludge utilization. National legislation, the national strategic program for the management program of this specific waste stream, and the national level of public awareness of the usefulness of the sludge as a raw material for the CE are also important.

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A case study of the composition of treated sewage sludge, generated at Central wastewater treatment plant Ljubljana (CWWTPL) has been performed. The CWWTPL treats the municipal wastewater of the capital city Ljubljana and is the largest UWWTP in Slovenia [10]. The purpose of the analysis and the research was to evaluate the feasibility of sewage sludge pre-treatment at the site of origin, anaerobic stabilization of excess sludge and biogas production, seasonal fluctuations in the quality of treated sludge, and the comparability of quality of the annual representative samples. The purpose is also to evaluate the sewage sludge as a smart material. The obtained results are the basis for sustainable and predictable use of treated sludge in the CE [11], both in the field of WtE and material utilization. The most important legal requirements for specific purposes of sewage sludge use are given. The chapter combines specifications, guidelines, and limit values regarding WtE processes, pyrolysis, and fertilizing products with real data of treated sludge quality and its potential. Quality data of the CWWTPL sludge were collected over a ten-year period of operation, from 2010 to 2020. The last year is also the starting year for a number of forecasts on improving the environment and preventing climate change.

1.1 Pyrolysis: recovery operation R 3, thermal conversion of organic matter into new products

According to WFD [7] the recovery operation R 3 means recycling/reclamation of organic substances which are not used as solvents (including composting and other biological transformation processes), gasification and pyrolysis using the components as chemicals, waste preparing for reuse, and recovery of organic materials in the form of backfilling.

Pyrolysis is a thermochemical anaerobic decomposition of biomass into a range of useful products. The process is typically carried out in a temperature range from 300°C through 650°C [12]. During pyrolysis, large, complex hydrocarbon molecules of biomass break down into relatively smaller and simpler molecules, forming gaseous (non-condensable volatile compounds) and liquid products (bio-oil), and solid residue (biochar). Pyrolysis offers the potential of material utilization of UWWTS. The densified pyrolytic fraction of sewage sludge is suitable for energy utilization, and on the other hand, the resulting solid residue is potential for material utilization on fields or forests. Biochar is by mass the major pyrolytic product or resideous material. Its characteristics make it promising for application in agriculture due to its high immobilization affinity of heavy metals [13]. Biochar retains the main part of the carbon in stable solid form [12]. In addition, sewage sludge biochar contains significant content of phosphorus, potassium, and nitrogen, which further demonstrates the great potential of its use as a fertilizer [12].

There is no special EU legislation regarding the waste pyrolysis process. European Biochar Foundation (EBC) has launched the guidelines for specification and certification procedure for biochar evaluation [14]. As a specification for pyrolysis technology is prescribed: (i) the use of waste heat or the use of liquid and gaseous pyrolysis products, and (ii) compliance with nationally defined emission limit values. For the characterization of biochar properties, the limit values in **Table 1** must be observed. The biochar for all application classes must be analyzed at least according to the EBC Basic Analysis Package ([14], Annex 1). The latter reference also indicates which types of biomass are permissible for each application class.

As both biochar properties and the environmental footprint of its production are largely dependent on the pyrolysis parameter and the type of feedstock to be used, a secure control and assessment system for its production and analysis had to be introduced. According to reference [14], biochar is defined by its quality

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EBC—label, application classes	Parameter	EBC— feed	EBC— AgroBio	EBC—Agro	EBC— material
EBC—class		Class I	Class II	Class III	Class IV
Ultimate analysis		TC,	C _{org} , H, N, O	, S, ash	
Indicator of the degree	H/C _{org}			< 0.7	
of carbonization and stability	O/C _{org}			<0.4	
Physical properties	Water content, dry	y matter (D	M), bulk den pH, salt conte	sity, specific surfac ent	e area (BET),
Thermogravimetric analy	zsis				$ \geq $
Nutrients	707	At le	east N, P, K, I	Mg, Ca	-7
Potencially toxic metals (PTM)	Pb	10 g t^{-1} (88% _{DM})	$45~g~t^{-1}{}_{\rm DM}$	150 g t^{-1}_{DM}	250 g t^{-1}_{DM}
	Cd	$0.8 ext{ g t}^{-1}$ (88% _{DM})	$0.7 g t^{-1}{}_{\rm DM}$	$1.5 \mathrm{g} \mathrm{t^{-1}}_{\mathrm{DM}}$	$5 \mathrm{g} \mathrm{t}^{-1}{}_{\mathrm{DM}}$
	Cu	70 g	t^{-1}_{DM}	$100 \text{ g t}^{-1}{}_{\mathrm{DM}}$	$250 \; g \; t^{-1}{}_{\rm DM}$
	Ni	25 g	t^{-1}_{DM}	$50 \mathrm{g t}^{-1}{}_{\mathrm{DM}}$	$250 \; g \; t^{-1}{}_{\rm DM}$
	Hg	$0.1\mathrm{g}\mathrm{t}^{-1}$ (88% _{DM})	$0.4 g t^{-1}{}_{DM}$	1 g t ¹ _D	DM
	Zn	200	$g t^{-1}_{DM}$	$400 \text{ g t}^{-1}{}_{\text{DM}}$	750 g t^{-1}_{DM}
	Cr	70 g	t^{-1}_{DM}	$90 \text{ g t}^{-1}{}_{\text{DM}}$	$250~g~t^{-1}{}_{\rm DM}$
	As	2 g t^{-1} (88% _{DM})	13	$3 \text{ g t}^{-1}_{\text{DM}}$	$15 \mathrm{g} \mathrm{t}^{-1}{}_{\mathrm{DM}}$
Organic contaminants	16 PAH according to EPA priority list	4 ± 2	$g t^{-1}_{DM}$	$6.0\pm 2.2~g~t^{-1}{}_{DM}$	$30 \text{ g t}^{-1}{}_{\text{DM}}$
	Benzo(a)pyren	25 mg t ⁻¹ (88% _{DM})		_	
	PCB, PCDD/F	([14], chapter 9)	Once po production for PCDE	er pyrolysis unit for batch. For PCB: 0.2 D/F: 20 ng kg ⁻¹ (I-T respectively.	r the first 2 mg kg ⁻¹ _{DM} , TEQ OMS),
uble 1. mit values for biochar proj	perties.				

characteristics, the raw materials used, its sustainable production, and the end-use (**Table 1**).

The pyrolysis of non-plant biomasses such as treated sludge, livestock manure, certain digests or bones may also produce valuable raw materials and could be used in the interests of the bio-economy and climate protection, but these raw materials have not yet been included in the EBC feedstock list and are therefore not subject of the EBC guidelines [14].

According to the declaration of biochar properties, the organic carbon or TOC (C_{org}) must be defined. By the last version of EBC guidelines [14] the lower limit value of 50% m/m_{DM} has been reconsidered. All solid pyrolysis products below this limit value were considered only as pyrogenic carbonaceous materials (PCM).

The EBC certificate guarantees that only climate-positive biochar production technology is used and does not release unburned pyrolysis gases into the atmosphere. Reference [14] specified the conditions for the safe and harmless operation

of pyrolysis units. Regarding the environment protection and preventing climate change the most important conditions are: (i) with the exception of the preheating of the pyrolysis reactor, the use of fossil fuel for heating is prohibited, (ii) if the pyrolysis reactor is electrically heated, the use of renewable energy source or the use of surplus electricity is recommended, (iii) the non-condensable pyrolysis gas must be burned or it can be trapped and used for the chemical industry, (iv) the bio-oil can also be stored and used for other energy and material purposes, (v) syngas combustion must comply with national emission thresholds, and (vi) the heat produced by pyrolysis process must be used.

1.2 EU legislation regarding the energy recovery from waste

The IED Directive [15] shall not apply to pyrolysis and gasification plants if the gases resulting from this thermal treatment of waste are purified to such an extent that they are no longer a waste prior to their incineration and they can cause emissions no higher than those resulting from the burning of natural gas.

In the EU regulation on waste incineration and co-incineration, the limit values for polluting substances, related to substances in sludge are presented. There is a possibility of linking the characteristics of the sludge with environmental pollution and harm to human health, so the energy recovery from treated sludge must be provided safely and harmlessly. Data provision and assessment must be made from a holistic point of view to consider WtE processes. These processes must be evaluated from an economic as well as from the environment point of view regarding the emissions into the air and into the surface water, and last but not least also regarding the generated residues.

1.2.1 Technical provisions to waste incineration plants and waste co-incineration plants

Technical provisions to the new waste incineration plants and waste coincineration plants, according to IED Directive [15] are considered. In **Table 2** presented emission limit values of polluting substances into the air according to the standardized oxygen atmosphere. Limit values for waste incineration plants in **Table 2**, footnote a, apply for facilities: (i) that were in operation and have a permit in accordance with applicable Union law before 28 December 2002, and (ii) that were authorized or registered for waste incineration and have a permit granted before 28 December 2002 in accordance with applicable Union law, provided that the plant was put into operation no later than 28 December 2003. In the view of the competent authority, these facilities were the subject of a full request for authorization before 28 December 2002.

Limit value for NOx in **Table 2**, footnote b, applies for existing waste incineration plants with a nominal capacity exceeding 6 tonnes per hour or new waste incineration plants. The limit value for NOx in **Table 2**, footnote c, applies for existing waste incineration plants with a nominal capacity of 6 tonnes per hour or less. A new waste incineration plant means any waste incineration plant not covered by the existing plant.

Table 3 presents the limits values for polluting substances causing the emissions into the air according to transitional provisions of the IED Directive. The limit values shall be applied as follows: (i) in **Table 3**, footnote a, to combustion plants that co-incinerate waste from 1 January 2016 referred to the reference ([15], Article 30 (2)) and (ii) in **Table 3**, footnote b, to combustion plants that co-incinerate waste from 7 January 2013 referred to the reference ([15], Article 30 (3)).

Polluting substances/standard oxygen concentration in waste gas	Waste incineration plant ^a	Cement kilns co- incinerating waste				
	Sampling period of waste gas					
	daily	average				
	11% v/v	10% v/v				
Total dust	10	30				
ТОС	10 (gaseous and vapo	orous organic substances)				
со	50					
HCl	10	10				
HF	1					
SO ₂		50				
NO _x as NO ₂	200 ^b	500				
	400 ^c					
Heavy metals and their compounds	A minimum of 30 m	in and a maximum of 8 h				
Cd + Tl	$\sum t$	\sum_{tot} ; 0.05				
Hg		0.05				
Sb, As, Pb, Cr, Co, Cu, Mn, Ni, V	Σ	\sum_{tot} ; 0.5				
Organic pollutants	A minimum of 6 h	A minimum of 6 h and a maximum of 8 h				
Dioxins and furans	0.1					

Table 2.

Emission limit values for the following polluting substances in mg/Nm³ for heavy metals and in ng/Nm³ in combination with toxic equivalence factor (TEF) for dioxins and furans in their gaseous and vapor forms.

1.2.2 Technical provisions to technological wastewater from incineration plants and waste co-incineration plants

In flue gas cleaning technological wastewater is generated, which captures dust of fly ash and condensed volatile compounds of heavy metals. The generated process water must be treated in accordance with the limit values for pollutants in the generated wastewater, which are uniformly determined for all waste incineration and co-incineration plants [15]. Limit values for total suspended solids (TSS) in pre-treated technological wastewater as defined in Annex I of UWWTD [1] are: (i) 30 mg L⁻¹ by 95% of all results or (ii) 40 mg L⁻¹ by 100% of all results.

