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Biochar from organic waste: characterization and use

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Preface

This MSc thesis was inspired, initiated, and supported by the SiEUGreen project (EU grant no: 774233) (SiEUGreen, 2020), which pursues the goal to develop a coherent and sustainable future city, by achieving maximum utilization of resources through the concept of circularity, zero waste, and minimum footprint. This will contribute to people's well-being and the global circular economy.

Biochar is a product of pyrolysis obtained from waste biomass (food residues, wood, waste sludge, and other biosolids). It has a potential for environmental impact reduction by carbon sequestration and decrease of greenhouse gases emissions, as well as nutrient recycling. Despite all the benefits, biochar is still considered to be quite debatable because of the high variability in the physical and chemical properties due to heterogeneity of the source material that is used for biochar production. Also, even biochar with the same feedstock varies a lot depending on the pyrolysis conditions.

Depending on the biomass origin it can also contain potentially dangerous compounds, that limit biochar use. However, if treated properly and correct application is chosen, risks associated with biochar application can be eliminated. To remove prejudices regarding biochar and to prepare the basis for future regulations/legislation, biochar should be characterized in detail. A holistic description of physic-chemical characteristics of biochar and its source would allow the prediction of biochar properties, based on similarities in the feedstock.

The main objective of this study is to make a necessary contribution to the biochar characterization and evaluate potential uses by comparing the chemical and physical properties of biochars produced from different feedstocks with different production temperatures.

The biochar samples were produced by Scanship (part of Vow), which works with solutions for wastewater treatment and resource recycling.

Initially, it was planned to also conduct the experiments on the sorption capacity of biochar, however, due to the pyrolytic system upgrade by Scanship as well limiting conditions of COVID-19 pandemic lockdown it was decided to focus only on the characterization of biochar.

Abstract

Growing population, rapid urbanization, economic boost, and improved living standard have increased the demand for energy, water, food, and other resources. At the same time, the increase in population has resulted in a significant increase in organic and inorganic waste generation which caused increasing the risk of pollution and degradation of the natural environment and further limiting resource availability. The safe disposal and utilization of sewage sludge, in particular, become challenging because of the potential environmental risks posed by heavy metals and emerging contaminants found in the sludge. Moreover, it became more obvious that the current practices of the linear economy are not able to meet sustainably the growing demand of resources particularly for energy, water, and food for the rapidly growing population. Thus, the shift to the circular economy concept is gaining more interest as it has potential for sustainable development, which includes resource use efficiency, material recycling/upcycling, and cascade use, where all materials are at each stage of the process are considered to be valuable sources but not wastes.

Conversion of sewage sludge and waste wood biomass into biochars is a promising approach for sludge management from the circular economy and environmental protection perspective. Production of biochar from sludge or other organic wastes allows recovery of nutrients and energy, contributes to carbon sequestration, and reduces greenhouse gas emissions. However, due to the concerns related to the legal and strict regulation of its application, biochar should be properly characterized for different uses and functions. In this study the biochar from three different feedstocks 1) – Softwood pellets from whole tree trunks of 60% of Norwegian spruce and 40% of Scots pine (W); 2) – Waste sludge (Bio-rest) from Lindum/Vesar (WS1); and 3) –Waste sludge from Ullensaker (WS2) produced by microwave-assisted pyrolysis (MAP) with the same exposure time (20 mins), but with different pyrolysis temperatures in the range of 500 – 800 °C. The sequence of analyses includes pH, electrical conductivity, total, fixed, and volatile solids, moisture and ash content, bulk density, specific surface area, optical characterization (including Scanning Electron Microscopy (SEM), and X-ray Diffraction microscopy), elemental and chemical analyses including heavy metals. Additionally, the molar ratio of H:C, O:C, and (N+O)/C was calculated as aromaticity, hydrophilicity, and polarity index, respectively and the C/N ratio for nitrogen availability were used for characterization of the biochars and to identify possible biochar uses for different applications and functions.

This study demonstrates that the composition of the different feedstock results in different biochar characteristics when produced at similar temperatures and exposure time. The SEM and XRD showed the differences in the morphology and distribution of elements on the surface of the different biochars. Wood pellet biochar showed more C (about 93%) than Ullensaker sewage sludge (about 30%) and food waste sludge (about 15%). Wood biochar had more surface area (313 m^2/g – 402 m^2/g) than the two sludge-based biochars (77 m^2/g – 122 m^2/g). Moreover, H/C and O/C ratio for wood biochar is <0.7 and <0.2 which indicates more carbonized and more stable material than the sludge-based biochar which have, on contrary, higher values. Whereas, the nutrient, mineral, and heavy metal concentrations were higher for the two sludge-based biochar. Due to concerns of high Cu, Ni, and Zn from the food waste sludge and sewage sludge the biochar may not meet the requirements for agricultural applications but the biochar from these sources can be utilized for industrial applications (EBC-Material, Class IV) as valuable elements like P, TiO_2 and others can be extracted. The biochar from wood pellet on the other hand can meet the EBC-AgriBio (Class I) requirements as feed or feed additives for animal husbandry. Characterization of biochar based on its source is therefore important to decide to which applications the biochar can be used.

Acknowledgments

I would like to thank the SiEUGreen project for this inspiration and support. First, I want to thank Prof. Petter D. Jensen and Dr. Melesse Eshetu Moges, who shared all their knowledge, experience, and thoughts with us, their students. I appreciate that you kept an eye on us and how we coped with the lab work, data processing, and writing and showed us the right direction when we needed it the most. Thanks for understanding what we were going through while writing a master thesis in time with very limited possibilities and tons of restrictions.

I would like to express my deep gratitude specifically to my main supervisor Melesse Eshetu Moges, who guided and supported me through the thesis writing. He always had time and the right words to motivate me and gave me good advice that helped me with problems that I had. I tend to overcomplicate things, but he always had simpler solutions.

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Thanks to Øyvind Enger, Senior Engineer from MINA at NMBU, who not only conducted chemical analysis for my thesis but also showed me how it is performed. This helped me to gain a deeper insight into the topic.

Thanks to Tore Krogstad, Professor from MINA at NMBU, and Line Tau Strand, Associate Professor from MINA at NMBU, who helped to make a final decision on the calculations for my thesis.

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List of abbreviations

ARGs – Antibiotic-resistant genes
BET analysis– Brunauer-Emmett-Tellertest surface area analysis
CEC – Cation exchange capacity
CNTs – Carbon nanotubes
COD – Chemical oxygen demand
DS – Dissolved Solids
EBC – European Biochar Foundation
EC – Electrical conductivity
ECs – Emerging contaminants
EPS – Extracellular Polymer Substances
ER – Equivalence Ratio
EU – Europeana Union
FS – Fixed Solids
He-KED - Helium Kinetic Energy Discrimination
HTB – High temperature-derived biochar
HTL – Hydrothermal Liquefaction
IBI – International biochar initiative
ICP-MS - Coupled Plasma-Mass-Spectrometry
MAP – Microwave-Assisted Pyrolysis
PAEs – Phthalate esters
PAH - Polycyclic aromatic hydrocarbons
PBDEs – Polybrominated diphenyl ethers
PCBs - Polychlorinated biphenyls
PCDD/Fs – Polychlorinated dibenzo-p-dioxins
PCP – Primary care provider
PFCs – Perfluorochemicals
PPCP – Pharmaceuticals and personal care products
PPS - Pigeon pea stalk
QBSD - Quadrant Backscatter Electron Detector
SEM - Scanning Electron Microscope
SS – Suspended Solids
SW – Sewage wastes
TMAH - Tetra-Methyl-Ammonium-Hydroxide
TS – Total Solids
USEPA – U.S. Environmental Protection Agency
VOC – Volatile Organic Carbon
VPSED - Variable Pressure Scanning Electron Detector
VS – Volatile Solids
W – Wood biomass
WAS – Waste Activated Sludge
WS1 – Waste sludge from Lindum/Vesar
WS2 – Waste sludge from Ullensakker
WWTP – Wastewater treatment plant
XPS – X-ray photoelectron spectroscopy
XRD – X-ray Diffraction

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1 Introduction

1.1 Current status of sludge and related challenges

Accelerated population growth coupled with rapid economic development, urbanization, improved living standards, and rural population migration to cities has significantly increased water, energy, food, and resource demand in cities and at the same time resulting in increased generation of wastewater and sewage sludge production. Elevation of wastewater and sewage sludge generation has become a new problem causing social, economic, and environmental challenges. Despite the investments in infrastructure and improvements in technology, managing wastewater and sludge remains complex with some new challenges. In most cases, disposal of sludge faces significant environmental problems related to contamination of air, soil, and water, and, therefore, it should receive appropriate treatment and careful management which would correspond to public health requirements. The increasing levels of sewage sludge production demand innovative research and development of technologies to introduce more commercially feasible options for value creation in the circular economy and reducing socio-economic and environmental problems associated with its current treatment. (Mateo-Sagasta et al., 2015).

Sludge is a semi-solid, muddy mixture of solid and liquid by-products from different industrial stages, drinking and wastewater treatment, and onsite sanitation systems (Lexico, 2020). Specific sludge production can vary widely in a range of 35-85 g of dry solids /person/day (IWA Publishing, 2014). Therefore, there are millions of tons of sludge (just from urban WWTP) generated each year (sludge production is shown in figure 1.1 (Eurostat, 2016)).

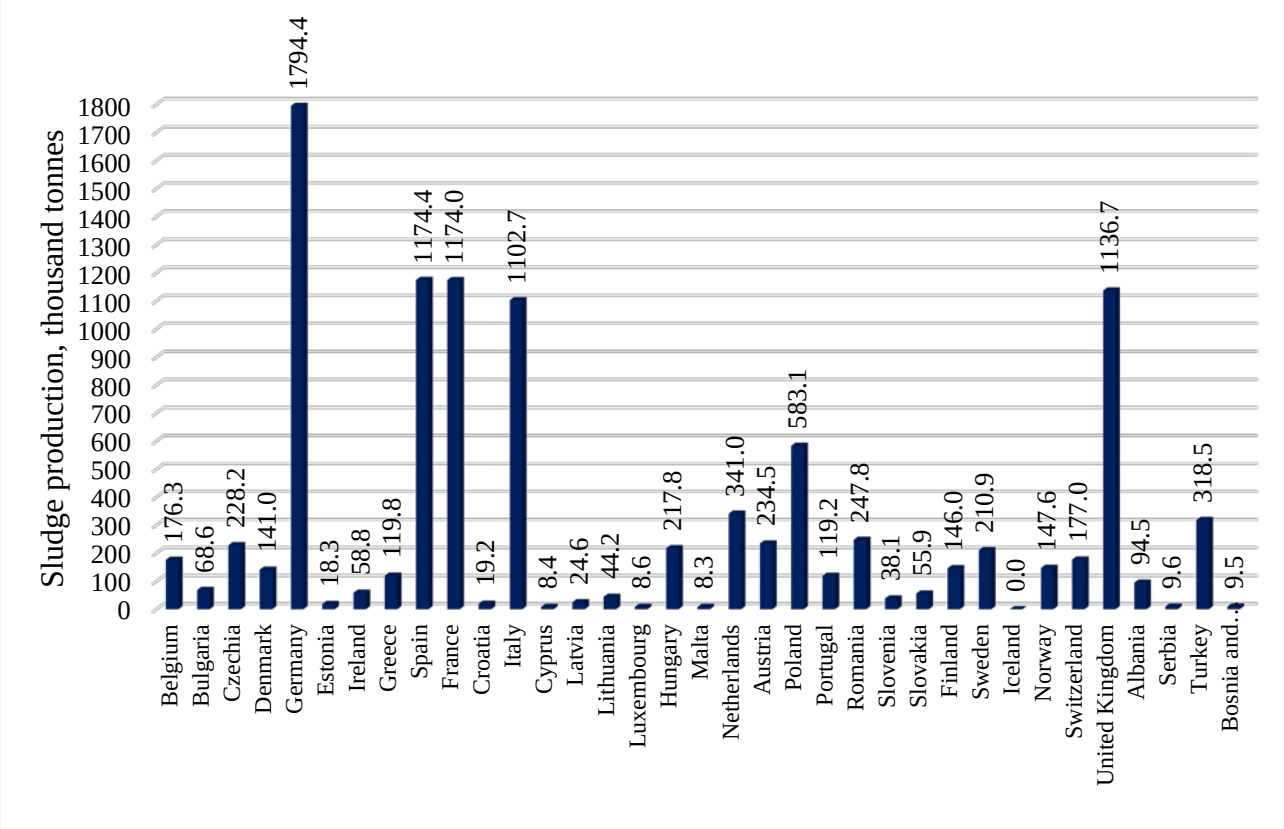


Figure 1.1 – Sludge production based on latest available data for each country (Eurostat, 2016)

The fate of these wastes is very different depending on the local context: they can be collected or not, treated or not, and finally used directly, indirectly, or end without any beneficial use. Sewage sludge is polluted with pathogens, pesticides, heavy metals, hazardous substances, etc. Therefore, it is essential to process the sludge, store it, and utilize it in a way it will not affect people's health and will not cause any further environmental problems and consequences (Baily, 2009; Eurostat, 2014).

1.1.1 Challenges of current sewage sludge management systems

Although municipal sewage sludge accounts for a small percentage of total waste production, its impact on the environment and the risks involved in the process of its application and use are considerable. The current sludge management strategy involves the integrated application of various separate sludge treatment steps (primary, secondary, and tertiary) or treatment processes. These treatment steps and processes including the conditioning step with inorganic or organic coagulants and flocculants and mechanical dewatering of the sludge, which requires a significant amount of chemicals and energy. For example, WWTP in China received about 53.52 billion m^3 in 2015 and considering about 0.47 kWh/m^3 (amount required for an average conventional activated sludge (CAS) system), it would make around 25.15 billion kWh (Y. Liu et al., 2020). Similarly, it was reported, that about 3% of national electricity is used for wastewater treatment, which is 30-60% of municipal energy demand. Considering that a big fraction of wastewater is not even treated, it is estimated that energy consumption for wastewater treatment may increase by up to 40% until 2030. Moreover, most of the current sludge management systems are not designed to recover resources except for direct applications of the processed sludge in the agricultural fields.

Besides all the mentioned problems, the increase of emerging contaminants (ECs) becomes a big concern of the modern world. The presence of ECs was found in human and animal tissues, food, air, soil, and water. These contaminants include (Bexfield et al., 2019; Sivaranjanee & Kumar, 2021):

- pharmaceuticals and drugs (retinoid, endocrine-disrupting compounds, non-steroidal anti-inflammatory drugs, per fluorinated compounds, benzothiazoles, etc.),
- industrial pollutants (plasticizers, microplastics, nanomaterials, carbon nanotubes (CNTs)),
- fire retardants,
- personal care and household cleaning products (PCP) (beauty-products, drugs, cleaning items, disinfectants, antioxidants, food additives, etc.),
- lawn care and agriculture-related products (pesticides: picloram, clopyralid, herbicides, etc.).

The use of sewage sludge currently is regulated by Council Directive 86/278/EEC, which is already over 30 years old and limits the use only by heavy metal content (Cd, Cu, Hg, Ni, Pb, Zn) (Hudcová et al., n.d.). However, the direct application of sludge in agriculture has been criticized strongly and was much more limited or completely banned in most European countries. The introduction of stricter regulations in the area of sewage sludge usage and better wastewater treatment, mainly due to its greenhouse gas emission effects, environmental pollution, and increased health risks, have increased the level of difficulties concerning sewage sludge management.

Current sludge disposal options include landfills (14%), incineration (27%), agricultural field applications (42%), and other industrial sectors (17%) like energy recoveries, adsorbent preparations, etc. (Faria et al., 2018). Agricultural use of raw sludge or other composting practices is encouraged by national authorities in most developing countries as the best way for recycling. Directive 86/278/EEC on Sewage Sludge in Agriculture requires, however, that no one may permit the use of

sewage sludge on agricultural land unless specific requirements are fulfilled. However, the development of sludge recycling systems to the great extent is dependent on the economic development of the countries and is currently only documented in developed countries. EU and USEPA developed policies and regulations that were implemented in some countries to lower shares of sludge that is not handled sustainably. However, many countries still utilize direct agricultural use or disposal landfills (figure 1.2 based on appendix A).

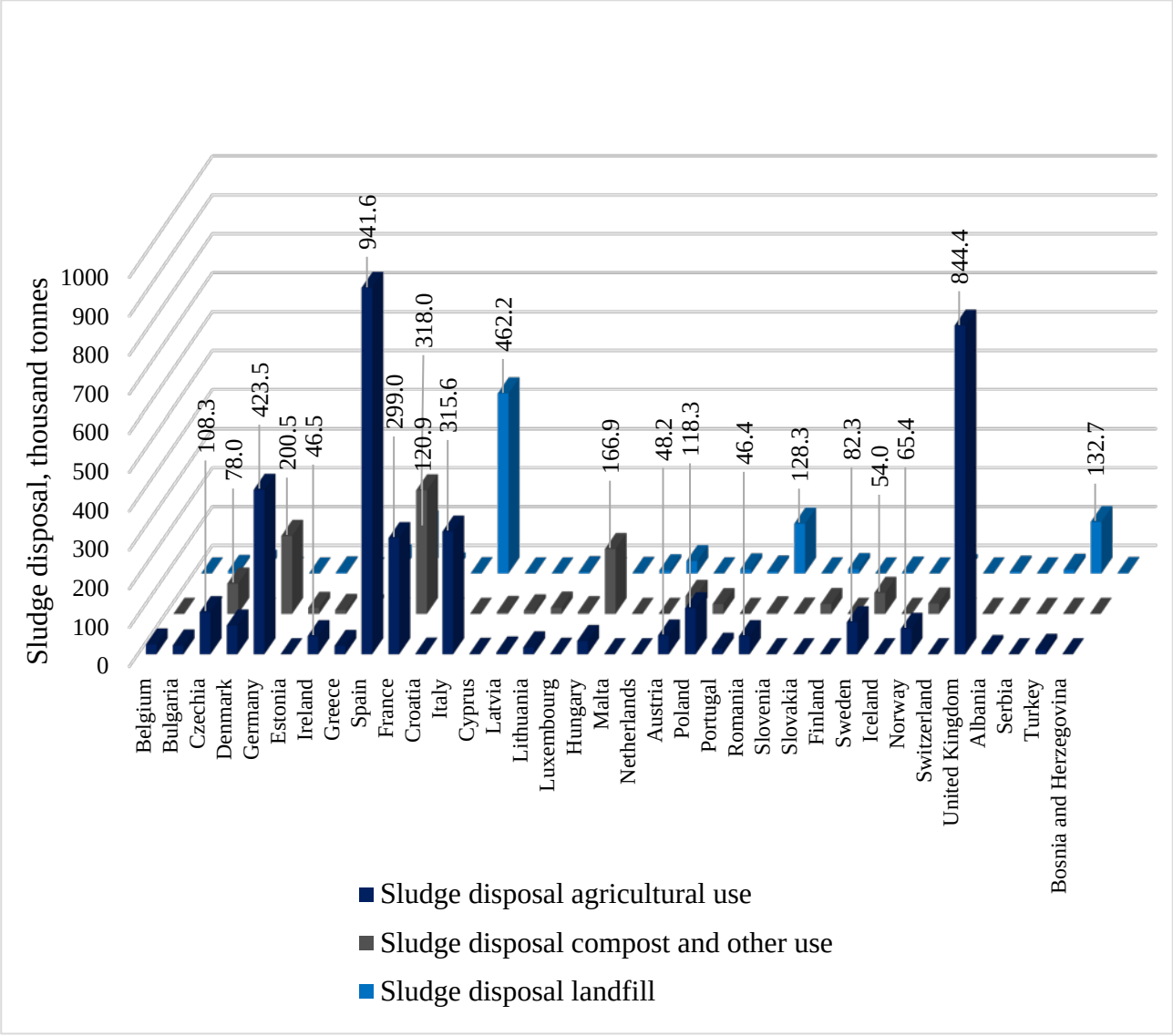


Figure 1.2 – Sewage sludge disposal from urban wastewater (Eurostat, 2014)

There are many constituents in the waste sludge, that are derived from wastewater and could be associated with sanitary, health, and environmental risks. Therefore, sometimes it is impossible to use sludge directly on land or for other applications without preliminary treatment. The most important contaminants are listed below in table 1.1, divided into 3 main sections: heavy metals, organic matter, pathogens and viruses.

Table 1.1 – Main contaminants of the sewage sludge

Contaminant			Consequences	References
Heavy metals	From where?	Industrial or consumer waste, soil leaching, coagulants.	**For plants:** • chlorosis, • photosynthesis dysfunction, • growth dysfunction, • low biomass, water, nutrient accumulation. **For people – increased risk of:** • headaches, • liver diseases, • gastrointestinal cancer, • mental growth retardation, • malnutrition.	(Geng et al., 2020; Rai et al., 2019; S. Singh et al., 2016)
	What?	Fe, Al, Cd, Hg, Mn, Cu, Zn, Pb, Cr, Ni		
	Possible removal methods	• electrokinetic method, • supercritical fluid extraction, • chemical treatment, • washing agent (plant-based), • ion-exchange treatment, • advanced oxidation method, • bioleaching.		

Contaminant			Consequences	References
Organic matter and traces	From where?	Pharmaceuticals, personal care productions, industries, etc.	**For environment:** • development of drug-resistant bacteria, • influence redox potential and pH of the soil, • influence grazing animals, causing some disease risks as well as for humans. **For people – increased risk of:** • cardiovascular disease, • cancers, • diabetes, • endocrine disruption, • birth defects, • reproductive systems disruption.	(Guo et al., 2019; Lü et al., 2021; Olowoyo & Mugivhisa, 2019)
	What?	• PAHs, • PCBs, • PCDD/Fs, • PBDEs, • PAEs, • PFCs, • ARGs, • PPCPs, • flame retardants, • hormones, etc.		
	Possible removal methods	• sludge composting with the previous pretreatment and bulking agents, • bioleaching, • sludge thickening.		

Continuation of table 1.1

Contaminant			Consequences	References
Pathogens and viruses	From where?	From wastewater of slaughterhouses, human excreta, etc.	Pathogens and viruses get in the fertilized soil, then into plants, which in turn can be consumed by animals or people, causing different diseases and disorders. **For people and animals:** • gastrointestinal infections, • respiratory infections, • leptospirosis, • meningitis, • hepatitis, • myocarditis, etc.	(Alegbeleye et al., 2018; Chahal et al., 2016; M. Wang et al., 2021)
	What?	**Pathogens:** • Salmonella, • Shigella, • Legionella pneumophila, etc. **Viruses:** • hepatitis A • norovirus, • rotavirus, • enteroviruses, etc. **Protozoa:** • Cryptosporidium • Giardia, • Cyclospora, etc.		
	Possible removal methods	• Electro-Fenton treatment, • Anoxic oxidation treatment, • Acidification treatment, • Methanol treatment, • Ultrasound treatment, etc.		

1.2 Sludge as a resource in the context of circular economy

Sewage sludge is formed at various stages of wastewater treatment. In conventional activated sludge systems, the core biological unit of the sewage treatment plants can produce about 0.3-0.5 kg dry biomass per 1 kg of COD removed (X. Zhang et al., 2019). As a result, an extremely large amount of biosolids, known as waste sludge, are inevitably generated through the biological oxidation of soluble COD to biomass. However, the COD in sewage is a chemical energy that should be captured and converted to electric energy and other value-added organic by-products via anaerobic digestion and recovery of nutrients with minimized energy consumption.

As the global demand for renewable energy and organic matter increases, organic wastes, including sewage sludge, could be one of the locally available and sustainable resources for this purpose. Sewage sludge can be used as an energy resource for power and heat generation with emerging technologies. Moreover, sewage sludge can be considered as a substrate for soil fertilization and remediation if the applied technology allows obtaining a safe quality product. Such re-uses of sewage sludge are economically viable and environmentally sustainable compared to the current linear waste handling and landfilling practice. The circular economy concept offers an approach that can be the basis for the creation of a new sewage sludge management strategy. The concept allows the combined goals of sewage sludge disposal and energy, nutrients, and another resource recovery to be achieved. With the concept of circular bioeconomy, the new strategies fit into the eco-innovation trend of “reduce, reuse, recycle and recover” as the most preferable and sustainable waste management hierarchy.

To develop a modern approach, the main principles of the circular economy should be applied (Defait, 2019):

- waste and pollution should be considered and minimized during the design stage,
- all the resources should be kept in use: maximum possible recycling.
- regenerate and restore natural systems.

Thus, as a linear approach is no longer satisfactory for the demands of the modern world, a more sustainable (nearly zero wastes and zero emissions) circular approach should be applied. Based on the above-stated principles, sludge should be perceived as a valuable source of biomass and nutrients and not as a waste product. Also, since sludge is a part of the wastewater treatment life cycle, new upgraded systems should combine solutions for both water and sludge (figure 1.3).

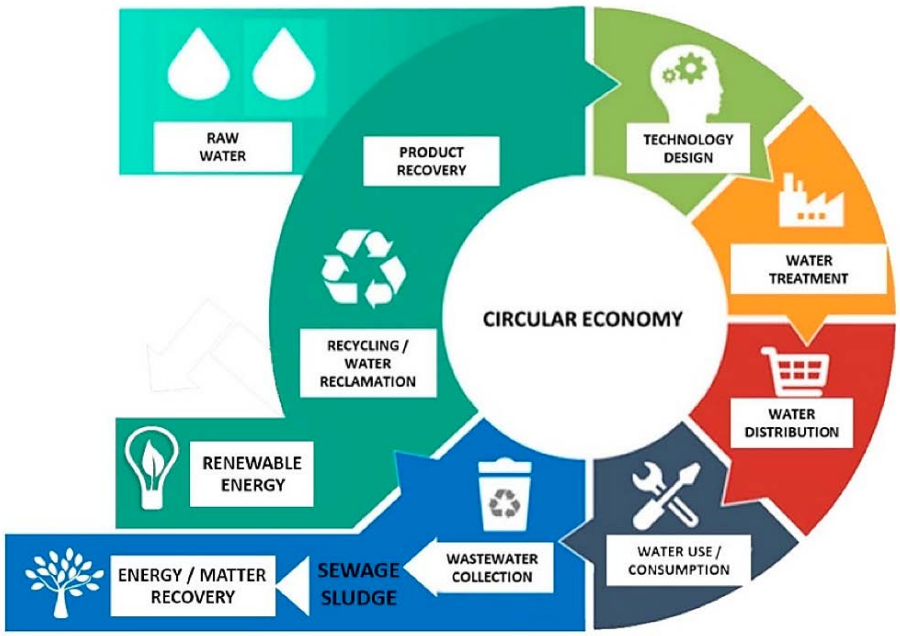


Figure 1.3 - Circular wastewater – waste sludge chain (Facchini et al., 2021)

According to J.Peccia and P. Westerhoff, sewage sludge should be considered as an asset that has nutrients, high-value metals, and big energy potential (Peccia & Westerhoff, 2015). It was estimated that for 1 million people, just 13 most valuable elements (Ag, Cu, Au, Fe, Pd, Mn, Zn, Ir, Al, Xd, Ti, Ga, Gr) would give a profit of about US $13 million/year. In the same case, phosphorus would give a profit of about US $55,000/year. Prices for the waste sludge resources are listed below in table 1.2 (Peccia & Westerhoff, 2015).

