

Örebro Studies in Chemistry 30



Charlotte Nilsson

**Phosphorus recovery from sewage sludge**

**Implications of incineration and enrichment potential of produced ashes**

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**Title:** Phosphorus recovery from sewage sludge, Implications of incineration and enrichment potential of produced ashes

**Publisher:** Örebro University, 2024

[www.oru.se/publikationer](http://www.oru.se/publikationer)

**Print:** Örebro University, Repro 05/2024

**ISSN:** 1651-4270

**ISBN:** 978-91-7529-561-9 (print)

**ISBN:** 978-91-7529-562-6 (pdf)

## **Abstract**

Sewage sludge is a promising source for phosphorus recovery, but it also contains contaminants (organics, metals) which must be removed. The most commonly used practice is incineration, where organic contaminants are decomposed. This treatment entirely alters the chemical profile of the material, and information regarding this transformation is crucial for development of durable handling and recovery processes. The aims of this project were to; <sup>1</sup>study the chemical speciation of phosphorus and metals in sewage sludge and their ashes after incineration; <sup>2</sup>evaluate the impact of iron and aluminium on the phosphorus redistribution following incineration, and <sup>3</sup>investigate the potential for sewage sludge ashes to function as sorbents for phosphorus and metals. Sludge and ashes from 10 municipal wastewater treatment plants in Sweden were sampled and characterized for their elemental composition, mineral components, leachability and chemical speciation. Major elements were Fe and Al (added in the wastewater treatment process), Ca, Mg, Na and K. Phosphorus was predominantly associated with aluminium and iron in the sludge, but after incineration there was a shift to calcium associated species, which is preferred for phosphorus recovery. This alteration was hampered by high concentrations of aluminium, why its concentration should be kept at a minimum. The incineration caused changes in speciation, where more ordered mineral phases were created, hematite being the major component. The ashes were successfully used as sorbents for both metals and phosphorus. Adsorption isotherms and inter particle-diffusion modelling indicated that the sorption takes place in two stages, where the first is a rapid process on the surfaces, while the second is slower and includes interactions with the pores of the material.

**Keywords:** Wastewater, sewage sludge, ashes, phosphorus, metal, speciation, adsorption, recovery, sustainability

## Dedication

This thesis is based on research conducted at Örebro University and Fortum Waste Solutions AB, Kumla, with funding from the Norrtorp-Kumla Environmental Foundation. The co-writers are acknowledged for contributing to the scientific papers, Prof. Monica Odlare (MDU) is acknowledge for reviewing the thesis.

The completion of this thesis, and the work behind it, would never have been possible without the contribution from several persons; My main supervisor, Prof. Stefan Karlsson (ORU), now we can agree that there isn't that much time left, but we made it! Prof. Bert Allard (ORU), without you this journey would never have begun, and without your support it wouldn't have finished. I will be forever grateful for all your support! Dr. Thomas von Kronhelm, you have grown to be not only one of my co-supervisors and my manager, but also a friend, what would I have done without your support? And more importantly, without all laughter, hard work and odd projects? Strangely enough, we always find a way, be it to memorable visits or to reach the target of a specific project – I look forward for more of both!

My dear co-workers and friends at the R&D department at Fortum (past and present), without you I would have been reduced to a wet patch on the floor a long time ago. Radwa, Raimo, Karin, Marina, Anna, Helene, Tomas – thank you for your support and all fun memories – I am sure that there are more to come. Ulrika, you are amazing and without you my life would be so much more boring! Edvin, I am truly excited to take on a new journey, but from another perspective – what could possible go wrong? Carl-Johan, what can I say – your support and commitment mean the world to me, you are unique and amazing – don't ever change! Staff, colleagues and friends at the laboratory, I truly appreciate all help and support, as well as inspirational discussions during lunch and coffee-breaks. And, to all colleagues at Fortum, thank you for keeping me connected to the real world.

To all of you who I have been lucky to work together with at MTM during these years – Thank you for being there, for interesting discussions, and for sharing this time with me. Viktor, you have been there throughout this long journey and provided help, support and

encouragement along the way, thank you! Josefine, I am impressed by your determination and efficiency throughout your journey, Anna – you are a true inspiration. Kristina – you are one of a kind, and I really value getting to know you.

To friends and family, who have been there in ups and downs, I am so lucky to have you in my life, and I will forever be grateful for you keeping up with my “small” outbreaks. Special thanks to: Madde, I can only hope that you know how much I appreciate you. Frida, even though we are terrible in keeping contact, you are always there, thank you for being you! Amanda, my vent and one of my dearest friends, what would I do without you (Britta kom!)? Pillis you mean so much to me. Martina, Anni and Ina, spending time with you provides well needed energy and I am so glad to have you in my life. Hobbe, where would I be if it wasn't for you? Thank you for everything – you are a rock!

To my mother, the strongest person I know, thank you for always believing in me – I love you! Fredrik, thank you for being there and for supporting me in everything! Lina, my amazing sister who has never lost faith in me, what would I do without you? I love you! Adam and Calle – the world's best nephews, Daniel – I am so happy to be able to call you a part of my family! Kerstin and Åke, thank you for all help and support, both in general and with the children – you are lifesavers!

Henrik, what a journey this has been – I will forever be grateful for your love and support. Although things didn't turn out the way we planned and hoped for, you will always have a special place in my heart. Signe and Filip, you are truly the meaning of my life – always stubborn, curious and energetic, I love you to the moon and back.

In addition, I would also like to acknowledge the well-needed energy, without which the completion of the thesis would not have been possible: Coffee – as well as the person who brought the coffee, and chocolate!

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## List of papers

This thesis is based on the following studies, referred to in the text by their Roman numerals.

- I. Nilsson, C., Sjöberg, V., Grandin, A., Karlsson, S., Allard, B., von Kronhelm, T., 2022. Phosphorus speciation in sewage sludge from three municipal wastewater treatment plants in Sweden and their ashes after incineration. *Waste Management & Research*, 40:8, 1267-1276
- II. Nilsson, C., Karlsson, S., von Kronhelm, T., Sjöberg, V., 2018. Leaching behaviour of principal elements (Al, Ca, Fe, K, Mg, Mn, Na) and P in incinerated sewage sludge. *Submitted to Water Air and Soil Pollution*
- III. Nilsson, C., von Kronhelm, T., Karlsson, S., Phosphorus speciation in sewage sludge and their ashes after incineration as a function of treatment processes. *Accepted for publication in Waste Management & Research*, 2024-04-12.
- IV. Nilsson, C., Karlsson, S., Sjöberg, V., von Kronhelm, T., 2016. Municipal sludge ash for abatement of ARD. In Drebenstedt C, Paul M (Eds). *Mining Meets Water – Conflicts and Solutions. Proc. 12th IMWA Congress, Leipzig, Germany*, 699-705
- V. Nilsson, C., Sjöberg, V. Phosphorus sorption to sewage sludge ash, *Manuscript*

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Relevant publications not included in the scope of this thesis:

- Nilsson, C., Renman, G., Westholm, L.J., Renman, A., Drizo, A., 2013. Effect of organic load on phosphorus and bacteria removal from wastewater using alkaline filter materials. *Water Research*, 47:16, 6289-6297
- Nilsson, C., Lakshmanan, R., Renman, G., Rajarao, G.K., 2013. Efficacy of reactive mineral-based sorbents for phosphate, bacteria, nitrogen and TOC removal – Column experiment in recirculation batch mode. *Water Research* 47:14, 5165-5175
- Allard, B., Nilsson, C., Sjöberg, V., Karlsson, S., 2023. Leachability and speciation of elements in municipal wastewater treatment sludge and the ashes after incineration – application of new sequential extraction procedures based on alkaline aqueous solutions and organic solvents as leachants. *Manuscript*

## List of Abbreviations

The following abbreviations are used throughout this thesis:

Al-P	Phosphorus associated to aluminium
ANOVA	Analysis of variance
AP	Apatite phosphorus (phosphorus associated to Ca
ATP	Adenosine triphosphate
Ca-P	Phosphorus associated to calcium
Fe-P	Phosphorus associated to iron
IP	Inorganic phosphorus
ISSA	Incinerated Sewage Sludge Ash
MWWTP	Municipal Wastewater Treatment Plant
NAIP	Non-apatite inorganic phosphorus
OP	Organic phosphorus
p.e.	Person equivalents: the volume of wastewater corresponding to that produced by one person on a daily basis
rcf	Relative centrifugal force
SMT	Standard Measurements and Testing
TP	Total phosphorus
WtE	Waste to Energy

# Introduction

## Phosphorus

Phosphorus was discovered in 1669 by the German alchemist Henning Brand, who was able to isolate its elemental form as white phosphorus, which is the most commonly used form of phosphorus. It is also the least stable form, and it gradually changes into the other common forms, such as red phosphorus, a process which is accelerated by light and heat. White phosphorus with a lower grade of purity is often referred to as yellow phosphorus, because of the discoloration caused by red phosphorus contamination. Due to its high reactivity towards oxygen, phosphorus is never found as a free element; in nature it is exclusively found in a combined state, notably as calcium phosphate in phosphate rock (ZumdaHL and ZumdaHL, 2003).

## Phosphorus use in agriculture

Phosphorus is an essential element in all living organisms and is therefore an irreplaceable component in food production (Cornel and Schaum, 2009).

In their studies on phosphorus usage through history, Ashley *et al.* (2011) and Naden *et al.* (2016) described the cycle of consumption and recycling of phosphorus that has been the norm throughout history, thereby gaining higher crop yields. Examples of this practice include the burning of plants and thereby release of previously plant-unavailable phosphorus to crops, as performed by hunter-gatherers 40 000 years ago. In China, human excreta have been used to increase crop yields for at least 5 000 years and during the medieval period in England, the nobility allowed peasants to graze sheep on their land in exchange for the sheep droppings. However, this recycling of phosphorus has changed over time. During the Industrial Revolution, urbanization resulted in rapid expansion of cities. By 1854 London was one of the largest cities in the world, with some 2.5 million residents within a circumference of 20 km. As the population density increased, so did the outbreaks of infectious diseases such as plague

and cholera. The previous practice of returning of ‘night soil’ to agricultural land was hampered by increase in waste quantities as well as transport distance, why most households let the waste accumulate in the immediate vicinity of their homes. The turning point occurred in 1854, when a cholera outbreak in London resulted in 616 deaths. It was concluded that the outbreak was a result of poor waste management, representing an important milestone in the ‘Sanitary Revolution’, and the focus for sewage treatment shifted towards health and hygiene. As a result, the disposal of human wastes was made by water-based systems, with the aim to move the waste downstream, away from the citizens (Ashley *et al.*, 2011; Naden *et al.*, 2016). This shift in waste disposal practice also reflected on the phosphorus management, particularly in urban areas, and the previous phosphorus recycling society became a phosphorus throughput society. Instead of being reused for crop production on arable land, the phosphorus was used once and then discarded (Ashley *et al.*, 2011), typically into water courses and the ocean.

In the 17th and 18th centuries, decreased nutrient content in arable soil resulted in an intense search for fertilizers in order to increase, or even maintain, the crop yields to produce food for the growing population. Crushed bones and guano were discovered to contain high levels of phosphorus and were therefore imported to the UK. In the 20th century, deposits of natural occurring calcium phosphates with high concentrations of phosphorus (typically 10-20%), commonly referred to as phosphate rock, were discovered. Phosphate rock was considered as a cheap, abundant and inexhaustible source of phosphorus and the use of mineral fertilizers grew exponentially. In order to keep up with the rapidly growing population, urbanization and increasing shortage of food, the use of fertilizers sextupled between 1950 and 2000. Processed fertilizers, originating from phosphate rock, contain higher concentrations of phosphorus compared to organic sources, and the use of these have saved millions from starvation. From a Swedish context, the low phosphorus content in agricultural soils following World War II led to increased concentration of mineral fertilizer, with a peak in the 1970s (Linderholm *et al.*, 2012) Although the fertilization recommendations have changed, and the use of fertilizers have decreased, the amounts

of phosphorus imported for fertilization adds up to almost 13 000 metric tonnes (SCB, 2020b). Today, these fertilizers are crucial to produce enough food for the global population; thus, we have been addicted to phosphate rock (Cordell *et al.*, 2009).

## **Phosphorus – a limited resource**

According to the U.S. Geological Survey, phosphate mineral deposits must meet certain criteria in order to be classified as a reserve (USGS 2013). The criteria encompass the quality of the mineral, as well as the volume of the deposit. Furthermore, the exploitation of the deposit must be economically advantageous using the technology available at the time of characterization. Deposits that do not meet these requirements are classified as resources. Following technical development and changes in price, the distribution between these two categories is likely to change, thereby affecting the lifetime of the phosphate reserves. Although there are different opinions on the size and longevity of these reserves, it is clear that the amount of phosphate rock is limited (Scholz and Wellmer, 2016).