In terms of sustainable energy utilization of sewage sludge, in order to prevent the circulation of already removed polluting substances back to nature, it is necessary to assess the quality of treated technological wastewater and prevent deterioration of the chemical and ecological status of the receiving surface water. **Table 4** shows a comparison of the limit values for the discharge of treated technological wastewater from the incineration and co-incineration plant [15] with the limit values for good chemical status and very good and good ecological status of receiving surface water. The chemical status of waters is assessed by the content and concentration of Environmental quality standards (EQS), expressed as priority substances (PS) or priority hazardous substances (PHS) [16, 17]. The ecological status is assessed, among other conditions, by the presence and concentration of non-synthetic special pollutants (SP) [16]. Since the dilution factor of some polluting substances in the treated wastewater from the incineration and co-incineration

Polluting substances/standard oxygen concentration in wa gas	ste Tot	2 Total rated thermal input MWth				
	<50	50– 100	100– 300	>300		
	Samj	oling perio	od of waste	e gas		
		daily a	verage			
		6%	v/v			
Total dust ^a	50	30	25	20		
Total dust ^b		()	20	10		
SO ₂ ^a) A	400	200			
SO ₂ ^b			200	150		
NO _x as NO ₂ ^a		300	200			
NO _x as NO ₂ ^b			200	150		
Heavy metals and their compounds	A m	A minimum of 30 min and a maximum of 8 h				
Cd + Tl		\sum_{tot}	; 0.05			
Hg 0.05						
Sb, As, Pb, Cr, Co, Cu, Mn, Ni, V \sum_{tot} ; 0.5						
Organic pollutants A minimum of 6 h and maximum of 8 h				a		
Dioxins and furans		0	.1			

Table 3.

Emission limit values for combustion plants co-incinerating solid fuels with the exception of biomass for the following polluting substances in mg/Nm^3 and in ng/Nm^3 in combination with toxic equivalence factor (TEF) for dioxins and furans in their gaseous and vapor forms ([15], Articles 30(2) and 30(3)).

Polluting substances	IED Directive [15]
Emission limit values	for unfiltered samples (mg L^{-1} except for dioxins and furans)
Hg	0.03
Cd	0.05
Pb	0.2
Ni	0.5
Dioxins and furans, TEQ	$0.3 \text{ ng } \mathrm{L}^{-1}$
As	0.14
Tl	0.05
Cr	0.5
Cu	0.5
Zn	1.5

Table 4.

Emission limit values for discharges of wastewater from the cleaning of waste gases.

plant into the environment must be around 1000, it is necessary to pay full attention to this sustainability aspect of the WtE process.

EU Member States may, when assessing the monitoring results against the relevant EQS, take into account: (i) natural background (NB) concentrations for metals and their compounds where such concentrations prevent compliance with the relevant EQS, (ii) hardness, pH, dissolved organic carbon or (iii) other water quality parameters that affect the bioavailability of metals, the bioavailable concentrations being determined using appropriate bioavailability modeling.

Mercury is an atmospheric deposit and is behaving like a ubiquitous persistent, bioaccumulative and toxic substance (PBT). Due to its volatility mercury is often present in the environment. Limiting the circulation of mercury in the atmosphere as much as possible is an important task in establishing the sustainability of sewage sludge utilization in the CE.

Establishing the sustainable utilization of sewage sludge with WtE processes is based on a holistic assessment of the environment in which the facility is located. Sewage sludge is a specific waste stream with a complex composition and only a good knowledge of all aspects of environmental impact and properties of sewage sludge allows the design of sustainable WtE technologies from treated sludge.

1.3 EU legislation regarding material recovery from treated waste in the agriculture

The framework European Sewage sludge Directive (SSD) [6] regulates the use of sewage sludge in agriculture for the EU Member States. According to reported quantities on recovery procedures for sewage sludge for the period 2013–2015 in Europe, 48.5% m/m sewage sludge is used for agriculture [3]. The data in Ref. [3] show that in many EU Member States this process is still the most topical.

The selection of polluting substances, for which a limit value is set, include heavy metals, which are potentially toxic and are essential in a small amount for various biochemical and physiological functions within the plants, animals, and human [18] (**Table 5**). A pH limit is additionally prescribed for the quality of the soil. In adapting its national legislation EU Member States may permit the limit values they fix to be exceeded in the case of the use of soil and sludge for cultivation of commercial food crops exclusively for animal consumption (**Table 5**, footnote a).

Treated sludge and soil properties	Soil ^a	Treated sludge ^a	The maximum annual quantities of PTM introduced into soil ^c
рН	6–7	Not relevant	
PTMs	mį	g kg ⁻¹ _{DM}	kg ha $^{-1}$ y $^{-1}$
Cd	1–3	20–40	0.15
Cr		Limit value is	not defined yet
Cu	50–140 ^b	1000–1750	12
Hg	1–1.5	16–25	0.1
Ni	30–75 ^b	300–400	3
Pb	50-300	750–1200	15
Zn	150–300 ^b	2500-4000	30

Table 5.

Limit values for use of sewage sludge in agriculture according to SSD [6].

EU Member States also may permit the limit values they fix to be exceeded in respect of these parameters on soil with a pH consistently higher than 7 (**Table 5**, footnote b). The maximum authorized concentrations of PTMs may not exceed those values by more than 50%. The EU Member States must also seek to ensure that there is no resulting hazard to human health or the environment and in particular to ground water. The amount of PTMs annually spread on soil is calculated on a 10-year average (**Table 5**, footnote c).

National legislation of the EU Member States regarding the use of sludge in agriculture is not uniform, there are differences in the limit values for the key parameters, and there is also a difference in the legislation demands between USA and EU [20].

Given the strategic objectives of the CE philosophy and the reduction of waste, it is necessary to give priority to the use of recovered waste over the depletion of raw materials. In order to include as much recovered waste as possible in the raw material cycle, the EU has adopted a Fertilizing Resolution (FR) [21] for the use of recovered waste in fertilizer, which aims to unify the European fertilizer market. According to the vision of FR, the 'EU fertilizing product' means a fertilizing product which is labeled with the logo CE ("conformité européenne") when made available on the market. It includes fertilizers produced from recovered or organic materials. The FR, which will not enter full force until 16 July 2022, will not affect the implementation of SSD [6]. The possibility of using sewage sludge as a fertilizer product is still ambiguous. From the conditions for the selection of possible treated waste for use as a fertilizer, it can be understood that this can be all wastes that are composted or anaerobically stabilized [21].

FR does not prescribe the extent of plant response when applying a particular fertilizer. Slovenian legislation is more restrictive in this area and prescribes the quantity and quality of the digestate used for the purpose of a fertilizer (**Table 6**) [19].

1.3.1 Designation of component material categories for the potential EU solid fertilizer

According to FR sewage sludge could be used as input material for the component materials categories (CMC) for fertilizer as a blending compost (CMC 3) and treated digestate (CMC 5), if it does not contain more than 6 mg PAH kg_{DM}⁻¹. **Tables 7** and **8** provide the basic starting conditions for the quality of the recovered waste that can be used as input material for the production of a fertilizer.

Biological criteria	Unit	Quality class 1	Quality class 2
Plant (Chinese cabbage in pot) germination 15% m/m or 25% (v/v) granules: fresh vegetable mass (FVM)	[% m/m]; [% v/v]	≥ 100% of control substrate; germination: ≥95%, germination delay: 0 days	No limits
Germination rate (Cress in Petri dish) 30% m/m or 50% v/v granules: FVM		≥90% of control substrate; germination: ≥90%, germination delay: 0 days	
Green mass (Chinese cabbage), granules: peat moss 20% m/m	%	No limit	
Determination of the content of unwanted weed soil i	seeds and j mprovers	plant propagules in growing subs	strates and
Weed seeds and plant propagules, granules: peat moss 20% m/m	$\rm N^{o} \ L^{-1}$	<2	

Table 6.

Determination of the plant response. Digestate with >20% m/m_{DM} : Characterization of the effect of digestate granules as soil improvers and growth substrates on plant germination and growth [19].

Parameter/ criteria	Unit	Compost (CMC 3)	Digestate other than fresh crop digestate (CMC 5)
	Macroscop	pic impurities (MI); Glass,	metal, plastics
Particles >5 mm	% m/m _{DM} [19]	^{1th} Class, ^{2sd} Class: < 5	^{1th} Class, ^{2sd} Class: < 5
Particles >2 mm ^a		^{1th} Class: < 0.5 ^{2sd} Class: < 2	^{1th} Class, ^{2sd} Class: < 2
	$g kg^{-1}_{DM}$ [21]	3	3
MI _{total}		5	5
$rac{1}{2}$		POPs	
PAHs ₁₆ ^b	${ m mg~kg^{-1}}_{ m DM}$	6	6

Table 7.

Designation of component material categories (CMCs) for the potential EU solid fertilizer incorporating sewage sludge [19, 21].

Parameter/criteria	Unit	Compost (CMC 3)	Digestate other than fresh crop digestate (CMC 5)
	Stability criter	ria [21]	
Oxygen uptake rate	mmol O ₂ kg ⁻¹ _{OM} h ⁻¹	Max 25	Max 25
Residual biogas potential	L biogas $g^{-1} VS^a$	_	0.25
	Stability criter	ria [19]	
(AT ₄)	$mg \ O_2 \ g^{-1}{}_{DM}$	< 15	No limit
Acetic acid	mg L^{-1} (mass/volume)	< 100	< 300
Propionic acid			
	Micro-organisms to be	tested/pathogens	
Salmonella spp.	CFU in 25 g		Absence
Escherichia colli or Enterococcaceae	CFU in 1 g		1000 ^b

The significance for footnotes a and b are provided in the main text of sub-subsection 1.3.1.

Table 8.

Designation of component material categories (CMCs) for the potential EU solid fertilizer incorporating sewage sludge [19, 21].

Conditions for use include the content of total MI, polycyclic aromatic hydrocarbons (PAHs) as persistent organic pollutant (POPs), adequate stability and content of pathogens as evidence of hygienic integrity.

According to FR stricter limit values will apply in the future for the presence of plastics above 2 mm (**Table 7**, footnote a): (i) from 16 July 2026 the maximum limit value point shall be no more than 2.5 g/kg dry matter, and (ii) by 16 July 2029 this limit value shall be re-assessed in order to take into account the progress made with regards to separate collection of bio-waste.

According to FR, sixteen PAHs have been identified as polluting substances indicative of POPs contamination (**Table 7**, footnote b): naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo[a] anthracene, chrysene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, indeno[1,2,3-cd]pyrene, dibenzo[a,h]anthracene and benzo[ghi]perylene.

Residual biogas potential of digestate (**Table 8**, footnote a) is an indicator of mineralization efficiency of excess sludge into the digestate and is expressed as a produced biogas per unit of material that is lost on ignition of the dry solids at 550° C. Loss on ignition is expressed as volatile solids (VS). The treatment process of the digestate must include the hygenization process. It must be free of *Salmonella* spp. and the maximum number of *Escherichia coli* or *Enterococcaceae* expressed in colony-forming units (CFU) is 1000 (**Table 8**, footnote b).