Table 1.2 – Value of sewage sludge resources (Peccia & Westerhoff, 2015)

Resource		Price *[$/ton]*
Nutrients	Nitrogen in form of NH_4^+ *	24
	Phosphorus **	7
Metals	Ag, Cu, Au, Fe, Pd, Mn, Zn, Ir, Al, Cd, Ti, Ga and Gr	480
	Au, Ag	103
Energy	Energy contents as coal ***	50

** for calculation was used $700/ton for anhydrous NH_4^+ with N = 3.4% in dry biosolids.*

*** for calculation was used $115/ton for rock phosphate with P = 35%.*

**** Based on the assumed energy content of sludge 18 MJ/kg, while 24 MJ/kg for coal.*

1.2.1 Waste sludge origin and types

This study focuses on sludge that derives from sanitation systems, water, and wastewater treatment facilities. Sludge characteristics will differ to a great extent depending on its source since different types of sludge will have different elemental compositions and properties. There are two main types of waste sludge (Figure 1.4): fecal/septage and sewage (Mateo-Sagasta et al., 2015). The first type is excreta collected from toilets that are obtained on-site or off-site. The term fecal sludge is mostly used for on-site excreta and septage sludge is for off-site. The second type is sewage sludge produced by wastewater treatment plants during removal of the suspended solids and can be subdivided, based on the stage it was obtained from, as primary and secondary sludge.

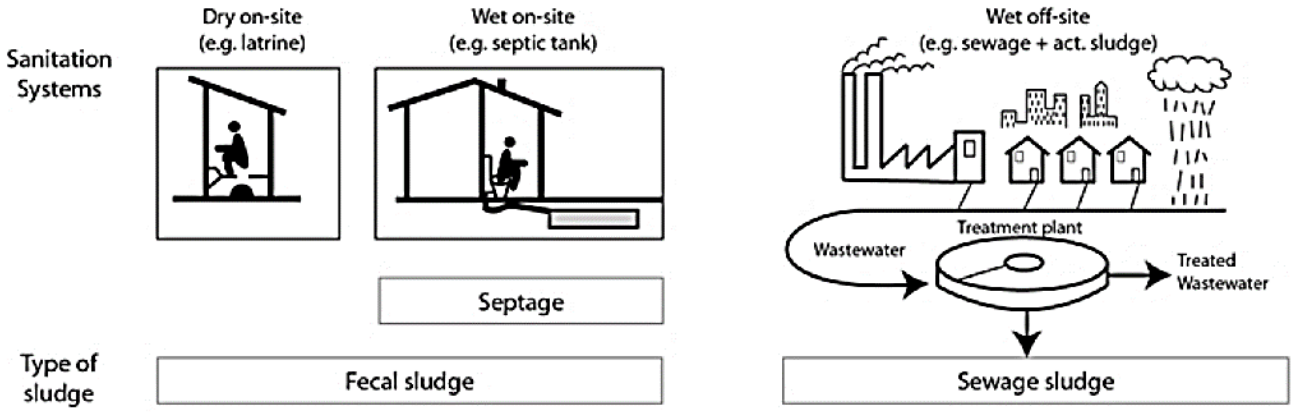


Figure 1.4 – Types of sludge by source (Mateo-Sagasta et al., 2015)

1.2.2 Characterization of sewage sludge as a substrate

As it is mentioned above sludge characteristics depend on the list of the followed parameters:

- Sludge origin: volume of received sludge, what wastes sludge originates from, etc.
- Quantity of flushing water (type of toilet) (how much water it uses, does it have source separation, does it include greywater, etc.).
- Collection type (on-site, off-site).
- Treatment level of sludge (sludge after thickening, dewatering, digestions, etc.).

Sludge includes total solids (TS) and water. In its turn total solids consist of suspended and dissolved solids, where each can be fixed (FS) or volatile (VS) (Tambo et al., 1982):

$$\text{Sludge} = \text{TS} + \text{H}_2\text{O} \tag{1.1}$$

$$\text{TS} = \text{SS}_{\text{org}} + \text{SS}_{\text{in}} + \text{DS}_{\text{org}} + \text{DS}_{\text{in}}, \tag{1.2}$$

where TS – total solids;
SS_{org} – organic/volatile suspended solids;
SS_{in} – inorganic/fixed suspended solids;
DS_{org} – organic/volatile dissolved solids;
DS_{in} – inorganic/fixed dissolved solids.

VS/TS ratio allows to estimate organic fraction in the sludge and also the level of digestion. Usually, digestion would reduce VS with an efficiency of 40–55% (Tambo et al., 1982).

Sludge contains a lot of valuable resources including organic carbon (needed for energy recovery and soil conditioning), macro elements (N, P), and usually less K and relatively low concentrations of Ca and Mg (Tambo et al., 1982). However, K is easily available for plants, so this element will be easily absorbed by roots. As for microelements, including Fe, Cu, Zn, B, Mo, they vary a lot from sludge type to sludge type. The presence and concentration of those elements depend on influent sewage quality and the sludge treatment process. All those elements are essential for agriculture and aquaculture (Mateo-Sagasta et al., 2015).

1.3 Sludge processing/treatment and potential use

Sludge is treated differently depending on the disposal place, and the way of its further use. However, all sludge treatment aims for the same objectives:

- organic matter stabilization and pathogen destruction,
- dewatering (volume reduction by removing accessible water) and drying,
- extraction of valuable resources from sludge,
- sludge disposal or recycling.

Usually, before the final disposal place, sludge undergoes a combination of processes (for possible options see Table 1.3). For instance, for biochar production sludge should be processed in the pyrolytic reactor, but before that is should be dewatered until specific water content value.

Table 1.3 – Groups of sludge treatment processes (Miklas, 2006; R., 2010)

Treatment method	Processes	Options
Thickening	Sludge remains in a liquid state, but solid content is increasing to 5-6%	Gravity, flotation, centrifuge, elutriation, constructed wetland.
Dewatering	Solid content increases up to 15-30%, pathogen reduction if dried, nutrient loss if filtered or centrifuged	Drying beds, filter press, centrifuge, vacuum filter, belt press, and lagooning, constructed wetland.
Stabilization	Increase in solid content, reduction of odor, pathogens, VS, possible loss of N.	Anaerobic and aerobic digestion, lagooning, heat treatment, constructed wetland.
Disposal	Volume, odor, VS reduction, elimination of most pathogens, a decrease of nutrients.	Incineration, pyrolysis, wet air oxidation, composting, sanitary landfill, cropland, ocean.

During the recent decade, a lot of modern sludge handling techniques are developed, a short overview of different ways of waste activated sludge (WAS) management is presented in table 1.4.

Table 1.4 – Possible directions of WAS use

Possible use	Explanation	References
"Sludge = waste" logic		
Landfill disposal	The conventional method of waste sludge handling that now is considered to have many disadvantages including wasting the fertilizing value of WAS, risk of environmental pollution, increasing cost due to fines increase and sludge still should be treated to meet disposal requirements.	(European Commission, 2001, 2002)
Incineration	Considered one of the most expensive methods, that requires special equipment to prevent air pollution and does not allow organic recovery. However, this method is still considered to be more progressive for excluding dangerous potential contaminants "from food chain".	(European Commission, 2001, 2002)
Land spreading	Using sludge as fertilizer on fields, directly or with pretreatment. Concerning approach due to high metal content in sludge as well as other possible pollutants concerning health safety.	(European Commission, 2001, 2002)
"Sludge = product" logic		
Land use	WAS is very good for soil restoration and conditioning unless it contains a big number of heavy metals. Land use is possible only if sludge properties satisfy the local legislation system, otherwise, it is sent to a landfill or managed in another way. Biosolids can be applied to the soil directly by injection equipment.	(Epstein, 2002; R. P. Singh & Agrawal, 2008)
Construction material	Sludge can be used to produce a variety of materials for construction as cementitious material, concrete, mortar, bricks, tiles, etc. In this case, the maximum replacement or regular material by sludge is up to 30-40% (depending on the type of producing material or production methodology) without losing durability and performance.	(Rao Meda et al., 2021), (Godoy et al., 2019), (Erdogmus et al., 2021)
Fuel source for cement industry	The use of preliminarily treated sludge in the cement kilns would produce a relatively high net calorific value (around 10-20 MJ/kg) with lower CO_2 emission in comparison with coal. This would allow to reduce the industry's influence on the environment and reduce greenhouse gas emissions. This approach has already been implemented in multiple countries in Europe including Germany and Switzerland.	(Bioenergy Consult, 2020)
Biogas production	Use of preliminary treated or enriched sludge as a source for methane production together with other materials as lignocellulosic waste (waste that origins from agriculture or forestry), free ammonia,	(Zhu et al., 2021), (X. Liu et al., 2018)
Waste granular sludge	Waste granular sludge is generated by biogranular treatment units that are much more compact than regular activated sludge systems. Those systems allow having great settleability, toxicity tolerance, and being able to treat big loads of carbon/nutrient polluted wastewater. Furthermore, obtained granules are used later to extract extracellular polymer substances (EPS) (proteins, polysaccharides, DNA, etc) that in its turn would be used to obtain concentrated EPS and hydrogel with potential application for paper coating, biosorption, flame retardant materials, cement curing.	(Feng et al., 2021)

Continuation of table 1.4

Possible use	Explanation	References
Incineration	Ash and hydrochar are used as technology that can be used for efficient phosphorus recovery. For the HTL process, P recovery is just a by-product, while the main goal is energy production. For both processes, it is challenging to extract P since acidic extraction has high efficiency (up to 100%) but also extracts heavy metals, while alkaline has lower efficiency (up to 70%) but avoids metals extraction.	(H. Liu et al., 2021)
Hydrothermal liquefaction (HTL)		
Biochar production + energy recycling	Production of highly porous adsorbent reaches in phosphorus, potassium, and other micronutrients by thermo-chemical treatment under oxygen-limited conditions. Biochar can be used as an adsorbent for specific compounds or enriched and used as soil fertilizer and conditioner.	(Karim et al., 2019), (Zhai et al., 2017)

2 Literature Review

2.1 Sewage sludge biochar: characterization and evaluation

The important and effective management of wastewater sludge materials environmentally and economically can be addressed through pyrolytic conversion of the sludge into biochar and its associated products for agricultural and different industrial applications. Biochar is a solid, stabilized, recalcitrant organic carbon material obtained by pyrolysis of the biomass (in this case waste sludge) under limited or deficient oxygen concentration with increased temperature, usually between 300 to 1000 °C. The produced biochar can be used for different purposes depending on the feedstock biomass source and the characteristics of the pyrolysis process. In the last decade, biochar received increasing attention due to its multiple applications including carbon sequestration (Laird et al., 2010), bioenergy production (Field et al., 2013), and improving the physical, chemical, and biological fertility of the soil. Moreover, it plays an important role in environmental remediation (Mohan et al., 2014), particularly in heavy metal removal of contaminated water and soil. Biochar has proved itself as an innovative soil ameliorant, which can solve numerous problems of the emerging contaminants (Department of Agriculture in Australia, 2019) and is applied for:

- sludge recycling and management,
- nutrient and biomass recovery (improves nutrient storage and availability),
- soil restoration (improves soil structure, water holding capacity, an abundance of fungi, which help with nutrient uptake),
- carbon sequestration (long-term carbon transfer in the biochar, production of alternative to fossil fuel energy source – syngas, reduction of N_2O gas emissions with fertilizer application).

This study focuses on the biochar characterization of properties and to fully understand it, biochar should be traced from the beginning till the end:

origin of sludge -> sludge properties ->biochar production methods-> biochar properties

Originally the definition of “biochar” was given to a solid product after pyrolysis of biomass of different origins mostly used as a soil amendment material. However, since recently biochar was obtained as a product (or by-product) of other biomass treatment processes and its application range widened significantly according to its newly gained properties, it would be more accurate to define “biochar” generally as a solid carbonized product of thermochemical decomposition of biomass in an oxygen-limited environment.

In the work of Suddapuli-Hewage (Suddapuli-Hewage, 2016), the evolution of the “biochar” definition was nicely studied. Indeed, one may find difficult to group the materials of various distant sources of origin, a wide range of application, different production methods and different properties of the final product in one term. Thus, alternative notations for clearly differing products can be found – such as black carbon, hydrochar, charcoal. Including biochar, they are all enclosed in terms of pyrogenic carbonaceous material (PCM), and one should be cautious that materials of distinct nature in various sources are still referred to as “biochar”. An example of sludge and biochar made of it is shown in figure 2.1.

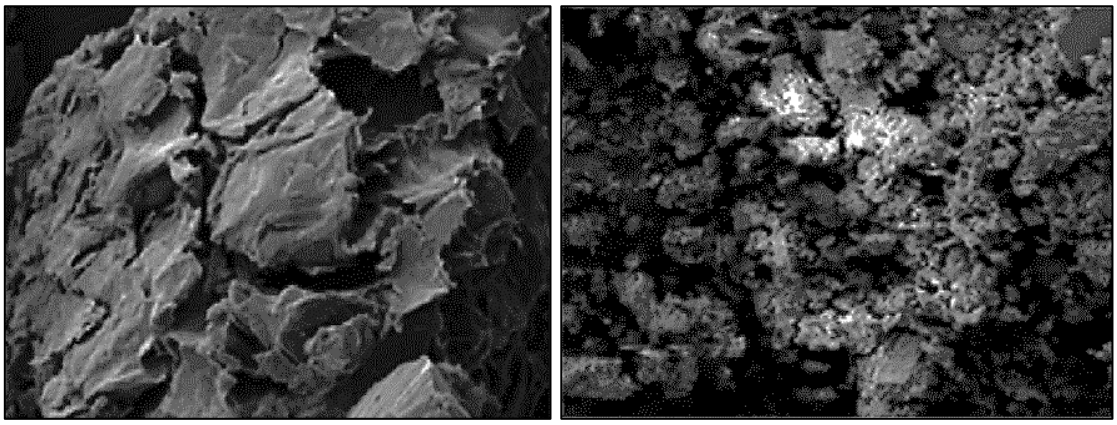


Figure 2.1 – Scanning electron microscope (SEM) images of (a) sewage sludge and (b) biochar produced from sewage sludge (Kim et al., 2013)

The physical-chemical properties of produced biochar stem from the biomass source and thermal conversion procedure, but overall biochar can be characterized as high carbon content (50-90%), porous, from medium to high specific surface area (1-500 m^2/g), nutrient-containing (N, P, K) material (D. Wang et al., 2020). Biomass source strongly affects the chemical composition of the final product, not to mention that it is an important factor for the selection of appropriate thermal treatment techniques and processing conditions. Thus, primary biomass sources can be separated into the next categories:

- high cellulose content easy degradable plant remains (wheat straw, rice husk, corn stalks, bamboo),
- high lignin content poorly degradable plant and trees remain (pine, spruce, palm, eucalyptus, larch sawdust, and bark),
- livestock wastes and manure,
- organic human wastes in the form of domestic wastes and sludge from wastewater treatment plants (Kazemi Shariat Panahi et al., 2020).

Numerous studies report that biochar produced from high lignin sources exhibits higher carbon content, increased porosity, and therefore higher specific surface area (A. Tomczyk, 2020). Utilization of lignin-rich materials fosters as well higher mechanical strength of biochar. Meanwhile, animal and human wastes originated biochar possesses higher nutrient content (Yaashikaa et al., 2020) and dependently on the treatment method exhibits comparable Cation Exchange Capacity (CEC) to high lignin source.

It is hard to address how the source of raw material solely influences the properties of final biochar since it is rather an interplay of treatment approach and processing conditions together with the chemical composition of source material define the characteristics of the end product. Above some generalities, that were highlighted based on the available literature, more context will be provided for each method of production in the next section.

2.2 Biochar production

Generally, 4 different methods of biochar production are reported in the literature: slow pyrolysis, fast pyrolysis, gasification, torrefaction. In fact, only slow pyrolysis is utilized as an approach for primary biochar production, the fast pyrolysis and gasification aim for the production of bio-oil

(liquid fraction of biomass pyrolysis) and syngas accordingly (D. Wang et al., 2020; Yaashikaa et al., 2020). On the other hand, the torrefaction's main focus is the production of solid fuel pellets alongside maximization of their energy content and solidification of charred products. It is clear, that these processes are hard to compare in terms of biochar production since they have different final goals. Some address biochar as a by-product, and another aim for biochar with distinctly different properties. However, a comprehensive overview of these methods is to provide a better understanding of how the processing conditions influence the final biochar. A short overview of biochar production methods is given in table 2.1.

Table 2.1 – Comparison of 4 methods of biochar production

Technique	Temperature	Residence time	Biochar yield	Carbon content	Nitrogen content	Specific surface area	References
	[°C]	*[min]*	*%*	*%*	*%*	*m^2/g*	
Slow pyrolysis	300-700	30-120	20-50	50-90	1-3	1-500	(B. Tomczyk et al., 2021; D. Wang et al., 2020; Yaashikaa et al., 2020)
Fast pyrolysis	500-1000	<0.03	10-30	30-70	1-2	1-500	(Chatterjee et al., 2020; D. Wang et al., 2020; Yaashikaa et al., 2020)
Gasification	750-900	0.2-0.3	<10	60-90	<2	1-400	(James et al., 2020; D. Wang et al., 2020; Yaashikaa et al., 2020)
Torrefaction	200-300	10-60	70-90	40-70	-	0-300	(Nai et al., 2020; D. Wang et al., 2020; Yaashikaa et al., 2020; Zheng et al., 2017)

2.2.1 Slow pyrolysis

Pyrolysis is the process of thermal decomposition of biomass at elevated temperatures (300-700 °C) in the inert atmosphere. The difference between "slow" and "fast" pyrolysis is in the heating rate and therefore residence time of the biomass. Slow pyrolysis occurs at the heating rate of 5-7 °C/min with common residence times of 30-120 min, meanwhile fast pyrolysis heating rate can reach 1000 °C/min and residence time of vapor being <2 s. Naturally, this strongly affects the properties of the final biochar. Slow pyrolysis provides sufficient time for each fraction of biomass to decompose. Hemicellulose starts depolymerizing at 170–240 °C, cellulose at 240–310 °C, and lignin as the most stable fraction decomposes at 300–550 °C, thus each fraction requires its optimal temperature range and residence time to be optimally depolymerized and for exhaust gases and volatiles coming from each fraction to transfer out from reacting bulk mass(Giudicianni et al., 2013). Steady heating also gives sufficient time for the solid carbon flushed with the gaseous phase to deposit back on a solid fraction. Generally, the resulting biochar has high carbon content and presumably should be more biodegradable for the plant when used for agricultural remediation purposes (A. Tomczyk, 2020; D. Wang et al., 2020).

The higher temperature of pyrolysis also promotes better removal of volatile organic carbon (VOC) from biochar and increase of carbon content, solid density alongside with higher specific surface area of biochar, however, reducing the overall yield. An increase in the temperature of pyrolysis facilitates the formation of micropores to a certain limit (of around 800 °C) after which the destruction of micropore walls and shrinkage of solid matrix occur resulting in lower specific surface area but higher total porosity (Kazemi Shariat Panahi et al., 2020).

2.2.2 Fast pyrolysis

As it was mentioned, fast pyrolysis is conducted at significantly higher heating rates to extract liquid and volatile fractions from the biomass, which later is condensed in the form of bio-oil. Rapid heating causes quick vaporization of the volatile fraction which fast transfers from the bulk mass resulting in higher microporosity of obtained char. However, after reaching a certain point fast depolymerization of organic compounds at the surface of solid particles negates the positive effect of fast vaporization on the formation of porous structure (Chatterjee et al., 2020).

2.2.3. Gasification

Gasification is another thermal conversion approach. Biomass in the gasification is subjected to incomplete combustion under the limited oxygen supply. Gasification is conducted under the temperature of 750-900 °C (sometimes up to ~1200 °C), with an oxygen flow rate of 0.1-1.0 kg/h. The primary product of gasification is syngas (figure 2.2, (Mysior et al., 2019)), meanwhile, char is a rather undesirable by-product. Airflow or the so-called equivalence ratio (ER) is the controlling parameter of the process alongside pressure and temperature. An increase in ER, oxygen content, and reduction of pressure results in smaller yields of biochar and lower carbon content, which also can adversely affect the mechanical strength and particle size uniformity (Kazemi Shariat Panahi et al., 2020; D. Wang et al., 2020).

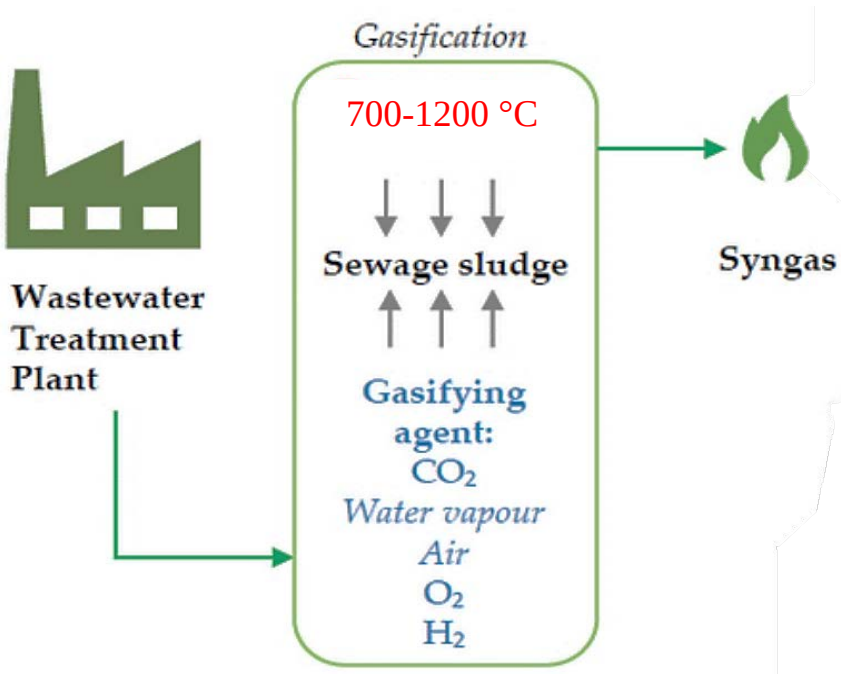


Figure 2.2 – Principal scheme of the syngas production over gasification method (Mysior et al., 2019)

2.2.4. Torrefaction

Torrefaction is considered an emerging alternative technique suitable for biochar production. During torrefaction, biomass undergoes heating and limited pyrolysis in the inert atmosphere. The main goal of torrefaction is the removal of moisture and highly volatile/low energy-to-mass ratio compounds. Since biomass after torrefaction should retain a maximum of original energy content and has maximum possible energy density, the pyrolysis rate is kept at a minimum, thus operating temperatures do not exceed 300 °C (Nai et al., 2020; D. Wang et al., 2020; Zheng et al., 2017).

2.3 Biochar application

The development of biochar led to the formation and advancement of research fields including waste management, agriculture, environment, material, and energy. New biochar applications allow the introduction of a new approach to environmental problems. The application of biochar and its relationship with its properties is shown in figure 2.3 (Lu et al., 2020). Biochar structure and surface reactivity should be considered for effective and efficient use.

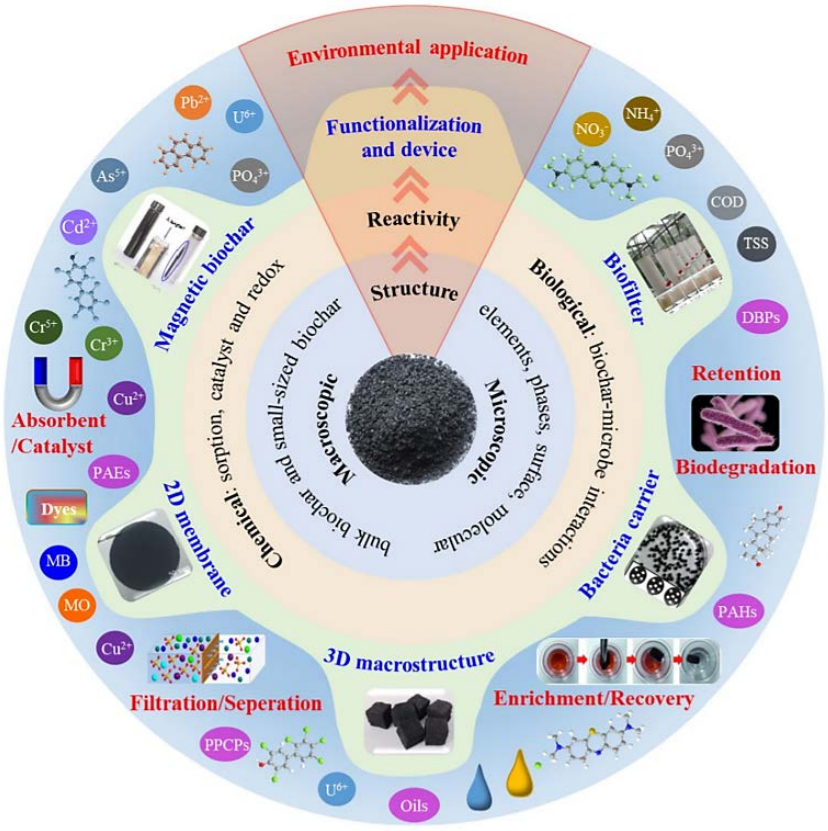


Figure 2.3 – Relationship between properties related to structure, biochar reactivity, functionalization, and environmental application of biochar (Lu et al., 2020)

Big bulk biochars with a size up to 1 cm are usually used for agricultural or environmental purposes (if chemical composition allows to apply it), otherwise, they should be reduced in size for uniform properties and heat transfer ability (Lu et al., 2020). During the carbonization process, which is increased with the increase of pyrolysis temperature, biochar gets smaller in size, and more nano-particle-sized biochar is formed. In fact, the structural difference in biochar causes a difference in

many physic-chemical characteristics including pH, polarity/aromaticity, chemical composition, specific surface area, surface reactivity (charge - zeta potential, surface functional groups, free radicals), pore volume (Yaashikaa et al., 2020).

Depending on its reactivity, the biochar can be divided into 2 categories: chemically active (reactivity towards inorganic/organic contaminants) and biologically (reactivity towards microbes) active biochars. All of this then defines the purpose of biochar:

- **Sorption:** biochar can adsorb organic compounds, metals, nutrients, gases, and microorganisms. C, H, O, and N form biochar matrix, while Si, P, and S play a major role in sorption ability. In general, different structures and compositions would generate regions with a strong affinity towards specific elements.
- **Catalyst:** biochar has redox properties: the specific capacity to give/accept electrons. Biochar can be used for the transformation/ degradation of pollutants into the desired form or can directly react with pollutants. Biochar surface activates some oxidants and produce reactive radical or reacts directly.
- **Biochar-microbe interactions:** Biochar can interrupt microbial cell communication.