## **Limitations in phosphorus production**

Besides the limited reserves of phosphate rock, the mining and productification of them into fertilizers are also hampered by technical challenges. One of these is the accessibility to water in several of the countries where phosphate rock is present, since mining and refining consume large quantities of water. In regions with limited access to water this may therefore result in conflicting interests, e.g., agriculture or drinking water production. (Ridder *et al.*, 2012). In addition, phosphate rock also contains other minerals, which may have negative impact on the processes or the product (Nziguheba and Smolders, 2008; Derhy *et al.*, 2020). The refining process is dependent on the superficial properties of mineral, and parameters such as surface charge, wettability and solubility plays an important role in the process optimization. The great variety of phosphate rock also entails a diversity in processes, and high concentrations of other minerals further adds on to the complexity. From a study on two different types of phosphate ore, Elbendari *et al.*

(2019) reported high concentrations of SiO<sub>2</sub> (19% and 32%), Al<sub>2</sub>O<sub>3</sub> (3% and 15%) and CaO (38% and 18%). While all three constituents may have positive effects on the production process if their content is kept at acceptable levels, too high concentrations (>2% SiO<sub>2</sub>; >3% Al<sub>2</sub>O<sub>3</sub>; CaO:P<sub>2</sub>O<sub>5</sub> > 1.6) entail increased production costs (Derhy *et al.*, 2020). In addition, several commercial phosphate fertilizers have been shown to contribute to increased concentrations of trace elements such as As, Cd, and Cr (notably Cr(VI)) in agricultural soils, depending on the origin of the phosphate rock (He and Singh, 1994; Guttormsen *et al.*, 1995; Nziguheba and Smolders, 2008; Shahid *et al.*, 2019; Sharma *et al.*, 2020; Suci *et al.*, 2022).

## A geopolitical perspective

Even though deposits of calcium phosphate can be found in the earth's crust throughout the world, high grade calcium phosphate rock, is found only in a few locations (Driver *et al.*, 1999). According to the U.S. Geological Survey (U.S.G.S., 2021), the global reserves hold a total of approximately 72 billion metric tons of phosphate rock, while the annual consumption amounts to 220 million metric tons (**Table 1**). China, the U.S., Morocco and Russia are the four leading nations in terms of phosphate rock mining, with an annual production of 85, 22, 38 and 14 million metric tons, respectively. In total, these four nations account for more than 70% of the global phosphorus production.

**Table 1.** Reserves and annual production of phosphate rock for 2021 and 2022 (estimated), given in million metric tons.

	Mining		Reserves
	2021	2022*	
China	90	85	1 900
Morocco	38	40	50 000
U.S.	22	21	1 000
Russia	14	13	600
Other	62	63	18 700
World total	226	220	72 000

Data compiled from U.S.G.S., 2023

However, most of the mined phosphate rock is consumed domestically, and less than 20% reach the global market (AEEP, 2022). As a consequence, the majority of the world's nations depend on import of phosphorus raw material or fertilizer products, and thereby also vulnerable to geopolitics (Brownlie *et al.*, 2022). An example is the 100-135% export tax on fertilizers introduced by China in 2008, as a means to ensure the availability on the domestic market. More recently, the global phosphate prices have spiked 400% since 2020 because of disruptions in the supply chain, export bans and sanctions. This development is most likely to continue, leading to further decreases in phosphorus availability on the world market, and thereby increasing prices. As for now, the amount of phosphate rock exported from the largest producer, China, is steadily decreasing and the export in May 2022 was only 20% compared to the same period in 2021 (Chow and Patton, 2022). In addition, although being one of the biggest producers, the U.S. is actually importing phosphorus in order to meet their fertilizer demands (AEEP, 2022). Thus, the export from two of the dominating phosphate rock producers is much lower compared to the theoretical capacity, leaving Morocco and Russia as the possible providers to the world market. However, due to the Russian attack on the Ukraine in February 2022, several major economies (including the U.S., the EU and the UK) have imposed economic sanctions on export and imports from and to Russia, including fertilizers. Therefore, the only candidate for phosphate rock export is Morocco, which also is the nation holding the largest phosphate rock reserves, constituting more than 70% of the global reserves (U.S.G.S., 2021). However, the majority of these reserves are in fact located in Western Sahara, which has been occupied by Morocco for the last 35 years, thus making it a highly disputed region.

It is clear that the geopolitical situation is far from stable in terms of phosphate rock trading. Due to its economic importance and high risk associated with the supply, the Raw Materials Supply Group, an expert group of the European Commission, has included phosphate rock on their list of critical raw materials (EC, 2020).

## **A sustainable approach?**

As stated in the report from the Brundtland Commission (UN, 1987), *sustainable development* can be defined as “a development that meets the needs of the present without compromising the ability of future generations to meet their own needs”. It is clear that the “end-of-line” use of phosphorus that has been the standard practice up till now is not sustainable. Mining rock with high concentration of phosphorus in order to produce fertilizers that are used to increase crop yields strongly affects the phosphorus balance of arable land. Since the applied phosphorus is removed from the fields through harvest and food production, recirculation is effectively hampered, while the consumed phosphorus is excreted and eventually released to the nature.

In this manner the reserves of phosphate rock are being depleted as the phosphorus is accumulated in the water, leading to eutrophication of lacustrine and oceanic systems. This results in an increased biological consumption of oxygen and, in the long run, problems with anoxic waters. Fertilization is, however, necessary to maintain high enough crop yield, if no nutrients would be added it can therefore be assumed that the soils would be depleted, resulting in decreased food production. In addition, the few nations with large phosphorus resources are in control over the global market and therefore have an economic advantage of other countries.

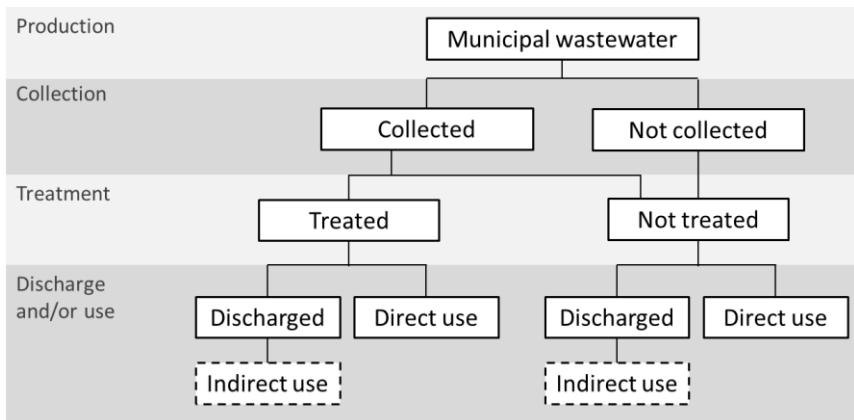
In order to sustain the agriculture of today and to enable the possibility to feed the growing global population, it is crucial to once again start to recycle the spent phosphorus and return to the phosphorus-recycling society.

## **Wastewater as a phosphorus resource**

Approximately 90% of the mined phosphate rock is used for food production (Cordell *et al.*, 2009). Due to extensive losses in the phosphorus cycle, during mining, erosion, runoff, missed recycling opportunities and accumulation of phosphorus in soil due to overfertilization etc., only 20% of the phosphorus that is mined reaches the food that is consumed (Smit *et al.*, 2009). Nearly all

phosphorus consumed through food is excreted; the global population annually excretes approximately 3 million metric tonnes of phosphorus through urine and faeces (Cordell *et al.*, 2009), making domestic wastewater an important resource for phosphorus recovery.

As visualized in the municipal wastewater chain (**Figure 1**), wastewater can, be collected, treated, used or disposed of. Direct use means that treated or untreated wastewater is used directly for different purposes such as agriculture, forestry, gardening etc. Indirect use implies that the wastewater is released to a water body, thereby being diluted, before being used on agricultural land for irrigation purposes (Mateo-Sagasta *et al.*, 2015). In their work to monitor the Sustainable Development Goal 6, to ensure availability and sustainability management of water and sanitation for all, the Food and Agriculture Organization of the United Nations has created a global database for information on water resources (Aquastat, 2018). Here, it is possible to retrieve information regarding the production and treatment of wastewater on a national level. Although the amount of wastewater produced and treated on a global scale is hard to determine, estimations based on reported national data suggest a total production of 310 billion m<sup>3</sup>, of which 50-60% is collected and



**Figure 1.** The municipal wastewater chain; possible options for collection, treatment and usage of municipal wastewater (Mateo-Sagasta *et al.*, 2015).

treated (Aquastat, 2018). These numbers are, however, rather uncertain and the lack of available data constitutes an important limitation for evaluation of wastewater production and treatment, on a global basis. In a study on the need for data regarding generation, treatment and use of wastewater, Sato *et al.* (2013) reported that only 55 out of the 181 countries studied had available data on all three parameters. Furthermore, different use of the word “treatment” also presents a challenge since it makes comparison more difficult; Although most countries report only secondary and tertiary treated wastewater as “treated wastewater”, some include primary treated wastewater. In addition, many wastewater treatment plants, especially in low-income countries, are functioning below expectation, leading to treatment efficiencies below the reported levels (Mateo-Sagasta *et al.*, 2015).

According to their study on wastewater production, collection, treatment and reuse, Jones *et al.* (2021), estimated the annual global wastewater production to almost 360 billion m<sup>3</sup>, with a global average of 49 m<sup>3</sup> year<sup>-1</sup> per capita. This estimation differs from the previously mentioned volume of 310 billion m<sup>3</sup>, retrieved from the Aquastat database, possibly because of the different sources used for retrieval of the data. Assuming an average total phosphorus concentration of 7.8 mg L<sup>-1</sup> (Quadir *et al.*, 2020), the annual potential of phosphorus recovery from wastewater adds up to 2.8 million metric tons (MMT). This can be compared to the 19.5 MMT of phosphorus that is mined each year, or the annual losses (e.g., erosion and removal of plant material) from arable land which amounts to 10.5 MMT phosphorus (Liu *et al.*, 2008). Thus, it is obvious that recovering of phosphorus from wastewater constitutes an important piece in the puzzle of a sustainable phosphorus management.

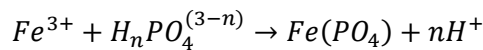
## **Phosphorus removal from wastewater**

There are numerous techniques which have been developed to remove phosphorus from liquid streams, such as municipal wastewater (Morse *et al.*, 1998; de-Bashan and Bashan, 2014; Desmidt *et al.*, 2015; Wu *et al.*, 2015), the most commonly used ones are described below.

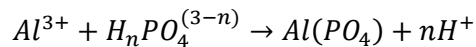
## Chemical precipitation

Because of its high efficiency and ease of operation, chemical precipitation is the most commonly used method for phosphorus removal in Swedish MWWTPs (SCB 2020). Briefly, this technique is based on addition of solutions with di- or trivalent salts to the wastewater, thereby inducing formation of insoluble phosphate compounds, which are settled out and incorporated in the sludge (Morse *et al.*, 1998). The most frequently used metals for removal of phosphorus from the liquid phase are iron and/or aluminium, which react with the phosphate ions according to Equation 1 and Equation 2, respectively. In addition to direct precipitation, co-precipitation with hydrous oxides also has an important role in the phosphorus removal process. Both iron and aluminium salts added to the water will form hydrous oxides with very high sorption capacities, as well as entrapping colloids and particles in the forming amorphous matrices (Equation 3) (Smith *et al.*, 2008).

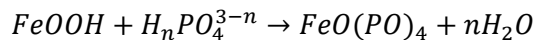
### Equation 1



### Equation 2

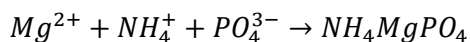


### Equation 3



Commercial processes with the aim to recover phosphorus from the wastewater are, however, often based on precipitation of struvite ( $NH_4MgPO_4$ ) or calcium phosphate (hydroxyapatite), as shown in Equation 4 and Equation 5, respectively.

#### Equation 4



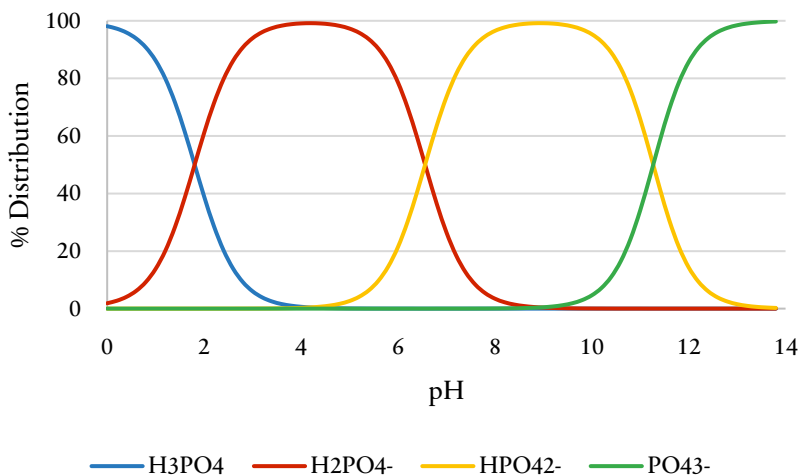
#### Equation 5



Spontaneous precipitation of struvite in pipes and other parts of the wastewater treatment plant is a common problem since it leads to increased maintenance costs (Desmidt *et al.*, 2015). Controlled formation of struvite, on the other hand, represents a possible approach to recover phosphorus and several studies have been conducted on the formation, the properties and fertilizer-potential of this compound (c.f. Uysal *et al.*, 2010; Ye *et al.*, 2014). In most MWWTPs, the formation of struvite is limited by the concentration of magnesium, why this is added as MgCl<sub>2</sub> or MgOH (Desmidt *et al.*, 2015).