1.3.2 Limit values and declaration for product function categories of the EU fertilizing products

According to FR the product function categories are: (i) liquid or solid fertilizer (organic or inorganic straight or compound macro and micronutrients), (ii) liming material, (iii) organic or inorganic soil improver, (iv) growing medium, (v) non-microbial plant biostimulant, and (vi) fertilizing product blend [21]. In a solid organo-mineral fertilizer, each physical unit shall contain organic carbon (C_{org}) and all the nutrients in their declared content. A physical unit refers to one of the component pieces of a product, such as granules or pellets. Inorganic micronutrient fertilizers shall be made available to the end-user only in packaged form.

If sewage sludge is pre-treated at the site of fertilizer production, the final product line must be separate from the processing of other input materials, and there must be a strictly prevented physical contact between the input and output material during storage.

An organic fertilizer shall contain organic carbon (C_{org}) and primary nutrients (PN) (P, K, Ca, Mg, Na, S) of solely biological origin, but no other material which is fossilized or embedded in geological formations. It shall be derived from plant residues or livestock manure (**Tables 9** and **10**).

Table 9 provides the technical specification of product function categories (PFC) of the EU fertilizing products, which could potentially contain the sewage sludge.

In a solid organo-mineral fertilizer, each physical unit shall contain C_{org} and all PN in their declared content (**Table 9**, footnote a). Limit values shall not apply where copper or zinc has been intentionally added to an organo-mineral fertilizer for the purpose of correcting a soil micronutrients (MICN) deficiency and is declared in accordance with Annex III of FR (**Table 9**, footnote b).

Straight or compound inorganic fertilizer shall contain one or more primary macronutrients (P MACN) and one or more secondary macronutrients (S MACN). **Table 10** presents the minimal content for nutrients for those two groups of fertilizer: (i) content of only one P MACN (**Table 10**, footnote a), (ii) content of only one P MACN and one or more S MACN (**Table 10**, footnote b), (iii) content of more than one P MACN (**Table 10**, footnote c), and (iv) content of no P MACN and more than one S MACN (**Table 10**, footnote d). The total sodium oxide (Na₂O) content shall not exceed 40% by mass (**Table 10**, footnote e). If an inorganic fertilizer contains more than 1% by mass of C_{org} derivated from chelating or complexing agents, nitrification inhibitors, denitrification inhibitors or urease inhibitors, coating agents, urea (CH₄N₂O), or calcium cyanamide (CaCN₂) (**Table 10**, footnote f), shall meet pathogen requirements set out in **Table 8**. Limit values shall not apply where copper or zinc has been intentionally added to an organo-mineral fertilizer for the purpose of correcting a soil micronutrients deficiency and is declared in accordance with Annex III of FR (**Table 10**, footnote g).

Declared minimum content of the total sum of (MICN) boron, cobalt, copper, iron, manganese, molybdenum, and zinc for compound solid inorganic micronutrient fertilizer, PFCs 1(C)(II)(b) shall be 5% by mass. That type of fertilizer shall be made available to the end-user only in packaged form. Contaminants in an inorganic micronutrient fertilizer must not exceed the limit values presented in **Table 11**.

Parameter	Unit	Unit Organic fertilizer, PFC 1(A)(I)			Organo-mineral fertilizer, PFC 1 (B)(I)					
		Content of only one PN	Content of n than one P	nore N	Co only	ntent o y one F	of PN	Conto tha	ent of r n one F	nore PN
]	Declaration							
	P	rimary nutrien	ts (PN), maximı	um co	ntent	:				
NH ₄ NO ₃	% N						<	:16		
]	Primary nutries	nts (PN), minim	al cor	itent					
N _{org}	% N					1		6	0.5	6
N _{tot}	% N	2.5	1		//	2.5)		2	
P _{tot}	% P ₂ O ₅	2	1					2		
K _{tot}	% K ₂ O	2	1					2		
Sum of N, P, K	%	_	4			_			8	
		Oı	ganic carbon							
C _{org}	% C		15				7	.5 ^a		
		Ι	Limit values							
		Pollu	ting substances							
Cd	$mg \ kg_{\rm DM}{}^{-1}$		1.5				-	_		
Cd (<5% P ₂ O ₅)			_					3		
Cd (>5% P ₂ O ₅)	mg Cd kg ⁻¹ of P_2O_5						6	60		
Cr ^{VI}	mg kg_{\rm DM}^{-1}			2	2					
Нg	_ •			1						
Ni				50	C					
Pb				12	0					
As (in inorganic compounds)				4	0					
Biuret (C ₂ H ₅ N ₃ O ₂)	$g k g_{DM}^{-1}$	No	ot present				:	12		
1717	(\bigtriangleup)	Potent	ially toxic metal	s))	(\supset	6
Cu	mg $\mathrm{kg_{DM}}^{-1}$		300)		60	00 ^b	-7	
Zn			800				15	00 ^b		

Table 9.

Limit values and declaration for solid PFCs of EU fertilizing products.

Table 12 presents the limit values and declaration of nutrients for organic soil improver, inorganic soil improver, growing medium, and non-microbial plant biostimulant. Declared organic soil improver may contain peat, leonardite, and lignite, but no other material which is fossilized or embedded in geological formations. Growing medium could be solid or liquid materials/substrate in which plants (including algae) grow (**Table 12**, footnote a).

The plant biostimulant shall be an EU fertilizing product which stimulates plant nutrition processes independently of the product's nutrient content with the sole aim of improving one or more of the following characteristics of the plant or the

Parameter	Unit Sti ferti		Straight inorganic fertilizer, PFC 1(C)(I) (a)(i)		d inorganic PFC 1(C)(I) (ii)
		1 ^a	2 ^b	3 ^c	4 ^d
De	eclaration (% by m/m in th	e form as ava	ailable on the	market)	
	Primary macronutrients	(P MACN),	minimal cont	tent	
N _{tot}	% N	10		3	_
P _{tot}	% P ₂ O ₅	12			
K _{tot}	% K ₂ O	6			
	Secondary macronutrient	s (S MACN)	, minimal cor	ntent	
Ca	% CaO	12	1.5		1.5
Mg	% MgO	5	1.5	_	1.5
Na ^e	% Na ₂ O		1	_	1
S	% SO ₃	10	1.5	_	1.5
Sum of P MACN and	S MACN %			18	
	Orga	nic carbon			
C _{org} ^f	% C			<1	
	Lim	it values			
	Polluting substar	nces, maxima	l content		
Cd (>5% P ₂ O ₅)	mg kg ⁻¹ of P_2O_5	i		60	
Cd (<5% P ₂ O ₅)	$mg \ k{g_{\rm DM}}^{-1}$			3	
Cr ^{VI}				2	
Hg				1	
Ni				100	
Pb				120	
As				40	
Biuret (C ₂ H ₅ N ₃ O ₂)	${\rm g}~{\rm kg_{DM}}^{-1}$			12	
Perchlorate (ClO ₄ ⁻)	mg kg_{\rm DM}^{-1}			50	
	Potentially toxic n	netals, maxin	nal content		
Cu	mg kg _{DM} ⁻¹			600 ^g	
Zn			1	500 ^g	

Table 10.

Limit values and declaration of nutrients for solid inorganic fertilizer declared as a PFCs 1(C)(I).

plant rhizosphere: (i) nutrient use efficiency, (ii) tolerance to abiotic stress, (iii) quality traits, or iv) availability of confined nutrients in the soil or rhizosphere (**Table 12**, footnote b). The plant biostimulant shall have the effects that are claimed on the label for the plants specified thereon (**Table 12**, footnote c).

Pathogens content of EU fertilizing products declared in **Table 12** must not exceed the limits set out in **Table 8**. Evaluation of the sewage sludge, its solid pyrolytic residue (PCM), and its mixture with other treated waste as a fertilizer according to FR will be a complex procedure. In addition to the physicochemical evaluation, the EU fertilizer products label will require a number of other administrative procedures - from packaging to sale.

Polluting substance	Fertilizer with more than one MICN, expressed in mg/kg of total micronutrients content
Cd	200
Hg	100
Ni	2000
Pb	600
As	1000

Table 11.

Upper limit values of polluting substances for compound solid inorganic micronutrient fertilizer, PFCs 1(C) (II)(b) of EU fertilizing products.

Parameter	Unit	Organic soil improver, PFC 3 (A)	Inorganic soil improver, PFC 3 (B)	Growing medium, PFC 4ª	Non-microbial plant biostimulant ^{b;c}
D	eclaration	of nutrients (% by r	n/m in the form as av	ailable on the	market)
Biological origin	%	>95	_	—	_
Dry matter	-	≥20	_	_	_
		Organic car	bon, minimum conte	nt	
C _{org}	% C	7.5	_	_	_
]	Limit values		
		Pollu	uting substances		
Cd	mg	2	1.5	1.5	1.5
Cr ^{VI}	kg _{DM} ⁻¹	2	2	2	2
Hg	-	1	1	1	1
Ni	-	50	100	50	50
Pb	-	120	120	120	120
As (in inorganic compounds)	-	40	40	40	40
	5/	Poten	tially toxic metals		
Cu	mg	300	300	200	600
Zn	kg _{DM} ⁻¹	800	800	500	1500

Table 12.

Limit values and declaration of nutrients for PFCs 3(A), PFCs 3(B), PFCs 4 and non-microbial plant biostimulant (PFCs 6(B)) of EU fertilizing products.

2. Materials and methods

In terms of reviewing basic data on morphological, thermal, and physicochemical properties of sewage sludge, a case study for the CWWTPL was conducted [10]. It is an urban one-stage mechanical-biological wastewater treatment plant aimed at conventional secondary treatment of municipal wastewater, a small amount of industrial wastewater, and providing the public service for acceptance and treatment of excess sludge from the small WWTPs and the contents of septic tanks.

The findings of long-term morphology, physicochemical investigations, and thermal analyses of pelletized dehydrated digestate (granules), produced at CWWTPL, which were carried out in the period from 2010 to 2020, are presented. Predominantly accredited methods for physicochemical characterization and non-accredited methods for morphological properties (bulk density, particle size distribution, and specific surface area determination) and thermal properties were applied. Chemical elements that are the basis for WtE processes, the elements that are important for the use of residues after thermal treatment (combustion or pyrolysis), and elements that are important for the use of granules as a fertilizer or as a material for soil remediation and improvement of the ecological condition were determined. Additional research of thermal properties was done with the conventional accredited methods for organic matter content, loss on ignition, and volatile matter. Enabling more extensive information in the change in weight of granules under the thermal load was derived with simultaneous thermal analysis of granules and mass spectroscopy of the released gases.

Confidence in the results of research into the properties of sewage sludge is based on an appropriate quality control system (including sampling), targeted enduse, and a list of required parameters. Only high-quality performed analysis enable credible results and the setting of optimal guidelines for the successful CE.

2.1 Materials

After thickening by mechanical equipment, along with the addition of a strong cationic polyelectrolyte, the surplus sludge is anaerobically stabilized under mesophilic conditions at 37–40°C and pH of 7.4 in a digester by a hydraulic retention time of at least 20 days. The produced digestate is a thick black-gray suspension of anaerobic biomass with 3.6% m/m of dry matter. Anaerobic stabilization is followed by centrifugal dehydration (cake production) and granulation in a drum dryer at 90°C [20]. The drying process is conducted in batch mode. Simultaneously the digestate cake gets hygenized and granulated. The selection and execution of the cake drying are in accordance with Technical Standard (TS) from the group CEN/TC 308, Characterization of sludges, CEN/TR 15473:2007, Good practice for sludge drying.