In this study, the focus will be on the agricultural application of the biochar produced from waste sludge. Therefore, the main purpose is the sorption of nutrients with further use as a soil fertilizer. It would give a lot of benefits not just to the land, but also to the entire involved infrastructure (figure 2.4) that includes a barn, manure/slurry, biogas plant, composting system, field, trees/forest, and soil. The main importance between all of the advantages is an increased yield of crops, higher soil quality (better water holding capacity, nutrient buffer, humus formation), increased stress tolerance for plants, stable climate as well as animal welfare and stable gas yield (Bioenergy Europe & EBI, 2021).

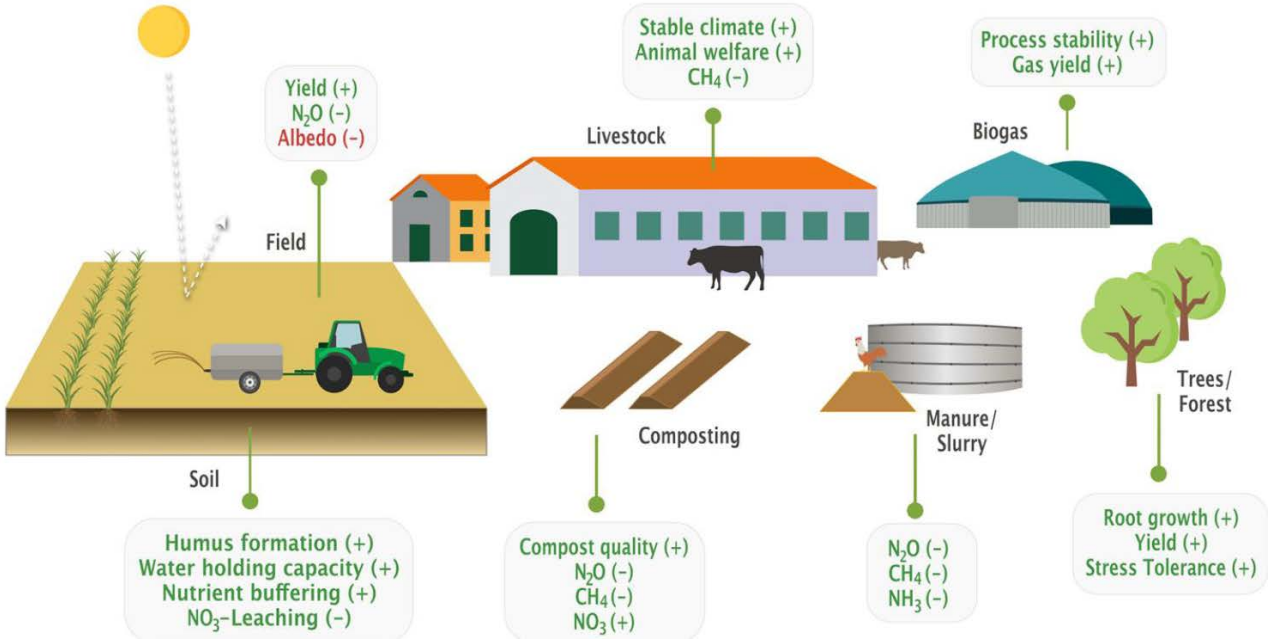


Figure 2.4 – Biochar application benefits (Bioenergy Europe & EBI, 2021)

The biochar market is growing constantly with the production of about 17.000 t in 2020 (Bioenergy Europe & EBI, 2021). Production capacity was doubled during 2018-2020. Also, it is estimated that the number of biochar production system installations will reach at least 100 systems in 2021 (72 at the end of 2020) (Bioenergy Europe & EBI, 2021).

3 Problem statement of the thesis

The disposal of sewage sludge (SS) into landfills or sending it to incineration has been gradually criticized due to environmental and health risks. The increased population and subsequently higher sludge generation have put legislators and environmental policymakers to develop the most stringent regulations in waste sludge disposal and reuse of sludge in agriculture or other applications. Because of the restrictions and stringent legislation, the use of traditional disposal methods has been reduced due to land limitations, secondary contaminant production, and the risk of polluting farmland and surface or subsurface water.

Sewage sludge from wastewater treatment has received more attention: from feedstock to anaerobic digestion to produce biogas and reined biomethane. More recently, interest is growing for the use of sludge as a biomass source for biochar production and is used in agriculture because of its high phosphorus, macro-, and micronutrient content. Moreover, due to the surface chemistry and physical characteristics of sludge-driven biochar can be used for different industrial applications. One of the advantages of using sewage sludge from wastewater treatment plants as a sustainable source for biochar production is its wide availability. However, information on the characterization of sewage sludge biochar and its application for different uses is limited. Characterization of biochar generated from sewage sludge is thus important in identifying agronomic and environmental applications and for guiding future research towards safe management and utilization of sewage sludge in the circular economy.

The main objective of this MSc thesis is, therefore, to characterize sewage sludge-derived biochar and to evaluate the potential applications for safe utilization of the biochar for soil amendment purposes or nutrient recovery and as filtration media for wastewater, as adsorbent for removal of contaminants, construction material, etc.

4 Materials and methodologies

Methods

4.1 Production

4.1.1 Source materials and preparation for pyrolysis

- Source description and origin
- Sludge processing and drying with KENKI drying until satisfactory moisture content.

4.1.2 Pyrolysis:

- Biogreen® pyrolysis technology.

Preparation of the source material for pyrolysis and pyrolysis itself was performed by Scanship AS.

4.2 Characterization

4.2.1 Sample preparation

4.2.2 Physical properties:

- Scanning electronic microscopy + X-ray diffractometry mapping *(used equipment in Imaging Center).*
- Surface area (BET-test performed in UiO), pH, electrical conductivity, ash and moisture content, bulk density.

4.2.3 Chemical properties:

- Elemental composition (C-H-N-O) – EDTA *(performed by specialists in NMBU laboratory)*
- Mineral content, (macro- and micro-elements, heavy metals) – ICP-MS *(performed by specialists in NMBU laboratory)*

4.1 Biochar production

4.1.1 Source materials and preparation for pyrolysis

Materials for biochar production should pass through a bio-sludge treatment system to reduce material volume via dewatering, and subsequent drying.

Different dryers can be used depending on the source material properties. However, since wood and sludge have different characteristics, they require different drying technic for different materials. The dryers that were used for our samples are shown in figure 4.1 (Biogreen ®, 2021a, 2021b).

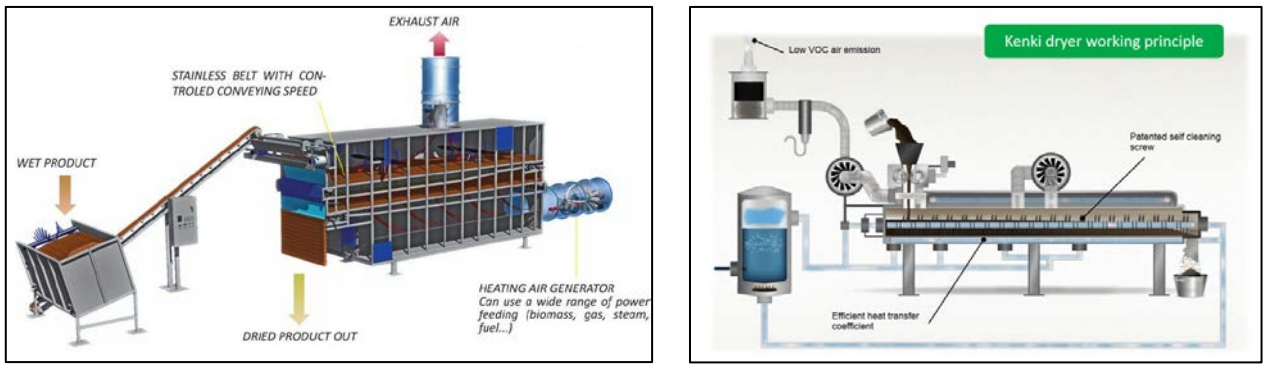


Figure 4.1 – Equipment for biomass drying: a) continuous belt dryer;
b) KENKI dryer (Biogreen ®, 2021a, 2021b)

A continuous belt dryer (figure 4.1a) allows to dry divided products such as wood pellets, solid wastes, sawdust and reduce the moisture content down to 8-12 %, while the KENKI dryer (figure 4.1b) is more used for highly humid, slurry, pasty, or sticky material: different kinds of sludge, food waste, other materials with high moister content or viscosity; reduces water content down to 10% or lower. During material dewatering and drying, biological material reduces volume by up to 90%.

For the characterization was decided to pick 3 different sources that are displayed in table 4.1 below. Samples were collected and processed by Scanship AS.

Table 4.1 – Type and origin of source material

#	Source material	Origin	Type
1	Wood pellets	Hallingdal	Wood*
2	Slam-biorest	Lindum/Vesar	Waste sludge
3	Slam-biorest	Ullensaker	Waste sludge

** "Commercial wood pellets made of softwood, 60/40 by volume of Norway spruce (Picea abies) and Scots pine (Pinus sylvestris). The pellets were produced using whole tree trunks and represent all parts of the trunk: bark, inner bark, cambium, sapwood, and heartwood." - Scanship*

4.1.2 Pyrolysis

After the source material is dried to acceptable moisture content (about 15% or lower) and pelletized it was forwarded to Microwave-Assisted Pyrolysis (MAP) (Scanship AS, 2019), which allows producing biochar and syngas out of dry waste materials as shown in figure 4.2. Availability of syngas allows avoiding fossil fuel use as it is usually containing a lot of energy-rich components.

Biochar is produced by heating in the full or partial absence of air. Pyrolysis is the most common method for biochar production (EBC, 2021). Production is usually conducted under a temperature in the range of 350 to 1000 °C. All the biochar samples were produced with the same heat exposure time (20 mins) but with different temperatures in the range of 550-800 °C.

Figure 4.2 – Microwave-Assisted Pyrolysis system (MAP) (Scanship AS, 2019)

4.2 Characterization of biochar

The analyses are planned according to sample amount availability, as well as consideration of which parameters are the most relevant for biochar characterization as an adsorbent, which can be used as a soil amendment or for nutrient recovery and as filtration media for wastewater. Planned work with general information about samples is summarized in table 4.2.

Table 4.2 – Sample list with information and planned analyses for characterization

				Physical characterization							Chemical characterization	
#	Samples source	t, °C	Remark	pH	Electrical conductivity	Specific surface area	TS+VS	Ash + moisture content	Bulk density	Image analysis	EDTA	Decomp + ICP-MS
1	Wood pellets Hallingdal	550	Unwashed	+	+			+	+	+	+	+
2		600	Unwashed	+	+	+		+	+	+	+	+
3		600	Treated in air/oxygen 900 °C	+	+	+		+	+	+	+	+
4		700	Unwashed	+	+	+		+	+	+	+	+
5		700	Washed							+		
6		750	Unwashed	+	+			+	+	+	+	+
7	Slam-biorest Lindum/Vesar	-	Source	+	+		+	+	+		+	
8		500	Unwashed	+	+			+	+	+	+	+
9		600	Unwashed	+	+	+		+	+	+	+	+
10		700	Unwashed	+	+	+		+	+	+	+	+
11		700	Washed							+		
12		800	Unwashed	+	+			+	+	+	+	+
13	Ullensaker slam	-	Source	+	+		+	+	+		+	
14		700	Unwashed	+	+	+		+	+	+	+	+
15		800	Unwashed	+	+			+	+	+	+	+

4.2.1 Sample preparation

All the samples were prepared according to ISO 11464:1994(E) (Technical Committee ISO, 1994). Originally most of the standards are developed for the characterizing of the soil properties, however, these methods were advised to use by European Biochar Foundation (EBC) (EBC, 2021), as biochar reassembles soil structure. While soil samples usually undergo a sequence of pretreatment procedures, which includes drying and crushing of the samples, drying is not needed for biochar since it is produced by pyrolysis (unless it was stored in high humidity conditions).

The biochar sample should be homogenized and dried (by air-drying or drying under 40 °C after that divided into representative portions. These portions are taken by the quarter method of the preliminary homogenized biochar (Eija Alakangas, 2015) and then used for further physical and chemical analyses.

4.2.2 Physical properties characterization

4.2.2.1 pH (in H_2O) and Electrical conductivity

pH was measured according to (Coleman et al., 1951) and EC according to (EBC, 2021; Marshall, 1978; Technical Committee ISO, 1996; VDLUFA, 2003). For pH/EC measuring, a mixture of 1 (dry sample): 2.5 (distilled water) was placed in the tube, thoroughly mixed, and left overnight for equalization. The next day, after all the particles are settled, first EC is measured by Conductometer 712 (Metrohm) and then pH by digital standard pH-meter PHM210 (Meterlab) with combined pH electrode. For more detailed methodology see appendix B.1.

4.2.2.2 Total Solids (TS) and Volatile Solids VS

Total solids and volatile solids were determined according to Method 1684 (Telliard, 2001). For this purpose, about 10 g of each source material (2 parallels for each source) were placed into metal plates weighted, dried in the drying oven (105 °C for 2 h), weighted again, dried in the ignition furnace (550 °C for 20 mins). For more detailed methodology see appendix B.2. All the values are then used for further calculations of total, fixed, and volatile solids by using followed formulae:

$$\%\, Total\ solids\ (TS) = \frac{m_{dried} - m_{blank}}{m_{sample} - m_{blank}} \cdot 100\% \quad (4.1)$$

$$\%\, Fixed\ solids\ (FS) = \frac{m_{volatile} - m_{blank}}{m_{dried} - m_{blank}} \cdot 100\% \quad (4.2)$$

$$\%\, Volatile\ solids\ (VS) = \frac{m_{dried} - m_{volatile}}{m_{dried} - m_{blank}} \cdot 100\% \quad (4.3)$$

where: m_{blank} – weight of empty evaporation dish, g;
m_{sample} – weight of the dish and wet sample, g;
m_{dried}– weight of the sample and dish after drying 105 °C, g;
$m_{volatile}$ – weight of the sample and dish after ignition 550 °C, g.

It is very essential to keep temperature stable and time should neither exceed nor be less than it is stated in the method as different processes can take place that can influence weight to a great extent:

- weight loss due to volatilization of organic material on the drying stage;
- weight gain due to the oxidation;
- mechanical occlusion and crystallization of water;
- heat-induced chemical decomposition, etc.

4.2.2.3 Moisture and ash content

Moisture and ash content method according to (EBC, 2021; Mclauglin, 2010). Raw samples should be homogenized and crushed to obtain uniform powder-like material. Then 1 g of sample is weighed with accuracy 0.01g, spread evenly on the drying metal dish, and dried in an oven (preheated to 40 °C) until constant mas. After the drying, samples should be put into the desiccator (to avoid absorbing air humidity) and weighed. Recorded values are used for moisture calculations according to the followed formula:

$$W, \% = \frac{m_{sample} - m_{dried}}{m_{sample}} \cdot 100\% \quad (4.4)$$

where m_{sample} – weight of the wet sample, g;
m_{dried} - weight of the sample after drying at 40 °C.

After that place samples in the muffle oven preheated to 550 °C and ignite until constant mass. Repeated the same weighing procedure and use recorded numbers to calculate ash content as follows:

$$Ash(dry\ basis), \% = \frac{m_{ash}}{m_{dried}} \cdot 100\% \quad (4.5)$$

where m_{dried} – weight of the sample after drying 40 °C;
m_{ash} - weight of the sample after ignition 550 °C.

4.2.2.4 Bulk density

The bulk density of the biochar was determined according to ISO 11272:20117(E) (EBC, 2021; ISO 11272:2017, 2017). Graduated cylinder filled with sample biochar that determined by the weighting of compressed by falling biochar. Bulk density is calculated from the mass and volume of the sample [kg/m^3]. For each sample weigh measurements were performed 10 times as some of the biochar pieces are quite fragile and were breaking easily.

4.2.2.5 Specific surface area

Specific surface area using BET measurement according to ISO 9277 (Technical Committee ISO, 2010). Preliminary dried samples are placed in the Belsorb MINI X, which is shown in figure 4.3 (Microtrac Retsch GmbH, 2021).

Figure 4.3 – Equipment for BET-analysis: Belsorb MINI X (Microtrac Retsch GmbH, 2021)

N_2 gas is dosed in the equipment chamber and adsorbed on the biochar surface (Figure 4.4, (MCA Services, 2020)). First, it fills micropores and covers the surface of mesopores and macropores, creating a monolayer on the biochar surface. Then multilayer starts to appear, filling first mesopores and then macropores. Based on adsorbed nitrogen gas and relative pressure adsorption/desorption isotherms are built.

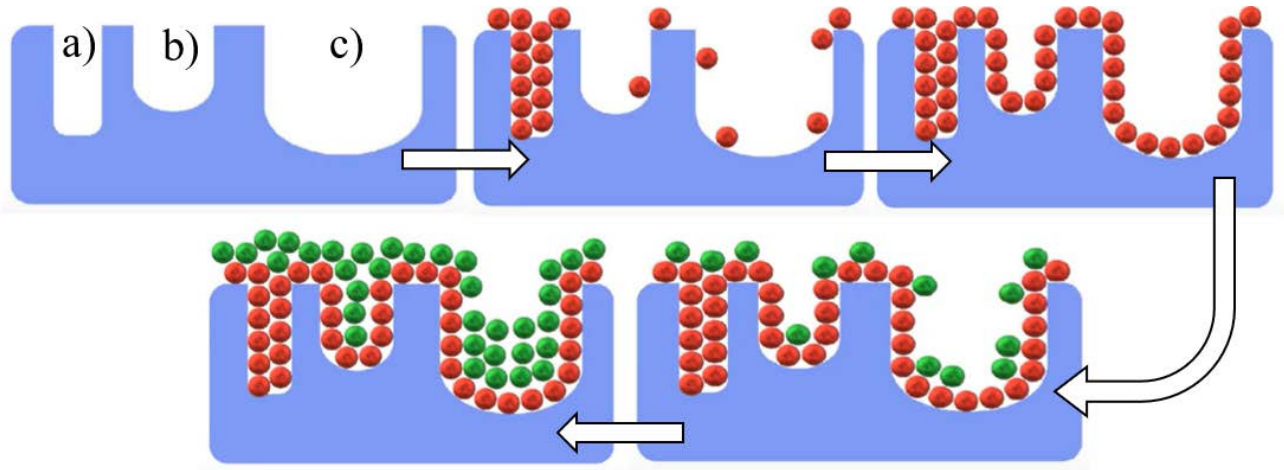


Figure 4.4 – N_2 adsorption on the biochar surface: a) micropores; b) mesopores; c) macropores (MCA Services, 2020)

4.2.3 Optical characterization

Representative sample pieces for each biochar sample picked and placed on the sample holder as it is shown in figure 4.5. After samples are placed in Zeiss EVO scanning electron microscope (figure 4.6 (Zeiss Germany, 2021)), the most important parameters that were used for taking images is shown in table 4.4.

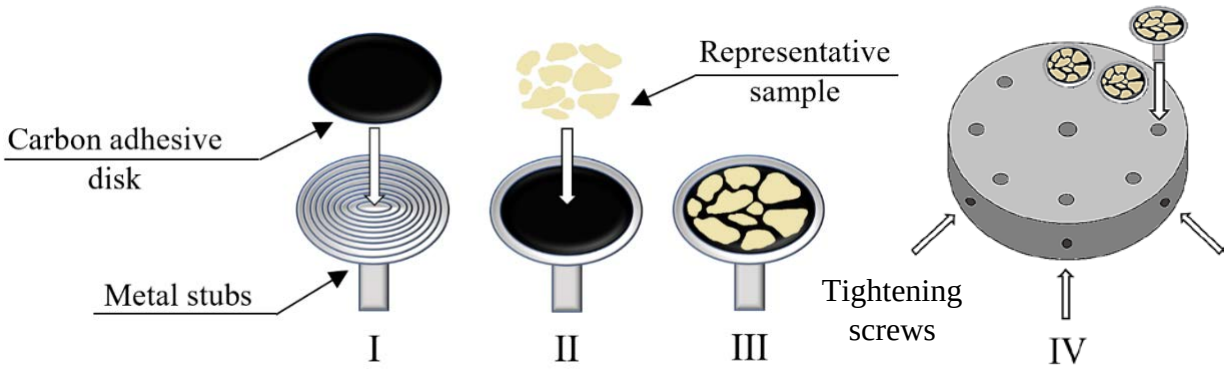


Figure 4.5 – Sample mounting: I – place the disk on stub; II – place sample pieces on disk; III – make sure that all the pieces are well attached; IV – place stubs into the holder disk and tighten screws

Figure 4.6 – Zeiss EVO 50 EP microscope with BEI and X-ray (Zeiss Germany, 2021)

Table 4.3 – Important parameters for optical characterization

Parameter	Details or specific values
Focal distance	7.5-8.5 mm
Pressure	50 Pa
Magnification levels (SEM)	1500x, 800x, 100x
Magnification level (XRD)	800x
Used detectors	VPSED – Variable Pressure Scanning Electron Detector, QBSD – Quadrant Backscatter Electron Detector
Amount of imaging points per sample	2-3 points

After all the equipment is ready for imaging it was picked 2-3 points on one sample that has a relatively uniform flat surface. Then for each point, it was manually adjusted focal distance, sharpness, and brightness. As soon as all preparations are finished images can be saved directly to the PC.

4.2.4 Chemical properties characterization

4.2.4.1 Elemental composition (C-H-N)

The elemental analyses (C, H, and N) of the sewage sludge (source material), sewage sludge biochar, and wood pellet biochar were determined using an automatic elemental analyzer using the C-H-N method according to (Bremner & Mulvaney, 2015; Nelson & Sommers, 2015).

Samples were taken according to section 4.3.1 crushed with a pestle and mortar into fine powder. For the determination of main components ($C_{\%}$, $H_{\%}$, $N_{\%}$), 200 mg of each sample was weighed into a tin foil and placed for combustion into LECO CHN628 (figure 4.7). Each element is then measured as a volume of CO_2, H_2O, and N_2 and recalculated to elemental percentage. For detailed methodology see appendix B.3.

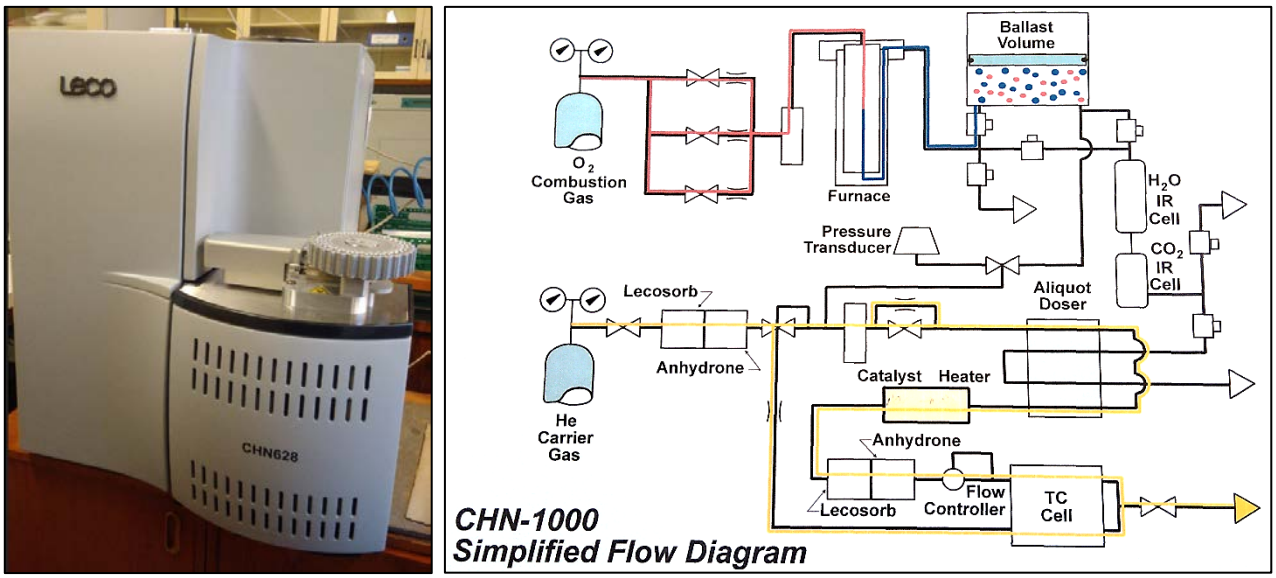


Figure 4.7 – LECO CHN analyzer EC628 and its simplified flow diagram

Preliminary to further calculation proximate oxygen content should be estimated. However, this is associated with a lot of difficulties due to inaccuracy and little reliability of available methods.

Calculated oxygen will not reflect actual content, but will help to estimate dependencies. Oxygen was calculated as by **difference method** (a difference between 100% and concentrations sum of elements measured by elemental and chemical analysis):

$$O_{\%} = 100\% - (C_{\%} + H_{\%} + N_{\%} + Min.c._{\%}) \quad (4.6)$$

$$Min.c._{\%} = \sum Na, Mg, Al, Si, P, S, K, Ca, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Mo, Cd, Hg, Pb\ (\%) \quad (4.7)$$

where $A_r()$ – atomic weight of the specified element, g/mol;
$Elem_{\%}$- percent concentration of the specified element, %;
$Min.c._{\%}$ - percent concentration of minerals in the biochar, as a sum of elements, %.

Organic oxygen is then can be estimated as a difference of total oxygen and inorganic oxygen calculated stoichiometrically.

$$org\ O_{\%} = O_{\%} - in\ O_{\%} \quad (4.8)$$

where $in\ O_{\%}$ - percent concentration of inorganic oxygen, %;
$org\ O_{\%}$ - percent concentration of organic oxygen, %.