Although several different calcium phosphates can be formed from precipitation, hydroxyapatite (Ca<sub>10</sub>(PO<sub>4</sub>)<sub>6</sub>(OH)<sub>2</sub>) is the most likely. Since calcium phosphate is the major component in phosphate rock, it should be possible to use in fertilizer production (Driver *et al.*, 1999).

Phosphorus precipitation is a complex process, determined by several parameters. Besides the concentration of phosphorus and the counter ions (e.g., Al, Ca, Fe or Mg), time, temperature and the ionic-strength and types of ions present in the solution play important roles for the composition of the resulting solids. Despite the different ions used to remove phosphorus through precipitation, the processes are generally favoured by high pH (Harrison *et al.*, 2011), causing the phosphate to exist in a more reactive form (i.e. as PO<sub>4</sub><sup>3-</sup> as opposed to HPO<sub>4</sub><sup>2-</sup>, H<sub>2</sub>PO<sub>4</sub><sup>-</sup> or H<sub>3</sub>PO<sub>4</sub>), as visualized in **Figure 2**.



**Figure 2.** Fractional speciation of phosphate in aqueous solution as a function of pH

## Sorption

The concept of sorption is used for several in principle different processes (see below) where phosphorous, or other elements, in an undersaturated solution adheres to the surface of a solid substrate. The process typically has two stages where the first interaction binds the solution species to the surface with mechanisms described below. Secondly, if the porosity of the sorbent allows, the sorbed species diffuse into its matrix because of the concentration gradient. These processes are of great quantitative importance since they determine the physical and biological properties of an element in undersaturated systems. In nature, the reactivity of phosphate ions results in an almost quantitative sorption to a wide variety of available surfaces. The capacity of surfaces and net kinetics of the processes are determined by several factors where surface potential and properties of complexing surface groups are most important (Stumm, 1992; Langmuir, 1997). In addition, the composition of the solution phase and its impact on the distribution of dissolved species is also of importance. Particularly pH

and the presence of complex forming ions and molecules are important for the sorption process. Since the phosphate ion is a highly reactive ligand with a large variety of cations it is never free neither in natural systems nor in sewage water. Its chemical state, i.e., dissolved or sorbed to carrier phases, will in principle be controlled by the stability of available coordination compounds and if they are free in the water phase or a part of a solid surface. The sorption mechanisms, including phosphate, can be characterized by five different mechanisms (Loganathan *et al.*, 2014):

- *Ion exchange*: a stoichiometric process in which the counter ions leaving the sorbent are replaced by other counter-ions, in order to maintain the electro-neutrality of the sorbent. This process is rapid, driven by electrostatic forces, and it results in weak forces of attraction between the ion and sorbent and is therefore reversible.
- *Ligand exchange* includes the formation of a covalent bond with oppositely charged ions at the surface of the sorbent. For anions, this results in a release of negatively charged ions (e.g., hydroxyl groups), previously bound to the cation, with a subsequent increase in pH. Sorbents behaving in this manner typically have high sorption capacity as well as selectivity; the formed complex is strong and therefore not always reversible.
- *Hydrogen bonding* consists of the attractive forces between the hydrogen atom in a molecule and an electronegative atom, such as oxygen, in another. This sorption mechanism results in a stronger association compared to ion exchange, but weaker than ligand exchange. The process is fast and not always reversible.
- *Surface precipitation* consists of the formation of stoichiometric compounds between dissolved and surface bound species, typically ions. The mechanism is derived from the theoretical framework from reactions in saturation-controlled systems. Documented solubility products ( $K_s$ ) are, however, not directly transferable between the systems since the surface potential of the solid alters the chemical conditions. These kinds of reactions are rapid, and the resulting complexes are not easy to dissolve.

- Surface diffusion. Since the above stated mechanisms result in an increased surface concentration of sorbed species there is a concentration gradient directed towards the interior of the sorbent. For non-specific bonds it is frequently observed that there is a surface migration of sorbed species, driven by concentration differences. For this process to happen it is also important that the internal volume (porosity) allows for the migration of species. The process is slow, and highly dependent on the sorption mechanism.

Although sorption enables effective removal from wastewater, the process is hampered by solids or organic material (Nilsson *et al.*, 2013). In order to enable for an efficient sorption process, extensive pre-treatment of the water is therefore needed, which limits the applicability in full scale treatment, especially from a cost perspective.

### **Other techniques**

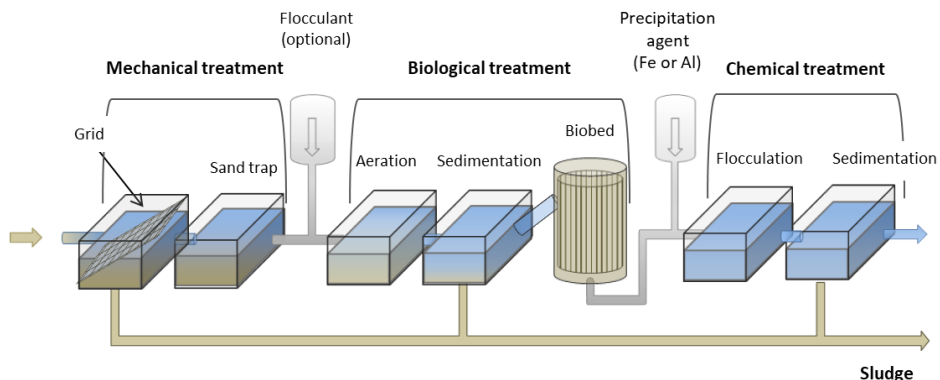
There are several alternatives for removal of phosphorus from wastewater, besides chemical precipitation and sorption discussed above. Two of these are enhanced biological phosphorus removal (EBPR) and constructed wetlands.

In enhanced biological phosphorus removal (EBPR), specific strains of bacterial are used to accumulate excess amounts of phosphorus, compared to the amount needed for growth (sometimes referred to as “luxury uptake”). The incubation conditions are altered in terms of concentration of carbon and availability of oxygen in order to achieve a net-uptake of phosphorus, and up to 90% phosphorus removal (de-Bashan and Bashan, 2014; Ramasahayam *et al.*, 2014). Even though EBPR offers a green approach to phosphorus removal, it is vulnerable to changes in terms of wastewater composition and incubation conditions.

Constructed wetlands are systems which are designed to mimic natural wetland systems, in which vegetation, soil and microorganisms work together to remove nutrients. This is a complex system which relies on a combination of physical, chemical and biological mechanisms (Wu *et al.*, 2015).

## Wastewater treatment

As the industrialization accelerated after the Second World War, many environmental problems escalated, from being of local nature to regional and national scales. As a consequence, national monitoring programs and guidelines were initiated in Sweden, as well as other countries (Herschy 1998; Fölster *et al.*, 2014), which has resulted in the wastewater treatment systems of today. Conventional wastewater treatment consists of a combination of processes; preliminary, primary, secondary and tertiary treatment, a schematic presentation of the treatment process is given in **Figure 3**. The initial treatment consists of physical removal of coarse solids, such as grit and large objects. This is followed by the primary treatment, where organic and inorganic solids are removed through flotation and sedimentation. Further removal of organics is achieved in the secondary treatment, which is a biological process. The wastewater is aerated, and microorganisms are used to digest organic matter, resulting in the formation of what is usually referred to as activated sludge. The last step is the tertiary treatment, which specifically aims at removing nutrients (mainly phosphorus) from the wastewater before being released to a recipient. One commonly used approach



**Figure 3.** Conventional wastewater treatment entailing primary (mechanical), secondary (biological) and tertiary (chemical) treatment.

for this is addition of metal ions (e.g., chloride or sulphate salts of iron or aluminium), which induce precipitation of phosphorus (notably phosphates) species, as previously described. Following this, phosphorus is precipitated as aluminium- or iron phosphates, or co-precipitated with hydrous oxides. In addition to phosphorus and the counter ions (e.g., Al, Ca, Fe or Mg), the precipitates also contain other constituents, which hampers direct use or recirculation. Once formed, these precipitates are removed by sedimentation (Pes-cod, 1992) and incorporated in the sewage sludge together with other substances removed in the wastewater treatment process. Due to this relocation of phosphorus, from liquid to solid phase, the concentration increases from approximately 4-15 mg kg<sup>-1</sup> to 10 000 mg kg<sup>-1</sup> sewage sludge (dry weight), thereby making the sludge a good candidate for fertilizer use. Besides the salt solutions added for precipitation, many facilities also use additives, often different kinds of polymers based on iron- and/or aluminium ions, in order to improve the physical properties of the sludge, e.g., to increase sedimentation efficiency and dewaterability.

All urban wastewater produced within the EU must be treated according to the Urban Wastewater Treatment Directive (91/271/EEC), which aims at protecting the environment from adverse effects of wastewater discharge. The directive states that urban wastewater should be collected and subjected to (at least) secondary treatment before discharge. Although removal of nutrients (i.e., phosphorus and nitrogen) is only required for “sensitive areas”, most freshwater bodies belong to this category and approximately 2/3 of the European population is connected to MWWTPs with tertiary treatment (Eurostat, 2022). In their analysis of phosphorus flows and balances in the European Union (EU-27), van Dijk *et al.* (2016) stated that 34.6% of the phosphorus that is lost through human consumption is accumulated in sewage sludge.

Given the apparent uncertainty regarding global production and treatment of wastewater, it is difficult to make a precise assessment of the amounts and quality of sewage sludge produced. However, in their comprehensive study on legislation for biosolids reuse in Europe, Collivignarelli *et al.* (2019), stated that the annual sewage

sludge production within the EU exceeded 10 M metric tonnes (dry weight). Assuming an average phosphorus concentration of 10 mg g<sup>-1</sup> (dry weight), this corresponds to 100 tonnes of phosphorus. Thus, the sewage sludge constitutes an important source for phosphorus recovery.

### **Phosphorus recovery from sewage sludge**

The simplest way to recover phosphorus from sewage sludge is by direct application of the sludge to agricultural soil. In addition to phosphorus, this practice also allows for recirculation of other components which are necessary for growing crops. Application of sewage sludge entails an increase in soil organic carbon, as well as porosity, which has a positive effect on the soil physical conditions (Singh and Agrawal, 2008). Sewage sludge also contains nitrogen and potassium, which are the two other components in commercial fertilizer products often referred to as NPK.

However, direct application of sewage sludge is disputed because of its content of potentially harmful substances originating from the wastewater. These include organic pollutants (e.g., PFAS, PAH, pharmaceuticals and their metabolites, etc.), pathogens and heavy metals. Informal use of untreated sewage sludge is common in low-income countries, where regulations are weak, whereas formal use is strictly regulated in developed countries (Mateo-Sagasta *et al.*, 2015). Currently, direct application of sewage sludge within EU is regulated by Council Directive 86/278/EEC, which states permissible concentrations of heavy metals in the sludge, as well as in the soil after sludge application. All member states have transposed the directive into their national legislations, and many nations have adopted even more stringent limits for metal concentrations in sludge or soil. In addition, several nations have also added limit values for metals not included in the directive, as well as for organic micropollutants and pathogens (Collivignarelli *et al.*, 2019; Hudcová *et al.*, 2019). Limiting values for regulation of sludge application to arable in land within the EU, are presented in **Table 2**.

**Table 2.** Limiting values for heavy metals in sewage sludge to be used on arable land for food production, maximum concentrations in soil, and maximum annual loading, given as average for a period of 10 years. Concentrations are given in mg kg<sup>-1</sup> dry weight (DW), maximum annual loadings are given as kg per hectare (ha)

	<b>Sludge</b>	<b>Soil</b>	<b>Annual load</b>
	<i>mg kg<sup>-1</sup> DW</i>	<i>mg kg<sup>-1</sup> DW</i>	<i>kg ha<sup>-1</sup> year<sup>-1</sup></i>
Cd	20 - 40	1 - 3	0.15
Cu	1 000 – 1 750	50 - 140	12
Ni	300 - 400	30 - 75	3
Pb	750 – 1 200	50 - 300	15
Zn	2 500 – 4 000	150 - 300	30
Hg	16 – 25	1- 1.5	0.1
Cr*	100	60	0.04

\* Limiting values for Cr is not stated in 86/278/EEC, given values are retrieved from SNFS 1994 (soil concentration and annual load) and SOU 2020:3 (sludge concentration)

Although direct application is regulated in the EU, it is still the main disposal route, accounting for 50% of the annual production within the EU. Other common disposal routes are incineration (28%) and landfilling (18%). The remaining fraction (4%) is disposed of using other methods, such as pyrolysis, storage, forestry, land reclamation and landfill coverage (Collivignarelli *et al.*, 2019; Eurostat, 2022).