Prepared and characterized were also laboratory samples of the basic solid residues generated after controlled thermal loading of granules in order to simulate pyrolytic biochar and incineration bottom ash.

2.2 Methods and techniques

Inflow and outflow of water at the CWWTPL are measured continuously with the Khafagi type venturi meter and an in-line flow meter. The wastewater samples are prepared, cooled, and stored in accordance with the standards from the group water quality—sampling: (i) ISO 5667-10:1992, Part 10: Guidance on sampling of waste waters, and (ii) ISO 5667-3: 2012, Part 3: Preservation and handling of water samples. The COD in raw and treated wastewater is monitored by measurements of daily representative 24 h time-proportional composite water samples using method from the group of standards ISO/TC 14/SC 2 "Physical, chemical and biochemical methods".

From the composite daily sub-samples, mass-proportional representative batch and monthly composite samples of dried and pelletized digestate (in granules) are made, tested, and stored at $5 \pm 1^{\circ}$ C. Similarly, mass-proportional representative annual composite samples according to monthly delivered amount were prepared out of the refrigerated monthly samples. For the granules sampling procedure, a quality system that includes a manual time-proportionate daily sampling in accordance to the standard ISO 5667-13:2011, water quality, sampling, Part 13: Guidance on the sampling of sludge from sewage and water treatment works, and EN 15002:2015, characterization of waste, preparation of test portions from the laboratory sample, was established, as well as a routine control of produced granules as they were shipped to the stakeholder (**Table 13**). The granules sampling plan takes into consideration the relevant technical standards (TS): (i) EN 14899:2005, Characterization of waste, sampling of waste materials, framework for the preparation and application of a sampling plan, (ii) CEN/TS 15442:2006, Solid recovered fuels, methods for sampling and (iii) CEN/TR 15310–3:2006, Characterization of waste, sampling of waste materials, Part 3: Guidance on procedures for subsampling in the field.

Most of the results for the annual representative samples are obtained from official evaluation prepared for the purpose of conducting a public tender for the transport and final treatment of granules from the place of origin. The evaluations were prepared by an authorized contractor [22] and are part of the tender documentation for the implementation of large value public contracts. The methods are selected according to the legal requirements depending on the sample matrix and the scope of the sample under consideration. Slovenian national legal requirements prescribe the quality of the sewage sludge used as a bioresource or as a material for the WtE, and the range of methods and techniques for quality parameters determination. Standard analytical methods for characterization of granules as a potential fertilizer (PF) and as a solid recovered fuel (SRF) were applied as specified by TSs: (i) CEN/TC 223 "Soil improvers and growing media", (ii) CEN/TC 292 "Characterization of waste", (iii) CEN/TC 308 "Characteritation of sludge", and (iv) CEN/TS 343 "Solid recovered fuels". In accordance with the CEN/TS 343, TS EN 15402:2011, Determination of the content of volatile matter (VM), the proportion of VM that causes the granules mass loss in a covered crucible at a thermal load of 900°C over a period of 7 min is determined.

2.2.1 Sampling pattern for representative samples of granules

Periodicaly, every 3 h, 200 mL samples of granules were manually collected from the conveyor belt. Preparation of representative composite daily sample for each shipment is provided by homogenizing and quartering the three-hour subsamples. Daily samples are stored in plastic bottles of 1 L at 5°C \pm 1°C. The sampling period runs from 1 January to 31 December. At the end of each batch of drying process preparation of the composite batch sample (sample increment of 400 mL in volume from each daily sample) is executed by homogenizing and quartering of sub-samples. Representative batch samples are stored in glass bottles of 0.75 L at $5^{\circ}C \pm 1^{\circ}C$. At the end of the calendar month preparation of a composite monthly sample (sample increment of 400 mL) from each daily sample is provided. Prepared are four composite samples $(4 \times 1 L)$ by homogenizing and quartering the daily sub-samples. The monthly samples are stored at $5^{\circ}C \pm 1^{\circ}C$ in brown glass bottles. At the end of the calendar year preparation of a composite massproportional annual sample is prepared from each monthly sample. Four annual composite samples $(4 \times 1 L)$ are obtained by homogenizing and quartering the monthly sub-samples. Storage is done at $5^{\circ}C \pm 1^{\circ}C$ in brown glass bottles.

All annual representative samples are still kept properly and are available for further investigation.

2.2.2 Granules characterization

At CWWTPL the quality control of granules is provided by performing regular quality control at all levels of sludge pre-treatment. To ensure the stable granules

quality, dry matter is regularly checked on an hourly and daily basis with moisture analyzers with a halogen heater. In addition, the quality of representative samples of batch, monthly and annual samples are checked in the laboratory using standard analytical methods for characterization of granules: (i) the oven dry method for moisture content at 103°C (CEN/TC 223, EN 13040:2007, Sample preparation for chemical and physical tests, determination of dry matter content, moisture content and laboratory compacted bulk density) and at 105°C (CEN/TC 444, Environmental characterization, Sludge, treated biowaste, soil and waste, EN 15934:2012, Calculation of dry matter fraction after determination of dry residue or water content), (ii) laboratory furnace (LF) for organic matter content (OM) at 450°C (LF) (CEN/TC 223, EN 13039:2011, Determination of organic matter content and ash), (iii) LF for loss on ignition (LOI) at 550°C (CEN/TC 292, EN 15169:2017, Determination of loss on ignition in waste, sludge and sediments), (iv) LF for ash content at 900°C in LF (CEN/TS 343, EN 15403:2011, Determination of ash content, modified), and (v) standard laboratory equipment for bulk density (as received) (CEN/TS 343, CEN/TS 15401:2010, Determination of bulk density, modified). The content of carbonates (inorganic source of carbon and CO₂) is determined as a mass difference between LOI at 550°C and LOI at 900°C due to the thermal decomposition of magnesium- and calcium carbonates, predominately caused by the latter.

Measurements of the specific surface area of granules by gas adsorption are performed using a Micromeritics ASAP 2020 analyzer according to ISO 9277:2010. The adsorptive gas was nitrogen, and the specific surface area (SSA) was calculated using the Brunauer-Emmett-Teller method (BET). A simple method for determining the ignition temperature in the granules layer was provided by a non-standardized method in an open LF with flues and with the isothermal temperature program.

To determine the chemical properties of granules the annual composite granular sample was milled to <1 mm using the Retsch SK1 hammer mill and, when necessary, down to <0.5 mm in the Retsch ZM 200 mill. Microwave-assisted digestion procedure for preparation of the PF to determine the PTMs content was done with aqua regia, while microwave-assisted digestion of granules as a SRF was done with a more invasive acid mixture of concentrated hydrofluoric (HF), nitric (HNO₃) and hydrochloric acid (HCl), and the results obtained are shown in separate tables.

The majority of the methods used for wastewater and granules characterization are accredited according to the Technical Standard SIST EN ISO/IEC 17025:2017, General requirements for the competence of testing and calibration laboratories and performed by authorized contractors.

Simultaneous thermal analysis (STA) with thermogravimetric analysis (TGA), derivative thermogravimetric analysis (DTG), and differential thermal analysis (DTA) of granules and mass spectroscopy of released gases are performed in an oxidative and in an inert atmosphere. STA apparatus (Netzsch's products were used) allowed the simultaneous acquisition of mass loss (TGA) and thermal effects (DTA) during thermal analysis. The DGT curve is obtained by calculating the derivative of the TG curve. The DTA measurement gives combustion curve or thermal change curve as a function of thermal load and information on the heat balance for each stage of thermal decomposition of granules. The DTG analysis enables a "fingerprint" of the thermal behavior and a thermal decomposition profile curve ($\Delta m/\Delta t$). Data manipulation and transformation are performed by Netzsch Proteus 6.1.0 software.

Fingerprint of thermal decomposition of granules for determination of their behavior at thermal load is carried out on the two representative annual samples (**Table 13**): (i) for the year 2010 and (ii) for the year 2012. In 2011 the annual sample 2010 (labeled as 2010/2011) was characterized with the TGA/DTG/DTA

2010	2011	2012	2013	2014	2015
165	141	203	165	145	167
45	60	46	45	42	45
		12			
		Jan–Oct			no s.
2016	2017	2018	2019	2020	
176	154	194	194	194	
40	40	37	37	37	
		12		$)(\simeq$	
Jan–Oct	no s.	Jan - Dec	no	o s.	7 []
	165 45 2016 176 40 Jan-Oct	165 141 45 60 2016 2017 176 154 40 40 Jan-Oct no s.	165 141 203 45 60 46 12 Jan-Oct 2016 2017 2018 176 154 194 40 40 37 Jan-Oct 12 Jan-Oct 12	165 141 203 165 45 60 46 45 Jan-Oct 2016 2017 2018 2019 176 154 194 194 40 40 37 37 12 12 12 Jan-Oct 194 194 40 40 37 37 12 12 12 12 Jan-Oct no s. Jan - Dec no	165 141 203 165 145 45 60 46 45 42 12 12 12 12 2016 2017 2018 2019 2020 176 154 194 194 194 40 40 37 37 37 12 12 12 12 12 Jan-Oct no s. Jan - Dec no s. Ioo s.

Table 13.

Sampling procedure for granules.

analysis in both atmospheres: (i) the inert atmosphere of Ar (purity 99.999%) and in (ii) the oxidizing atmosphere (80% v/v of Ar and 20% v/v of O_2 , purity 99.999%). The findings are presented as a short review of the study in Ref. [23]. In 2012 TGA analysis for the annual sample 2012 is performed in both atmospheres (labeled as 2012/2012), and additional the TGA analysis in both atmospheres for the sample 2010 (labeled as 2010/2012) for the purpose of comparison was repeated. In 2016 the TGA analysis (inert atmosphere) was repeated on the sample 2012 (labeled as 2012/2016), and again in 2018 on both samples: (i) the sample 2010 (labeled as 2010/2018), and (b) the sample 2012 (labeled as 2012/2018). Both representative samples, 2010 and 2012, are still properly stored (closed packaging, in a dark and cool room). Each time, 100 mg of finelly ground granules were weighed into the TG/DTA crucible (0.3 mL, Al₂O₃) and exposed to heating from T_{room} to 1500°C at the heating rate of 10 K min⁻¹. Protective and purge gas flows were set to 30 and 50 mL min⁻¹, respectively.

In the year 2017, using a method described by CEN/TS 343, CEN/TR 15716:2008, Determination of combustion behavior (Combustion behavior), the proximate analysis was performed on the representative annual sample 2012 (labeled as 2012/2017) with the TGA technique in the combination with: (i) isothermal and non-isothermal temperature program in the temperature range from room temperature (T_{room}) to 900°C in the inert atmosphere, and (ii) the isothermal temperature program in the oxidative atmosphere at 900°C. The proximate analysis was performed in Netzsch STA 449 F3 Jupiter. 50.0 ± 0.5 mg of the milled granules were used to provide the analysis. The sample was weighted into the TG/DTA crucible $(0.3 \text{ mL}, \text{Al}_2\text{O}_3)$. The contents of moisture, volatile matter (VM), fixed carbon (C_{fix}), and ash were determined with this single analysis of the granules consisting of several stages. In the first stage, moisture is determined by sample heating to 110° C with 20 K min⁻¹, keeping the temperature constant for 15 min in an inert Ar atmosphere (purity 99.999%). VM is determined by consecutive heating to 900°C at 20 K min⁻¹, followed by an isothermal hold for 15 min. In the last stage, the purge gas is changed to the oxidizing atmosphere (80% v/v of Ar and 20% v/v of O₂, purity 99.999%), and the temperature is kept constant at 900°C for 120 min. The mass loss in this stage is attributed to C_{fix} , and the residual mass is ascribed as ash.