From obtained C%, H%, N%, and O%, it is possible to calculate parameters that are necessary for characterization of the biochar: H/C – aromaticity index, C/N – nitrogen availability, O/C – hydrophilicity index, and (O + N)/C – polarity indices.

$$\frac{H}{C} = \frac{H_{\%}/A_r(H)}{C_{\%}/A_r(C)} = \frac{H_{\%} \cdot A_r(C)}{C_{\%} \cdot A_r(H)} = \frac{H_{\%} \cdot 12}{C_{\%} \cdot 1} = 12 \cdot \frac{H_{\%}}{C_{\%}} \quad (4.9)$$

$$\frac{C}{N} = \frac{C_{\%}/A_r(C)}{N_{\%}/A_r(N)} = \frac{C_{\%} \cdot A_r(N)}{N_{\%} \cdot A_r(C)} = \frac{C_{\%} \cdot 14}{N_{\%} \cdot 12} = 1.17 \cdot \frac{C_{\%}}{N_{\%}} \quad (4.10)$$

$$\frac{O}{C} = \frac{O_{\%}/A_r(O)}{C_{\%}/A_r(C)} = \frac{O_{\%} \cdot A_r(C)}{C_{\%} \cdot A_r(O)} = \frac{O_{\%} \cdot 12}{C_{\%} \cdot 16} = 0.75 \cdot \frac{O_{\%}}{C_{\%}} \quad (4.11)$$

$$\frac{O+N}{C} = \frac{(N_{\%}/A_r(N)) + (O_{\%}/A_r(O))}{C_{\%}/A_r(C)} = \frac{(N_{\%}/14) + (O_{\%}/16)}{C_{\%}/12} = \frac{24 \cdot N_{\%} + 21 \cdot O_{\%}}{28 \cdot C_{\%}} \quad (4.12)$$

4.2.4.2 Mineral content, (macro- and micro-elements, heavy metals)

Depending on the feedstock and therefore differences in elemental composition this analysis requires different types of digestion. According to Table 4.2, there are 11 samples for analysis. Before elemental analysis by Inductively Coupled Plasma-Mass-Spectrometry (ICP-MS), digestion was performed by followed chemicals in Milestone Ultraclave at 260 °C (figure 4.9a):

- combination HNO_3 + HCl,
- combination HNO_3 + HF,
- tetra-methyl-ammonium-hydroxide (TMAH) extraction for Cl determination.

A short overview of samples digestion is shown in Table 4.4.

The samples were analyzed by using an Agilent ICP-QQQ-MS in He-KED and oxygen reaction mode (figure 4.8b 9a (Ghent University, 2021)). Samples are placed into the ICP-MS where it is dosed as

aerosol drops (into the heating chamber under a temperature around 7226.9-9726.9°C (7500-10000 K). At this temperature sample changes from liquid matter into a plasmic state of matter. Mass spectrometer separates single charged ions, based on atomic mass. For more detailed methodology see appendix B.4.

Table 4.4 – Digestion summary for all the samples

Sample number	HNO_3/HCl	HNO_3/HF
1, 2, 3, 4, 6 (Wood biochar Hallingdal)	Digested in both HNO_3 and HNO_3/HF	The HNO_3/HF is closer to complete digestion, but some elements like Ca and Mg will precipitate as fluorides, while Fe and Al will co-precipitate.
8, 9, 10, 12 (WS Lindum/Vesar)	Samples, as well as reference material (sewage sludge 3), were not fully digested in HNO_3, a lot of undigested samples were left. Therefore, HNO_3 digestion with additional post digestion by HCl was used for extraction.	
14, 15, 16 (WS Ullensaker)		
	Method is best for followed elements	
	Mg, Al, Ca, Fe, Hg	Na, (Si*), P, S, K, Cr, Mn, Co, Ni, Cu, Zn, As, Mo, Cd, Pb

* *it is hard to identify Si as it won't be dissolved in HNO_3 and HNO_3 / HF digestion Si will form SiF_4 as this is volatile species.*

a)

b)

Figure 4.8 – Equipment for elemental analysis a) digestion set-up; b) ICP-QQQ-MS in He-KED (Ghent University, 2021)

5 Results and Discussions

5.1 Physical properties characterization

5.1.1 pH (in H_2O) and Electrical Conductivity

The pH value of biochar is an important parameter when biochar is used as a substrate in a targeted application, for instance, for nutrient retention and recovery, as a filter media for water and wastewater treatment, as well as in industrial products. The results for pH measurements and EC [mS/cm] are shown in table 5.1. As indicated in the table, the biochar from wood pellets generally showed higher pH than the biochar derived from sewage sludge. As it is stated in many publications, biochar pH can vary a lot based on the source and production temperatures in the range of 3.1-12.0 (B. Singh et al., 2017). pH commonly increases within the same biochar source type with the increase of pyrolysis temperature. This happens due to the followed reasons (Hailegnaw & Karim, 2021):

- with an increase in temperature, ash content also increases, which influences the pH (ash is considered to be a liming material, and about 10% of pH increased resulted from gradual removal of acid functional groups (phenolic, carbonyl, carboxylic (Gaffar et al., 2021)));
- carbonates of Ca and Mg are increasing with pyrolysis temperature (also have alkaline nature);
- oxygen and hydrogen concentrations are decreased with the degree of carbonization due to the weak chemical bound in compounds that make biochar structure.

Table 5.1 – pH and Electrical Conductivity results

#	Sample source	t *[°C]*	Remark	pH	Conductivity *[mS/cm]*
1	Wood pellets Hallingdal	550	Unwashed	8.55	0.458
2		600	Unwashed	9.15	0.860
3		600	Treated in air/oxygen under 900 °C	9.32	0.597
4		700	Unwashed	9.58	0.874
6		750	Unwashed	9.77	1.059
7	Slam-biorest Lindum/Vesar	-	Source	6.72	2.909
8		500	Unwashed	7.49	1.216
9		600	Unwashed	8.08	0.720
10		700	Unwashed	8.90	0.579
12		800	Unwashed	9.25	0.521
13	Ullensaker slam	-	Source	6.41	2.015
14		700	Unwashed	8.11	0.322
15		800	Unwashed	8.35	0.405

Most of the biochar samples show relatively high pH, which would define possible application for the biochar. If talking about the application of biochar as a soil amendment agent, then soil properties also should be considered. According to Colorado State University for healthy growth of most types of plants pH value of soil should not exceed 8.3. pH value 7.5 and higher would result in high iron availability, which can, in turn, lead to plant metal poisoning (Horiba, 2011). The best pH range should be maintained in a range of 6.0 – 7.5, which is acceptable for most plants. Therefore, if any of the biochars presented in the table below are to be used for land application, then they should be applied only for neutral or acidic soil types.

Electrical conductivity value is also an important parameter for biochar as a fertilizer, as it characterizes soluble salts content, which has a great impact on salt-sensitive plants. Biochar electrical conductivity was recorded to be in the range of 0.04-54.2 mS/cm (B. Singh et al., 2017). In the same way as pH, EC is also changing with carbonization degree and type of feedstock. Biochars with high carbon content are typically associated with higher EC values. As is shown in table 4.1 EC value changed differently for wood and WS biochars.

Wood biochar EC increased with carbonization degree, however, samples that had the same production temperature and exposure time (2 and 3) have almost 0.3 mS/cm difference, where second samples (additionally treated in air/oxygen atmosphere under 900 °C). It can be due to an increase in oxygen content. WS from Lindum/Vesar has a relatively low concentration of carbon, and on the contrary to the wood biochar, it was observed EC decrease. Meantime WS from Ullensaker shown an increase of EC with temperature, however, it has higher C content compared to MS from Lindum/Vesar. Both types of biochar shown a rapid decrease in EC between feedstock value and biochar with the lowest production temperature.

5.1.2 TS and VS of source material

To characterize the difference between 2 WS from Lindum/Vesar and Ullensaker a TS + VS test was conducted (results are displayed in table 5.2). All the values were calculated according to formulae in section 4.2.2.2. While %TS for both sources were about the same (around 95.5%), they differed a lot by %FS and %VS. It is clear, that WS2 is much higher in organic matter content but has much less fixed solids (different kinds of salts).

Table 5.2 – Total, fixed, and volatile solids content in the source material

#*	Sample source	TS	FS	VS
		[%]	*[%]*	*[%]*
7	Lindum/Vesar (WS1)	95.8	51.8	48.2
13	Ullensaker (WS2)	95.5	28.9	71.1

** According to the table in section 4.2*

Remaining ash already can characterize samples (figure 5.1). For instance, WS1 had an intense rusty color (sand-like, slightly brownish before the test), which is an indication of Fe^{2+} to Fe^{3+} oxidation. WS2 meanwhile had many black spots, that most likely an organic residue, which can be proved by high %VS.

a) b)

Figure 5.1 – Source material after ignition: a) Lindum/Vesar WS; b) Ullensaker WS

5.1.3 Moisture and ash content

Moisture and ash content analysis results are shown in Table 5.3. All the values were calculated according to formulae in section 4.2.2.3. According to the obtained data, moisture content at first is

lower if compared to the source material, but with the degree of carbonization, it is increasing. This is due to the increase of voltage and % of micropores, which hold water much tighter compared to macropores; this water can not be removed by 40 °C drying. Biochar produced under high pyrolitic temperatures more easily absorbed air humidity and treated samples (wood with treatment in air/oxygen environment at 900 °C), show the highest moisture content and even visually moister look.

Table 5.3 – Moisture and ash content for biochar samples and source material

#	Sample source	t [°C]	Remark	Moisture content [%]	Ash content [%]
1	Wood pellets Hallingdal	550	Unwashed	5.2	4.9
2		600	Unwashed	5.9	4.7
3		600	Treated in air/oxygen under 900 °C	29.5	2.8
4		700	Unwashed	6.2	3.5
6		750	Unwashed	6.9	3.4
7	Slam-biorest Lindum/Vesar	-	Source	1.6	54.8
8		500	Unwashed	0.03	80.3
9		600	Unwashed	0.2	85.9
10		700	Unwashed	0.4	88.4
12		800	Unwashed	0.4	91.6
13	Ullensaker slam	-	Source	2.1	31.1
14		700	Unwashed	0.8	52.4
15		800	Unwashed	1.0	68.0

Sewage sludge is different compared with other biosolids as it contains a much higher percentage of ash. Subsequently, an increase in ash content leads to an increase in the adsorption ability of polar molecules.

Ash content (%) is increasing for WS samples, while for wood samples only decreasing (too high temperature for this type of biomass). This happens since WS sludge contains many minerals that are still stable under 550 °C. For full decomposition higher temperature is required or specific conditions (for instance ignition in the oxygen atmosphere). Ash content results correlated with findings in other studies (Table 5.4) and slight variations depend on the source of the biochar and its mineral content.

Table 5.4 – Ash content for different feedstocks and biochars produced from them

Pyrolysis temperature, °C	Ash, content for different feedstocks, %				
	Waste sludge		PPS*	Bamboo	Pine wood
Source	32.80	-	-	-	0.3
400	-	-	3.08	2.98	2.0
500	57.42	74.21	4.23	4.12	3.1
600	63.24	77.90	4.80	4.65	4.7
700	66.66	81.53	-	-	-
800	68.32	83.93	-	-	-
References	(J. Zhang et al., 2015)	(Chen et al., 2014)	(Sahoo et al., 2021)		(H. Yang & Sheng, 2012)

** PPS – pigeon pea stalk*

5.1.4 Bulk density

Bulk density results are shown in Table 5.5. Typically biochar dry bulk density varies from 80 to 320 kg/m^3, however, the sizable difference in values depends on the density and elemental composition of original biomass feedstock (Brewer & Levine, 2015). The same can be observed for described samples: 3 samples with the same pyrolysis temperature (700°C) have different values. Since wood has much more organic matter compared to WS, it has much lower bulk density as organic matter attributes to high sample volume with a relatively lower weight. At the same time, WS1 and WS2 are highly mineralized and therefore are more compact and denser, with smaller particle sizes if compared with wood biochar.

Figure 5.5 – Bulk density results

#	Sample source	t [°C]	Remark	Bulk density [kg/m^3]
1	Wood pellets Hallingdal	550	Unwashed	290.6
2		600	Unwashed	298.8
3		600	Treated in air/oxygen under 900 °C	342.2
4		700	Unwashed	294.5
6		750	Unwashed	283.7
7	Slam-biorest Lindum/Vesar	-	Source	774.1
8		500	Unwashed	880.2
9		600	Unwashed	849.8
10		700	Unwashed	733.9
12		800	Unwashed	769.3
13	Ullensaker slam	-	Source	496.5
14		700	Unwashed	507.0
15		800	Unwashed	542.4

Relatively high bulk density values of WS are also explained by the way of sludge preparation. For characterized biochar, sludge was pelletized, which caused additional compactness. Overall, bulk density decreases with pyrolysis temperature, however, at a certain point when the pyrolysis temperature is too high it will ruin biochar structure resulting in higher ash content, which fills biochar pores and makes biochar denser.

Low bulk density is likely to reflect the internal porosity of the biochar: the lower the bulk density the more porous biochar is (Yargicoglu et al., 2015). If biochar is applied as a soil conditioning additive, it changes soil properties, resulting in an overall bulk density decrease. This leads to an increase in soil porosity, soil aeration, and potential improvement of microbial respiration (Askeland et al., 2019), increased root growth, improved water management (Joseph et al., 2018).

In general, bulk density values for wood and WS2 biochar correspond to previously reported data (table 5.6), while WS1 biochar reaches quite high numbers.

Table 5.6 – Bulk densities for some dried feedstocks and biochars produced from them

Material	Bulk density *[kg/m³]*	References
Air-dried wood samples (source material) *	572-960	(Werdin et al., 2020)
Wood samples from Eucalyptus *	140-323	
Agricultural residues (source material)	230	(Sun et al., 2017)
Agricultural residues biochar ($t_{pyrol.}$ = 650 °C)	137	
Nutshell and fruit peel (source material)	387	
Nutshell and fruit peel biochar ($t_{pyrol.}$ = 650 °C)	248	
Livestock manure (source material)	658	
Livestock manure biochar ($t_{pyrol.}$ = 650 °C)	570	
Residual sludge (source material)	690	
Residual sludge biochar ($t_{pyrol.}$ = 650 °C)	539	
Sewage sludge (source material) **	620	(Khanmohammadi et al., 2015)
SW biochar ($t_{pyrol.}$ = 500 °C) **	560	
SW biochar ($t_{pyrol.}$ = 600 °C) **	530	
SW biochar ($t_{pyrol.}$ = 700 °C) **	520	

** Wood samples from Eucalyptus*

*** A secondary anaerobically digested sewage from Isfahan WWTP, Iran*

5.1.5 Specific surface area (N_2-BET)

Specific surface area is a particularly important adsorbent characteristic, which is influenced rather by particles' shape, texture, and porosity than their size (Wolfrom, 2021). Biochar with higher surface area typically has better adsorption properties, however, biochar performance to the great extent is also dependant on the chemical composition, more specific functional groups on the biochar surface. Therefore, it is possible that biochar with lower surface area, but higher surface reactivity might have higher adsorption capacity. From N_2-BET were obtained specific surface area, average pore diameter, total pore, and micropore volume, as well as sorption-desorption isotherms (table 5.7 and figure 5.2). Isotherms are obtained under standard temperature and pressure (STP) conditions.

Table 5.7 – Results from N_2-BET measurements

#*	**Sample source**	**t** *[°C]*	**Remark**	$a_{s\ BET}$** *[m² g⁻¹]*	Average pore diameter *[nm]*	Total pore volume, P/P_0 = 0.99 *[cm³ g⁻¹]*	V_3*** *[cm³ g⁻¹]*
2	Wood pellets Hallingdal	600	Unwashed	313.25	5.4824	0.4293	0.1235
3		600	Treated in air/oxygen under 900 °C	132.26	2.5499	0.0843	0.0527
4		700	Unwashed	402.03	1.8946	0.1904	0.1591
9	Slam-biorest Lindum/ Vesar	600	Unwashed	77.97	7.1359	0.1391	0.0165
10		700	Unwashed	112.76	5.8864	0.1659	0.0195
14	Ullensaker slam	700	Unwashed	122.53	5.8150	0.1781	0.0221

** According to the table in section 4.2*

*** $a_{s,BET}$ – specific surface area*

**** V_3 – micropore volume*

Wood biochar produced with an increase of temperature from 600 to 700 °C also showed an increase in specific surface area $a_{s,BET}$ as well as micropore volume V_3, however average pore diameter and total pore volume at the same time reduces ~2.9 and ~2.3 times respectively. Biochar obtained by pyrolysis with temperature 600 °C, that additionally went through air/oxygen treatment under the temperature 900 °C got much lower in all parameters, due to excessive temperature. Therefore, according to the BET method wood biochar that was produced under 700 °C, without any treatment might have the best sorption potential.

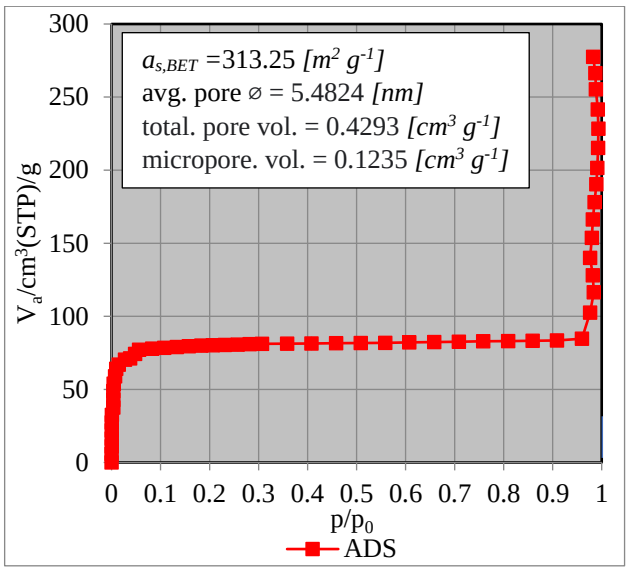
Overall, results obtained from the BET- test have shown relatively high values if compared to findings reported in the articles (summarised in table 5.8), especially surface area for waste sludge. Surface area parameters for characterized WS were about 4-6 times higher, average pore diameter – 2 times lower, and total pore volume – almost 10 times higher than reported by (Chen et al., 2014) and more corresponds to other biochars (from other feedstocks) in table 5.8. As for the wood biochar samples – they correlate with biochars produced out of biological matter with high carbon content.

Table 5.8 – BET-test results for biochars with different feedstocks

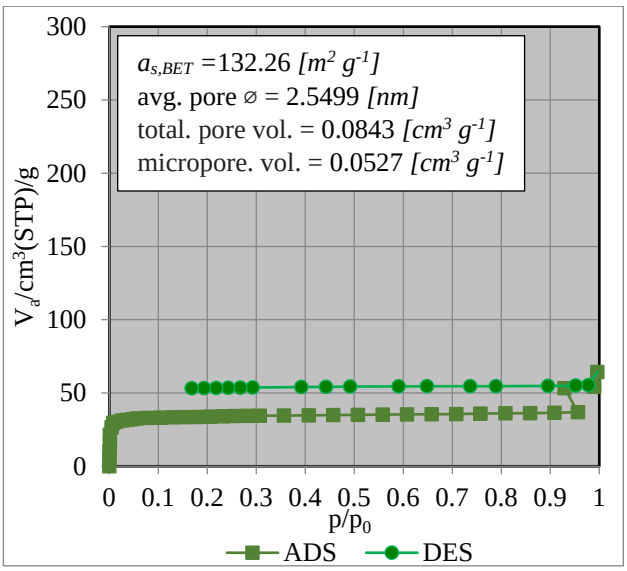
Sample source	**t**	$a_{s\ BET}$*	Average pore diameter	Total pore volume	References
	[°C]	*[$m^2\ g^{-1}$]*	*[nm]*	*[$cm^3\ g^{-1}$]*	
Waste sludge	500	10.79	-	-	(J. Zhang et al., 2015)
	600	10.79	-	-	
	700	18.28	-	-	
	800	19.11	-	-	
	500	25.42	3.74	0.056	(Chen et al., 2014)
	600	20.27	3.76	0.053	
	700	32.17	3.75	0.068	
	800	48.50	3.77	0.090	
Pig manure	600	15.9	-	-	(Kołodyńska et al., 2012)
Pigeon pea stalk	400	16.90	5.66	0.024	(Sahoo et al., 2021)
	500	186.08	2.56	0.120	
	600	261.78	2.42	0.160	
Bamboo	400	63.52	3.64	0.057	
	500	225.33	2.55	0.140	
	600	307.10	2.37	0.180	

* $a_{s,BET}$ – *specific surface area*

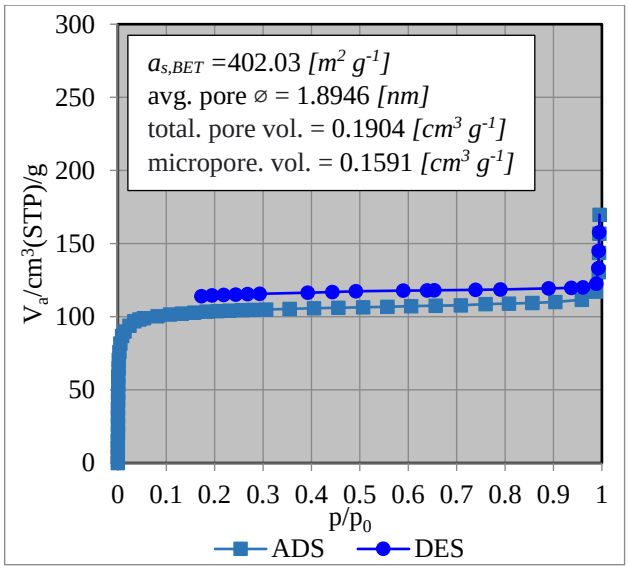
In figure 5.2 low p/p_0 (relative pressure) can be associated with the filling of micropores (rapid increase section of the plot), as relative pressure increases the adsorbate will continue to fill meso- and macropores until monolayer is formed (1 atom thick layer of adsorbate on the biochar surface). This stage forms a plateau section of the plot. And rapid increase in adsorbed volume happens when macropores are filling in. According to figure 5.2a, b, c, when relative pressure reaches ~0.15, biochar 2,3 and 4 adsorbs ~79.5, ~33.6, and 102.9 cm^3 of N_2/g of biochar. All plots can be classified as type IV isotherms, where hysteresis between adsorption and desorption occurs, which means that adsorption is reversible but not at the same rate.



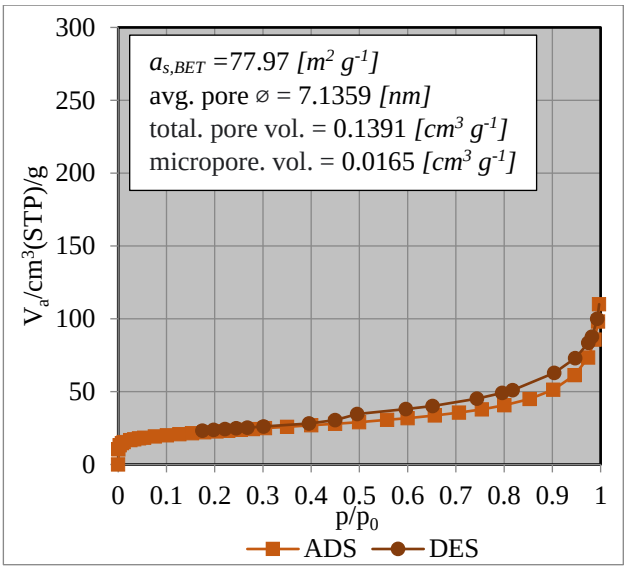
a) Wood biochar: $t_{pyrol.}$ = 600 °C, Hallingdal



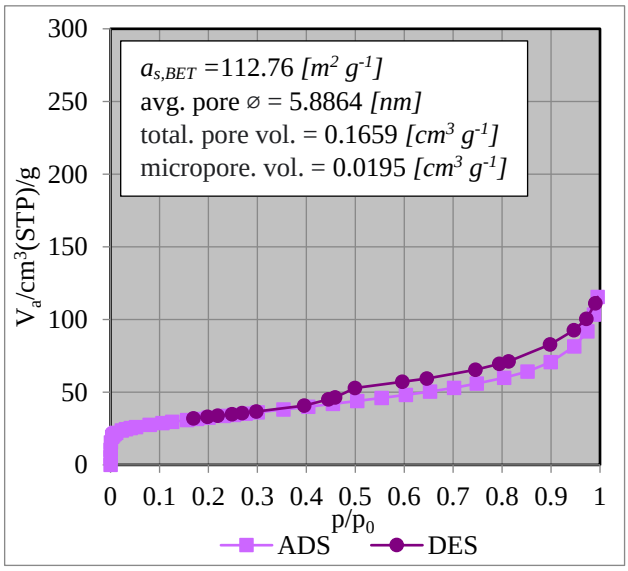
b) Wood biochar: $t_{pyrol.}$ = 600 °C + air/oxygen with 900 °C, Hallingdal



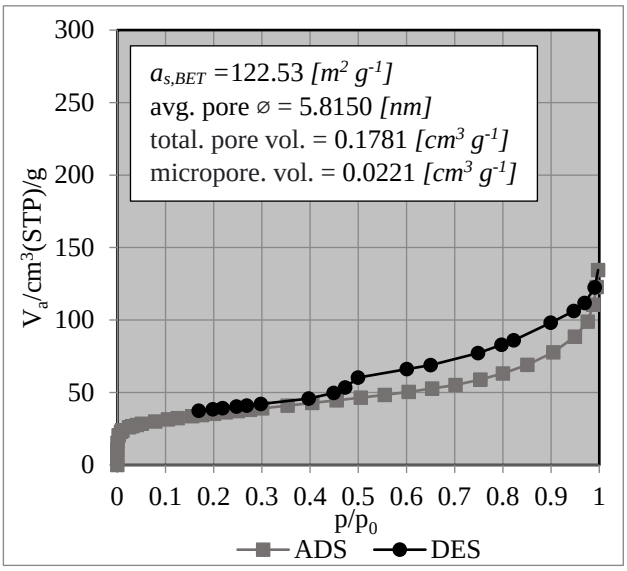
c) Wood biochar: $t_{pyrol.}$ = 700 °C, Hallingdal



d) WS: $t_{pyrol.}$ = 600 °C, Lindum/Vesar



e) WS: $t_{pyrol.}$ = 700 °C, Lindum/Vesar



f) WS: $t_{pyrol.}$ = 700 °C, Ullensaker

Figure 5.2 – Isotherms for biochar samples: ADS – adsorption carve, DES – desorption carve

Biochar produced from the WS that origins from Lindum/Vesar have the same tendency as wood biochar: increase of total pore and micropore volume as well as reduction of other parameters. However, there is a significant difference in pore size distribution for wood and sludge-derived biochars. In the case of waste sludge pore proportion of micropores is much lower (figure 5.2d, e) and the biochar surface has all kinds of pore sizes, which is represented in the absence of the plateau section of the plot and gradual increase of adsorbed volume instead.

Everything written above is also applicable for Ullensaker biochar (figure 5.2 f) as it has a very similar sorption/desorption isotherm as Lindum/Vesar biochar at 700°C productions, as well as main parameters (slightly higher in everything, but average pore size). Therefore, both waste biochars from this perspective should perform similarly.