### **Sludge application – pros and cons**

Direct application of sewage sludge does not only allow for recirculation of phosphorus, but also of other crucial components which are needed for growing of crops, e.g., nitrogen and organic carbon. This practice of sludge management has been widely studied in relation to its effect as a fertilizer on a variety of crops with positive results. The range of plants include rye grass (*Secale Cereale*) performed by Kelling *et al.* (1976) to willow (*Salix viminalis*; Wyrwicka and Urbaniak, 2018), maize (*Zea mays*; Kidd *et al.*, 2007) and raspberry (*Rubus idaeus*; Angin *et al.*, 2017). However, in order for the sludge to properly function as a fertilizer, the phosphorus has to be in a chemical form that is available for the plants. Addition of

iron and/or aluminium ions in the wastewater treatment process generates the corresponding phosphates (Morse *et al.*, 1998). Although both categories of compounds have a potential to supply phosphorus to plant roots, the effect is much lower compared to sludge from biological phosphorus removal (Krogstad *et al.*, 2005). In a study on the impact of iron-dosing on phosphorus and metal speciation in sludge, Carliell-Marquet *et al.* (2010) concluded that the bioavailability of phosphorus in iron-dosed sludge (dosed with an iron: phosphorus molar ratio of 2:1) to be only 30% compared to undosed sludge. These results are consistent with those reported by Contin *et al.* (2015), who stated that addition of FeCl<sub>3</sub> (added at a rate of 40 g Fe kg<sup>-1</sup> DW) resulted in less shoot dry matter compared to sludge where no iron had been added, especially in acidic soils.

The sludge is not only a valuable product, but also a bulky by-product that has to be disposed of in a proper way, which is the main driver for the development of regulatory frameworks in several countries (SOU 2020:3). As mentioned previously, in addition to the beneficial components in sewage sludge, it also contains compounds and elements that may be harmful to the environment, such as toxic metals and organic molecules, as well as pathogens, and there are several reviews highlighting the risks associated with direct sludge application (Lake *et al.*, 1984; Lewis and Gattie, 2002; Singh and Agrawal, 2008; Hlava *et al.*, 2017; Seleiman *et al.*, 2020). There is a significant body of research indicating metals in sewage sludge to be available for plant uptake (c.f., Rieuwerts, 2007; Khan *et al.*, 2015; Nunes *et al.*, 2021). In addition, the risks associated with organic contaminants is of growing concern as more compounds and their biological responses are revealed, especially the fate of pharmaceuticals (Puckowski *et al.*, 2016; Zhang *et al.*, 2017). Consumer use is considered to be the most important source of pharmaceuticals in the environment; and depending on the kind of molecules some 30% to 90% of the orally administered dose is expected to be in its active form when excreted (BIO Intelligence Service, 2013). The degradation and removal rates of these in the wastewater treatment process, and thereby also their potential presence in the effluent water and sludge phases, are highly dependent on the type of pharmaceuticals. Even though many of the

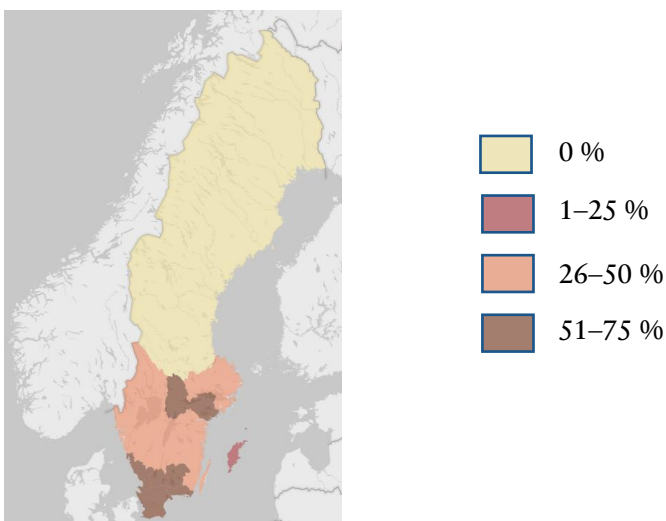
pharmaceuticals in the influent wastewater are removed in the treatment process, significant amounts are still present in the effluent water and in the sludge (Jones *et al.*, 2007; Muños *et al.*, 2009; Verlicchi *et al.*, 2012; Seleiman *et al.*, 2020). Several studies have reported results that indicate the possibility for plants to accumulate pharmaceuticals, thereby constituting a possible pathway for human exposure (Prosser and Sibley, 2015).

## Sludge production and utilization in Sweden

The most commonly used approach to remove phosphorus from municipal wastewater in Sweden is by dosing of iron and/or aluminium salts (SEPA, 2018). In total, the Swedish MWWTPs (>2 000 p.e.) annually treat more than 1 000 000 000 m<sup>3</sup> wastewater, resulting in over 200 000 metric tonnes (DW) of sewage sludge, with an average phosphorus concentration of 26.5 mg g<sup>-1</sup> (SCB, 2020). In total, this corresponds to 5 300 metric tonnes of phosphorus, which equals to more than 40% of the amount of phosphorus purchased as mineral fertilizers in 2018/2019 (SCB, 2020b). Despite the high nutritional value of the sludge, only 40% is used directly on agricultural land, while 25% is used for construction. The remainder is disposed of as landfill coverage (17%), stored (6%) or used in other ways (10%). Only 2% of the sludge is deposited to landfills or incinerated (SCB, 2020). However, since Sweden is an elongated country with great diversity regarding conditions for agriculture, there are differences in disposal routes, which can be seen in **Figure 4**. In the strive towards higher quality of sewage sludge, as well as effluent water from the MWWTPs, the branch organization Swedish Water has created a certification system (REVAQ). The system is controlled by the Federation of Swedish Farmers (LRF), the National Food Administration (Livsmedelsverket), Swedish Water and representatives from MWWTPs, and was founded in 2008. Facilities holding the certificate is actively working towards reducing the flow of hazardous substances to the treatment plant, and thereby to ensure a good quality of the sludge. In addition, before utilized on agricultural land, the sludge must be treated to avoid spreading of infectious disease. These processes are often referred to as hygienization of the sludge, and the treated sludge has to be tested

negatively for salmonella before spreading (Revaq, 2021). Besides long-term storage (> 6 months), approved processes include

different kinds of thermal treatments, composting and treatment with additives, such as urea and lime (Revaq 2021b; SEPA, 2013). In order for the produced sludge to be allowed for spreading on agricultural land, it has to be properly documented. Besides basic parameters, such as origin and time period for production, this includes concentrations of nutrients (nitrogen and phosphorus) and metals, as well as a negative test for salmonella. The producer also must state, the amount of sludge spread during a specified period of time, and calculated amounts of metals and nutrients added on an annual basis, based on the given time interval. In practice, the amount of sludge that can be spread is limited by the concentration of cadmium, specifically the Cd/P ratio, and the resulting net effect on soil Cd concentration. In 2020, 60% of the sewage sludge from MWWTPs was produced at certified facilities, of which 78% (40% of the total amount of sludge) passed the qualitative tests required for spreading on agricultural land (Revaq, 2021b).



**Figure 4.** Graphical illustration of the difference in sludge application on farmland in Sweden, based on the geographical location. Data divided in groups based on the percentage of produced sludge (SCB, 2020).

## Phosphorus extraction from sewage sludge

Phosphorus can be extracted and recovered from the sludge, or from its ashes following thermal treatment. Although there are a multitude extraction processes applicable on sewage sludge (Desmidt *et al.*, 2015), most of them have been optimized for treatment of ashes. One of the reasons for this is the significant reduction in volume following thermal treatment. This results in increased concentration of phosphorus, thereby increasing the value of the material as a potential phosphorus resource. The removal of organic material also allows for a more efficient process, since it eliminates the need for oxidization of organic matter prior to phosphorus extraction. In addition, by incineration of the organic content in the sludge, potentially toxic or harmful substances are destroyed, thereby enabling safe handling of the residues. Therefore, thermal treatment is considered to be an efficient method for decontamination of sewage sludge. As the regulations governing sewage sludge disposal become more stringent, an increasing number of nations are converting to thermal treatment, and this is expected to be the dominant technology in the future (Syed-Hassan *et al.*, 2017).

### Thermal treatment

There are several viable options for thermal treatment of sewage sludge, the most common ones are summarized below:

- *Incineration* (including both mass burn incineration and fluidized bed combustion) is a widely used method for treatment of wastes, including sewage sludge, and several European large scale MWWTPs incinerate their sludge on-site. This is an exothermic process which is generally performed within a temperature range of 800-1450 °C, with access to oxygen and at atmospheric (or higher) pressure (Kwapinski *et al.*, 2021). The result is an ash with high concentration of phosphorus (>20% as P<sub>2</sub>O<sub>5</sub>), as well as metals. The major draw-back for incineration for treatment of sewage sludge is the need for pre-drying of the sludge in order for the process to be self-sustaining. It is possible to avoid this costly pre-treatment step by the means of co-incineration, where materials with higher calorific values are mixed with the sludge.

The added material must, however, be chosen with precaution, since it may limit the usability of the ashes for phosphorus recovery. If the material renders a large amount of ash, this will result in a dilution of the sludge ash, reducing the phosphorus concentration and consequently its value for phosphorus recovery.

- *Gasification* entails high-temperature treatment (500-1800 °C) with limited access to oxygen, and often under elevated pressure. The process aims for production of fuel in the form of syngas, but also renders a solid residue (tar) in which the metals and phosphorus is retained (Raheem *et al.*, 2018).
- *Pyrolysis* is an endothermic process which operates with deficit of oxygen and at moderate temperature (250-900 °C), thereby forming of gases and oil or char, depending on the operating temperature range of the process. Because of the nature of pyrolysis (low temperature and lack of oxygen), the process is accompanied by production of furans and dioxins (Zhu *et al.*, 2022).
- *Hydrothermal carbonization (HTC)* is a wet endothermic process which operates at autogenous pressure (i.e., the pressure that is created during the process) and at low temperatures (180-250 °C). Following the procedure, the phosphorus is accumulated in the solid char fraction, which can hold a final concentration of around 5% (Schneider and Haderlein, 2016).

Due to the decomposition of organic matter, thermal treatment processes lead to a significant reduction in volume: approximately 90% of the sludge volume is lost during incineration. As a consequence, the phosphorus concentration increases, from approximately 5% in the sludge (DW) to approximately 10% in the ashes (corresponding to >20% as P<sub>2</sub>O<sub>5</sub>) (Adam *et al.*, 2009; Steckenmesser *et al.*, 2017). The concentration after thermal treatment is com-parable to those in phosphate rock, the mineral mined for phosphorus extraction (Kumar Haldar, 2018). However, because of the differences in chemical composition, the ashes cannot be treated in the extraction processes de-signed for phosphate rock,

why recovery of phosphorus from these are more costly. In order to make it economically favourable to use the sludge ashes as a phosphorus resource within a reasonable timespan, it is therefore important to increase the value of this matrix. One possibility for achieving this would be to increase the both the concentrations and number of elements of value to recover, such as phosphorus or metals of economic interest. This can either be done before the thermal treatment, by adding materials which contain significant amount of the desired element, or by treating of resulting ashes.

### **Enrichment and refining of ISSA**

Given its high concentration of iron and/or aluminium, incinerated sewage sludge ash (ISSA) from municipal sewage sludge contains high concentration of metal oxides. These have been widely studied as scavengers for metals in solutions, and for their applicability as sorbents for treatment of different kinds of wastewater (Hua *et al.*, 2012). Several studies have shown that particularly iron oxides, have the potential to retain phosphate from aqueous solutions (Yoon *et al.*, 2014; Ajmal *et al.*, 2018; Lyngsie *et al.*, 2019). Hence, it would be possible to increase the value of the produced ISSA by enriching them with valuable metals and/or phosphate ions before extraction. There are several examples of full-scale processes where fly ashes from WtE incineration are treated with the aim to recover valuable, or to remove toxic, metals prior to landfilling or recirculation as construction material (Becidan and Johansson, 2020). By utilizing the ISSA as a sorbent, it should be possible to combine the synergically effects and to create an eco-nomically sustainable process where also the phosphorus and/or metals could be recovered.

Although the literature on the use of ISSA for removing of metals from real wastewater is limited, there is a large number of reports on the removal of metal cations from synthetic solutions, from which promising results are reported (c.f. Ma *et al.*, 2019; Wang *et al.*, 2019; Militaru *et al.*, 2020). No studies have been identified on the removal of phosphorus from water by means of ISSA. However, from their study on utilization of sludge-derived adsorbents for phosphorus removal, Xia *et al.* (2020) concluded that the material could

successfully remove phosphorus from both synthetic solution and wastewater.

The literature indicates that the performance of ISSA as a sorbent for metals is stable in a wide pH range, most likely due to the combination of several mechanisms in the removal process. In general, the retention is governed by a combination of cation exchange, precipitation and co-precipitation. One of the most prominent mechanisms for retention of metals to the material seems to be cation exchange, while the contribution of precipitation and complexation remains to be determined (Pan *et al.*, 2008; Wang *et al.*, 2019). Furthermore, although the reported adsorption capacities for the individual metals are high (Wang *et al.*, 2019), this is rarely the case in full scale applications, which rather aims at treating complex solutions with a multitude of contaminants. Several studies have been conducted using multi-element solutions, and the results from these clearly indicate a competitiveness between the different ions (Wang *et al.*, 2019; Militaru *et al.*, 2020).

## **Aims of Study**

The overall aim of this thesis was to increase the understanding of the chemical speciation of principal elements in sewage sludge and their ashes following incineration, with the overarching aim to recover phosphorus and metals from them. In order to limit the research topic, the study is focusing on the Swedish wastewater treatment conditions. In addition, the focal point is to evaluate the technical prerequisites for future industrial solutions, and not to evaluate or discuss such processes.