The year 2012 is chosen also as the reference year for further investigations of representative annual samples of CWWTPL and comparisons of results obtained in future research.

2.2.3 Characterization of solid residues after thermally treated granules

Two types of techniques for solid residue preparation were used: (i) pyrogenic residue, prepared with TGA technique using inert atmosphere (pyrolysis, Ar, 99.999 vol%)—2000 mg of granules were isothermally heated for 60 min at 450°C, in TG crucible 3.4 mL, Al₂O₃; the procedure was repeated until enough amount of sample has been achieved, and (ii) simulation of four type of bottom ash - the ignition (incineration) of granules in the laboratory heating furnace (LF) at 450°C (240 min), 550°C (180 min), 700°C (120 min) and 900°C (60 min). In the resulting residues were determined the content of nutrients (TOC, N, P, K, and Mg), the proportion of volatile part of nutrients with the extraction method in accordance with the TS CEN/TC 223, EN 13652:2002, Extraction of water-soluble nutrients.

3. Results and discussion

3.1 Sewage sludge treatment at the CWWTPL

Because of the mixed sewer system, the amount of treated wastewater over a 10year period varies between 1.5 million and 4.045 million m^3 per month and 32.6 million m^3 in the year 2010 to 24.6 million m^3 in 2020. The removed COD varies between 550 t of O₂ to 1770 t of O₂ per month and is lower at the higher quantity of inflow in the period of wet weather.

The average daily amount of excess sludge over a 10-year period is about 17.5 t_{DM} or 51 g PE⁻¹_{COD} (18.6 kg PE⁻¹_{COD} year⁻¹). The produced amount of excess sludge is lower than that reported in the literature (20–25 kg of sludge per one PE year⁻¹) [5]. Due to the fluctuations of the raw municipal wastewater inflow and related removed COD (**Figure 1**), the amount of generated granules, and also their useful matter content delivered to the stakeholder, varied accordingly (**Figure 2**). On average, the daily amount of granules production over a 10-year period is 10.6 t_{DM} or 31 g PE⁻¹_{COD} (11.3 kg PE⁻¹_{COD} year⁻¹). Over the year, these values fluctuate more markedly due to the influence of wastewater temperature on the properties of activated sludge and consequently on the final quantity and quality of granules.

Dynamics at CWWTPL is very important for the granules stakeholder to be able to make a risk assessment and adjust his procedures to the quantities and energy



Figure 1. *Dynamics of the amount of treated wastewater and COD removal rate.*



Figure 2.

Dynamics of granules production in their net calorific value (NCV) for the consecutive months in the 10 years time period.

content of granules (**Figure 2**). The problem for the sustainable use of granules in agriculture is the seasonal demand for fertilizer, while the granules are generated over the whole year with the highest production rate in the summer [20]. On average, 6.380 t_{DM} of excess sludge is produced annually (**Figure 3a**) with content of organic matter of 73.0% m/m_{DM}. The anaerobic stabilization reduces the amount of sludge for 39% m/m_{DM}, yielding about 3880 t_{DM} to be transformed into granules having average organic matter content of 67.4% m/m_{DM}. By taking over the granules, the stakeholder gained an average of 55,300 GJ of energy per year in the ten years period (**Figure 3b**).

Biogas production in digestor contributes to a double economic benefit. The amount of sludge is reduced and fuel is obtained for site heat supply (heating the digester and drying the cake). Biogas production has its seasonal fingerprint as well. Due to summer conditions at the biological stage of wastewater treatment, the biogas production (**Figure 4a**) and the granules NCV (**Figure 4b**) are lowest. On average, 17.2 L of biogas per one PE_{COD} was produced at CWWTPL over the 10 years period.



Figure 3.

Dynamics of 10 years period: (a) excess sludge production and an organic load of inlet wastewater and of excess sludge, and (b) annual dynamics of granules production, their organic matter content, and calorific value.



Figure 4. Seasonal dynamics over the 10 years period: (a) biogas production and (b) NCV_{ar} (as received) of granules.

3.2 Granules characterization

3.2.1 Morphologic properties

Table 14 presents data for the morphological characteristics of annual representative granules samples. Granules are a dry, homogeneous non-hazardous hygienized fine-grained waste with a grain size distribution of 2–4 mm (**Figure 5a**). No foreign solid particles are observed with the eye. Granules do not contain macroscopic impurities or solid particles of glass, plastic, and metals exceeding 2 mm in diameter. Also, no other mineral particles exceeding 5 mm in diameter are present. Granules' response to mechanical stress expressed as mechanical durability is 95.6%. Mechanical durability is a measure of the resistance of compressed fuels toward shocks and/or abrasion during handling and transportation.

Seasonal fluctuations in bulk density in the period from 2017 to 2020 are not significant, the bulk density of granules is highest in early spring. There is also no significant fluctuation in bulk density at the annual level. Only the value for the annual sample 2010 differs significantly (**Table 14**), and that is also determined for other quality parameters of that sample, which will be presented below. The volume of 1m³ granules for the period 2017–2020 has a mass of about 640 kg (**Figure 5b**).

Granules are slightly basic. Their electrical conductivity is 2.38 mS cm⁻¹, which means that they contain a small proportion of salts. The granules are compacted, difficult to break, which is evident in their low value for the specific surface area (BET) from 0.9 m² g⁻¹ to 1.4 m² g⁻¹ (**Table 14**).

Parameter	Unit	2010	2011	2012	2014	2016	2018	
Electroconductivity _{25°C}	${ m mS~cm^{-1}}$	No a.	3.81	2.38	No a.	2.48	2.71	
Specific surface area, BET	$\mathrm{m}^2\mathrm{g}^{-1}$		0.954	0.934	1.406	No) a.	
pH	_	No a.	7.1	7.9	No a.	8.0	7.3	
Bulk density	${\rm kg}~{\rm m}^{-3}$	704	656	641	683	646	628	
Compacted bulk density		No a.	683	No) a.	702	809	

Table 14.

Basic morphologic and physical properties of granules.



3.2.2 Basic thermal properties of granules: determination with conventional laboratory methods

Organic matter is the main component of granules, which releases energy during combustion, rendering steam and CO₂. In general, sewage sludge is semi-biomass, its main constituents being water, organic matter, which is a mixture of residual decomposition products of excess aerobic biomass and anaerobic decomposition products, which are mostly denatured proteins (due to cationic polymer addition, dehydration, and drying of the digestate), carbohydrates, lipids, fatty acids and inorganic substances (salts and complex natural minerals) are also present. Granules behavior under thermal load with conventional laboratory methods in the oven dryer, LF, or combustion chamber (determination of NCV) is an indicator of their proximate properties: moisture, volatile and organic matter (VM, OM), carbonates, and ash content (**Table 15**). The organic fraction or biomass content that can burn in the presence of oxygen at 450°C is 66.9% m/m_{DM}, the further fraction that can burn at 550°C is 0.7% m/m_{DM} higher. The share of VM is 53.9% m/m_{DM}, which means that a high volume of gaseous products is formed during incineration (**Table 15**).

Parameter	Unit	2010	2011	2012	2013	2014	2016	2018
DM, 103°C ¹	% m/m	No a.	No a.	91.3	90.8	91.3	90.5	89.9
DM, 105°C ²		91.3	90.7	91.5	90.7	91.5	91.0	90.4
OM, 450°C ¹	% m/m _{DM}	No a.	62.7	66.9	65.7	65.7	65.6	66.6
LOI, 550°C ²		61.1	67.6	67.6	66.3	67.4	66.3	68.6
Ash, 900°C, modif. ³		33.2	31.8	28.5	29.6	29.4	29.8	28.1
VM, 900°C ²		No a.	No a.	53.9	54.0	53.3	53.0	No a.
T _{ignition}	°C	540	560			No a.		
Heat content	GJ/y	46.58	51.67	55.61	54.50	54.13	57.83	59.27
NCV	MJ/kg _{DM}	12.91	13.68	14.90	13.31	14.43	14.16	14.48

¹*Temperature prescribed for biodegradable waste or biomass.*

²*Temperature prescribed for treated waste into solid recovered fuel.*

³Prescribed temperature is 550°C, but the determination of the residue at 900°C also includes the thermal decomposition of carbonates.

Table 15.Basic thermal properties of granules.

The granules ignition point is determined by a non-standardized method and apparatus. It means the temperature at which, when heated in an oxidizing atmosphere, the granules spontaneously ignite and immediately continue to burn. The granules temperature of the ignition ($T_{ignition}$) is at 550°C on average (**Table 15**).

Tables 14 and **15** provide the results, which are taken from expert assessments of granules, which were published in the period from 2010 to 2018 in expert reports prepared by an authorized waste assessment contractor. Only the results for the year 2010 differ significantly due to extensive floods on Ljubljana city area and the inflow of background water to the CWWTPL.

On average, the granules' dry matter content is at least 90% w/w. Fluctuations in the results for dry matter content are due to the drier operating conditions, the choice of analytical method, and determination temperature. It is characteristic of the granules that they lose most of their mass even at a low temperature of the thermal load, namely at a temperature of 450°C. With further heating, the weight loss is smaller.

The loss on ignition is often used as an estimate for the content of organic matter in the sample. Inorganic decomposition products (e.g. H_2O , CO_2 , SO_2) are released and some inorganic substances are volatile under the reaction conditions. Determination of LOI at 550°C and 900°C allows us to determine the proportion of organic matter (at 550°C) as well as the proportion of CO_2 (at 900°C) resulting from the thermal decomposition of naturally occurring carbonates that cause CO_2 emissions for which it is not necessary to purchase emission coupons (6a). In 2010, the contamination of raw wastewater with inorganic impurities led to an increase in the ash content in the granules (**Table 15**) and especially an increase in the carbonate content, which continued in 2011 (**Table 15**, **Figure 6a**). **Figure 6b** also shows the fluctuation of the calorific value on an annual basis, which is not always logically related to the fluctuation of the LOI and carbonates.

Granules production at CWWTPL is not a continuous process. Due to the specific layout of facilities and machine capacity, this process is performed in batch mode. The quality of representative samples of individual batch series for the year 2020 (**Table 13**) fluctuates markedly seasonally (**Figure 7**). The contents of the biomass (LOI at 450°C) are characterized by the lowest content over the summer. At that time, the mineral content, determined as the difference between LOI at 550°C and LOI at 450°C, is also the lowest (**Figure 7**). The latter mass loss is probably due to the thermal decomposition of MgCO₃ or minerals containing magnesium, phosphorus, and carbonates.



The summer period is characterized by higher wastewater temperatures, less precipitation, lower concentration of activated sludge because of more intensive

Figure 6.

(a) Dynamics of LOI of granules at 550°C and carbonates content, and b) comparison of annual dynamics of LOI of granules at 550°C and NCV.



removal of excess sludge, and consequently higher granules production, which is consequently reflected also in their final quality.

At CWWTPL the biogas production is also the lowest during sommer and early autumn (**Figure 4a**), the same is true for NCV_{ar} (**Figure 4b**).