5.2 Optical characterization: SEM and XRD

For optical characterization scanning electron microscopy (to investigate changes and differences in biochar morphology) and X-ray diffraction (element distribution on the biochar surface) were performed. During these analyses, it was observed differences between:

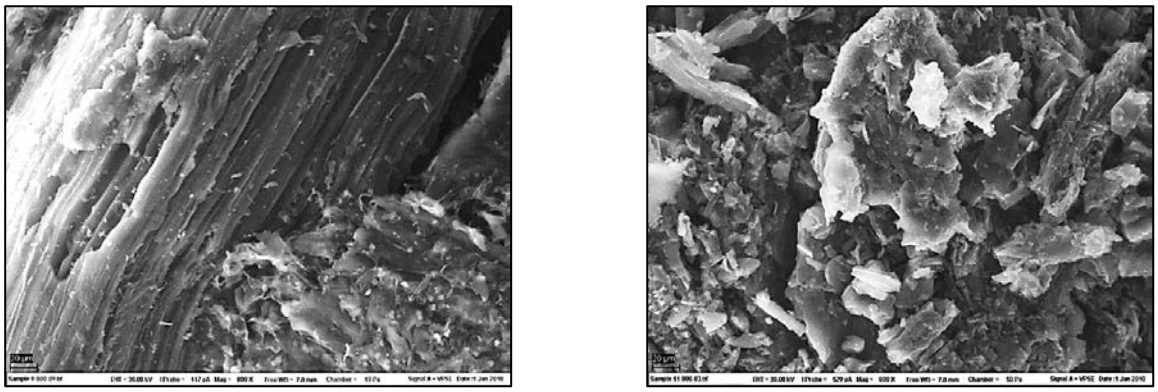
- biochar with the same feedstock, but different temperature;
- treated and not treated biochar;
- washed and unwashed biochar;
- biochar sample produced under the same temperature but from different feedstocks;
- special features on the biochar surface.

5.2.1 Effect of pyrolysis temperature on biochar production

Pyrolysis temperature has a significant effect on the chemical and surface charge properties, cation and anion exchange capacity, elemental composition, surface area, and pore volume of the biochar produced from wastewater sludge. With the change of the production temperature, the same trend was observed for all kinds of biochar (SEM for all biochar types is shown in appendix C): with an increase of carbonization, most of the elements are getting brighter and more visible on the biochar surface, more organic matter is burned away and all the biochars tend to be smaller in size with temperature increase. Also, the concentration of many elements is increasing due to mineralization, while oxygen content is decreasing, due to the breakage of weak bonds in compounds.

5.2.2 Modified and unmodified biochar

One of the biochar samples (wood biochar from Hallingdal produced under 600 °C) was additionally treated in the presence of oxygen at the temperature of 900 °C to improve the sorption characteristics of the biochar. According to SEM images shown in figure 5.3, the modified biochar showed a structural modification, which resulted in a reduced size and higher fragility than the unmodified biochar. As for XDR results shown in figure 5.4, Potassium (K) showed increased concentration in the modified biochar. However, the Ca concentration remained relatively the same.



Unmodified wood biochar Modified wood biochar

Figure 5.3 – SEM for unmodified and modified (additionally treated) wood biochar

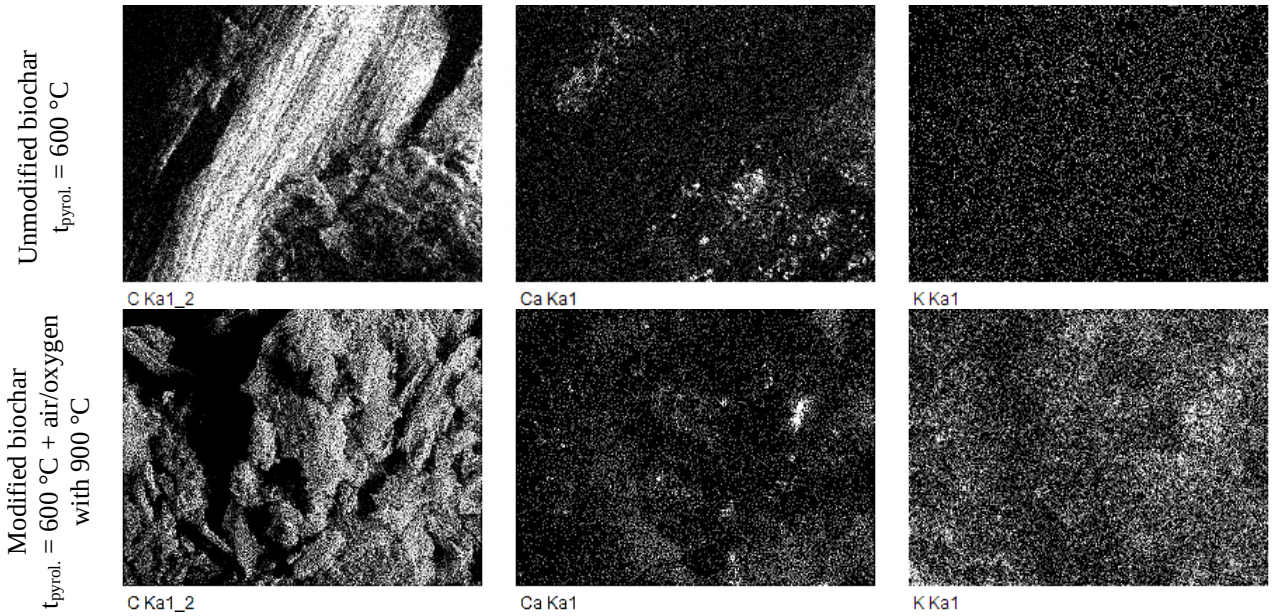


Figure 5.4 – Full mapping for unmodified and modified biochar by XRD

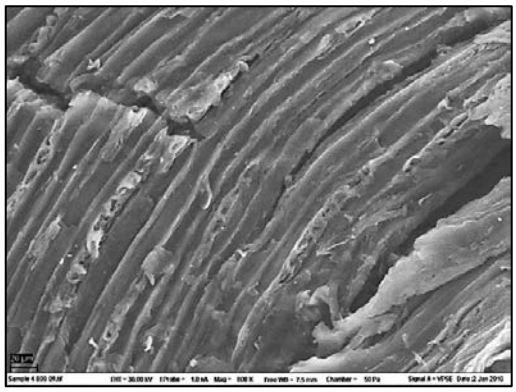
5.2.3 Different feedstock, same pyrolysis temperature (washed/unwashed)

To estimate nutrient availability for the plant, biochar samples were washed with water several times and the SEM + XRD was performed from the sample before and after washing. For this test samples produced at 700 °C were picked for wood and WS biochar. In the case of wood biochar, originally it was covered with many particles (figure 5.5) of different sizes, which is considered to contain high concentrations of Ca^{2+} and K^{+} according to XDR results (figure 5.6).

However, after intensive washing, most of the elements were washed out leaving a clear wood structure. Potassium was reduced to the extent that it wasn't picked by XDR measurements, while there is still some calcium left, that is strongly attached to the biochar surface.

As for WS (Lindum/Vesar was analyzed) biochar, visually it did not show too much difference (figure 5.7): water washed away ash, which wasn't attached to the biochar surface. As for elemental distribution such elements as P, Na, and K were washed away, as well as pieces of Ca and Mg (figure 5.8 and 5.9). According to the results for biochar produced from Ullensaker WS, it looks very similar to the waste sludge biochar from Lindum/Vesar, however, according to XRD WS2 biochar has much relatively higher concentrations of C, Al, P, and much lower Fe concentration compared to WS1 (figure 5.10).

Unwashed wood biochar



Washed wood biochar

Figure 5.5 – SEM for wood biochar samples without and with washing

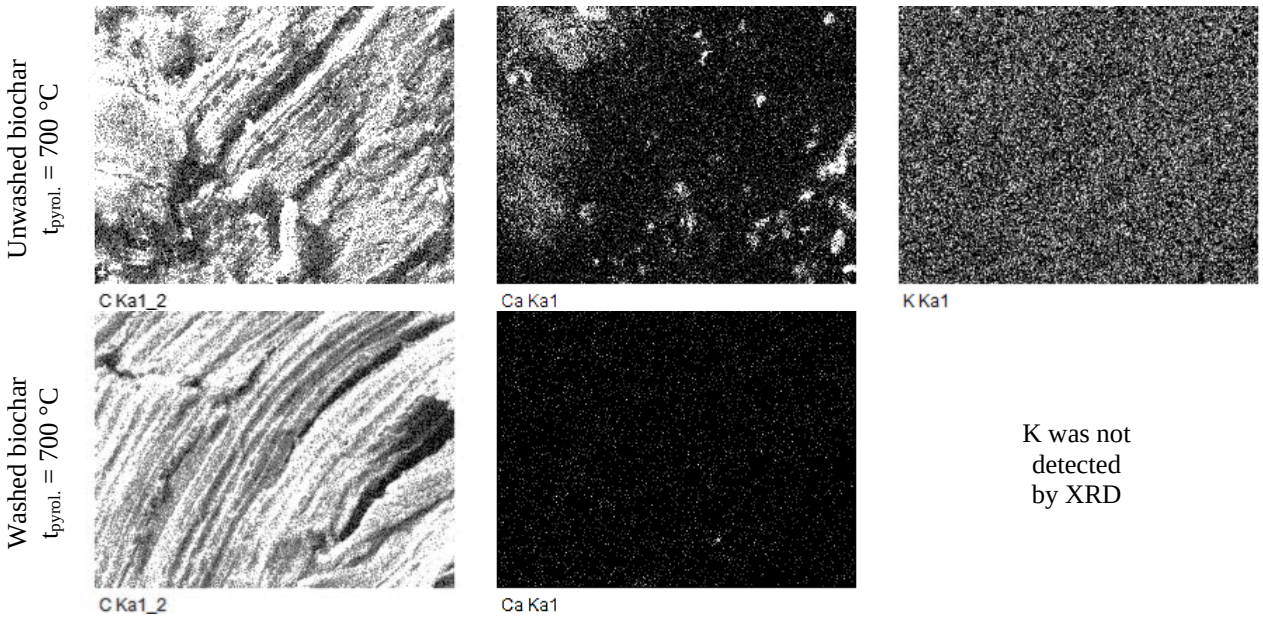
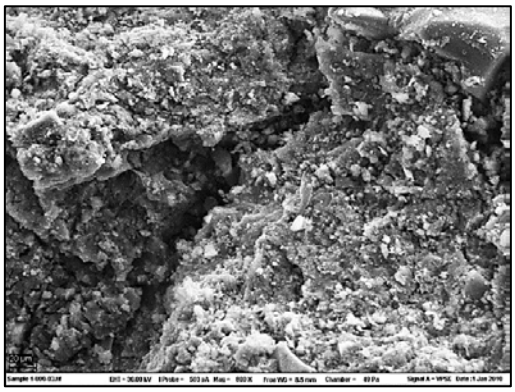
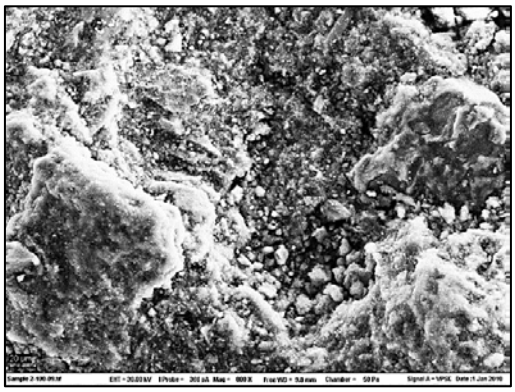


Figure 5.6 – Full mapping for unwashed and washed biochar by XRD



Unwashed WS biochar (Lindum/Vesar)



Washed WS biochar (Lindum/Vesar)

Figure 5.7 – WS biochar samples without and with washing

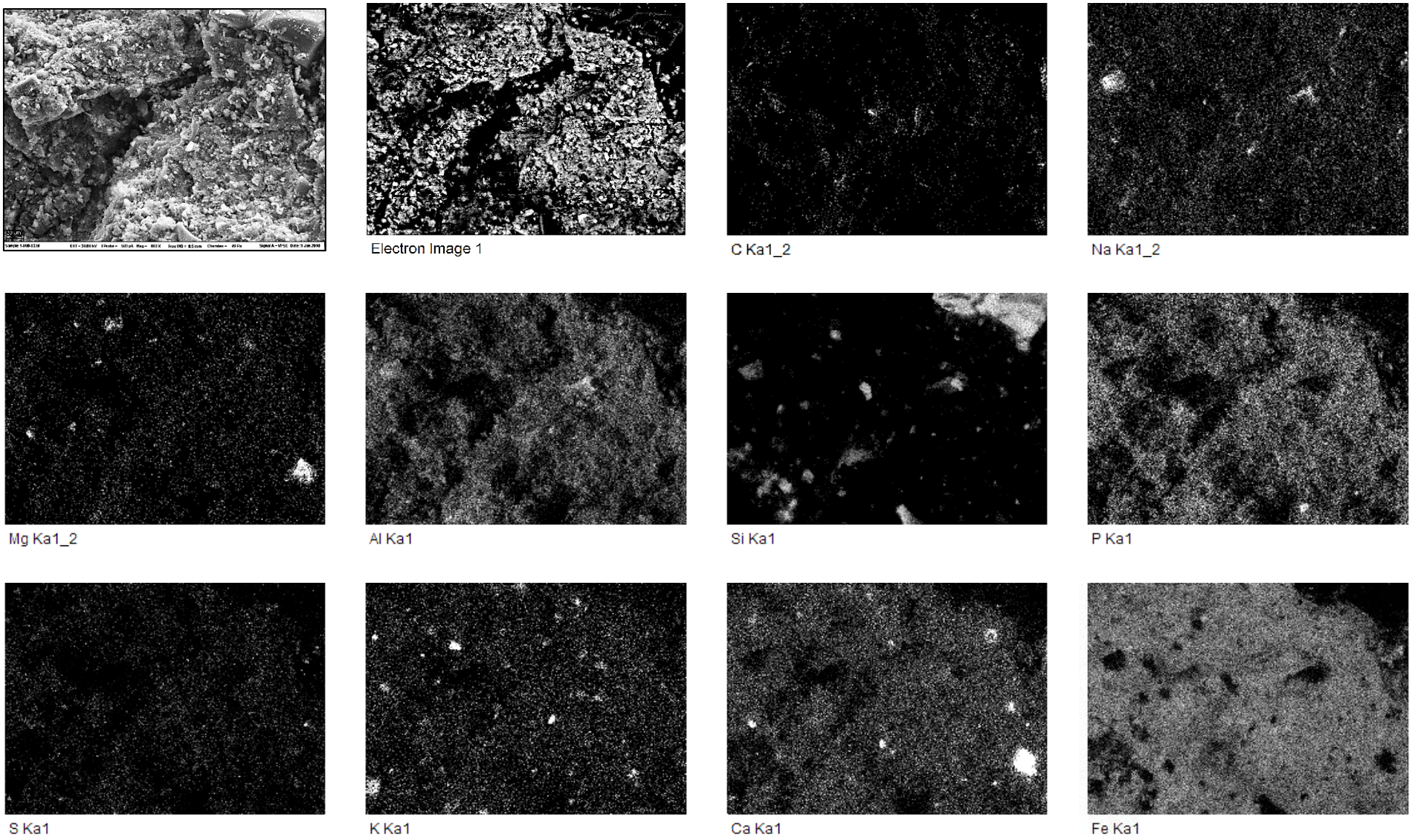
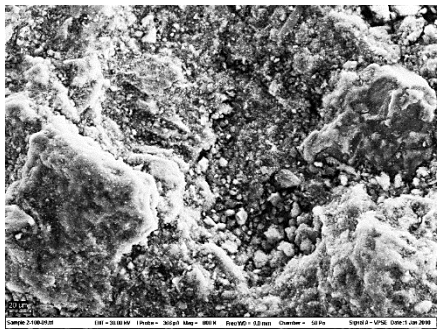
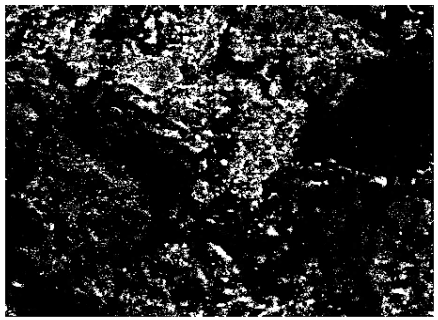
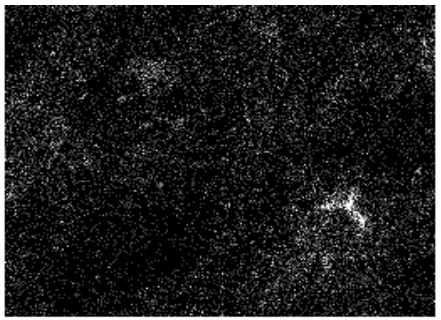


Figure 5.8 – Full mapping for unwashed biochar from Lindum/Vesar; $t_{pyrol.}$ = 700 °C by XRD



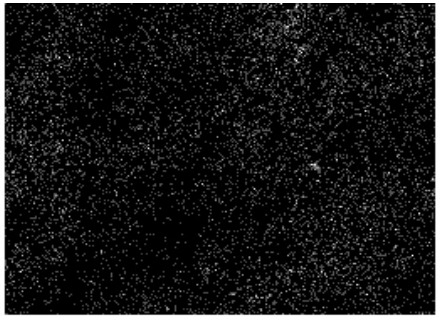


Electron Image 1

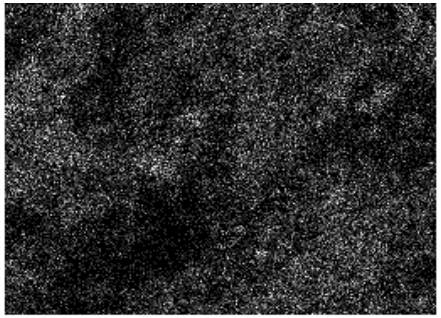


C Ka1_2

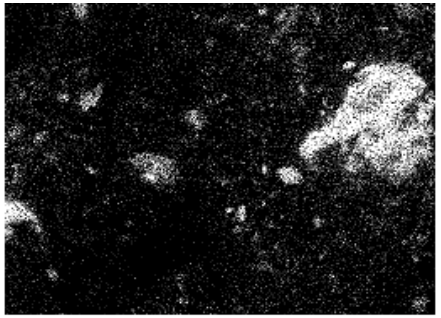
Na was not detected by EDX



Mg Ka1_2



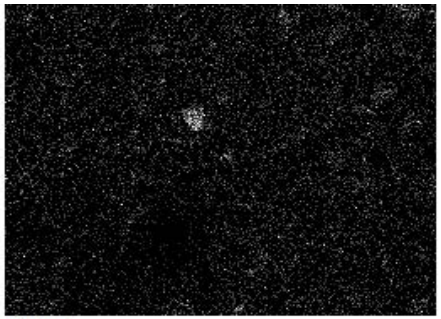
Al Ka1



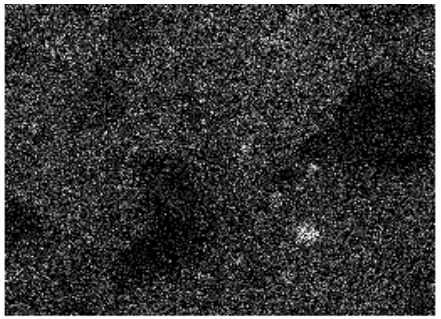
Si Ka1

P Ka1

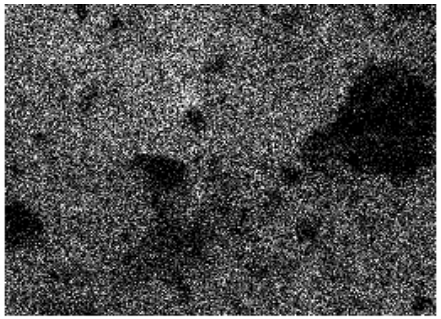
S Ka1



K Ka1



Ca Ka1



Fe Ka1

Figure 5.9 – Full mapping for washed biochar from Lindum/Vesar; $t_{pyrol.}$ = 700 °C by XRD

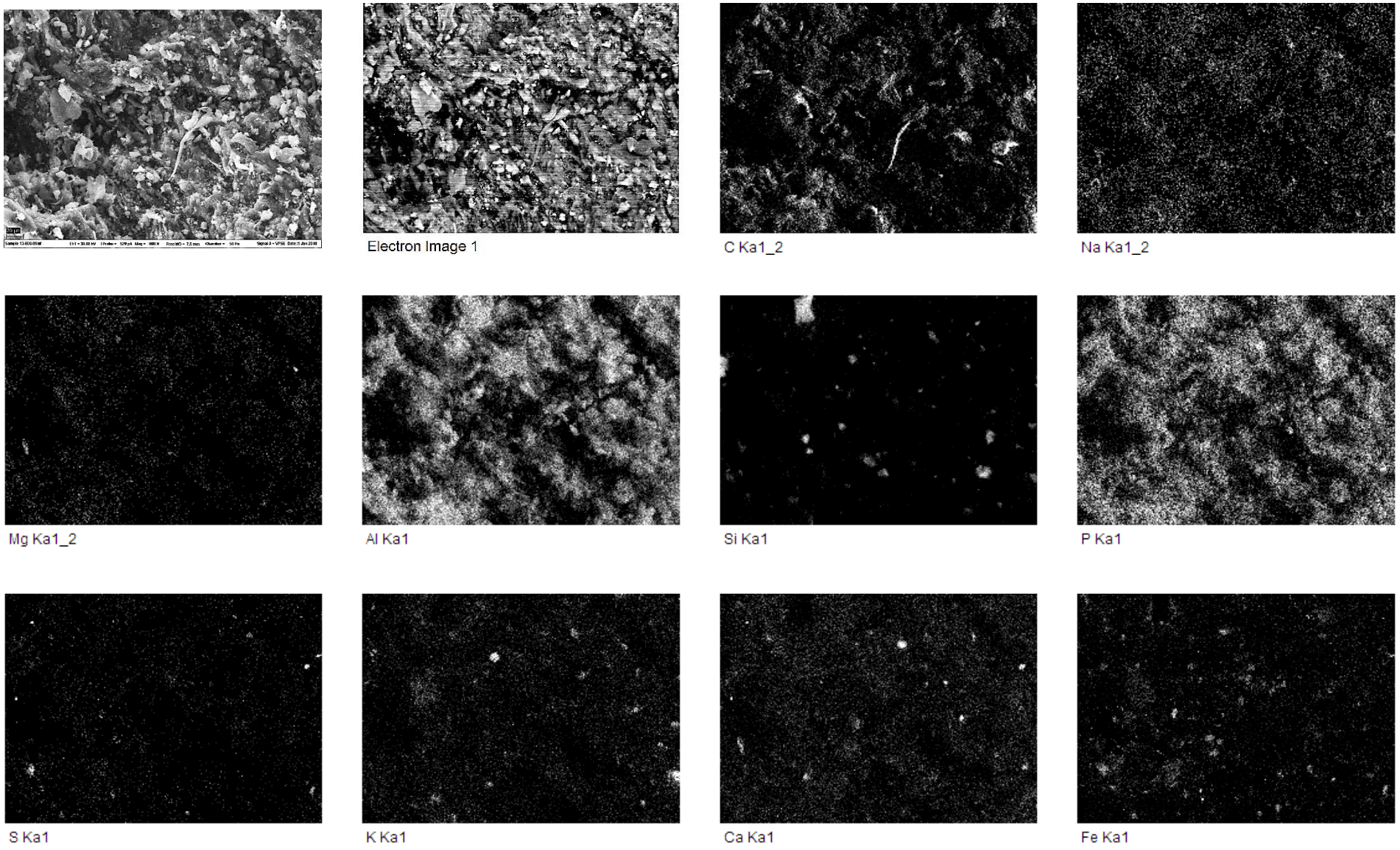
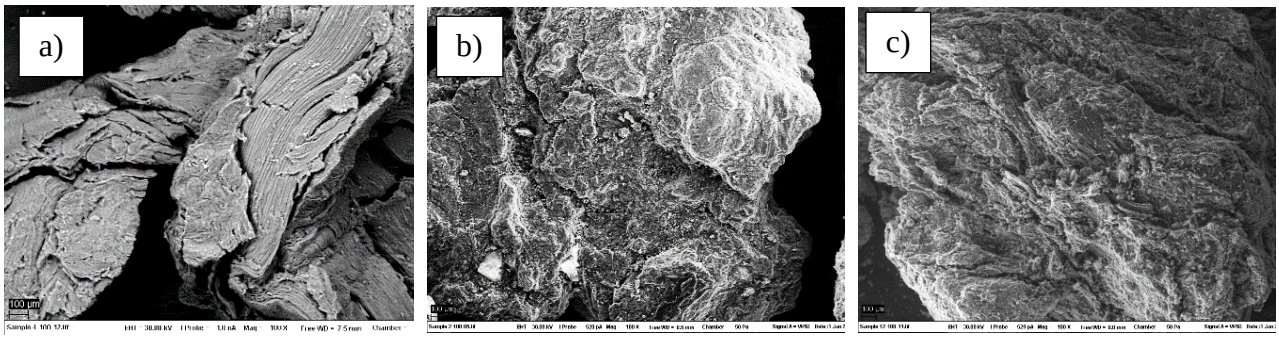


Figure 5.10 – Full mapping for unwashed biochar from Ullensaker; $t_{pyrol.}$ = 700 °C by XRD

5.2.4 Biochar produced from different sources

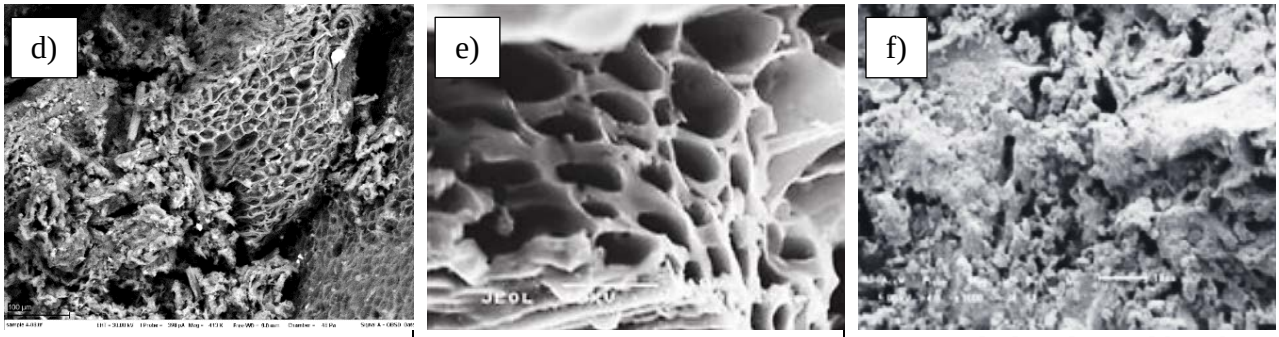
Biochar feedstock is one of the most important parameters, that defines physical and chemical properties, which in its turn will identify possible uses and final destination of the biochar. In figure 5.11 different biochars are displayed. According to figure 5.11b, c, f, WS biochar surface tends to look highly mineralized with a lot of small sediments attached to the surface, some are easy fall off, and some are tightly attached to the surface. Meanwhile, biochar produced from sources with relatively low mineral content keeps the structure of the original material: wood structure for Hallingdal biochar (Figure 5.11a) or honeycomb-like highly porous structures.