Accordingly, the specific aims are summarized as follows:

- To study the chemical speciation of phosphorus and metals (Al, Ca, Fe, K, Mg, Mn and Na) in sewage sludge and their ashes after incineration (paper I, II and III);
- To evaluate the impact of iron and aluminium on the phosphorus redistribution following incineration (paper III);
- To investigate the potential to utilize ash from incineration of sewage sludge as adsorbents for phosphorus and metals (Co, Cr, Cu, Ni, Pb, V, Zn) (paper IV and V)

## Materials and Methods

A total of ten municipal wastewater treatment plants (MWWTPs) were included in this thesis, and three (MWWTP 1, 2 and 3) were studied in more detail (paper I, II, IV and V). All the included facilities are considered as fair representatives for average wastewater treatment plants in Sweden, both with regards to the connected population and their treatment processes.

Dimensioning capacities and actual loadings given as p.e., as well as the annual volumes of influent wastewater and amounts of produced sludge, are presented in **Table 3**. The included facilities treat an average of 17.8 million m<sup>3</sup> wastewater annually (8-50.5 Mm<sup>3</sup> year<sup>-1</sup>), from an average population of 179 000 p.e. (65 000 – 560 000).

### Experimental

All experimental work was done on sludge and/or ashes from the MWWTPs presented in **Table 3**. For full details of the studies, the readers are referred to the individual papers appended in the end of this thesis.

**Table 3.** Dimensioned (Dim) and connected (Tot.) population, including industries (Ind) for the 10 facilities in the study, given as person equivalents (p.e.). Included is also the annual loading of incoming wastewater (WW), given as million m<sup>3</sup>, and the sludge produced, presented as metric tonnes of dry weight (DW).

MWWTP	p.e. (x 1000)			WW (10 <sup>6</sup> m <sup>3</sup> )	Sludge (Tonnes DW)
	<i>Dim.</i>	<i>Tot.</i>	<i>Ind.</i>		
1	220	121	5.7	15.9	3 200
2	125	100	8	15.3	2 900
3	130	85	7.3	16.9	3 000
4	700	560	5.3	50.5	8 400
5	340	216	55	14.8	3 200
6	125	92	5.3	11.9	1 300
7	97	74	11	8.4	1 500
8	200	178	42.5	16.8	2 600
9	200	172	25	18.2	3 500
10	100	70	16.8	5.9	1 400

## Sludge sampling and sample preparation

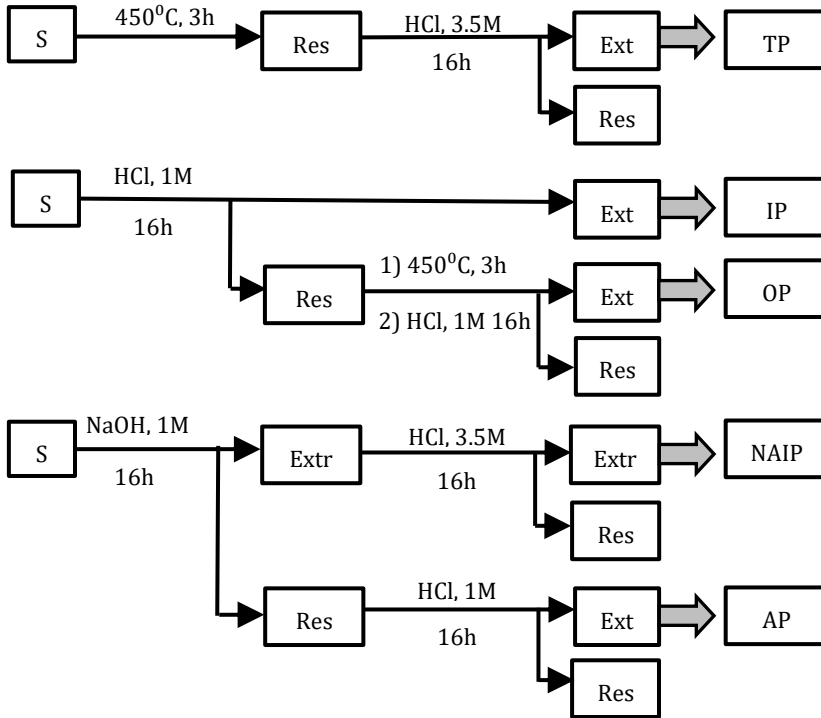
Samples of dewatered sludge were collected in plastic containers and transported to the laboratory, where they were stored at 8 °C until further processing. The sludge was dried at 105 °C, after which a fraction was incinerated at 1000 °C in a chamber furnace at atmospheric pressure to produce the ash. Both dried and ashed samples were crushed to a particle size <0.1 mm and thereafter stored in a desiccator until used.

## Extraction protocols

In order to obtain information regarding the amorphous chemical forms and association of phosphorus (paper I and II) and metals (paper III) in sewage sludge, as well as ashes following incineration, three different protocols for sequential extraction were used. By exposing the material to a sequence of extractants with increasing degree of aggressiveness, it is possible to gain information regarding the chemical nature of its constituents, including non-ordered species. All sludge and ash samples from MWWTP 1, 2 and 3 were treated according to the protocols be-low. Sludge and ash samples from MWWTP 4-10 were only extracted following protocol 1. A compilation of the extractions is presented in **Table 4**.

**Table 4.** Compilation of extractions performed on sludge (S) and ash (A) samples from the 10 facilities, following the SMT protocol (1), the modified Tessier scheme (2), and the protocol developed by Chang and Jackson (3). Samples extracted following the full protocol are indicated by “F”, while “p” indicate extraction following the last part of protocol 1 (distinguishing between non-apatite and apatite phosphorus).

MWWTP	1		2		3		4		5		6		7		8		9		10	
	S	A	S	A	S	A	S	A	S	A	S	A	S	A	S	A	S	A	S	A
1	F	F	F	F	F	F	F	p	F	p	F	p	F	p	F	p	F	p	F	p
2	F	F	F	F	F	F														
3	F	F	F	F	F	F														



**Figure 5.** Workflow of the Standards Measurement and Testing (SMT) protocol for phosphorus speciation. Samples (S) are extracted in the fractions Total phosphorus (TP); Inorganic phosphorus (IP); Organic phosphorus (OP); Non-apatite inorganic phosphorus (NAIP); and Apatite phosphorus (AP).

1. The Standards Measurements and Testing (SMT) protocol, developed within the European Commission program of Standards Measurements and Testing (Ruban *et al.*, 2001) (paper I and III). All sludge samples, and samples of ash from MWWTP 1, 2 and 3 were treated according to the complete protocol. The remainder of the ash samples (i.e., MWWTP 4-10) were extracted following part of the protocol (as shown in **Table 4**). The outline of the protocol is presented in **Figure 5**.

2. A modified version of the sequential extraction protocol for speciation of trace metals by Tessier *et al.* (1979) was used, as outlined in **Table 5**. The modification of this protocol entailed inclusion of a pre-step with deionized water (18.2 M $\Omega$ ) at a liquid to solid ratio (L/S) of 20, for 24 hours at room temperature, before the extraction targeting the exchangeable fraction. The final extraction in the original procedure, which targets the residual fraction, was excluded. Instead, total concentrations of metals were extracted following Aqua regia digestion at 121 °C for 90 minutes according to the European standard EN ISO 15587-1 (paper I and II).
3. A protocol developed for phosphorus association to Al, Ca and Fe in calcareous soil, developed by Chang & Jackson (1957) (paper I), described in **Table 6**.

Following each step in the sequential extractions, the liquid phase was separated from the solids by centrifugation (2885 rcf, 20 minutes) and subsequent decantation. The liquid samples were measured for pH and thereafter acidified for preservation and stored at 8 °C for less than 48 hours (phosphorus analysis, paper I and III) or 30 days (metal analysis, paper II). Extractions for quantification of total amounts of metals were done on fresh samples of sludge and ash, using a L/S ratio of 100.

**Table 5.** Outline of the modified sequential extraction procedure, based on the protocol developed by Tessier *et al.*, 1979.

	<b>Fraction</b>	<b>Extractant</b>	<b>Temperature</b>
1	Water extractable	Deionized water (18.2 M $\Omega$ )	RT
2	Exchangeable	1 M NH <sub>4</sub> OAc (pH 7)	RT
3	Bound to carbonates	1 M NH <sub>4</sub> OAc (pH 5)	RT
4	Bound to oxides	0.04 M NH <sub>2</sub> OH·HCl in 25% (v/v) CH <sub>3</sub> COOH	96 °C
5	Bound to organic matter	H <sub>2</sub> O <sub>2</sub> /HNO <sub>3</sub>	85 °C

RT=Room temperature

**Table 6.** Fractionation protocol for identification of phosphorus associated to different principal elements (Al, Ca and Fe), developed by Chang and Jackson (1957). Times are given as hours in an orbital shaker (OS), stationary (S) or intermittently shaken (IS), temperatures are given in °C (Wang *et al.*, 2010)

	<b>Fraction</b>	<b>Extractant</b>	<b>Time</b>	<b>Temp.</b>
1	Ca <sub>2</sub> -P	0.25 M NaHCO <sub>3</sub>	1 (OS)	20
2	Ca <sub>8</sub> -P	0.5 M NH <sub>4</sub> Ac (pH 4.2)	4 (S) + 1 (OS)	20
3	Al-P	0.5 M NH <sub>4</sub> F	1 (OS)	20
4	Fe-P	0.1 M NaOH+ 0.1 M Na <sub>2</sub> CO <sub>3</sub>	2(OS)+16(S)+2(OS)	20
5	Occluded P	0.3 M C <sub>6</sub> H <sub>5</sub> Na <sub>3</sub> O <sub>7</sub> + Na <sub>2</sub> S <sub>2</sub> O <sub>4</sub> +0.5 M NaOH (followed by digestion)	0.5 (IS)	80
6	Ca <sub>10</sub> -P	0.5 M H <sub>2</sub> SO <sub>4</sub>	1 (OS)	20

All extractions were done in triplicates, except for total extractions of metals, which were done in duplicates. The reagents were of analytical grade and deionized water (18.2 MΩ) was used for preparation of solutions. Nitric acid was prepared by sub boil distillation in a class 10 clean room.

### Solid phase analysis

Total concentrations of Al, Ca and Fe in the sludge samples were analysed with X-ray fluorescence spectroscopy (XRF) (XLAB 1000, Xepos 03). Qualitative determination of ordered crystalline phases in sludge and ash samples from MWWTPs 1, 2 and 3 were done using X-ray powder diffraction (XRD), using an X'pert PRO Powder diffractometer (PANalytical) (paper II). The radiation source consisted of a copper electrode that was operated at 45 kV and 40 mA. The sample was continuously rotated between 5°-70° at 0.1° sec<sup>-1</sup> for the 5 min. scans and 0.02° sec<sup>-1</sup> for the 22 min. scans. Data evaluation was performed using the Profex software (Döbelin *et al.*, 2015).

## Stability and release of metals (paper IV)

Stability and potential release of elements (Al, As, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Na, Pb, V and Zn) from the ashes, as well as the impact of washing the ashes with deionized water (18.2 M $\Omega$ ) before extraction, were studied in batch experiments. A mixture of ashes from MWWTPs 1, 2 and 3 (mixing ratio 1:1:1) was used. Washing was done by shaking the ashes with 18.2 M $\Omega$  deionized water for 24 hours at room temperature (approximately 20 °C), after which the water was removed by centrifugation (2885 rcf, 20 minutes) and subsequent decantation. Samples of original and washed ash mixtures were equilibrated with distilled water at five different pH values ranging from pH 2 to 10 for 24 hours at room temperature, using a rotary shaker and a liquid to solid ratio (L/S) of 5.

## Metal sorption (paper IV)

To evaluate the useability of ISSA as a sorbing agent for metals, artificial acid rock drainage (ARD) was prepared from sulphidic mine waste from Ljusnarsberg, Sweden. The ARD was prepared by equilibrating 750 g mine waste with 1 L of 18.2 M $\Omega$  water for three years (timespan other projects). The composition of the ARD is summarized in **Table 7**.

In the sorption studies, a composite sample of ashes from MWWTP 1, 2 and 3 (mixing ratio 1:1:1) was mixed with the ARD (L/S 10) and shaken at room temperature for 24 hours at three different pH values (3, 5 and 8). The resulting equilibrium concentrations at pH 8 were used for geochemical modelling of saturation conditions using Visual Minteq (Gustafsson, 2021).

**Table 7.** Chemical profile of the produced ARD after equilibration; pH and selected ions, given as mg L<sup>-1</sup>

pH	SO <sub>4</sub> <sup>2-</sup>	Ca	Mg	Zn	Al	Mn	K	Cu
2.9	5 000	450	440	386	320	33	11	10
	Na	Fe	Cd	Pb	Co	Cr	Ni	V
	5	3	1.8	1.8	0.8	0.5	0.5	0.5

## Phosphorus sorption (paper V)

The potential use of ashes from incineration of sewage sludge to retain phosphate was evaluated in batch tests. Synthetic solutions with increasing concentrations of phosphate ions (0 – 1000 mg L<sup>-1</sup>) were prepared by dissolving KH<sub>2</sub>PO<sub>4</sub> in deionized (18.2 MΩ) water. The solutions were then mixed with ashes (L/S 5) and shaken for 24 hours, after which the liquid phase was recovered and filtered (0.45 µm cellulose acetate syringe filters) before phosphate quantification, as described in section 3.2.1. The concentration differences in solution before and after contact with ISSA were used to estimate the amount of phosphorus sorbed by the solids. The results were used to estimate the sorption capacity of the material, as evaluated by the Langmuir, Freundlich and SIPS isotherms. In addition, the adsorption process was further evaluated using the intra particle diffusion model (IPD model).