3.2.3 Basic thermal properties of granules: determination with the advanced techniques

According to TS Combustion behavior solid fuel combustion consists of three relatively distinct but overlapping phases: (i) heating phase (time to thermal decomposition), (ii) pyrolysis, and gas phase combustion (time of gas-phase burning), and (iii) char combustion (time to char burnout). The STA is the most used technique in thermal analysis to give us sufficient information about the thermal behavior of solid fuel.

The results of two techniques of the STA method are provided on granules: (i) proximate analysis and (ii) fingerprint of thermal decomposition of granules in the oxidative and inert atmosphere provided by the non-isothermal temperature program. The proximate analysis of solid granular fuel executed with the TGA technique is a standard procedure for the determination of behavior regarding volatile release and combustion. This technique is comparable with the method as specified in TS EN 15402:2011 for volatile matter (VM) determination. The proximate analysis was performed according to the prescribed procedure (TS Combustion behavior) on the annual sample 2012/2017.

The obtained results of the performed technique (**Figure 8**), moisture (8.12% m/m), VM (51.9% m/m_{DM}), and ash (30.8% m/m_{DM}), are comparable to those obtained with the conventional methods (**Figure 6**, **Table 15**). The proximate analysis performed with a TGA gives us an additional parameter of solid fuel properties, and that is a combustible carbon content or fixed carbon ($C_{\text{fix}} = 11.8\%$ m/m_{DM}). When switching an inert atmosphere of thermal loading at 900°C to an oxidizing atmosphere, further mass loss can be attributed to the carbon remaining in the sample as elementary carbon, which was bound in substances that were depolymerized, and thermochemically converted to carbon. 88.2% m/m_{DM} of granules carbon content is bound in substances which, in an inert atmosphere when heated to 900°C, are volatile or are thermo-chemically converted into volatile gaseous compounds. The content of TOC for the annual sample 2012 is 38.4% m/m_{DM} (**Table 15**), and only 30.7% m/m_{DM} of carbon as a part of TOC is presented as a non-volatile matter and is burnout in the third phase of combustion.

The proximate analysis was performed in six stages (**Table 16**, **Figure 8**). The moisture was determined in the first stage, when the sample was heated to 110°C with



Figure 8.

The proximate analysis of granules (the annual sample 2012/2017) with TGA/DTG/DTA technique: C_{fix}) the fingerprint of granules decomposition in an inert atmosphere combined with an oxidative atmosphere in a sequential mode, and time program) determination of the stages of granules mass loss.

20 K min⁻¹, keeping the temperature constant for 15 min in an inert Ar atmosphere. At the time of 4.8 min, the signal peak for DTG was -1.95% min⁻¹ and the heat balance was endothermic (**Figure 8**, C_{fix}). VM was determined by consecutive heating to 900° C at 20 K min⁻¹. This part of proximate analysis consists of three stages: (i) second stage with two signal peaks for DTG (at 27.0 min the first signal peak is -4.34% min⁻¹ and at 30.8 min the second signal peak for DTG is -3.98% min⁻¹), (ii) third stage with one signal peak for DTG at 51.8 min (-1.01% min⁻¹), and (iii) stage four followed by the isothermal hold at 900°C in an inert atmosphere for 15 min. In the fifth stage, the purge gas was changed to the oxidizing atmosphere (80% v/v of Ar and 20% v/v of O_2), and the temperature was kept constant at 900°C for 120 min. In this stage the carbonized sample was burnout (C_{fix}), the signal peak for DTG is -1.01 at 80 min, and the heat balance is exothermic. In the sixth stage, only insignificant mass change is recorded. The residual mass is ascribed as high-temperature ash, and the cumulative mass loss is 71.8% m/m (**Figure 8**, Time program). The mass loss followed in 8 steps of the time program is shown in **Figure 8b** and **Table 16**.

The TGA/DTG/DTA granules analysis gives us a useful picture and data on their behavior, with which we can predict or estimate the course of incineration and

Time program, step	Time period, minute	Stage	Temperature at the end of time step, °C	Cumulative mass loss, % m/m
1	0.0–18.0	1	98.5	-8.12
2	18.0–39.0	2	515.1	-50.7
3	39.0–53.4	3	801.8	-57.8
4	53.4–58.4		902.1	-59.0
5	58.4–74.0	4	900.2	-60.0
6	74.0-88.7	5	900.0	-71.7
7	88.7–133.3	6		-71.8
8	133.3–193.3			-71.8

Table 16.

Stages of proximate analysis of the sample 2012/2017—overview of the time program and cumulative mass loss (*Figure 8*, time program).

pyrolysis, the formation of emissions and residues on the full scale [23]. Using the TGA/DTG/DTA/EGA techniques, we can estimate the temperature range when substances characteristic of the decomposition of biological macromolecules take place, formation of the main decomposition gaseous products H₂O and CO₂, and determination of the temperature range when biologically inert substances react to thermal load. The latter allows us to determine the temperature range of CO_2 release resulting from naturally occurring carbonates that cause CO2 emissions for which no emission coupons need be purchased. Reference [23] conducted a STA study of the representative annual sample 2010/2011 in an inert (pyrolysis) and oxidative (incineration) atmosphere. The study shows that in a comparable temperature range from room temperature to 1000°C the decomposition in an oxidative atmosphere takes place in at least in two stages, while in an inert atmosphere it takes place in three stages. Due to the continuous decrease in mass by isothermal temperature program in an inert atmosphere, the STA was prolonged to 1200°C. In the last temperature range of the inert atmosphere, the residue mass was further decreased by 4.5% m/m, which means, that the decomposition in an inert atmosphere takes place in four stages. The study [23] reveals that the first stage of granules decomposition in the temperature range from room temperature to 185°C takes place equally regardless of the atmosphere, with the evaporation of H_2O . The mass loss in this temperature profile is 6.1% m/m, while the result for the mass loss for the annual sample 2010, determined with the conventional oven-dry method (non-isothermal temperature profile), is 8.7% m/ m (**Table 15**). In both atmospheres, the granules' thermal behavior in the temperature range from 185 to 420°C is very dynamic. The highest mass losses are observed: (i) in an inert atmosphere 32.5% m/m, the signal peak of DTG is -1.97% min⁻¹ at 324°C, and (ii) in an oxidative atmosphere 30.8% m/m, the signal peak of DTG is -2.14% min⁻¹ at 252°C. This stage in the thermal behavior of granules in both atmospheres presents the fingerprint for that type of material. It is a result of the decomposition of a major part of the granules' biomass. A comparison of the TGA curves profiles in both atmospheres shows that the TGA curves behave similarly to the temperature 486°C. At that temperature, the residue mass was 56.0% in the oxidative atmosphere and 56.4% by mass in the inert atmosphere. The further course of the TG curves was different.

Slightly different results were obtained in repeated analysis on the newer aparatous Netzsch STA 449 F3 Jupiter in the year 2012. For the sample 2010/2012 (**Figure 9a** and **b**) TGA curves behave similarly to the temperature of 346°C, whereby the residue mass was 70.1% m/m in the oxidative atmosphere and 71.2% m/m in the inert atmosphere. To the temperature of 486°C both TGA curves had a similar slope, with the residue mass being 58.0% m/m in the oxidative atmosphere and 55.2% m/m in the inert atmosphere. After that temperature TGA curves begin to behave significantly different.

This means that the presence of oxygen influences mass loss to differ significantly only above 486°C, while the dynamics of mass loss (DTG) and changes in heat balance (DTA) in different atmospheres begin to differ at temperature 185°C, immediately after the loss of free and bound water [23] (**Figure 9**). The determined temperature limit is close to $T_{ignition}$ of granules, which is 550°C (**Table 15**). The mass loss for the annual sample 2010 due to decomposition of carbonates determined with the combination of the two conventional methods in LF (nonisothermal temperature profile at 550°C and at 900°C) is 5.3% m/m_{DM} (**Figure 6a**). Carbonates content evaluated on the basis of the fingerprint for thermal behavior (isothermal temperature profile) for the sample 2010/2011 is 6.5% m/m, and for the sample 2010/2012 9.2% m/m (**Figure 9a**, pyrolysis mass loss from 550 to 900°C). Similar behavior was confirmed in the sample 2012/2012 analysis (**Figure 9c** and **d**), which had at 346°C the residue mass of 67.1% m/m in the oxidative atmosphere



Figure 9.

Comparison of the fingerprint of thermal decomposition in the oxidative and the inert atmosphere for (a) mass loss for each stage for sample 2010/2012, (b) thermogram for sample 2010/2012, (c) mass loss for each stage for sample 2012/2012, and d) thermogram for sample 2012/2012.

and 66.1% m/m in the inert atmosphere, and at 486°C the residue mass was 54.8% in the oxidative atmosphere and 49.1% m/m in the inert atmosphere.

In order to determine the impact on the stability of annual representative samples due to longer storage and in order to determine the repeatability of the TGA/ DTA/DTG techniques, repeated thermogravimetric analysis in an inert atmosphere were performed on annual samples 2010 and 2012 (pyrolysis) (Figure 10). Compared to the analysis in the year 2011 [23] when apparatus Netzsch STA 409 was used with the temperature range from room temperature to 1200°C, aparatous Netzsch STA 449 F3 Jupiter was used, which allows the temperature range from room temperature to 1500°C, and the heating rate was the same. Repeated analysis were performed in the years (Figure 10): (i) 2012 (sample 2010/2012 and sample 2012/2012), (ii) 2016 (2012/2016), and 2018 (2010/2018 and 2012/2018). The partial mass loss of samples at individual characteristic temperatures is repeated in the same way in all samples (Figure 11a), with only a slight upward trend at 400°C. The same is true for the peaks of the DTG signals (**Figure 11b**). There were no significant biological-chemical transformations or a significant change observed in the quality of granules after the storage period. Some substances became slightly more thermally stable, suggesting a smaller temperature lag for the DTG signal peaks toward higher temperatures (Table 17).

Pyrolysis is an anaerobic thermo-chemical decomposition process that enables the generation of various useful groups of substances from the treated sludge, which can then be utilized separately in various energy and material recovery



Figure 10.

Fingerprint of thermal decomposition in an inert atmosphere for annual samples 2010 and 2012 - analyzed in 2011, 2012, 2016, and 2018.



Figure 11.

Comparison of the fingerprint of thermal decomposition in the inert atmosphere (5 stages of mass loss) for the annual samples 2010 and 2012 (analyzed in the years 2011, 2012, 2016 in 2018) at the temperature of the DTG_{peak} for the sample 2012/2016 (**Figure 10**, **Table 17**): (a) Δ mass loss (% m/m) and (b) DTG (% min⁻¹).

Stage of thermal conversion, °C	1st Troom—190	2nd 90 191–550		3rd 551–900	4th 901–1230	5th 1231–1500
Sample/year of analysis			T _{pea}	_{uk} (DTG), °(C	
2010/2011	121	269	324	758	1114	_
2010/2012	120	277	329	759	1099	1383
2010/2018	121	282	337	768	1116	1393
2012/2012	123	279	332	753	1093	1345
2012/2016	123	278	338	757	1080	1360
2012/2018	127	279	339	763	1094	1366

Table 17.

Comparison of $T_{peak}(DTG)$ of the samples 2010 and 2012 analyzed in 2011 (only sample 2010), 2012, 2016 (only sample 2012), and 2018.

processes. Due to carbonization, part of the carbon remains in the residue (PCM) as bound carbon, so pyrolysis is useful as a technology that reduces the carbon footprint as opposed to the incineration procedure that generates greenhouse gases. The use of PCM in agriculture actually means carbon sequestration and thus a double bonus for the environment.