Hallingdal W biochar $t_{pyrol.}$=700 °C

Lindum/Vesar WS biochar $t_{pyrol.}$=700 °C

Ullensaker WS biochar $t_{pyrol.}$=700 °C



Spent coffee grounds biochar	Rice husk biochar	Sewage sludge-derived biochar
(Calabrese, 2020)	(Claoston et al., 2014)	(Leng et al., 2021)

Figure 5.11 – SEM of biochars produced from different sources

As biochar characteristics, along with the structural and visual differences vary to a great extent, it is too ambitious to predict biochar properties, unless biochars from similar or same feedstock are obtained. Also, it is important to identify the purpose of comparison, for instance, one biochar is considered to be “bad” for agricultural purposes, however, it might be much better than the other one for selective removal of toxic compounds, due to the high metal content.

5.2.5 Other observations

During XRD full mapping analyses, Ti presence was observed (most likely in form of TiO_2). It was not characterized by chemical analysis but will be discussed below.

As it follows from figure 5.12 Ti has higher concentrations with the increase of pyrolysis temperature (degree of carbonization). WS from Lindum/Vesar has the highest concentration, nothing was detected for the wood biochar, and relatively lower amounts are detected for WS from Ullensaker.

Titanium dioxide was detected in the Lindum/Vesar waste sludge. It naturally occurs in the soil (commonly present in many igneous and metamorphic rocks or sediments (Scheinost, 2005)) as well as it is increasingly used in different commercial products (as a white pigment in medicine, food, make-up, plastics, ceramics, paper, etc (University of Leeds, 2008)), therefore it is possible to observe its presence in food waste sludge and municipal wastewater sludge. According to the study by Paul Westerhoff et al., raw sewage water can have from 181 to 1233 μg/L of Ti (Westerhoff et al., 2011).

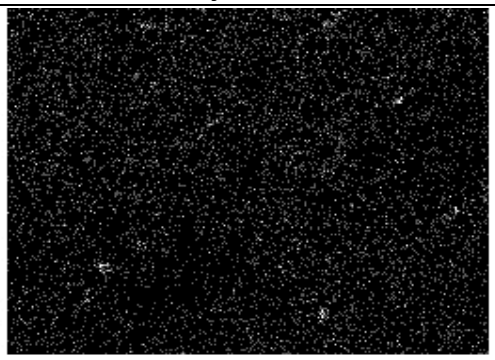
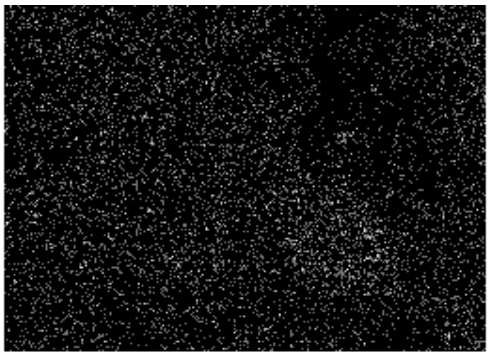
t_{pyrol}	WS from Lindum/Vesar	WS from Ullensaker
500 °C	Ti was not detected by XRD	The sample is not available
600 °C	 Ti Ka1	The sample is not available
700 °C	 Ti Ka1	Ti was not detected by XRD
800 °C	 Ti Ka1	 Ti Ka1

Figure 5.12 – Ti distribution from the full mapping analysis by XRD

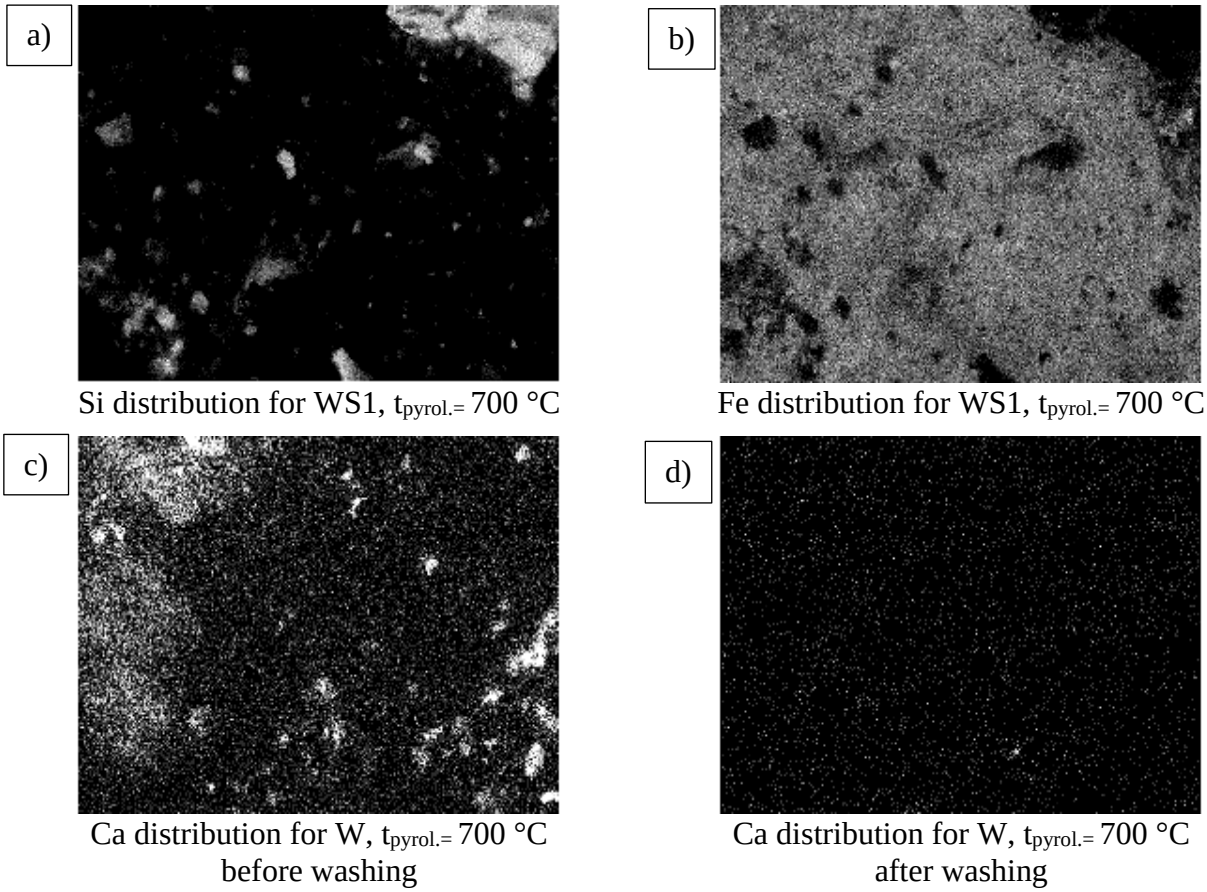
TiO_2 is not toxic, resistant to corrosion, has relatively low cost, physically and chemically stable. Because of its properties, it has a high variety of applications (it is widely known for application in nanotechnology, namely for immobilization of heavy metals, as a coagulant for wastewater treatment, as a catalyst, for nanomaterial synthesis, etc). It was documented the successful use of titanium dioxide as a catalyst for oily sludge treatment (Dang et al., 2021), for Cr (III) removal (S. Yang et al.,

2021), a combination of silver and titanium oxides for phenol removal (Mustapha et al., 2021), also TiO_2 can be used for the immobilization of heavy metals on the biochar surface.

It is hard to estimate the actual amount of Ti in the biochar from XRD scans, therefore before any considerations and potential uses additional chemical analysis should be provided. However, it was reported 87-828 mg/kg of Ti in the biosolids/sludge and 400-4000 mg/kg of Ti in sewage sludge ash (Mulchandani & Westerhoff, 2016).

5.2.6 Importance and interpretation of optical characterization

X-ray diffractometry results give information about the element distribution on the biochar surface. The more bright and coarse texture in the image shows higher concentrations of the elements. According to figure 5.13 elements can be distributed either irregularly or uniformly. For instance, Si in figure 5.13a is unevenly distributed, while Fe in figure 5.13b shows much concentration and uniform distribution. Similarly, when comparing unwashed (figure 5.13c) and washed (figure 5.13d) samples – elements can be loosely attached or tightly connected to biochar structure. This information is very important to identify possible applications of biochar as it shows the extraction potential of each element.



Si distribution for WS1, $t_{pyrol.=}$ 700 °C

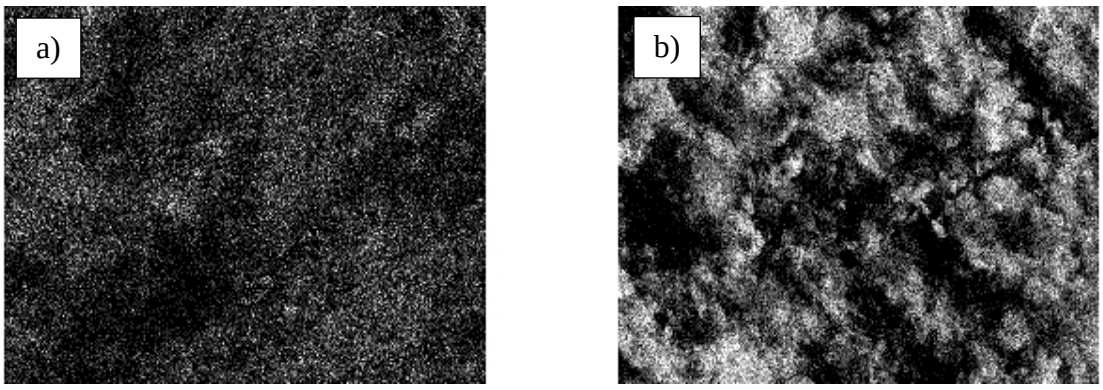
Fe distribution for WS1, $t_{pyrol.=}$ 700 °C

Ca distribution for W, $t_{pyrol.=}$ 700 °C before washing

Ca distribution for W, $t_{pyrol.=}$ 700 °C after washing

Figure 5.13 – Difference in element distribution on full mapping by XRD

However, since full mapping is based on the elemental ratio in the sample, sometimes it is hard to interpret and compare results for different samples. For instance, Al concentration for Ullensaker WS (figure 5.14a) seems to be much higher than for WS from Lindum/Vesar (figure 5.14a), however, chemical analysis shows similar Al concentration for WS1 and WS2, which is 20 g/kg and 19 g/kg respectively.



Al distribution for WS1, $t_{pyrol.=}$ 700 °C Al distribution for WS2, $t_{pyrol.=}$ 700 °C

Figure 5.14 – Misinterpretation of element concentrations

Therefore, the XRD results may be influenced by the concentrations and ratios of elements in the sample, analysis time, presence of possible interferences, etc. XRD results should be always supplemented with chemical analysis to provide full information about the surface characteristics of the different biochar samples. At the same time, elemental/chemical analysis alone reflects elemental composition in g/kg and does not give any information on the element distribution on the biochar surface. Overall, if both analyses are conducted it would reduce the risk of possible misinterpretation of data.

5.3 Chemical properties of the biochar

5.3.1 Elemental composition (C-H-N)

There are many challenges related to O% estimation, as the conventional difference method is not accurate, due to inorganic O% that remains in ash, and if acid washing is applied, it removes most of the ash as well as about 10-17% of organic O%. Oxygen calculation by stoichiometric ratios allows estimating only inorganic oxygen, as it is impossible to predict what kind of compounds are present in the biochar sample, especially for organic compounds. It is specifically hard to estimate O% for mineralized biochar samples (in our case waste sludge-derived biochar), due to the low carbon content while having high concentrations of oxygen (Bakshi et al., 2020). Direct oxygen measurements are quite rare (for instance X-Ray photoelectron spectroscopy (XPS) method), and therefore for biochars with low ash content, the conventional difference method is used more commonly (Söderqvist, 2019).

Results for oxygen calculation are displayed in table 5.9. All the values were calculated according to the formulae 4.6-4.8. Results of elemental and chemical (ICP-MS) analyses were used in the Modified difference method to estimate total oxygen content. Instead of ash content sum of all the elements measured by ICP-MS was used. However, there was a difficulty in measuring Si content, as in the lab, where analyses were performed, were no standards method. So, digestions did not give perfect results as Si does not dissolve in HNO_3 + HCl, and during HNO_3 + HF, digestion turns into SiF_4, which is a volatile compound. Therefore, the results obtained for ICP-MS for Si represent a minimum Silica content in each sample (which possibly can be much higher), which also would give maximum total oxygen content (minimum possible inorganic Oxygen content and maximum organic Oxygen).

Table 5.9 – Oxygen content calculations

#	Sample source	t	Remark	iO_1 *	oO_1 **	O_1 **
		[°C]		*[%]*	*[%]*	*[%]*
1	Wood pellets Hallingdal	550	Unwashed	0.57	2.79	**3.35**
2		600	Unwashed	0.58	3.00	**3.58**
3		600	Modified	0.48	4.28	**4.77**
4		700	Unwashed	0.67	2.87	**3.54**
6		750	Unwashed	0.62	2.39	**3.01**
8	Slam-biorest Lindum/ Vesar	500	Unwashed	17.67	37.29	**54.95**
9		600	Unwashed	17.99	37.50	**55.49**
10		700	Unwashed	16.18	44.56	**60.74**
12		800	Unwashed	19.32	36.14	**55.46**
14	Ullensaker slam	700	Unwashed	9.12	45.57	**54.69**
15		800	Unwashed	10.44	43.32	**53.77**

** Calculated based on formulae 4.6-4.8.*

*** Values are based on stoichiometric calculations, by using results from elemental and mineral composition analyses.*

The elemental composition of the raw material (excluding wood source), as well as biochar, is shown in Table 5.10. According to this data. C% and N%, content is increasing for wood biochar with a degree of carbonization, while H% was decreasing. At the same time, O% was increasing with temperature, however, it started reducing after 600 °C, this happens as some of the elements become volatile with temperature increase and detach from the biochar surface in form of oxides. Additionally, treated biochar ($t_{pyrol.}$ = 600 + treatment in air/oxygen atmosphere at 900°C), has shown much lower C%, N% and much higher H% and O%.

Table 5.10 – Content of the macroelements in the biochar (C, H, N)

#	Sample source	t	Remark	Total C	Total H	Total N	Total O
		[°C]		*[%]*	*[%]*	*[%]*	*[%]*
1	Wood pellets Hallingdal	550	Unwashed	92.24	2.43	0.60	3.35
2		600	Unwashed	92.70	1.71	0.60	3.58
3		600	Modified	91.54	1.93	0.56	4.77
4		700	Unwashed	92.93	1.31	0.65	3.54
6		750	Unwashed	93.68	1.04	0.74	3.01
7	Slam-biorest Lindum/Vesar	-	Source	20.73	3.29	2.16	N/A*
8		500	Unwashed	14.91	1.71	1.20	54.95
9		600	Unwashed	14.69	1.10	0.96	55.49
10		700	Unwashed	14.15	0.89	0.68	60.74
12		800	Unwashed	13.23	0.77	0.47	55.46
13	Ullensaker slam	-	Source	31.71	4.75	2.94	N/A*
14		700	Unwashed	28.93	1.42	1.08	54.69
15		800	Unwashed	30.23	0.97	0.78	53.77

** N/A – chemical composition by ICP-MS was not measured for source materials.*

Sludge biochar due to high mineral content behaves differently. WS1 from Lindum/Vesar had C%, N%, and H% decreasing, while O% was increasing until pyrolysis temperature did not exceed 700 °C. Due to the mineralization of the sample, it requires a higher temperature to break

down compounds. As for WS2, similarly to wood biochar it had decreasing H%, N%, and O% and increasing C%.

Overall, C% is increasing due to the elevation of carbonization degree and a higher degree of carbon clustering in the aromatic structures due to the temperature increase (Gaffar et al., 2021). O% decrease is explained by the loss of oxygen-containing groups (carboxylic, phenolic, and carboxyl). In general, biochar with the rise of thermal modification degree, loses functional and remaining elements polycondenses into a polyaromatic network (T. Wang et al., 2013).

Based on the Carbon content, materials that went through the pyrolytic process can be classified:

- by EBC as biochar if it has ≥ 50% of C, otherwise it is BioCarbon Mineral (BCM).
- by IBI, biochar should contain at least 10% minimum of organic carbon: class 1: ≥ 60%, class 2: ≥ 30 and < 60%; class 3: ≥ 10 and < 30%.

Obtained percentages of N, H, C, and O are then used for the calculation of aromaticity index (H/C), nitrogen availability (C/N ratio), hydrophilicity (O/C), and polarity index ((O+N) /C),. These parameters are considered to be the main characteristics (derived from elemental analysis results) of the biochar. All values are shown in table 5.11.

Aromaticity index (H/C) – indicates aromaticity and carbonization of the biochar related to long-term stability in the environment (Gaffar et al., 2021). The lower value is associated with higher aromaticity and carbonization degree. It is a common trend for high temperature derived biochars (HTB) with $t_{pyrol.}$ > 400 °C to mainly experience the aromatization process and formation of aromatic graphene-like structures (Xiao et al., 2016). As it follows from table 5.11, the H/C index was gradually decreasing for all biochars. H/C values, if compared between biochar with different feedstocks, show that waste sludge biochar was less carbonized compared to wood biochar. As stated above the molar H/C ratio is an indicator of the degree of carbonization and values exceeding 0.7 are an indication of non-pyrolytic chars or pyrolysis deficiencies (Schimmelpfennig & Glaser, 2012). The H/C ratio for Lindum slum-biorest is generally over 0.7 indicating non-pyrolytic chars.

C/N ratio for land application – indicates whether it can be used as a soil fertilizer. Soil microorganisms, that attribute to the nitrogen uptake, to stay alive should have specific ratios of C to N. C is burned by microorganisms to obtain energy and therefore part of it is lost during respiration. To acquire enough energy and nutrients for body maintenance, they should have about 24(C):1(N) ratio (soil microbes themselves without plants need about 8:1 ratio) (USDA-NRCS, 2011). If this ratio is higher, then it can cause nitrogen deficiency because microorganisms immobilize excessive nitrogen (if there is no additional N-source in the soil). Also, if the ratio is lower than 24:1, it will cause a temporary surplus of nitrogen (mineralization). Of course, the different plants would require different ratios (for instance hairy vetch cover crop need 11:1, while rye straw 82:1 ratio).

According to data in table 5.11 wood biochar has way too high C/N values (can be used if mixed with other N-containing material), exceeding the 24:1 ratio by 6-8 times. On the other hand, waste sludge biochar has close to the optimal value which can be utilized for soil conditioning as values vary in the range 11-45, which corresponds to some of the plants' requirements. At the same time, even though ratios are better for waste sludge, wood biochar has a much higher C carbon content, which has a higher energy value for microorganisms.

Table 5.11 – Main parameters based on molar fractions of macroelement

#	Sample source	t [°C]	Remark	H/C	C/N	O/C	(O+ N)/C
1	Wood pellets Hallingdal	550	Unwashed	0.314	178.123	0.027	0.033
2		600	Unwashed	0.220	180.566	0.029	0.035
3		600	Modified	0.252	189.714	0.039	0.044
4		700	Unwashed	0.168	167.139	0.029	0.035
6		750	Unwashed	0.132	148.273	0.024	0.031
7	Slam-biorest Lindum/ Vesar	-	Source	1.893	11.202	N/A*	N/A*
8		500	Unwashed	1.366	14.442	2.767	2.836
9		600	Unwashed	0.889	17.789	3.040	3.096
10		700	Unwashed	0.746	24.249	3.222	3.264
12		800	Unwashed	0.696	32.688	3.147	3.178
13	Ullensaker slam	-	Source	1.786	12.600	N/A*	N/A*
14		700	Unwashed	0.585	31.296	1.419	1.451
15		800	Unwashed	0.383	45.064	1.335	1.357

** N/A –oxygen content was not estimated, due to insufficient data.*

Hydrophilicity index (O/C) – indicates the reactivity and stability of the biochar in the environment. With the degree of carbonization, oxygen concentration tends to decrease, while the carbon content only increases. Therefore, the lower O/C the more stable the biochar is, and this index decreases with the degree of carbonization. O/C index is a measure of polar functional groups density on the biochar surface, which identifies biochar surface reactivity (Bakshi et al., 2020). Also, the hydrophilicity index is used to estimate the aging of biochar due to weathering in the soil.

It is expected that biochars with an O/C ratio less than 0.2 are more stable and have an expected half-life of over 1000 years, Biochar with O/C values of 0.3-0.5 has 100-1000 years, and over 0.6 – less than 100 years. In the case of biochar that has little to no oxygen groups and a very long half-life, considered to be not beneficial for soil interactions (CEC, water retention, etc) (Huff et al., 2018). Sequestering biochar carbon in soil contributes greatly to the reduction of greenhouse gases emissions. Biochar stability which is indicated by its O/C ratio is the most critical factor that determines its resistance to biotic and abiotic degradations in the soil can be used for the description of the carbon sequestration potential of biochar.

Overall, waste sludge biochars are much more hydrophilic if compared with wood biochar: hydrophilicity increases slightly with pyrolysis temperature until it doesn't reach a temperature over 700 °C, where hydrophilicity drops due to the change in biochar surface properties (wetting, dewetting, and adhesion characteristics of the surface). As for wood biochar, according to table 5.9, since it has an O/C index lower than 0.2% it can be classified as a mixture of soot and graphite, as it loses its original structure and has a low O/C ratio (Spokas, 2010); biochar shows relatively low hydrophilicity values. Overall, O/C ratio biochars show quite good performance as a filtration material for water treatment as well as can be used for carbon sequestration, as a soil additive.

Polarity index ((O+N) /C) – indicates the availability of polar functional groups and hydrophobicity. There is a common trend that with an increase of carbonization, biochar has polarity reduced and hydrophobicity increased. It was observed in some publications that for mineralized biochars might be no significant difference in polarity index for different production temperatures which can be

implied to the protection of polar groups by minerals (Qiu et al., 2014). Minerals can contribute to the high O% on the biochar surface.

An increase of aromaticity index and reduction of polarity is an indication of a higher sorption capacity of the biochar (Gaffar et al., 2021). For characterization of such complex samples was used so-called van Krevelen diagram (Fryda & Visser, 2015; Schimmelpfennig & Glaser, 2012), which uses ratios of elements on the axes and allows the interpretation of the chemical structure, decomposition rate, and maturity of samples (figure 5.15). Lower H/C and O/C ratios indicate fewer functional groups on the biochar surface and higher carbon stability. According to the European biochar certificate (EBC), biochar that can be applied for agricultural purposes should not exceed: H/C < 0.7 and O/C < 0.4, and only wood biochar is within the limits, while waste biochars have high polarity.

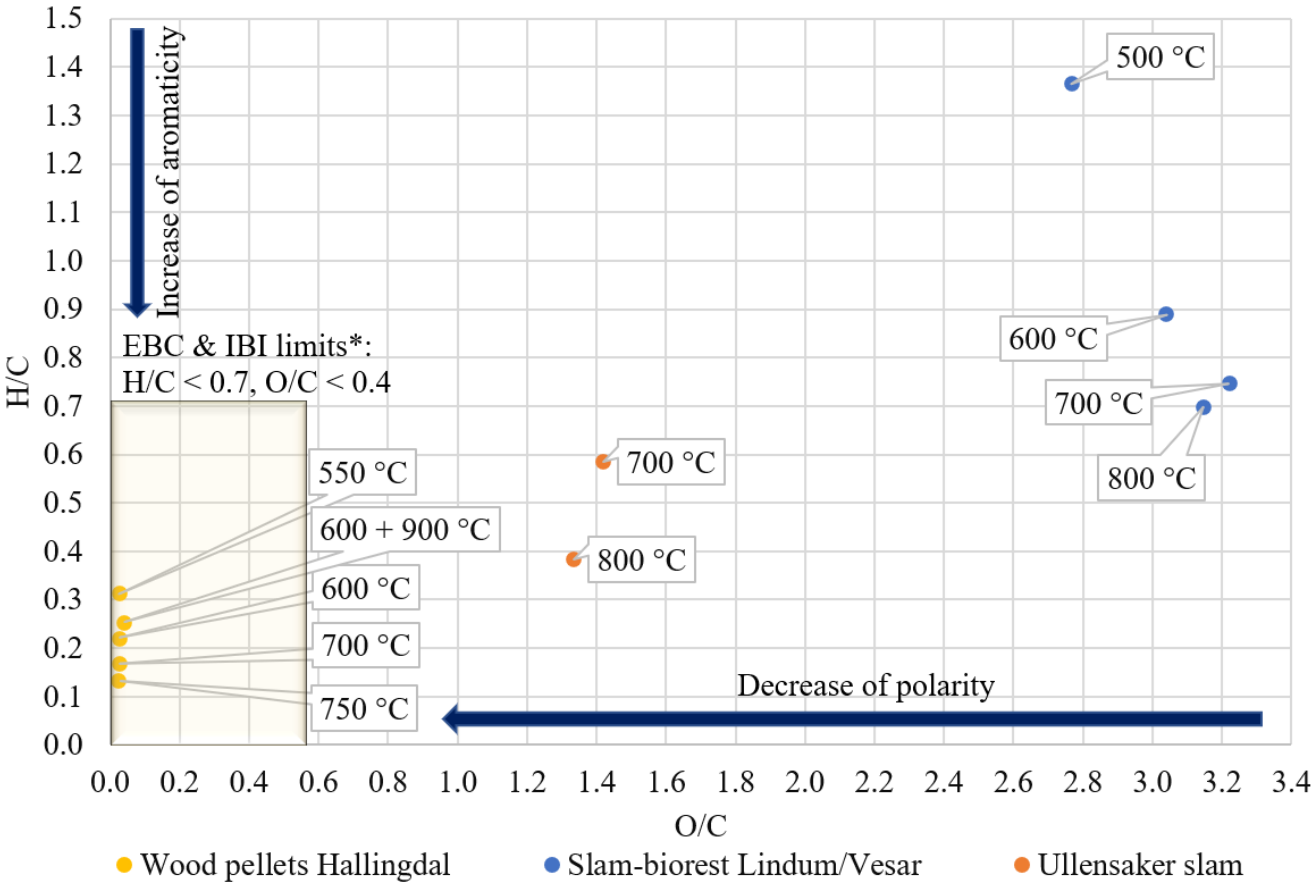


Figure 5.15 – Van Krevelen diagram for biochar samples:
H/C vs. O/C indices (* *by* (EBC, 2021; IBI, 2012))

5.3.2 Mineral content, macro-, and micro-elements, heavy metals

Results for chemical analysis of biochar samples are shown in table 5.12. Each of the samples was measured according to section 4.2.4 by ICP-MS and the content of 20 elements (Na, Mg, Al, S, K, Ca, Fe, Cr, Mn, Co, Ni, Cu, Zn, As, Mo, Cd, Hg, Pb, Cl, and Si) was analyzed and values were used for calculations in the previous section (for oxygen % estimation).