In these experiments both ionic strength and pH were allowed to vary in accordance with the response of the sorbent at the different concentrations.

## Analytical

This section aims at describing the analytical work on both liquid and solid samples, produced throughout the experiments.

## Phosphorus analysis

Analysis of phosphorus in the form of orthophosphate was done on all samples from the extraction protocols (paper I and II) and from the study on phosphorus sorption (paper V). In addition, extracts from sludge and ashes from MWWTPs 1, 2 and 3 (paper I) were analysed for total phosphorus following digestion with peroxydisulfate, according to the procedure presented by Ebina *et al.* (1983). All analyses were performed at room temperature (20 °C) on filtered (0.45 µm cellulose acetate syringe filters) samples following the ascorbic acid-molybdenum blue method (Murphy and Riley, 1962; APHA, 1992). The absorbance was measured at 880 nm using a 1 cm quartz-cell, external calibration was used in the interval of 0-1 ppm

phosphorus (prepared from  $\text{KH}_2\text{PO}_4$ ). Preparation of reagents, calibration solutions and dilution of samples was done using deionized water (18.2 M $\Omega$ ). Preparation of calibration solutions, as well as sample dilutions, were performed using plastic vessels, in order to avoid interaction between phosphorus and glass.

## Metal analysis

All samples from the extraction protocols and Aqua regia digestion (paper II), as well as from the study on release and sorption of metals (paper V) were analysed for metals using microwave plasma - atomic emission spectroscopy (MP AES model Agilent 4200). The instrument was equipped with a OneNeb (Agilent) nebulizer and a double pass Scott type spray chamber. External calibration was used in the interval of 0 - 10 ppm for each of the analysed metals. An internal standard mixture with Y, La and Lu was added to a final concentration of 1 mg L<sup>-1</sup> to monitor interferences. Plasma efficiency was controlled by continuous introduction of 2.5 g L<sup>-1</sup> CsNO<sub>3</sub> in 1% sub boil dis-tilled HNO<sub>3</sub> to the sample line. All analyses were performed on filtered (0.20  $\mu\text{m}$  polypropylene syringe filters) samples containing 1% HNO<sub>3</sub>. Calibration solutions and internal standards, as well as dilution of samples, were prepared to have a final concentration of 1% HNO<sub>3</sub>.

## Data evaluation

In order to facilitate for comparison between speciation of phosphorus (paper I and III) and metals (paper II), the results on phosphorus and metal concentrations in the ash samples were recalculated to sludge dry weight basis. Percentage change in AP and NAIP fractions in sludge and ash samples from the individual MWWTPs were calculated following **Equation 6** or **Equation 7**:

### Equation 6

$$AP_{incr} = \frac{\left(\frac{AP}{AP + NAIP}\right)_A - \left(\frac{AP}{AP + NAIP}\right)_S}{\left(\frac{AP}{AP + NAIP}\right)_S} \cdot 100$$

## Equation 7

$$NAIP_{decr} = \frac{\left(\frac{NAIP}{AP + NAIP}\right)_A - \left(\frac{NAIP}{AP + NAIP}\right)_S}{\left(\frac{NAIP}{AP + NAIP}\right)_S} \cdot 100$$

Where  $AP_{incr}$  and  $NAIP_{decr}$  refer to the percentage increase in AP and decrease in NAIP, respectively.

## Statistical analysis

Statistically significant relations between measured and added amounts of Al, Ca and Fe on the phosphorus speciation in sludge and ashes, as well as its alteration upon incineration, were evaluated by bivariate correlation analysis (paper III). The effect of pH on the metal distribution in the study on stability and release of metals (paper IV) was evaluated with ANOVA analysis and subsequent Tukey post hoc tests.

All statistical evaluations were done using the statistic software SPSS Statistics 19 (IBM, 2016).

## Chemical modelling

The chemical equilibrium model Visual MINTEQ was used (Gustafsson, 2021) in order to assess the mechanisms for retention of metals in the sorption study (paper IV).

The nature of phosphorus sorption to ISSA (paper V) was evaluated using sorption isotherms. This is a commonly used approach for describing the solid solution partitioning properties of a surface, that in general show the correlation between the concentration of the analyte in solution and on the surface of the sorbent. Although they are dependent on factors such as temperature, redox potential, concentration and (in particular) pH, the isotherms often allow for good estimations regarding the properties of a surface. It should, however, be kept in mind that processes in the system affect the

sorption over time, which would complicate the interpretation of the results. Two of the simplest, and probably also most commonly used, are the Langmuir (**Equation 8**) and Freundlich (**Equation 9**) isotherms. While the Langmuir isotherm assumes a surface with fixed number of sites, each with equal affinity to the sorbate, the Freundlich isotherm considers that most surfaces are heterogenous and contain sites with different affinity to the sorbate (Foo and Hameed, 2009; Corral-Capulin et al. 2019; Al-Ghouti and Da'ana 2020). However, the Freundlich isotherm does not allow for estimation of the theoretical maximum adsorption capacity of the sorbent. Therefore, these two isotherms can be combined in the SIPS isotherm (**Equation 10**), to evaluate the forces of attraction of a complex material (Foo and Hameed 2009, Corral-Capulin *et al.*, 2019).

**Equation 8**

$$Q_e = \frac{Q_m K_L C_e}{1 + K_L C_e}$$

**Equation 9**

$$Q_e = K_F C_e^{1/n}$$

**Equation 10**

$$Q_e = \frac{Q_m (K_S C_e)^{1/n}}{1 + (K_S C_e)^{1/n}}$$

Where  $Q_m$  is the theoretical maximum adsorption, calculated from the total amount of sorbate adsorbed to the sorbent ( $Q_e$ ) and the sorbate equilibrium concentration in solution ( $C_e$ ). The following specific constants are also used in the isotherms:

$K_L$  = Langmuir constant related to the free energy of adsorption

$K_F$  = Freundlich constant representing adsorption intensity

$K_S$  = SIPS constant representing the affinity between sorbate and sorbent

In addition, although the denotation “n” is included in both **Equation 9** and **Equation 10**, it has different meaning for the two isotherms: In the Freundlich isotherm it is an empirical constant indicating adsorption intensity and energy of adsorption (Torovazquez and Proctor, 2009; Mu and Sun, 2019). Values of “n” > 1 indicates a sorption process with a low energy barrier i.e., sorption is facilitated. In the SIPS isotherm it is an index of heterogeneity (Jeppu and Clement, 2012). Here, a completely homogenous material has an n-value that equals or is greater than 1, while a heterogenous material has a value below 1.

Further understanding of the mechanisms involved in the adsorption process can be obtained by fitting the data to an intra particle diffusion model (**Equation 11**).

#### Equation 11

$$q_t = K * \sqrt{t} + M$$

Where the model is fitted to the amount of sorbate at time t ( $q_t$ , in  $\text{mg g}^{-1}$ ) and the time (t, in minutes), and where K is the intra particle diffusion rate constant ( $\text{mg g}^{-1} \cdot \text{min}^{-0.5}$ ) and M is the adsorption capacity ( $\text{mg g}^{-1}$ ).

## Quality Assurance

Collected samples of sewage sludge were transported to the laboratory and stored for a maximum of one week before further processed, in order to avoid biodegradation of the material and redistribution in chemical speciation of phosphorus and metals. Measures were taken to avoid cross-contamination between the different samples during all handling of the samples (preparation, processing, extraction and analysis). All extractions performed were done using triplicate samples, except for Aqua regia extraction for which duplicate samples were used.

Quantification of total concentrations of metals in sludge and ash from MWWTP 1, 2 and 3 was performed after Aqua regia digestion, according to the European standardized method EN ISO 15587-1. All chemicals used were of analytical grade, preparation of all solutions, as well as dilution of liquid samples, was done using deionized water (18.2 M $\Omega$ ).

External calibration was used for quantification of phosphorus (0-1 ppm) and metals (0-10 ppm), and quality control samples were regularly included in the measurements to ensure stable analysis. All preparation of phosphorus containing solutions (calibration standards and samples) were done using plastic vessels in order to prevent interaction between phosphorus and glass. For the metal analysis, an internal standard mixture with La, Lu and Y was added to a final concentration of 1 ppm to monitor interferences. Plasma efficiency was controlled by continuous introduction of 2.5 mg L<sup>-1</sup> CsNO<sub>3</sub> (Karlsson *et al.*, 2015). Accuracy of the XRF analysis of Al, Ca and Fe was controlled by comparison of total amounts measured after Aqua regia digestion.

All produced data were stored according to the recommendations by Fortum Waste Solutions AB and Örebro University (i.e., file hosting services), which ensure continuous synchronization and backup of the files. All data stored or communicated by or with Örebro University is available to the public upon request, according to the principle of publicity as stated in Swedish law.

## Results and Discussion

Dry- and ash weights of the sludge from all included facilities are presented in **Table 8**.

**Table 8.** Dry weight (DW) and ash weight (AW) of sludge samples from the 10 MWWTPs in the study, given in percentage of dewatered sludge. Loss on ignition (LOI) is presented as the percentage mass loss after incineration of the dried sludge samples.

MWWTP	1	2	3	4	5	6	7	8	9	10
DW (%)	25	23	25	23	22	19	30	27	27	23
AW (%)	10	9	9	8	11	6	11	10	9	8
LOI (%)	61	61	64	65	52	68	64	63	65	64

Although there is a clear variation between the plants, most of the values are within one standard deviation from the average values of 24.5 % ( $\pm 2.9$ ) and 9.1 % ( $\pm 1.3$ ) for sludge and dry weights, respectively. For two of the facilities, both dry- and ash weights are lower (MWWTP 6) or higher (MWWTP 7) compared to the average range. In addition, the ash weight for sludge from MWWTP 5 is higher compared to the average range. These variations are most likely related to different composition of influent waters, as well as in the processes used for treatment. All the facilities use iron to remove phosphorus from the wastewater, and six of them also add aluminium for sludge conditioning (MWWTPs 1, 4, 5, 7, 9 and 10). Three of the remaining four facilities receive sludge from smaller MWWTPs that use aluminium in the treatment process (MWWTPs 3, 6 and 8). The amounts of added iron and aluminium, as well as concentrations of the principal elements Al, Ca and Fe (determined with XRF) in the sludge samples, are presented in **Table 9**.

From the results, it can be concluded that the facility with lowest dry- and ash weights (MWWTP 6) also has the lowest concentration of aluminium and iron. Both elements have an important role in formation and conditioning of the sludge, and a low concentration of them would therefore entail a higher concentration of water in the sludge. In addition, this facility also receives biowaste, which is included in the fermentation process, thereby increasing the organic

content of the sludge. Given the decomposition and loss of organic matter in the incineration process, high concentrations would result in a massive lowering of mass, and therefore a lower ash weight. On the other hand, MWWTP 7, has a rather high dosing ratio of aluminium and iron, as well as high total concentrations of these elements, probably connected to the large amounts of industries connected to this facility.

A high concentration of inorganic material, such as aluminium and iron, would result in a lower mass loss, and consequently higher ash weight. The fact that the ash weight for MWWTP 5 is higher than average, while its dry weight is within the range, may be related to a high concentration of organic matter in combination with a high concentration of inorganic principal elements. Besides domestic wastewater, this facility also receives high amounts of fat (> 2000 metric tonnes year<sup>-1</sup>) from different industries, which would contribute significantly to the concentration of organic material in the sludge.