Further pyrolytic experiments were performed on the sample 2012 [13, 24]. Under pyrolytic conditions two main processes were taken place—volatilization and carbonization. Despite the high temperature (up to 1.500°C) that was reached in the apparatus Netzsch STA 449 F3 Jupiter (Figure 9d and 10) the sample during pyrolysis remained solid. Melting of ashes occurs during granules incineration above temperature 1100°C. The pyrolytic products are [24]: (i) solid residue (pyrogenic material), (ii) aqueous light oily fraction (water condensate), (iii) pyrolysis oil as a heavy fraction (bio-oil), and (iv) non-condensable gas (syngas). The latter product was continuously withdrawn from the reactor and was co-fired (potential recovery procedure R 1). The semi-pilot scale experiment yielded [24]: 15.1% m/m syngas, 17.8% m/m water condensate, 16.8% m/m bio-oil and 50.3% m/m of PCM. Most of the water condensate originating from moisture, chemically or crystalline bound water, and water produced during thermal decomposition of the sludge was collected in the light oily fraction and contains a high concentration of condensed water-soluble substances. The yield of the most valuable product bio-oil was low due to the low content of macromolecules and their poor quality (oxidized and degraded organic matter). The bio-oil must be further refined and completely free of water to make it useful as a fuel. The produced PCM contained 32.4% of carbon by weight and had a calorific value of 11.1 MJ kg⁻¹.

3.2.4 Characterization of granules according to energy and material recovery operations

Despite anaerobic stabilization and biogas production (**Figure 4a**), there is still enough organic matter left in the granules that can be used for WtE process (**Figure 6**, **Tables 15** and **18**). **Table 18** provides the chemical properties of representative annual samples for the period from 2010 to 2018. In addition to energy recovery, the WtE processes enable also the material recovery of many inorganic compounds or elements present in the granules. They also contain some interesting elements that remain in the ash. These are primarily elements of the lithosphere (silicon, calcium, sodium, magnesium, aluminum, potassium, and iron, all in the form of oxides). They are in addition to carbon, nitrogen, hydrogen, sulfur and phosphorus the major elements in treated sludge (**Table 18**). Some other elements presented in **Table 18** are also on the list of critical raw materials [25, 26].

Untreated ash may be used in the construction industry. All procedures of material recovery must be used sensibly because during combustion granules substances are thermo-chemically converted, most of the elements are converted into oxides that are insoluble in water and their bioavailability is highly questionable.

Recovery procedures regarding ash utilization on the full scale, which purpose is to obtain only a certain element, e.g. extraction of phosphorus or other critical raw materials, are economically still unprofitable. WtE processes have economic benefits, but the facilities are also the source of emission of produced volatile compounds and particles into the air (**Tables 2–4**). **Table 18** presents the parameters, which are arranged in different groups: (i) elements relevant to the economic benefits, but are also the source of emission into the air (C, H, N, and S), (ii) halogens, which can cause corrosion of mechanical equipment (F and Cl), (iii) the major elements, which are important for material recovery of the ash (P), and (iv) volatile metals and their compounds, that are harmful to human health (Cd, Hg). Based on the given values for all the listed elements (**Table 18**), it is not possible to accurately

Parameter	Unit	2010 [*]	2011*	2012	2013	2014	2016	2018
Econor	nic benefits, source o C	f green C0 O ₂ /emissio	D ₂ of biolo on into the	ogical origin e atmosphe	n, and nati ere [15]	ural source	of inorga	inic
TC/C_{tot}	% m/m _{DM}	No a.	No a.	40.4	41.2	39.5	43.0	42.6
TOC/C _{org}		29.04	33.6	38.4	37.6	39.5	33.1	35.7
Н		4.57	5.58	4.38	4.21	5.08	No) a.
Ν	$\% m/m_{\rm DM} \rm NO_2$	16.1	17.9	20.2	19.4	18.3	18.9	19.7
S	% m/m _{DM} SO ₂	1.52	1.78	2.30	1.86	2.52	2.12	1.60
	$1 \Gamma (\frown) ($	C	Corosion p	otential		$\left(\right)$	$(\bigtriangleup$	
F	% m/m _{DM} HF	0.011	0.012	0.013	0.012	0.015	No	o a.
Cl	% m/m _{DM} HCl	0.011	0.066	0.088	0.098	0.113	0.123	0.076
	Potential resourc	e recovery	y of inorga	anic compo	unds/ash	componen	ts	
TIC	% m/m _{DM}	No a.	No a.	2.0	3.6	< 0.1	9.9	6.9
Р	_	1.07	2.18	2.22*	1.92	1.77	1.62*	1.45*
Fe	_	1.2	1.1	0.92	1.1	1.2	No	o a.
Al		1.0	0.97	0.88	0.78	0.88	No	o a.
SiO ₂	mg k ${ m g_{DM}}^{-1}$ Si	510	1700	1510	no a.	4700	No) a.
$\mathrm{Si}_{\mathrm{tot}}$	% m/m _{DM}	No a.	No a.	3.3	5.6	6.1	9.4	7.6
Ca	_	5.2	5.1	4.6*	4.8	4.7	3.65*	6.4*
Mg	_	1.0	1.1	0.96*	0.42		No a.	
Ti	_	No a.	No a.	0.14	0.15			
K _{tot}	_	0.22	0.23	0.30*	0.36	0.39	0.28*	0.32*
Na		No a.	No a.	0.12	0.14		No a.	
Environm	ental impact/volatile	metals an	d their co [8, 15	mpounds (].	VMs)/em	ission into	the atmos	sphere
Sb	$mg \ k{g_{\rm DM}}^{-1}$	< 20	< 20	4.3	3.7	2.6	3.5**	2.7
As	_	< 20	< 20	3.5	3.9	3.8	3.6**	3.3
Co		9.0	9.6	17	8.4	6.7	9.7**	6.8
Cu		310	300	350	410	540	230*	350
Mn		270	280	310	270	300	No a.	250
Cd	GOV	1.0	1.1	1.2	1.2	1.1	1.1**	0.80
Cr	_	84	100	120	110	110	130**	100
Hg	_	2.6	2.7	1.8	1.7	2.3	1.7**	1.14
Ni	_	54	60	86	82	80	73**	75
Pb	_	84	85	93	80	78	85**	66
V	_	<20	<20	17	18	19	No a.	20
Tl	_	<10	<10	< 0.5	< 0.5	< 0.5		0.13
\sum VMs		<885	<838	<1000	<985	<1264	_	874
	Scan of additional p	arameters	with ecor	nomic or en	ivironmen	tal signific	ance	
Ba	mg kg _{DM} ⁻¹	260	260	320	260	260	No) a.
Be		No a.	< 0.50	< 0.5	< 0.5	< 0.5		
Br		<50	30	<21	<37	62		

Parameter	Unit	2010*	2011 [*]	2012	2013	2014	2016	2018	
Se		<20	<20	3.4	3.1	4.4			
Zn		920	970	1000*	930	920	720*	790 [*]	
*Digestion for subsequent determination of aqua regia soluble portion of elements.									

** Average of ten representative monthly samples (Jan-Oct.).

Table 18.

Basic physicochemical properties of granules, interesting for WtE processes.

predict whether the WtE process will exceed the permitted emissions into the environment. The latter will certainly occur if the flue gas cleaning system is inadequate. For the sustainable energy use of granules, in addition to reducing their amount and economic benefits offered by this recovery procedure, it is very important that advanced flue gas cleaning and volatile metal removal techniques prevent the polluting substances their circulation in nature as much as possible. The granules produced at CWWTPL are a sustainable material for SRF is revealed by reference [27]. The latter is a case study of the establishment of an integral quality system for wastewater treatment and sludge management at CWWTPL according to TS CEN/TS 343, EN 15358:2011, Quality management system, Particular requirements for their application to the production of SRFs. For the period from 2012 to 2020, a classification of the granules defines their conformity as an SRF with Class code NCV 3–4; Cl 1; Hg 3. In Ref. [27] is also pointed out that mercury is one of the most problematic volatile metals regarding the quality of cleaned flue gases. It is transmitted to the environment through flue gas emissions [28]. By effectively cleaning the flue gases generated by WtE processes, we achieve the interruption of the circulation of substances that cause emissions into the air.

3.2.5 Granules and their solid residues after thermally loading evaluation as a fertilizer

In the EU the use of sewage sludge in agriculture is regulated by the framework directive SSD [6], which is summarized differently in each EU Member State. The limit values for soil and sewage sludge quality prescribed by SSD are presented in **Table 5**. The set of parameters for which the SSD prescribes limit values is short. It also does not prescribe a declaration for the content of C_{org}, primary nutrients, secondary nutrients, macronutrients, and micronutrients as does the Fertilizing Resolution (FR) (**Tables 9**, **10** and **12**). In general, the existing European market for fertilizers, which are produced from treated waste, is non-uniform. The latter will be addressed by (FR) [21], which will take full effect from 16 July 2022 (**Tables 7–12**). The use of granules in agriculture should be viewed in terms of soil quality (heavy metal content, pH, organic content) and in terms of granules quality. For their application, it is necessary to take into account the seasonal time, the type of plantation, the purpose of the crop usage, and the period of the plant growth.

Metals in the environment are usually in the form of compounds. Soil pH plays an important role in the bioavailability of heavy metals into the plant. If the soil is alkaline, soluble metal ions precipitate into less soluble compounds, e.g. hydroxides, which are less bioavailable and therefore less harmful. Elements in granules can have the function of nutrients if they are water-soluble or if they are bioavailable. This is especially important for phosphorus and potassium.

Table 19 presents the biological properties of representative annual samples for the years 2016 and 2018. Granules are anaerobically stabilized and hygienized waste, which therefore has limited biological properties and, depending on the degree of stabilization, still has the possibility of further self-degradation. In terms

Parameter	Unit	2016	2018
Stability criteria			
(AT ₄)	$mgO_2g^{-1}{}_{DM}$	43	35
Acetic acid	${ m mg}~{ m L}^{-1}$	236	530
Propionic acid	(mass/volume)	57.9	38
Soil improvers and growing media/determinatio	n of plant response		
The effect of granules as a soil improver and growth substrate	on plant germination a	and grow	vth
Plant germination and growth (Chinese cabbage)	% m/m	73 ¹	87 ⁴
Germination rate (Cress)		53 ²	47 ⁵
Green mass (Chinese cabbage)		0 ³	79 ⁶
Determination of the content of unwanted weed seeds and plant substrate and soil improver	propagules in granules	s as a gro	owing
Weed seeds and plant propagules, granules: peat moss 20% m/m	$\rm N^{\circ} \ L^{-1}$	<2	<2
¹ Granules: peat moss 30% m/m. ² Granules: peat moss 32% m/m. ³ The green part of the plant did not develop. ⁴ Granules: peat moss 15% m/m. ⁵ Granules: peat moss 33% m/m. ⁶ Granules: peat moss 15% m/m.			

Table 19.

Biological parameters/stability criteria of CWWTPL granules [19].

of the "stability" parameter, the limit value for short-chain fatty acids for 2018 was slightly exceeded (**Tables 8** and **19**). There is no limit value for parameter AT4 for granules as a digestate. The biological properties of the granules are suitable. By preparing an appropriate substrate, they enable germination and plant growth and do not introduce weeds into the plantation (**Table 19**).