Table 5.12 – Chemical analysis results *

		Wood biochar					WS1 biochar				WS2 biochar				
		550°C	600°C	600°C	700°C	750°C	500°C	600°C	700°C	800°C	700°C	800°C			
Elem.	Unit	1	2	3	4	6	8	9	10	12	14	15	LOD	LOQ	RS
Na	g/kg	0.066	0.029	0.034	0.034	0.033	1.4	1.5	1.7	1.8	2.0	2.5	0.0003	0.0011	0.98
Mg	g/kg	0.830	0.86	0.7	1.1	0.96	4.4	4.6	4.9	5.0	5.1	5.4	0.0004	0.0015	9.4
Al	g/kg	0.260	0.27	0.2	0.4	0.17	24	23	20	18	19	20	0.01	0.033	14
Si**	g/kg	0.43	0.39	0.34	0.66	0.28	53	12	54	60	43	15	-	-	-
P	g/kg	0.41	0.43	0.35	0.42	0.46	30	32	35	35	41	43	0.005	0.016	24
S	g/kg	0.077	0.08	0.075	0.086	0.1	11	13	13	13	5	4.1	0.009	0.03	13
K	g/kg	3.7	3.7	3.4	4	4.1	3.1	3.1	3.4	3.3	5.4	5.4	0.0003	0.0011	4.7
Ca	g/kg	7.3	7.7	6.1	8.2	8.4	24	29	27	28	21	21	0.003	0.0086	50
Cr	mg/kg	2.9	2.7	40	24	19	46	51	39	43	55	48	0.2	0.51	97
Mn	mg/kg	820	880	670	900	1100	310	330	330	370	350	390	0.2	0.52	1300
Fe	g/kg	0.21	0.15	0.3	0.31	0.19	150	150	110	170	54	40	0.001	0.0039	16
Co	mg/kg	0.31	0.42	0.65	0.57	0.51	9.6	11	11	12	7.8	7.5	0.01	0.047	92
Ni	mg/kg	2.5	2.2	24	14	12	39	43	36	41	46	43	0.2	0.78	230
Cu	mg/kg	5.3	5.3	4.8	5.6	6.5	240	260	280	290	230	220	0.4	1.3	620
Zn	mg/kg	28	12	70	<4,9	<5,5	630	680	720	730	550	380	2	5.4	1300
As	mg/kg	<0.17	<0.20	<0.19	<0.17	<0.19	4.4	4.8	5.1	6.1	2.9	2.2	0.06	0.19	84
Mo	mg/kg	0.28	0.17	4.4	2.4	2.2	17	19	20	20	9.5	11	0.03	0.11	59
Cd	mg/kg	<LOD	<LOD	<LOD	<LOD	<LOD	0.61	0.067	0.026	0.026	0.11	<0.026	0.008	0.025	81
Hg	mg/kg	<LOD	<LOD	<LOD	<LOD	<LOD	<0.031	<0.023	<0.030	<LOD	0.035	<0.032	0.002	0.0079	15
Pb	mg/kg	0.16	<0.11	0.46	0.18	<0.11	24	26	25	25	17	8.2	0.03	0.10	310
Cl	mg/kg	<LOD	<LOD	<LOD	<LOD	<LOD	0.48	0.58	0.50	0.48	0.62	0.30	0.03	0.10	-

where LOD – limit of determination; LOQ – limit of qualification; RS – reference sludge 3

numbers in green - do not exceed permissible values for the element;

numbers in red – exceeds the limit of at least 1 country regulation;

numbers in black – not regulated.

** Analysis was not performed for samples 5,7,11,13.*

*** Values are based on stoichiometric calculations based on elemental and mineral composition analyses.*

While wood biochar has high carbon content, waste sludge-derived biochar is rich in different minerals. Mineral content is an important parameter for the biochar which is produced for land application. The chemical compositions of biochar vary depending on the source material and the production condition (mainly pyrolysis temperature). Many elements showed higher concentration values in sludge biochar than in wood biochar (Table 5.12). this indicates the potential for the recovery of plant nutrients.

For healthy plant growth necessary 16 essential elements that include: primary elements (needed in big amounts), secondary and micro-nutrients (table 5.13). All the elements, however, should correspond to the plant need as both deficiency and excessive amount can cause serious damage to plant development.

Table 5.13 – Main functions of nutrients for plant growth (McFarland & Provin, 2018)

Type of nutrient	Nutrient	Main function
Primary	C	Plant structure
	O, H (water)	Respiration, energy production, carbohydrates synthesis, pH regulation
	N	Healthy vegetation growth, chlorophyll, formation of cells, basis for amino acids and proteins.
	P	Root growth, resistance to diseases, fruit and flower development, protein synthesis, cell formation, metabolism
	K	Resistance to diseases, fruit ripening, overall development, water regulation
Secondary	Ca	Plant structure, growth and strength, resistance to diseases,
	Mg	Vegetation development and growth, sugar formation, chlorophyll, fat formation, metabolism
	S	Maturity of seed and fruit
Micro	Cl, Fe, Zn, Mn, B, Cu, Mo	Plant growth, leaf color, formation of starch, enzyme development, and activity

According to the results of chemical analysis wood biochar contains a much smaller nutrient percentage as carbon takes up to 91-94% (wood biochar is lower in all the analyzed elements but K, which is nearly the same for all biochar samples and Mn, which is higher than if waste sludge biochar). At the same time, waste sludge biochar is rich in many different nutrients including all the elements from table 5.13. Even though some of the concentrations have excessive concentrations, if biomass is mixed with something else (for instance carbon reach biomass), it is possible to reach permissible element concentrations.

As it was mentioned before, biochar originating from sewage sludge generally contains high concentrations of metals, which remain in the final biochar product following pyrolysis. As shown in table 5.12 the concentration of heavy metals in Lindum biowaste sludge and Ullensaker waste sludge is higher than the concentration in the wood pellet. The concentrations in As, Cr, Co, Cu, Mo, Ni, Pb, and Zn in the biochar derived from sludge are 10 to more than 50 times higher than their corresponding values in biochar derived from wood pellet which could be a potential challenge for safe utilization of such resources. Many of the identified elements are not regulated if biochar is applied on land but increasing concerns might lead to the formation of new regulations. Currently regulated heavy metals are only: Cd, Cr, Cu, Hg, Ni, Pb, Zn, As (Table 5.14). For the comparison of

results with permissible concentrations of regulated elements in the Netherlands, Denmark, Sweden, and Norway were chosen as countries with the strictest requirements, as well as 86/278/EEC Directive values. The heavy metal concentration values, that do not meet the requirements of biochar for land application in at least 1 of chosen countries' regulations are marked in red in Table 5.12.

According to table 5.12 and table 5.14, the wood biochar meets all the requirements, but has Cr concentration for wood biochar under 600 °C has a value of 40 mg/kg which is the limit for Sweden. Sludge waste-derived biochars do not meet requirements to Cr (Sweden), Ni (Sweden, Denmark, Netherlands), Cu (Netherlands), Zn (Netherland and for some samples Sweden).

Table 5.14 – Maximum permissible concentrations of heavy metals for land application

Elem.	Unit	Directive 86/278/ EEC*	Netherlands **	Sweden	Denmark	Norway***	
						For agriculture	For green amenity areas
Cr	mg/kg	-	75	40	100	100	150
Ni	mg/kg	300-400	30	25	30	50	80
Cu	mg/kg	1000-1750	75	300	1000	650	1000
Zn	mg/kg	2500-4000	300	600	4000	800	1500
Cd	mg/kg	20-40	1.25	0.75	0.8	2	5
Hg	mg/kg	16-25	0.75	1.5	0.8	3	5
Pb	mg/kg	750-1200	100	25	120	80	200

* retrieved from (European Commission, 1986)

** retrieved from (Collivignarelli et al., 2019)

*** retrieved from (Whipps & Tornes, 2018)

Since Directive 89/278/EEC is outdated long ago, each country develops and implements its regulations. However, those regulations vary to a great extent. This makes it difficult for the international biochar market (to sell or buy biochar abroad). For instance, biochar with a Cu content of 100 would be allowed for all listed countries in table 5.14, but the Netherlands. Therefore, the development of international regulations would benefit all countries. There are multiple initiatives for regulation development including European Biochar Certificate (EBC) developed by Ithaka Institute in Switzerland, International Biochar Initiative (IBI) standards, Australia and New Zealand Biochar Standard, Korea Biochar Standard (Hu et al., 2021). Requirements for the metal content according to the European Biochar Certificate are listed in table 5.15.

According to the guidelines for EBC (EBC, 2012) for sustainable production of biochar, the following threshold values are set for basic and premium quality.

Basic grade (according to Germany's Federal Soil Protection Act (Bundes-Bodenschutzverordnung or BBodSchV)): Pb < 150 mg kg-1, Cd < 1,5 mg kg-1, Cu < 100 mg kg-1, Ni < 50 mg kg-1, Hg < mg kg-1, Zn < 400 mg kg-1, Cr < 90 mg kg-1

Premium grade (according to Switzerland's Chemical Risk Reduction Act (Schweizerische Chemikalien-Risikoreduktions-Verordnung or ChemRRV)): Pb < 120 mg kg-1, Cd < 1 mg kg-1, Cu < 100 mg kg-1, Ni < 30 mg kg-1, Hg < 1 mg kg-1, Zn < 400 mg kg-1

But most recently the European Biochar Certificate (EBC, 2021) defined four application classes as EBC-Feed (Class I), EBC-AgroBio (Class II for organic products, EU regulations for organic compost), EBC-Agro (Class III, based on the German Federal Soil Protection Ordinance (BBodSchV)), and EBC-Material (Class IV, based on the Swiss Ordinance on Waste for the Production of Cement and Concrete) that meet requirements for biochar application as feed and feed additives in animal husbandry, for agricultural use as fertilizer and in industrial applications. The biochar derived from wood pellet fulfills all the requirements for Class I. However, the high concentration in Cu, Ni, and Zn, the sludge biochar does not meet the requirements for Class II although the other heavy metal concentrations meet Class II except Ni. The two sludge biochars meet the requirements for EBC-Material and can be used for industrial applications.

At the same time, if compared with requirements of IBI standards, characterized waste sludge biochar does not meet the requirements by Cu, Zn, Mo (Se was not measured). IBI standards mostly correspond to the EBC class III, but additionally regulate Co, Mo, and Se.

Table 5.15 – Requirements of different application classes for EBC and requirements of IBI standard

Heavy metals	Unit	EBC*				IBI**
		EBC-feed Class I	EBC-AgroBio Class II	EBC-Agro Class III	EBC-Material Class IV	
Cr	mg/kg	70	70	90	250	93
Ni	mg/kg	25	25	50	250	47
Cu	mg/kg	70	70	100	250	143
Zn	mg/kg	200	200	400	750	416
Cd	mg/kg	0.8	0.7	1.5	5	1.4
Hg	mg/kg	0.1	0.4	1.0	1.0	1
Pb	mg/kg	10	45	150	250	121
As	mg/kg	2	13	13	15	13
Co	mg/kg	-	-	-	-	34
Mo	mg/kg	-	-	-	-	5
Se	mg/kg	-	-	-	-	2

* retrieved from European Biochar Certificate (EBC, 2021)

** retrieved from International Biochar Initiative (IBI, 2012)

As regulations are getting stricter it is important to have each parameter as low as possible, to avoid negative influence on the environment, before the application of biochar or any kind of organic fertilizer, it is necessary to analyze not only the fertilizer but soil parameters as well. For instance, it might have naturally high mineralogical content, and adding even more minerals will make the situation even worse.

6 Conclusions

The result of this study shows the importance of proper characterization of biochar derived from different sources for appropriate use and applications. Biochar from three different feedstocks 1)– Softwood pellets from whole tree trunks of 60% of Norwegian spruce and 40% of Scots pine(W); 2) – Waste sludge (Bio-rest) from Lindum/Vesar (WS1); and 3) – Waste sludge from Ullensaker (WS2) produced by microwave assisted pyrolysis MAP were characterized based on their physical characteristics and chemical composition after exposure to pyrolysis with the same exposure time (20 mins), but with different pyrolysis temperatures in the range of 500 – 800 °C. The biochars studied showed differences in chemical composition and physical properties mainly due to differences in their feedstock composition. All the biochars tested in this study showed an increase of pH, EC, ash content, active surface area, micropore and total pore volume with the increase in temperature or degree of carbonization.

Biochars derived from the waste sludge had higher ash content (WS1 - 54.8-91.6%, WS2 – 52.4-68%) compared to the wood-derived biochar (2.8-4.9%), due to much higher mineralization and lower organic matter content. Bulk density for wood biochar value was 2-3 times lower (290.6-283.7 kg/m^3) than for waste sludge biochars, (WS1- 880.2-769.3 kg/m^3, and WS2- 507.0-542 kg/m^3). On the other hand, the specific surface area was higher for wood samples (313 m^2/g – 402 m^2/g) and 3-4 times lower for waste sludge-derived biochars (77 m^2/g – 122 m^2/g).

With respect to aromaticity index (H/C), there is a general trend of decreasing with increasing pyrolysis temperature for all the samples. However, waste sludge biochars has shown lower aromaticity and carbonization degree than wood biochar. H/C value for the Lindum/Vesar derived biochar exceeded 0.7, indicating a non-pyrolytic chare or pyrolysis deficiencies. Wood biochar showed the lowest H/C ratio ranging from 0.13 to 0.31 indicating high C-sink potential. Like the H/C ratio, the O/C decreases for all samples after pyrolysis temperature reaches 700 °C, which is related to the decomposition of oxygen-containing functional groups. Wood biochar at 700 °C has shown O/C ratio equal to 0.03, which is 107 times lower than for WS1 and 45 times lower than for WS2, and is characterized as the more stable biochar, and the less hydrophilic. The same trend was observed for polarity index ((O+N)/C) which is nearly the same as hydrophilicity index as nitrogen content is relatively low for all biochar samples. Moreover, the C/N ratio indicates biochar feasibility as a soil fertilizer. Normally plants need in the range of 11:1 to 82:1 C/N ratio, depending on the plant species. According to the obtained data, the C/N ratio for wood biochar was on average 173 which exceeds the requirement for most plants, while waste sludge biochar with an average of 22 for Lindum sludge biochar and 38 for Ullensaker sludge biochar which is within the range to the optimum indicating their potential use as a soil amendment.

In terms of chemical composition, the wood biochar differs a lot from waste sludge-derived biochar. The wood biochar is mainly composed of organic C, C% ranging from 91.5 to 93.7% and the concentration of other elements and minerals low. Basically, all the elements are from 3 to 60 times lower than for the waste sludge biochar (except K, which is almost the same for all the samples, and Mn which is much higher for wood biochar). The results from chemical analyses of the biochar are closely linked with the XRD results. While chemical analyses show elemental content in the biochar, the XRD shows how elements are distributed (evenly or unevenly distributed) on the surface of the biochar.

Proper characterization of the biochar with the parameters mentioned above will therefore help to determine the potential application of the biochar, produced from the different feedstocks, for appropriate use depending on their characteristics. Accordingly, the biochar derived from the two waste sludges do not meet the EBC-Feed (Class I), EBC-AgriBio (Class II) and EBC-Agro (Class III) requirements due to elevated concentration in Cu, Ni, and Zn but can be used for industrial and construction purpose. Future biochar characterisation should also include analysis of organic pollutants as well as tests for the efficiency of biochar for specific applications: sorption tests, pot trials with plants, etc.

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Appendix A – Sewage sludge production and disposal

Table A.1 – Statistical data on sludge production and disposal of sludge for different countries

Country	Sludge disposal								Sludge production	
	Agricultural use		Compost and other use		Landfill		Total			
Belgium	2017	24.93	2017	0	2017	0	2017	153.09	2010	176.3
Bulgaria	2017	22.5	2017	3.8	2017	6.8	2017	45.3	2017	68.6
Czechia	2018	108.31	2018	78.01	2018	19.56	2018	228.22	2010	228.22
Denmark	2010	74	N/A	N/A	2010	1.4	2010	114.9	2010	141
Germany	2016	423.497	2016	200.503	2016	0	2016	1,773.186	2016	1,794.443
Estonia	2016	0.1	2016	15.44	2016	2.8	2016	18.34	2016	18.34
Ireland	2017	46.487	2017	10.065	2017	0.087	2017	58.773	2017	58.773
Greece	2016	21.528	2014	9	2016	34.03	2016	119.768	2016	119.768
Spain	2016	941.6	N/A	N/A	2016	120.9	2016	1,174.4	2016	1,174.4
France	2017	299	2017	318	2017	13	2017	809	2017	1,174
Croatia	2018	1.548	2018	0.153	2018	0.776	2018	3.954	2018	19.23
Italy	2010	315.6	N/A	N/A	2010	462.2	2010	953.7	2010	1,102.7
Cyprus	2018	0.937	2018	4.86	2018	0	2018	8.406	2018	8.406
Latvia	2018	4.288	2018	8.842	2018	0.071	2018	24.128	2018	24.591
Lithuania	2018	17.506	2018	15.892	2018	3.402	2018	38.684	2018	44.192
Luxembourg	2017	1.138	2017	4.557	2012	0	2017	8.618	2017	8.618
Hungary	2018	34.088	2018	166.948	2018	1.513	2018	231.349	2018	217.842
Malta	2018	0	2018	0	2018	8.28	2018	8.28	2018	8.28
Netherlands	2018	0	2018	0	2018	31.908	2018	303.745	2018	341.03
Austria	2018	48.17	2018	46.289	2018	0.262	2018	234.481	2018	234.481
Poland	2018	118.333	2018	25.196	2018	10.638	2018	583.07	2018	583.07
Portugal	2016	13.885	N/A	N/A	2016	5.137	2012	113.1	2016	119.17
Romania	2018	46.39	2018	4.15	2018	128.31	2018	247.76	2018	247.76
Slovenia	2018	0	2018	0.6	2018	0.3	2018	38	2018	38.1
Slovakia	2018	0	2018	25.45	2018	11.27	2018	55.93	2018	55.93
Finland	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	2015	146
Sweden	2018	82.3	2018	54	2018	2.3	2018	198.9	2018	210.9
Iceland	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
Norway	2018	65.4	2018	26.7	2018	8.7	2018	111.7	2018	147.6
Switzerland	2017	0	2017	0	2017	0	2017	177	2017	177
UK	2012	844.4	N/A	N/A	2012	4.7	2012	1,078.4	2012	1,136.7
Albania	2018	8.2	N/A	N/A	N/A	N/A	2018	94.5	2018	94.5
Serbia	N/A	N/A	N/A	N/A	2018	9.5	2018	9.5	2018	9.6
Turkey	2018	11.356	2018	0.023	2018	132.69	2018	288.907	2018	318.503
Bosnia and Herzegovina	0	0	2018	0	2018	1.3	2018	1.3	2018	9.5

* Retrieved from (Eurostat, 2016)

** N/A – data is not available.

Appendix B – Methodology

B.1 pH and Electrical Conductivity measurements

Apparatus and glassware:

- Sieves (with 2 mm mesh size and with no openings).
- Brush for sieve cleaning.
- Laboratory air compressor (optional).
- Pestles.
- Measuring spoon (5 and 10 mL).
- Plastic bottles with caps (50 mL).
- Beaker.
- Flask (500 mL).
- Distilled water.
- Calibration solutions (pH 4.0 and pH 7.0).
- Standard pH meter PHM210 (Meterlab) with a combined pH electrode.
- Conductometer 712 (Metrohm) with measuring electrode.

pH was measured according to (Coleman et al., 1951), and electrical conductivity measurements were conducted according to the (EBC, 2021; Marshall, 1978; Technical Committee ISO, 1996; VDLUFA, 2003).

Preparation: Representative dry sample of biochar sieved through 2.0 mm sieves. Sieve with mesh and without are used together to avoid sample loss and collect 2 fractions: <2.0 mm and >2.0 mm (figure B.1 a, b). Fraction of < 2.0 mm is then used for pH and electrical conductivity measurements and the remaining >2.0 is then returned to the original sample package. If there are a lot of big pieces that do not go through the mech then metal pestle can be used to crush them and porcelain to make sure that the whole sample went through the mesh (figure B.1 c). After each sieving, it is important to clean all used instruments. For this purpose, a brush can be used together with an air gun connected to an air compressor (figure B.1 c, d). This allows efficiently remove particles that are stuck inside the mesh and dust from the surface. In the end, also wipe everything with the paper. All of this is done to avoid any kind of interference in the further measurements.

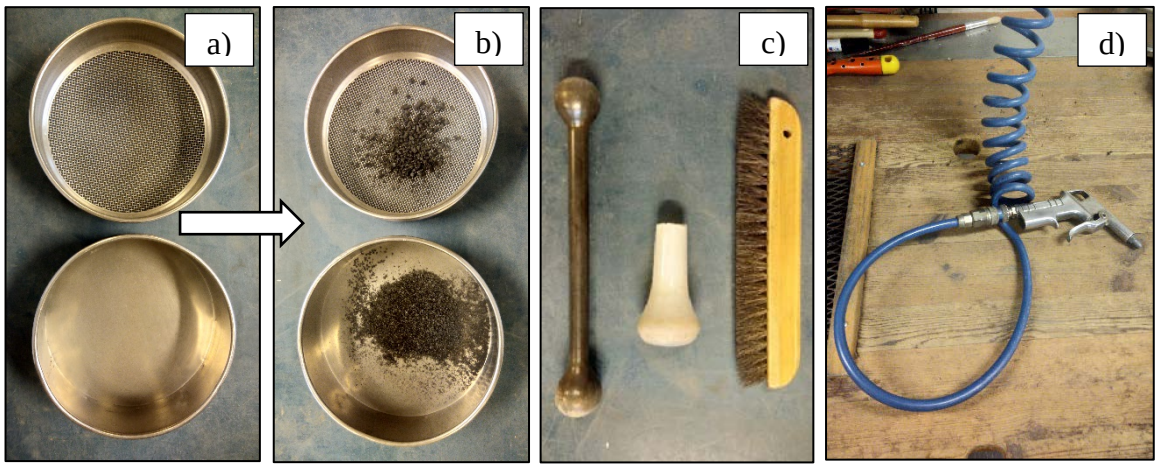


Figure B.1 – Equipment for sieving: a) sieves with 2 mm mesh size and with no openings; b) sieved material; c) brush, porcelain, and metal pestles; d) laboratory air compressor with a connected air gun

After sieving is completed for all the samples, 5 mL (for wood biochar considering that a limited amount of biochar is available) or 10 mL (for other samples) is placed in the plastic bottle with caps. To measure the specific volume of the dry loose material special measuring spoons are used (figure B.2 b). First, the spoon should be filled with a sample, and then the excess amount removed as shown in figure B.2.e. Then samples are placed in plastic bottles with caps together with a specific volume of distilled water: 12.5 and 25 mL respectively to 5 and 10 mL of sample. To measure distilled water volume water dispenser, plastic dropper, and graduated cylinder were used (figure B.2 a, c, d).

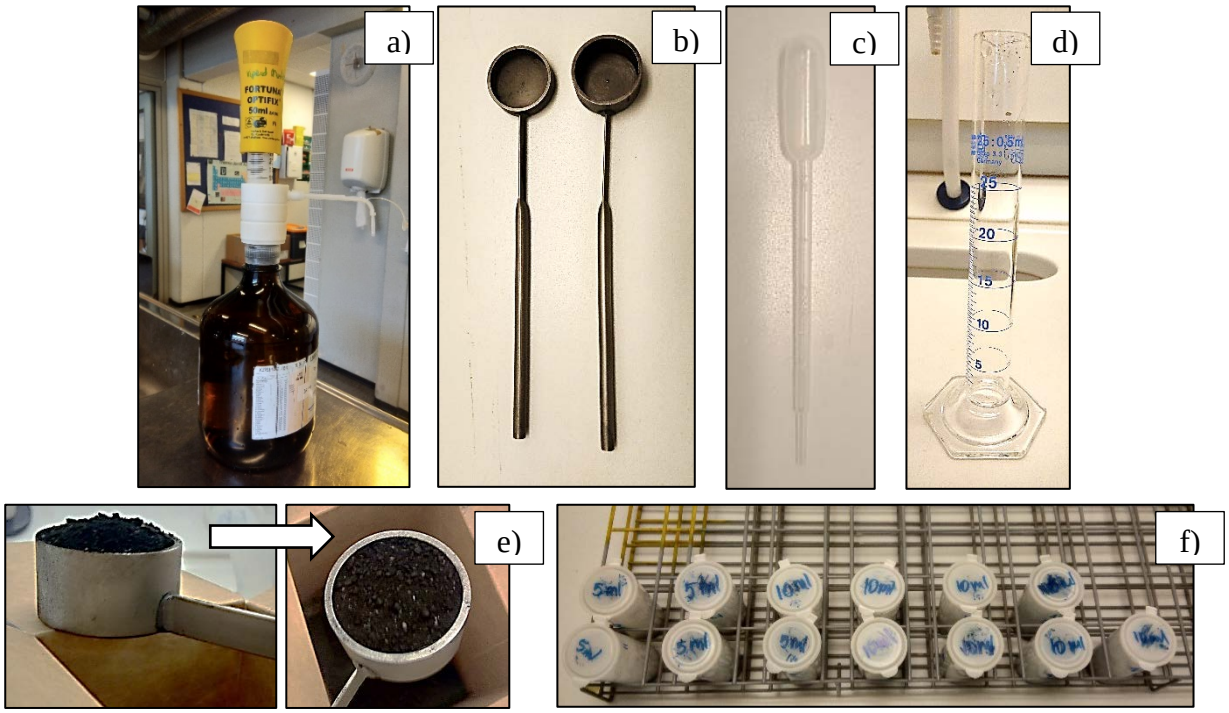


Figure B.2 Equipment for sample preparation: a) distilled water dispenser; b) measuring spoons; c) plastic dropper; d) graduated cylinder; e) sample volume measuring; f) prepared samples

After all the samples are ready (figure B.2 e) they should be closed with caps and thoroughly mixed for a couple of minutes and after 5-10 mins of standing mixed again. It is important to make sure that all particles are well mixed and wet. After the 2 shaking samples are left overnight and pH and conductivity measurements are performed the next day.

Conductivity measurements. The next day after the sample preparation, after samples are mixed again and settled the actual measurements finally can be done. It is important to measure conductivity first and the pH electrode is stored in KCl solution which will be slowly leaking into the solution that will influence conductivity measurements. The electrode (figure B.3 a) should be submerged into the sample-water mixture and the value is recorded from the conductometer screen (figure B.3 b) when it reaches stable values. Conductometer should be calibrated before the measurements.

Repeatability. Electrical conductivity measurements should meet followed requirements, which are shown in Table B.1. Variation in measurements for the same material should not vary more than it is stated in the table or results are not considered to be correct.

Table B.1 – Repeatability of the conductivity results (Technical Committee ISO, 1996)

Conductivity, mS/m at 25 °C	0–50	50–200	> 200
Deviation	5 mS/m	20 mS/m	10%

Figure B.3 Set-up for conductivity measurements: a) electrode; b) 712 Conductometer.

pH measurements. pH measurements are done with the same logistics. A combined pH electrode (preliminary calibrated with pH 4.0 and 7.0 solutions) is submerged into the liquors phase of the sample and should remain there until the pH meter (figure B.4) shows that the values are stable.