**Table 9.** Amounts of aluminum and iron added in the wastewater treatment process at the 10 municipal wastewater treatment plants (MWWTPs) in the study, and measured concentrations of Al, Ca and Fe in the sludge, given as mol metric tonnes<sup>-1</sup> dry weight (DW)

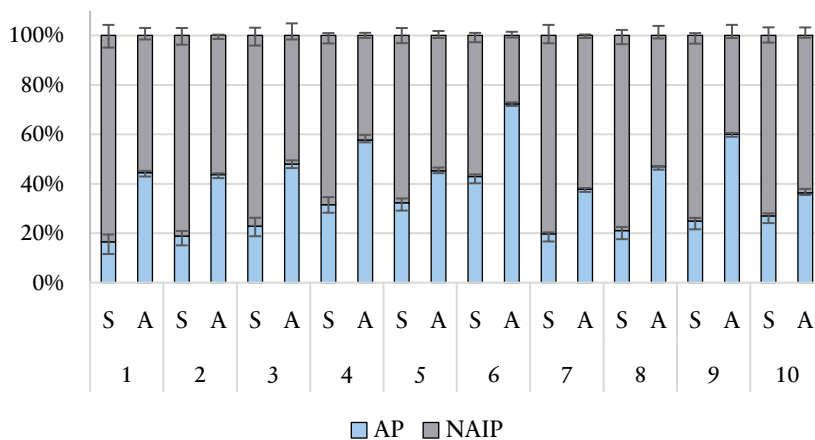
MWWTP	Added (mol tonne <sup>-1</sup> DW)		Total concentration (mol tonne <sup>-1</sup> DW)			
	<i>Al</i>	<i>Fe</i>	<i>Al</i>	<i>Fe</i>	<i>Ca</i>	<i>P</i>
1	78	780	1593	977	649	795
2	0	285	897	1404	515	1003
3	596	3263	1206	1719	653	1041
4	15	975	515	1123	780	1186
5	505	613	1225	962	805	1034
6	82	540	344	816	1041	922
7	725	663	911	1460	559	981
8	9	74	644	1384	563	1120
9	74	1570	356	1778	734	660
10	928	738	1827	818	738	872

Furthermore, as can be seen from **Table 9**, the concentrations of aluminium in the sludge exceed the added amounts from the treatment process for all facilities. This implies that a rather large fraction of the aluminium content in the sludge in fact comes from the incoming wastewater or other materials treated at the facilities. This is a clear example of the impact of the influent streams on the chemical composition of the sludge. The relationship between added and measured concentrations of iron is more diverse. For some of the plants there is a good correlation between them, while for others identified amounts exceed the addition. As for aluminium, the only reasons are the composition of the wastewater, as well as sludge from other facilities. However, for one of the plants (MWWTP 3), the iron content in the sludge only adds up to 50% of the addition in the treatment process. One possible explanation for this could be the sampling strategy in this case study: Only one composite sample was collected from each facility which might have obscured the variability that is caused by changes in the composition of incoming water and the effectiveness of the treatment process. The contents of calcium (**Table 9**) in the sludge are rather constant with an average of 704 moles tonne<sup>-1</sup>. The sludge from MWWTP 6 exceeds 1 000 moles tonne<sup>-1</sup>, a discrepancy that coincides with the treatment of dairy wastewater at this facility.

### **Phosphate speciation (paper III)**

Results from extraction of sludge and ash samples, following the SMT protocol, are presented in Table 10. Percentage distribution of the two subgroups of IP: AP and NAIP, is shown in **Figure 6**.

Despite the differences in total amounts of phosphate, IP is the dominant fraction in the sludge from all facilities and accounted for 85-94% of the total phosphate content, except for MWWTP 5, where it was 76%. One possible explanation for the lower IP fraction in this sludge could be that this plant receives fat from the food industry, which is mixed with the sludge and included in the fermentation process.



**Figure 6.** Percentage distribution of apatite inorganic phosphorus (AP) and non-apatite inorganic phosphorus (NAIP) in sewage sludge (S) and ashes (A) from 10 municipal wastewater treatment plants in Sweden.

As can be seen from **Figure 6**, it is obvious that the IP in the sludge is mainly present as NAIP, which is consistent with previous studies (Huang *et al.*, 2015; Xie *et al.*, 2011). The incineration process effectively altered the NAIP/AP distribution, resulting in a significant ( $p > 0.01$ ) increase in the AP fraction for all samples, with a corresponding decrease of NAIP (**Table 10**). This redistribution towards AP is probably caused by conversion of labile NAIP to more stable AP (Li *et al.*, 2014). It should be noted that the total amounts of AP and NAIP are lower compared to the IP fraction for all of the facilities, except for MWWTP 5. This discrepancy is most likely associated with limitations in distinguishing between NAIP and AP using this analytical protocol (c.f. Li *et al.*, 2014; Pardo *et al.*, 2003).

Regression analysis was used to statistically evaluate the relationship between added and measured amounts of principal elements (Al, Ca and Fe) and the distribution of phosphate species (AP and NAIP) in sludge and ash samples, as well as the percentage change in distribution following incineration. Significant effects ( $p < 0.05$ ) are indicated in **Table 11**.

**Table 10.** Non-apatite (NAIP) and apatite (AP) phosphate fractions ( $\text{mg g}^{-1}$ ) in sewage sludge and ashes following the SMT protocol, given as mean value  $\pm$  standard deviation ( $n=3$ ). Recalculated concentrations for ashes, presented as  $\text{mg g}^{-1}$  dry weight are given in brackets. Calculated increase and decrease in AP and NAIP fractions are given in percentage.

		<b>NAIP</b>	<b>AP</b>	<b>AP increase (%)</b>	<b>NAIP decrease (%)</b>
1	S	$17.1 \pm 1.2$	$3.4 \pm 0.4$	170	-34
	A	$34.6 \pm 3.6$ ( $13.4 \pm 1.3$ )	$27.8 \pm 1.7$ ( $10.1 \pm 0.6$ )		
2	S	$21.9 \pm 0.3$	$5.1 \pm 0.4$	133	-31
	A	$42.6 \pm 4.5$ ( $16.8 \pm 1.8$ )	$30.6 \pm 0.5$ ( $12.1 \pm 0.2$ )		
3	S	$19.0 \pm 0.9$	$5.6 \pm 0.6$	110	-33
	A	$35.1 \pm 2.1$ ( $12.5 \pm 0.7$ )	$29.9 \pm 0.4$ ( $10.6 \pm 0.2$ )		
4	S	$21.3 \pm 0.8$	$9.8 \pm 0.6$	83	-38
	A	$47.4 \pm 0.3$ ( $16.6 \pm 0.1$ )	$60.0 \pm 0.4$ ( $21.0 \pm 0.1$ )		
5	S	$21.9 \pm 0.8$	$10.4 \pm 0.8$	40	-19
	A	$59.7 \pm 3.3$ ( $28.5 \pm 1.6$ )	$45.8 \pm 0.9$ ( $21.8 \pm 0.4$ )		
6	S	$21.0 \pm 0.3$	$15.8 \pm 1.0$	69	-52
	A	$37.1 \pm 1.2$ ( $11.9 \pm 0.4$ )	$89.4 \pm 2.2$ ( $28.7 \pm 0.7$ )		
7	S	$25.7 \pm 1.0$	$6.3 \pm 0.6$	91	-22
	A	$67.6 \pm 2.0$ ( $24.5 \pm 0.7$ )	$38.0 \pm 1.3$ ( $13.8 \pm 0.5$ )		
8	S	$22.5 \pm 0.4$	$6.0 \pm 0.3$	122	-33
	A	$48.6 \pm 2.0$ ( $17.9 \pm 0.7$ )	$39.7 \pm 0.8$ ( $14.6 \pm 0.3$ )		
9	S	$22.8 \pm 1.4$	$7.6 \pm 0.2$	142	-47
	A	$41.9 \pm 0.5$ ( $14.8 \pm 0.2$ )	$58.3 \pm 0.6$ ( $20.5 \pm 0.2$ )		
10	S	$25.3 \pm 0.6$	$9.4 \pm 0.4$	35	-13
	A	$76.3 \pm 3.5$ ( $27.6 \pm 1.3$ )	$40.5 \pm 0.3$ ( $14.6 \pm 0.1$ )		

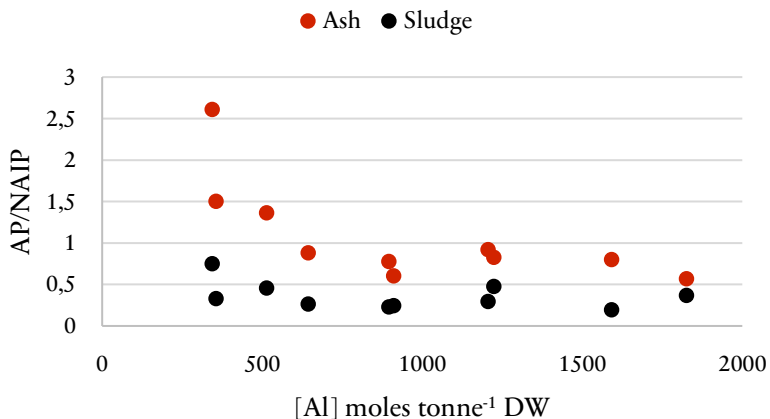
**Table 11.** Statistically significant ( $p < 0.05$ ) correlations between the phosphorus fractions in sludge (S) and ash (A) samples and the molar concentrations of Al, Ca and Fe in the sludge (dry weight), as well as the added concentration of Al ( $Al_{add}$ ) and Fe ( $Fe_{add}$ ). The nature of correlation are indicated by use of + (positive) or – (negative).

	AP incr	NAIP decr	[AP]		[NAIP]		[AP]/[NAIP]	
			S	A	S	A	S	A
[ $Al_{add}$ ]		-				+		
[ $Fe_{add}$ ]								
[Al]		-		-				-
[Fe]								
[Ca]			+	+			+	+
[Al]+[Fe]			-	-			-	-
[ $Al_{add}$ ] + [ $Fe_{add}$ ]								
[Al]/[Fe]								
[Al]/[Ca]		-		-				-
[Fe]/[Ca]			-				-	
[Al]/[P]				-				
[ $Al_{add}$ ]/[P]		-						
[Fe]/[P]	+		-				-	
[ $Fe_{add}$ ]/[P]								
[Ca]/[P]					-			
([Al]+[Fe])/[P]			-	-			-	-
([Al]+[Fe])/[Ca]			-	-			-	-

As can be seen from the results (**Table 11**), the concentration of AP, as well as the AP/NAIP ratio, in both sludge and ashes are significantly affected by the concentration of calcium in the sludge. A corresponding negative correlation can be seen for the total concentrations of aluminum and iron in the sludge ( $[Al]+[Fe]$ ). Furthermore, the results suggest that the concentration of aluminum has a negative impact on the concentration of AP and the AP/NAIP ratio in the ashes, while no such correlation can be seen for iron. In fact, neither total nor added concentrations of iron alone have significant impact on the phosphorus speciation in sludge or ashes, or the change in speciation upon incineration.

Moreover, the concentration of AP in the sludge was affected by the ratios between iron and calcium or phosphate ( $[\text{Fe}]/[\text{Ca}]$  or  $[\text{Fe}]/[\text{P}]$ ), while these correlations were shifted in the ash samples to corresponding ratios with aluminium ( $[\text{Al}]/[\text{Ca}]$  or  $[\text{Al}]/[\text{P}]$ ). It should also be noted that although the added or total concentrations of aluminium alone have no significant impact on the speciation of phosphate in the sludge samples, there is a significant correlation to its the speciation in the ashes. This may be related to the means and timing of the introduction of aluminium to the sludge. When added as sludge conditioners, it is polymers and should therefore not have any effect on the phosphorus, which already would have been precipitated as iron-phosphate. Following this reasoning, it is possible that aluminium entering the MWWTPs with the influent wastewater could affect the phosphorus speciation, given that these are present as free ions or in complexes (coordination compounds) with lower stability. More information is, however, required in order to draw any general conclusions regarding the possible impact of aluminium on the phosphorus speciation in sludge.

The overall results clearly show that the redistribution between NAIP and AP upon incineration is mainly controlled by the concentration of aluminium in the sludge, irrespectively of its origin (added in the treatment process or introduced through influent wastewater or sludge fractions). This relationship is visualized in **Figure 7**, and can be further exemplified by the mere 30% decrease in NAIP upon incineration of sludge from MWWTP 2 (**Table 10**). Although no aluminium is added in this facility, the aluminium concentration in the sludge is still rather high, probably related to the chemical composition of the influent wastewater. Besides domestic wastewater the plant also receives leachate from a landfill and condensate from a heating plant.



**Figure 7.** AP/NAIP ratio as a function of total concentration of aluminum in sewage sludge and ash

Although aluminium-P can be converted to AP, this redistribution requires higher temperature compared to the conversion of iron-P (Li *et al.*, 2015) why the latter would be preferable in order to decrease the amount of energy needed to ensure quantitative transformation to AP. Hence, to help in creating the best possible prerequisites for phosphorus recovery from sewage sludge ash, the concentration of aluminium in the sludge should be kept at a minimum.

### **Total phosphorus speciation (paper I)**

In order to further evaluate the impact of thermal treatment on the chemical speciation of phosphorus, samples from MWWTP 1, 2 and 3 were studied in more detail. Samples from extraction of phosphorus following the SMT protocol were analysed as total phosphorus (measured after digestion of the extracts), and the results are presented in **Table 12**. As can be seen from the table, the dry weight concentrations of phosphorus in sludge and ashes from MWWTP 1, 2 and 3 are rather constant even after incineration, which is a clear indication that no significant ( $p < 0.01$ ) amounts of phosphorus is lost. These results are inconsistent with those for analysis of phosphate (without prior digestion of the extracts) presented in Paper III. This

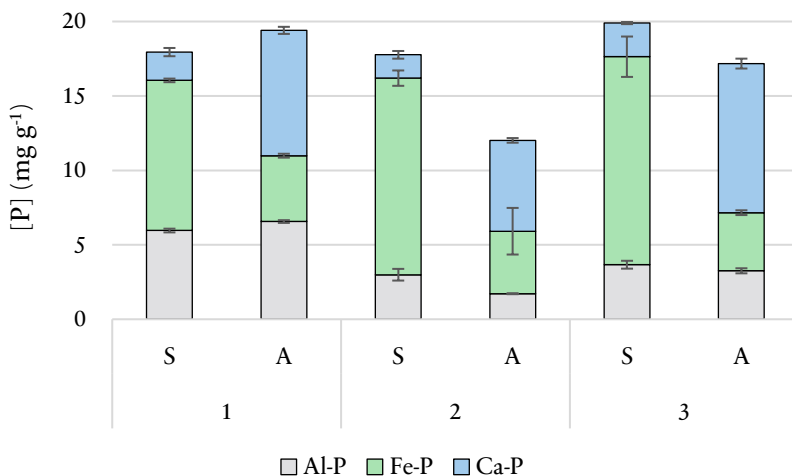
dissimilarity is most likely caused by formation of more stable phases following incineration, which were not quantifiable without digestion prior to analysis. Moreover, the concentration of TP in the ashes is comparable to that of phosphate rock (65-130 mg g<sup>-1</sup>), which is used for fertilizer production (Kumar Haldar, 2018). Hence, this material could be a viable option as phosphorus resource. As can be seen in **Table 12** IP is the dominating fraction, which would be expected. However, some organic phosphorus (OP) was still present in the samples even after incineration. Given the high incineration temperature of 1000 °C and free access to atmospheric oxygen the organic content should have been decomposed during the process. The incomplete decomposition of OP could possibly be related to formation of ordered iron and aluminium oxides, which could encapsulate organic material and thereby favour pyrolytic conditions. Such a mechanism merits further investigation since it would hamper the thermal decomposition of organic compounds in all materials with a high content of amorphous ferric oxides.