In addition to C_{org}, the granules contain a wide range of other elements, which are declared as either primary nutrients, secondary nutrients, or macro-and microelements. **Table 20** presents the chemical composition of representative annual samples for the period from 2010 to 2018. The values of the elements are expressed in units, as prescribed for the declaration and limit values of the elements or their relevant compounds according to FR [21] (Tables 9–12). Among the polluting substances in the granules, the most critical is mercury, the value of which exceeds the limit values for fertilizers (Tables 9, 10 and 12). Mercury is an environmental pollutant from atmospheric deposition, which enters with precipitations to a municipal treatment plant. The effect of biological removal of mercury from wastewater at CWWTPL is 84.6% on average with standard deviation of \pm 17.0% [20, 27], so municipal wastewater treatment plants play an important role in preventing the circulation of mercury in the environment and protecting human health. The phenomenon of Hg content in Slovenia is historically linked to the operation of a mercury mine in Idrija, where cinnabarite ore mining was supposed to begin in the last decade of the 15th century, and ceased in 1977. It was the secondlargest cinnabarite mine in the world. In the period from 2010 to 2018, a decrease in Hg content in granules produced at CWWTPL is observed (**Tables 18** and **20**). It is likely that the Hg content will continue to decline.

The general finding regarding the possible use of granules as compost or digestate is that these two treated forms of treated sludge are useful primarily as an additive to other processed waste, which then forms a mixture corresponding to the quality declaration and limit values set by FR.

Parameter	Unit	2010	2011	2012	2014	2016	2018
		Declara	tion				
		PN (Tab	le 9)				
C _{tot}	% C	No a.	No a.	36.6	36.1	35.9	38.5
C _{org}	% C	26.51	30.4.	34.8	36.1	30.1	32.3
NH ₄ -N	% N	No) a.	0.63		No a.	
	mg kg $^{-1}$ _{DM} , soluble in water		No a.		2271	2260	2600
NO ₃ -N					No a.	<2.5	16
N _{org}	% N	No a.	No a.	4.8		No a.	
N _{tot}	% N	4.17	4.94	5.57	5.07	5.20	5.49
	$kg N m^{-3}$	26.7	31.7	35.7	34.8	33.6	34.4
Р	% P ₂ O ₅	2.25	4.99	4.62	3.72*	3.36	3.01
К	% K ₂ O	0.244	0.255	0.326	4.30 [*]	3.09	3.44
	S N	ACN (T	able 10)				
Ca	CaO, %	6.69	6.50	5.80	6.02 [*]	4.64	8.10
Mg	MgO, %	1.53	1.64	1.49	1.67*	No a.	
Na	Na ₂ O, %	No a.	No a.	0.147*	0.109*	_	
S	SO ₃ , %	1.72	2.02	2.60	2.88	2.41	1.86
	Ν	IICN (Ta	ble 11)				
Fe	%	1.10	1.00	0.836*	1.10*	No	o a.
Mn	_	0.0248	0.0255	0.0281*	0.0274*	No a.	0.0226*
Cu	_	0.0285	0.0273	0.0281	0.0494*	0.0209	0.0325
Zn	_	0.0846	0.0884	0.0906	0.0842*	0.0655	0.0714
В	${ m mg~kg^{-1}}$			N	o a.		
Со	_	8.3	8.7	15.4*	6.1*	8.8*	6.2*
Мо	_	<50	<50	7.5	8.2*	No	o a.
	Env	ironment	al aspects				
	Polluti	ing substa	nces, PTN	⁄Is			
Cd	mg kg _{DM} ⁻¹	1.0	1.1	1.1	No a.	0.82	0.88
Cr	tltSlU	84	100	93	FU,	90	110
Hg		2.6	2.7	1.6		0.83	1.4
Ni	_	54	60	73		49	72
Pb		84	85	85	_	61	66
	_						

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^{*}*Microwave-assisted digestion with hydrofluoric (HF), nitric (HNO₃), and hydrochloric (HCl) acid mixture for subsequent determination of elements.*

Table 20.

Basic physicochemical properties of granules, relevant for fertilizing.

Solid residues generated at thermally treated sludge are an interesting substitute for phosphorus-potassium fertilizers and, in addition, a good conditioner for acidic, mineral-poor soils. At the laboratory level, the study was carried out regarding the water solubility of nutrients in resulting residues from the sample 2012 after its exposure to inert and oxidative thermal treatment (**Table 21**). PCM is by mass the major pyrolytic product with the organic carbon content of 29.4% m/m_{DM}, BET surface area of 6.82 m² g^{-1,} and bulk density of 820 kg m⁻³. The study on the water solubility of generated PCM shows that pyrolysis offers a much greater opportunity for material recovery from sewage sludge than from incineration ashes. It was found that the water solubility of phosphorus in treated sludge's PCM produced at 450°C is higher compared to the residues from the oxidizing atmosphere; in contrast, the water solubility of K and Mg is lower (**Table 21**). According to ashes properties, it was found that the highest water solubility and the highest BET

Parameter	Unit	Granules 2012	Technique for residues preparation; temperature of thermal load (°C)					
			Pyrolysis, TGA		Incinera	ation, LF		
			450	450	550	700	900	
			PCM 2012	ASH 450	ASH 550	ASH 700	ASH 900	
		Solid fra	ction					
Shape	_			Granules				
	1	Mass loss by p	reparation					
Mass loss	% Volatile $_{\rm DM}$	_	57.3	55.4	68.0	71.5	71.5	
P _{volatile}	% m/m_DM of $P_{\rm total}$		No a.		< 0	.001		
$Mg_{volatile}$	% m/m_DM of Mg_{total}				< 0.02		77.3	
K _{volatile}	% m/m_DM of $K_{\rm total}$			< 0.02	16.4	No a.	16.2	
	Pl	nysicochemica	al properties					
BET area	$m^2 g^{-1}$	0.934	6.82	52.4	31.6	18.2	8.49	
Bulk density	$\mathrm{kg}~\mathrm{m}^{-3}$	641	820	590	360	440	530	
ТОС	% m/m _{DM}	38.4	29.4		N	o a.		
ТС		40.4	29.4					
N _{tot}		6.15	4.12	<u>, </u>				
Р	${ m mg~kg^{-1}}_{ m DM}$	22,253	40,870	69,150	70,517	76,050	83,155	
Mg		9949	18,985	30,270	32,233	34,500	7700	
К		2989	4085	6205	7801	7810	8800	
		Water-soluble	e nutrients					
рН	—	7.8	8.0	6.8	9.1	12.4	12.4	
Р	% m/m _{DM} of P_{total}	5.76	5.37	0.16		< 0.01		
	mg kg $^{-1}_{\rm DM}$	1282	2195	112		<10		
Mg	% m/m _{DM} of Mg _{total}	1.91	1.30	4.66	4.64	<0.	002	
-	${ m mg~kg}^{-1}{ m _{DM}}$	184	246	1411	1496	<	2	
К	% m/m_DM of K _{total}	23.6	3.82	26.14	12.1	9.47	3.20	
-	${ m mg~kg}^{-1}{ m _{DM}}$	706	156	1622	943	740	282	

Table 21.

Fraction characterization of granules and their solid residues after thermal treatment.

surface area has the ash generated at 450°C. At higher temperatures of oxidative thermal treatment, the nutrients are chemically converted to a form that is no longer water-soluble, reducing the possibility of nutrient recovery of the residue (**Table 21**) [29]. The advantage of extracting phosphorus from PCM is also that pyrolysis does not cause sintering or melting, as happens with incineration at temperatures above 1000°C. According to the guidelines for sustainable production of biochar [14], it is potentially useful as a fertilizer for non-agricultural land, for reclamation of degraded land, and for the preparation of artificial soils. It could be used to amend depleted soil to increase fertility, porosity, and water retention. However, the concentration of copper and nickel increases due to the volatile and decomposed fraction of the pellets, while the concentration of mercury decreases [13, 20].

To increase the useful bioavailable components new economically viable technologies need to be developed to liberate the nutrients from sewage sludge ash. Some materials recovered from the UWWTS are still considered waste even if they are of good quality and have a market value [9]. At the moment, European legislation does not favor the recycling of these materials in the economy. The example of the FR, explicitly defining the conditions or processes under which struvite or ashes produced from UWWTS could cease to be a waste and become a product, is a good starting point [9]. Due to the impoverishment of natural sources of phosphorus, it is especially important to find opportunities for recycling it.

4. Conclusions

Municipal wastewater is a product of human life. With the help of natural processes, man has created suitable conditions for its biological treatment. Generated sewage sludge is of biogenic origin, its production is dynamic, and that is reflected in seasonal fluctuations of its quality and quantity. The results of dried sludge granules analysis over a 10-year period of operation at the CWWTPL are presented, as well as the year 2020, which is the starting year for the upcoming new ten-year period. 2020 is also a control year for many forecasts of improving the environment and preventing climate change. The data provide a comprehensive insight into the properties and potentials of treated sludge and allow thoughtful studies for use of this smart material in WtE, critical raw material recovery, organic matter recovery with pyrolysis, and agricultural use of the solid pyrolytic product or as raw granules.

The sewage sludge composition during the period 2010–2020 is similar, only 2010 differs markedly, which was characterized by heavy floods. They did not spare the capital of Slovenia, when a lot of urban area were under the water. Normal changes of anthropogenic or meteorological behavior do not have any special effect on the average annual values of granules. Within a year, these values fluctuate more markedly due to the influence of wastewater temperature on the properties of activated sludge and consequently on the final quality of granules.

Knowledge of the sewage sludge properties enables quick adaptation to the requirements of the revised legislation and, above all, prudent use. The chapter brings together and comments on existing legislation and also legislation in preparation. The data make it possible to compare the quality of granules with other UWWTPs and confirm the feasibility of the drying technology of dehydrated digestate.

For energy recovery, sewage sludge must be used in technically advanced facilities to prevent harmful emissions of substances into the air and prevent the circulation of harmful substances in nature. For the use of sewage sludge in agriculture, it is important to emphasize that this is a material that would make sense to add to the mixture of components for fertilizer and not just as a stand-alone substrate, while controlling the quality of the soil and that the application to the soil is in the form of a dynamic approach. Annual application amount, soil quality control, seasonal application period, and type of crop must be planned. With a dynamic approach, it is necessary to prevent the limit values for polluting substances per hectare of agricultural land from being exceeded.

Pyrolysis is a specific thermochemical decomposition of biomass into a range of useful products without oxygen. Pyrogenic carbonaceous materials are by mass the major pyrolytic product of treated sludge, but it has not yet been included in the EBC feedstock list and is therefore not subject to the EBC guidelines.

The study on the water solubility of generated residues after thermal treatment of granules shows that pyrolysis offers a much greater opportunity for material recovery from sewage sludge. It was found that the water solubility of phosphorus in biochar produced at 450°C is higher compared to the residues from the oxidizing atmosphere; in contrast, the water solubility of K and Mg is lower.

Without good sludge quality control, a sustainable strategy for the use of treated sludge in the CE cannot be achieved. To have confidence in the results of research into the properties of sewage sludge, it is necessary to have a good sampling procedure, targeted end-use, and a list of required parameters. Only high-quality analysis enables confidence in the results and the setting of optimal guidelines for a successful CE. Such an approach to sewage sludge quality control improves the public acceptance of this material in the CE.

The scope of analysis to determine the properties of sewage sludge can be reduced if the quality of sewage sludge is well known and the technology of municipal wastewater treatment and its quality does not change significantly.

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