Figure B.4 Set-up for pH measurements: a) combined electrode; b) standard pH meter PHM210

B.2 TS and VS measurements

Apparatus and glassware:

- Pestle and mortar.
- Evaporation dishes (thermo-resistant).
- Drying oven.
- Muffle furnace.
- Analytical balances.
- Sampling handling: spatulas, small spoons, tweezers.
- Desiccator.

TS and VS were measured according to (Telliard, 2001). Representative samples of the source material are crushed by using a pestle and mortar to ensure proper drying and incineration (figure B.5 a, b). 10 g of crushed samples are then placed into the numbered evaporation dishes. To ensure the representativity of the sample 2 parallels for each material were taken. Dishes with samples are then placed into the drying oven for 2 hours with a drying temperature of 105 °C. The residue after drying is cooled in the desiccator (to avoid air humidity adsorption), weighted, and placed in the muffle

furnace for ignition under 550 °C (20-30 mins) to remove volatile solids (first of all organic material). After ignition samples should be cooled down and weighted again.

Figure B.5 Source material for TS and VS measurements: a) Lindum/Vesar WS; b) Ullensaker WS

B.3 C-H-N% measurements

Apparatus and glassware:

- Pestle and mortar.
- Glass fiber filter (Whatman GF/F).
- Analytical balances (with accuracy at ± 0.0001 g).
- 2M HCl solution.
- Glass pipette for HCl solution transfer.
- Distilled water.
- Drying oven.
- Porcelain crucible.
- Iron and Copper chip accelerators.
- Leco Carbon Analyser EC12.
- Leco CHN628.

Samples taken according to section 3.3.1 should be crushed with a pestle and mortar into fine powder.

Total Carbon. This analysis was performed according to "dry combustion" proposed by Allison and described by Nelson and Sommers (Nelson & Sommers, 2015). As in the previous methods sample should be crushed into powder and dried at 55 °C to remove residual moisture, before proceeding further.

200 mg of each sample is weighed into a tin foil (reduced weight for the sample with high organic matter content: ~100-150 mg) as shown in figure B.6.a, b and placed into analyzed in LECO CHN628 (figure B.6.c & 4.7). During analysis, the sample undergoes so-called "complete combustion" (figure B.6.d), where all carbon in the form of CO is oxidized to CO_2 (under temperature 1050 °C). The concentration of CO_2 is then measured by infrared light in the IR cell (figure B.6.e).

Total Nitrogen. Analyses are performed according to the Dumas method, which is described by Bremner and Mulvaney(Bremner & Mulvaney, 2015). This method followed the same principle as for Total Carbon, with the difference that nitric oxide compounds (NOx) are reduced by the copper to N_2. Then the concentration of N_2 is measured by thermal conductivity in TC cell, using LECO CHN 628.

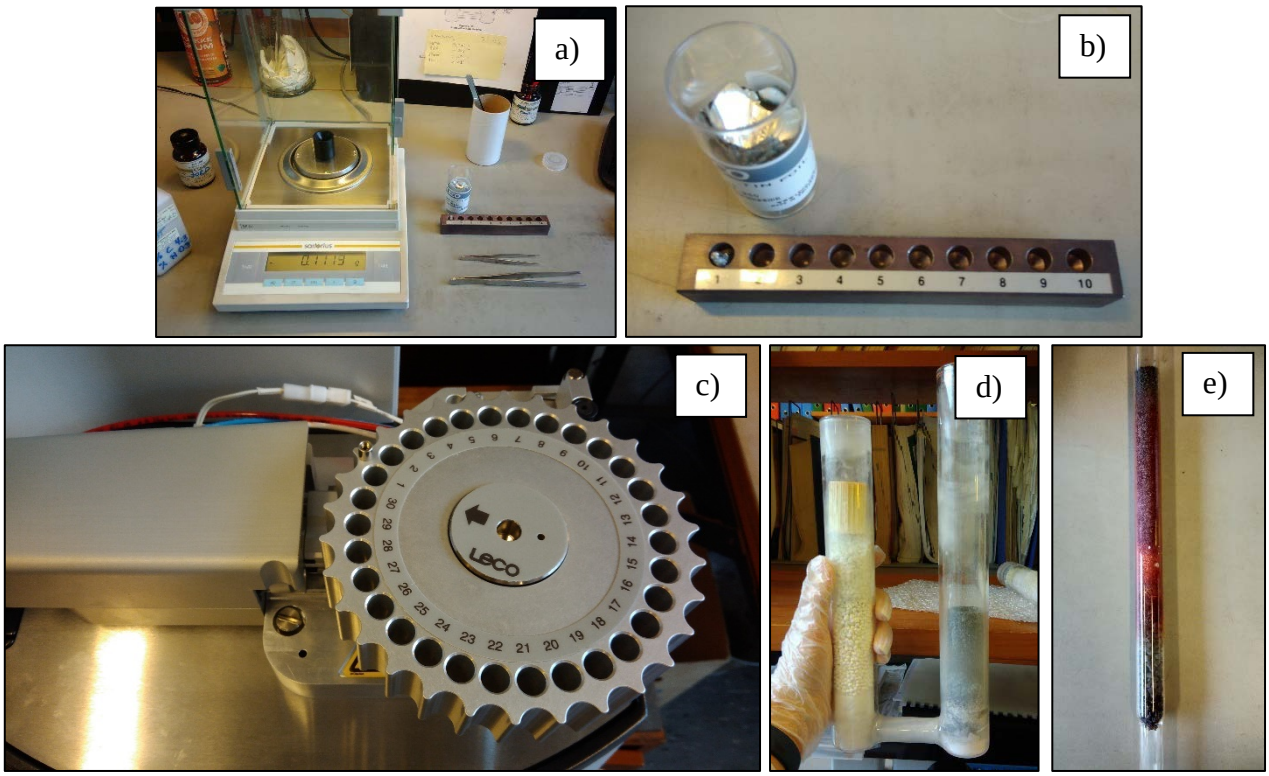


Figure B.6 – Important steps for EDTA performance

B.4 Elemental composition

Depending on the feedstock and therefore differences in elemental composition. This analysis will require different types of digestion. According to table 4.2, 11 samples were analyzed. Before elemental analysis by Inductively Coupled Plasma-Mass-Spectrometry (ICP-MS), digestion should be performed. 2 different digestions were performed: HNO_3/HCl and HNO_3/HF.

HNO_3/HCl digestion: Weighted exactly 0.25 g of sample (sample crushed into a fine powder with a pestle and mortar). Samples are then placed into teflon tubes (figure B.7a) and 5 mL HNO_3 is added. All the tubes are placed into a water bath container (also made of teflon (figure B.7b)). It is then placed for digestion in a Milestone Ultra clave at 260 °C (figure B.7c).

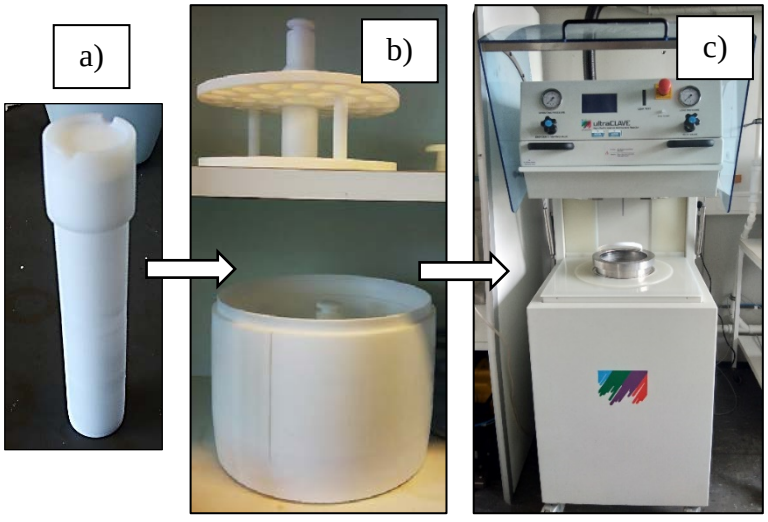


Figure B.7 – Digestion set-up

After the digestion, 1 mL of HCl is added to all the samples and then diluted to 50 mL with mq-water. Samples 1, 2, 3, 4, 6, and blanks were analyzed without any further dilution. To prepare samples 8, 9, 10, 12, 14, 15, and sewage sludge 3 for analysis, they were diluted 4x (to analyze all elements except Al and Fe). To analyze Al and Fe samples 9 and 12 were diluted 50x and the rest of the samples were diluted 20x.

The samples were analyzed by using an Agilent ICP-QQQ-MS in He-KED and oxygen reaction mode (figure B.8a, b). Samples are placed into the ICP-MS where it is dosed as aerosol drops (figure B.8c) into the heating chamber under the temperature around 7226.9-9726.9°C (7500-10000 K). At this temperature sample changes from liquid matter into a plasmic state of matter. Mass spectrometer separates single charged ions, based on atomic mass (figure B.8d). Then ions that are exiting the mass spectrometer enter the detector chamber, where they hit the active surface of the detector (dynode) (figure B.8e). Each hit generates a measurable electronic signal.

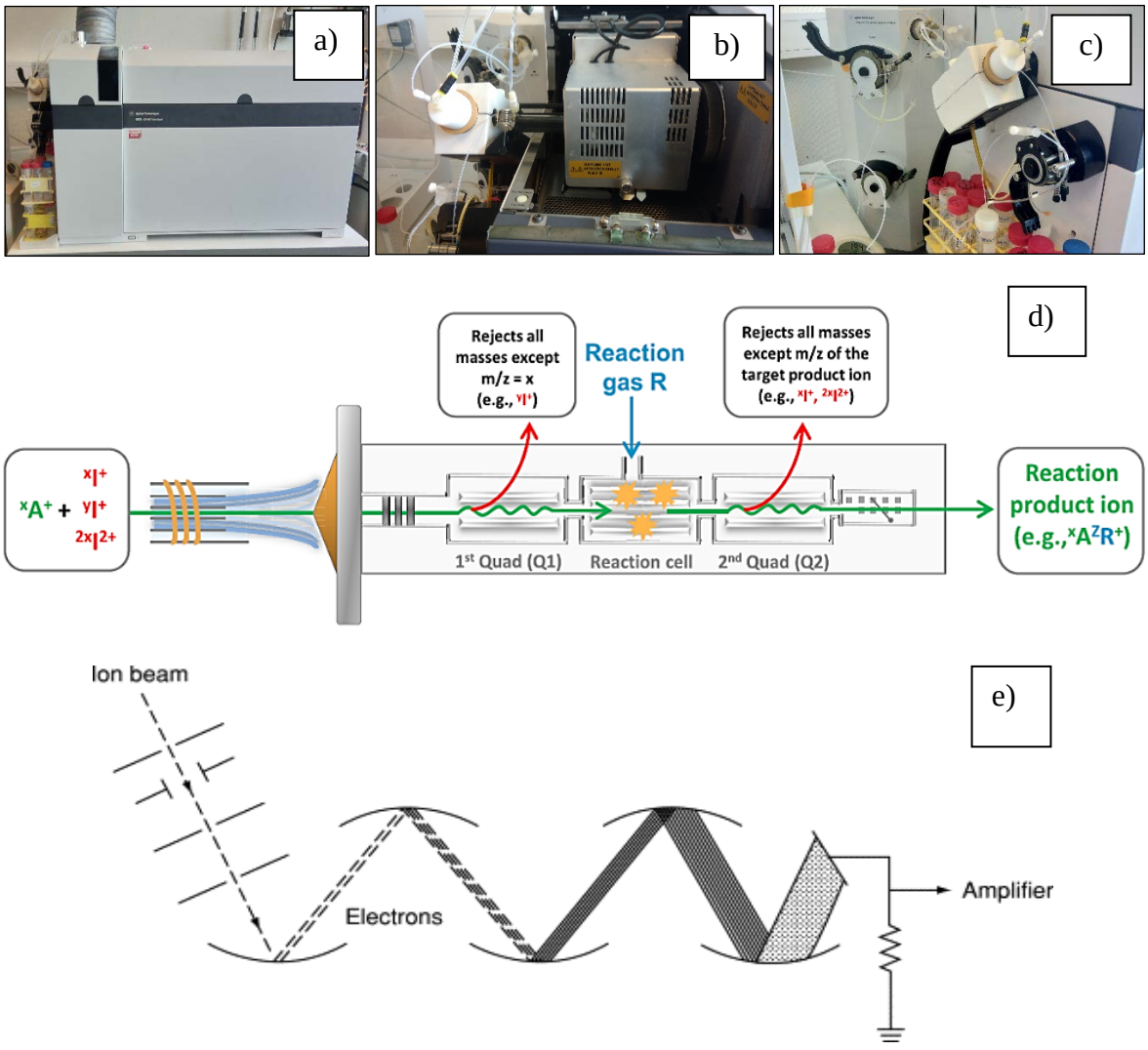


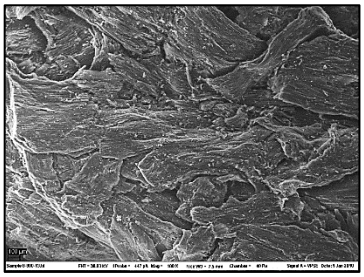
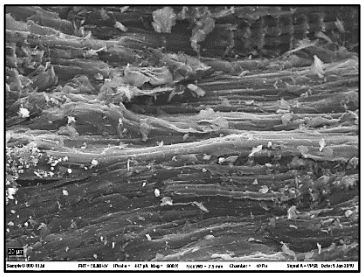
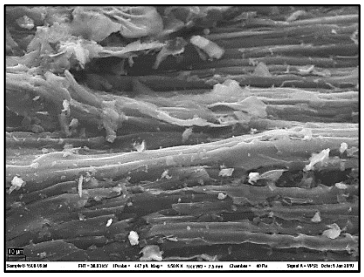
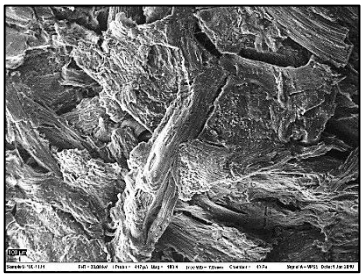
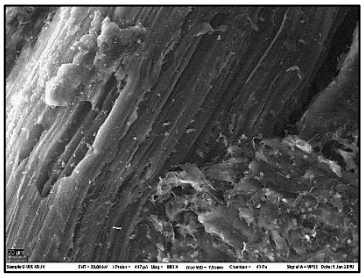
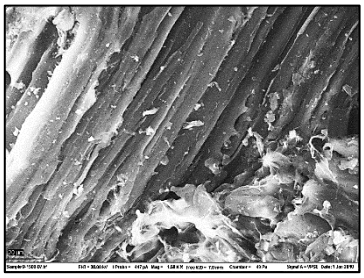
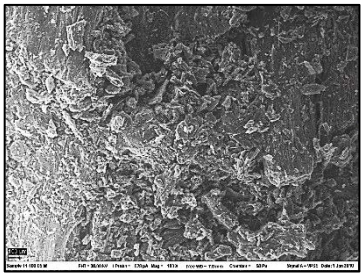
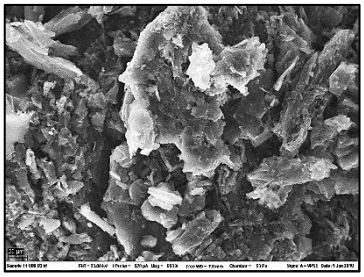
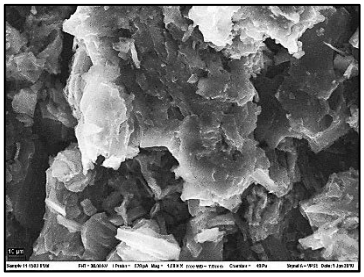
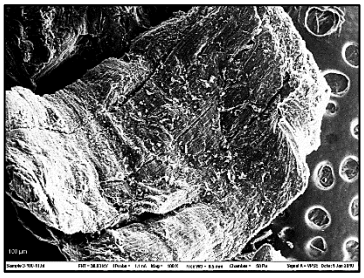
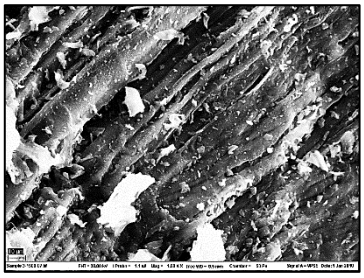
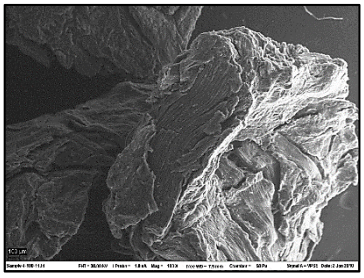
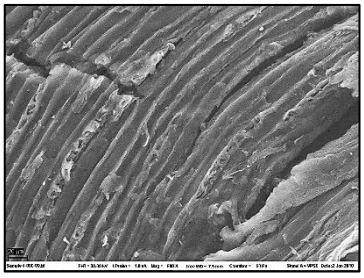
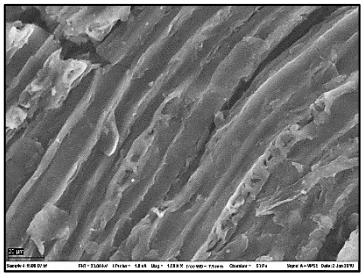
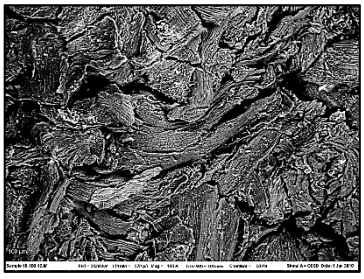
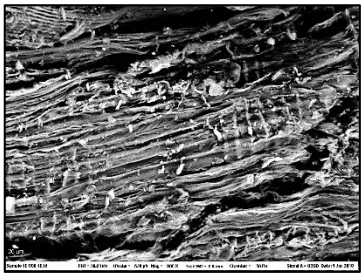
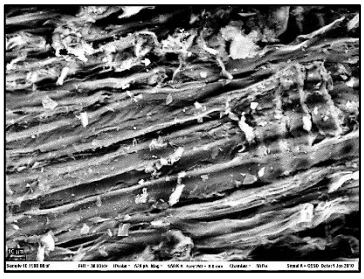
Figure B.8 – ICP-QQQ-MS in He-KED (Ghent University, 2021)

HNO_3/HF digestion: Weighted exactly 0.1 g and then placed in the teflon tube together with 5 mL of HNO_3 and 1 mL HF, and then digested in a Milestone Ultra clave at 260 °C the same way as with previous digestion. After digestion samples were diluted with mq- water up to 50 mL. To prepare samples for analysis they were diluted additionally 20x. The samples were analyzed by Agilent ICP-QQQ-MS in He-KED and oxygen reaction mode.

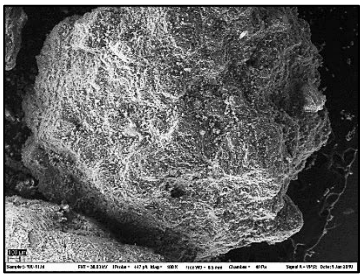
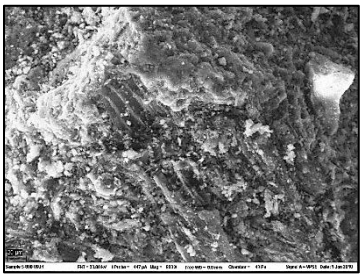
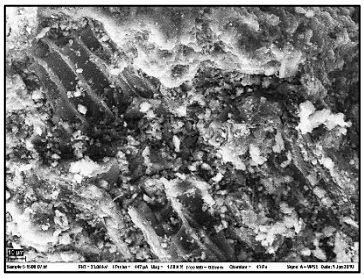
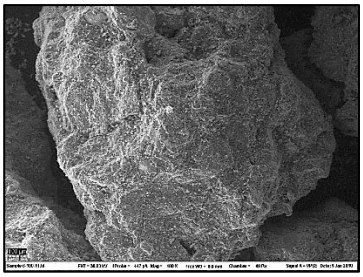
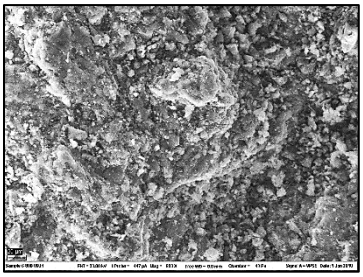
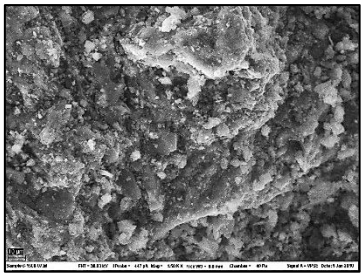
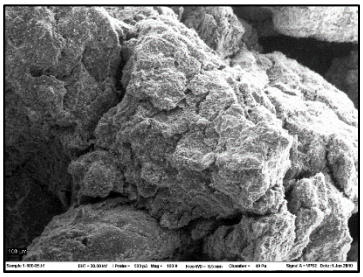
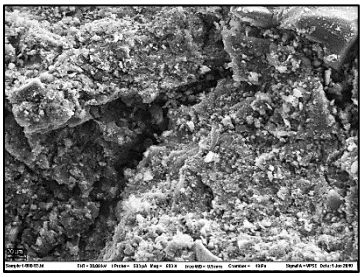
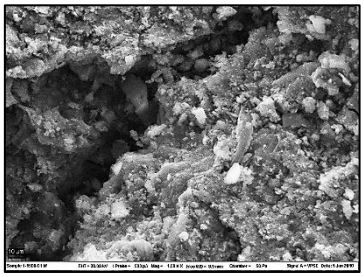
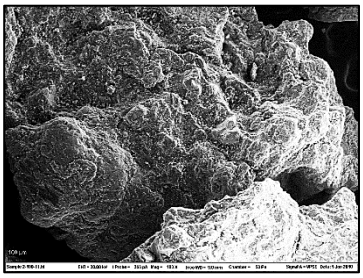
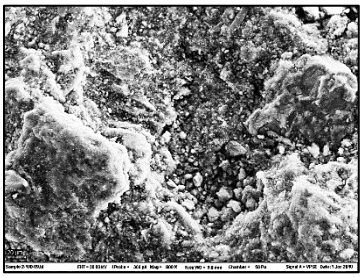
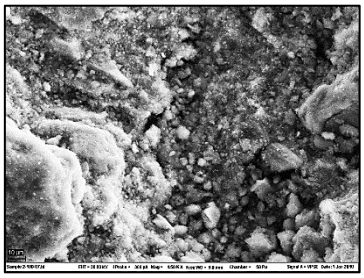
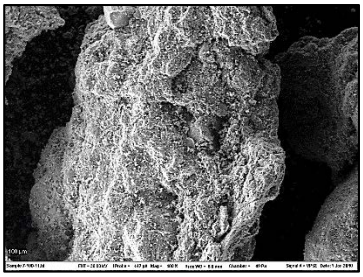
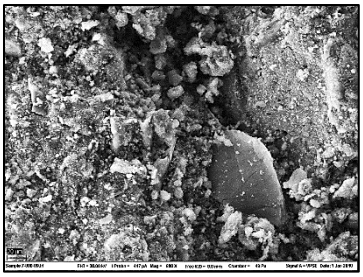
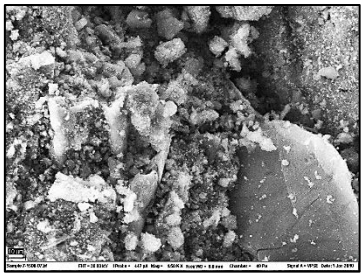
Preparation for Cl measurements: Weighted exactly 0.25 g of sample and added 2 mL of tetra-methyl-ammonium-hydroxide (TMAH). The samples were heated for 3 hours and then diluted to 10 mL with mq- water. Then samples are left to settle and then an aliquot part of 1 mL was transferred to a new tube and diluted to 10 mL with mq- water. The samples were then analyzed by Agilent ICP-QQQ-MS in He-KED and oxygen reaction mode.

Appendix C - Scanning Electron Microscope results

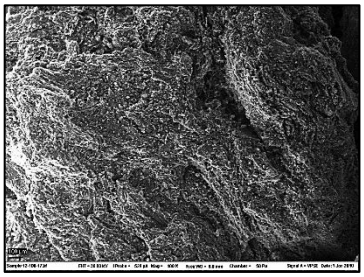
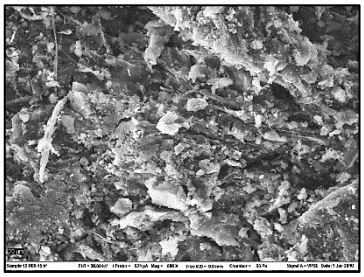
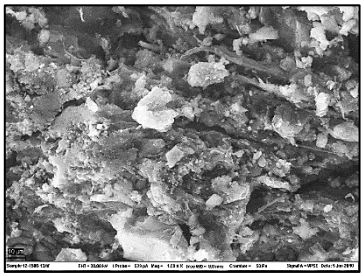
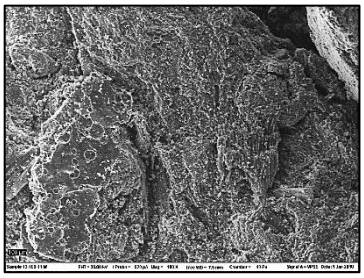
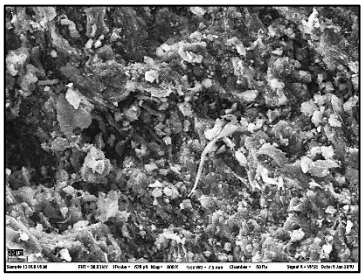
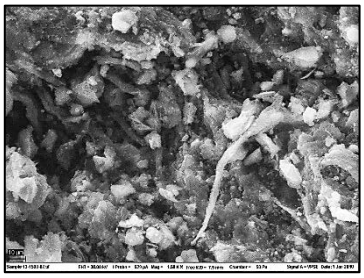
C.1 Wood biochar from Hellengdal

Note	Magnification: 100x	Magnification: 800x	Magnification: 1500x
Pyrolysis: 550 °C unwashed			
Pyrolysis: 600 °C unwashed			
Pyrolysis: 600 °C-unwashed, treated			
Pyrolysis: 700 °C unwashed			
Pyrolysis: 700 °C washed			
Pyrolysis: 750 °C unwashed			

C.2 Waste sludge biochar from Lindum/Vesar

Note	Magnification: 100x	Magnification: 800x	Magnification: 1500x
Pyrolysis: 500 °C washed			
Pyrolysis: 600 °C unwashed			
Pyrolysis: 700 °C unwashed			
Pyrolysis: 700 °C washed			
Pyrolysis: 800 °C unwashed			

C.3 Waste sludge biochar from Ullensaker

Note	Magnification: 100x	Magnification: 800x	Magnification: 1500x
Pyrolysis: 700 °C washed			
Pyrolysis: 800 °C unwashed			

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