**Table 12.** Concentrations of phosphorus in the fractions of the SMT protocol: Total phosphorus (TP), inorganic phosphorus (IP), organic phosphorus (OP), non-apatite inorganic phosphorus (NAIP) and apatite phosphorus (AP) in sludge (S) and ash (A) samples from MWWTP 1, 2 and 3. Concentrations are given as average concentrations (mg g<sup>-1</sup>) ± standard deviation (n=3). Recalculated concentrations in the ash samples, presented as mg g<sup>-1</sup> sludge dry weight are given in brackets.

		<b>TP</b>	<b>IP</b>	<b>OP</b>	<b>NAIP</b>	<b>AP</b>
1	S	29.4±0.3	24.7±3.9	3.6±0.2	24.0±3.4	6.4±0.4
	A	72.6±4.3 (28.1)	66.6±4.9 (25.8)	3.9±0.1 (1.5)	42.7±2.9 (16.6)	33.2±2.4 (12.9)
2	S	26.3±1.0	23.2±1.0	4.7±0.6	23.9±0.9	6.5±1.0
	A	77.5±3.7 (26.2)	61.2±1.2 (20.7)	13.2±0.8 (4.5)	32.9±1.3 (11.1)	42.0±3.5 (14.2)
3	S	32.2±0.7	30.2±2.4	4.2±0.2	26.8±1.3	10.6±1.4
	A	75.3±4.4 (31.3)	70.4±7.5 (29.3)	6.6±0.8 (2.7)	40.7±0.8 (17.0)	44.3±1.6 (18.4)

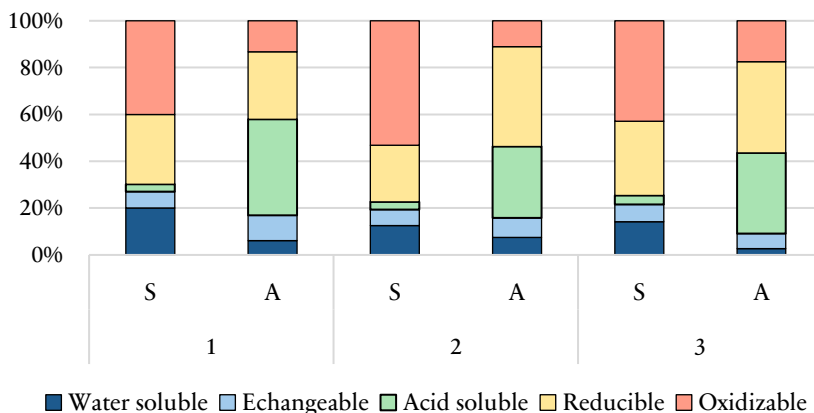
In addition, the incineration process induces a transformation of amorphous aluminium and iron hydrous oxides to ordered oxides, which would result in a decreased porosity of the material, and thereby lower the oxygen diffusion rate to the interior of the solids. Thus, it is likely that pyrolytic conditions were present, at least in parts of the material, why alteration of the organic compounds would take place, rather than a quantitative formation of carbon dioxide. As the ashes are crushed during the sample treatment, the interior of the particles are exposed, thereby making the organic content extractable. Another possible explanation to the findings might be limitations of the SMT protocol to quantify the OP fraction in incineration residues. The protocol was originally designed for quantification of bioavailable phosphorus in sediments, and is therefore relying on solubilization of inorganic phosphorus in acid solution. Organic phosphorus is converted to inorganic species by thermal treatment (450 °C) and are thereafter assumed to be soluble in acid, which allows for extraction and quantification. There is, however, a possibility for both under- and overestimation of the OP content (Chen *et al.*, 2019), which would explain the difference in TP and the sum of IP and OP (**Table 12**). Although the present results indicate that pyrolytic conditions were present during the incineration process, further studies are needed to obtain conclusive evidence.

Result from analysis of phosphorus association to principal elements (aluminium, calcium, and iron), performed according to the procedure by Chang and Jackson (1957), are shown in **Figure 8**. The amount of phosphorus extracted in this protocol was significantly lower ( $p < 0.05$ ) compared to the results from the SMT protocol, which is attributed to lower extraction efficiency of the different phosphorus species. In total, 35-78% and 54-78% of the AP content was accounted for in the extracts targeting different species of Ca-P in the sludge and ash samples, respectively. In comparison, the total amounts extracted in the fractions targeting aluminium and iron associated phosphorus amounted to 87-100% of the NAIP content in the sludge samples and 36-87% in the ashes.



**Figure 8.** Chemical associations of phosphorus in sludge (S) and ashes (A) from MWWTPs 1, 2 and 3, (given as  $\text{mg g}^{-1}$  DW, according to the fractionation procedure by Chang and Jackson, (1957). Average values ( $n=3$ ), standard deviations are indicated with error bars.

As can be seen in **Figure 8**, the concentration of calcium associated phosphorus (Ca-P) increased upon incineration, which is consistent with the observed increase in the AP fraction with regards to phosphate (**Table 10**) and phosphorus (**Table 12**). In addition, a corresponding decrease could be seen for Fe-P in all plants upon incineration, while no significant change was seen for Al-P. Overall, these results indicate that mainly Fe-P was transformed to Ca-P during incineration, probably because of the lower stability of this complex, compared to Al-P (Li *et al.*, 2015). The transformation of phosphorus species following incineration agrees with the results from the Tessier protocol, (**Figure 9**). Although the extraction efficiency was low with this protocol (1-2.5% in sludge samples and 0.3-0.4 % in ash samples), the results can still provide some qualitative indications on the redistribution of phosphorus species after heating.



**Figure 9.** Distribution of extractable fractions of phosphorus in sludge (S) and ashes (A) from MWWTP 1, 2 and 3, following the sequential extraction protocol by Tessier *et al.* (1979).

As can be seen from the results, the amounts of reducible species are only slightly affected by the incineration process, thus indicating that the vast majority of these were formed already in the sludge. There is, however, a notable increase in acid soluble species following incineration, which is attributed to the increased concentration of AP.

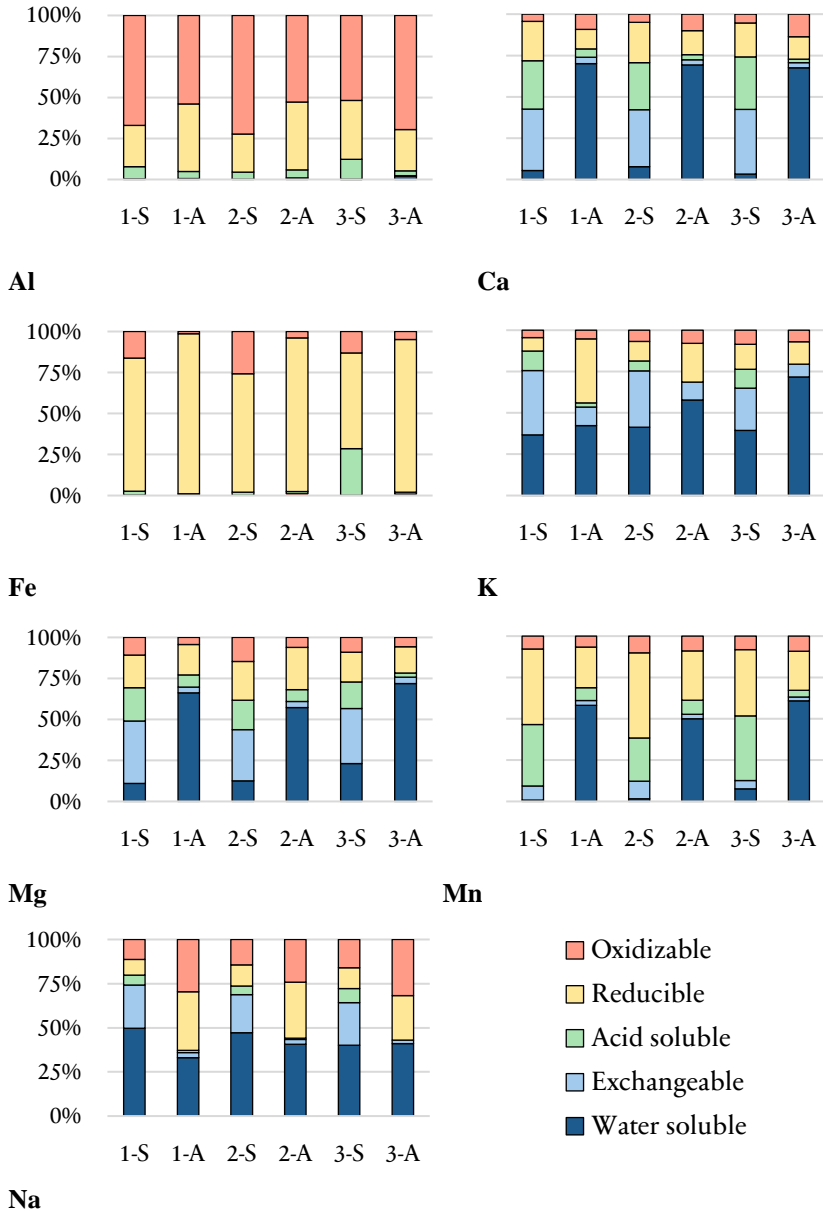
### Extraction of metals (paper II)

Concentrations of total metal (Al, Ca, Fe, K, Mg, Mn, Na) concentration in sludge and ash samples from MWWTP 1, 2 and 3, measured after digestion with Aqua regia, as well as extractable amounts following the SMT and Tessier protocols, are presented in **Table 13**. Percentage distributions of the extractable fractions are shown in **Figure 10**.

**Table 13.** Total amounts of elements in sludge (S) and ashes (A) from the three MWWTPs, determined after Aqua regia digestion, and extracted amounts following the Tessier protocol (Tes) and the SMT protocol, mean values (n=3) given as g kg<sup>-1</sup> DW.

			Al	Ca	Fe	K	Mg	Mn	Na
1	Total	S	42.7	28.5	57.7	3.0	3.0	0.4	1.1
		A	39.7	24.7	55.9	2.8	3.5	0.4	2.3
Ext.	Tes	S	6.0	19.1	21.3	1.8	1.6	0.3	0.8
		A	0.5	5.0	1.4	0.9	0.9	0.1	0.3
	SMT	S	38.6	24.0	44.2	1.8	2.2	0.4	1.2
		A	27.8	27.4	23.2	1.9	2.5	0.4	2.1
2	Total	S	13.9	21.6	81.9	2.9	2.9	0.5	1.2
		A	12.2	20.1	82.8	1.7	3.4	0.4	1.8
Ext.	Tes	S	3.7	15.2	20.2	1.6	1.5	0.2	0.7
		A	0.2	3.2	0.9	0.3	0.5	0.1	0.2
	SMT	S	11.8	23.9	72.2	2.3	2.1	0.4	1.1
		A	8.5	19.4	33.2	0.7	2.8	0.4	1.4
3	Total	S	28.8	27.8	77.0	3.4	4.3	0.4	1.0
		A	30.0	27.4	81.9	2.9	4.5	0.3	2.2
Ext.	Tes	S	6.4	17.8	21.8	1.8	2.2	0.2	0.6
		A	0.7	4.6	1.7	0.6	0.9	0.1	0.3
	SMT	S	30.7	29.1	71.8	1.7	2.9	0.3	0.9
		A	20.7	31.6	37.4	1.4	3.1	0.3	2.0

As can be seen, the metal concentrations presented in **Table 13** differ from the measured concentrations presented in **Table 9**. This difference is especially pronounced for aluminium in sludge and ash from MWWTP 2. One possible explanation for the general inconsistency is obviously the different methods used for analysis. Although XRF is generally considered to provide less precise quantifications of the content of several elements in a solid sample, it has been shown to provide reliable data for aluminium and iron in organic sediments (Kern *et al.*, 2019). Because of the organic content in the sludge samples, this could be an indication that XRF would be a reliable method for also this material.



**Figure 10.** Fractions of Al, Ca, Fe, K, Mg, Mn and Na released in the different steps of the sequential extraction procedure by Tessier et al. (1979), given in percentage of the extractable fraction.

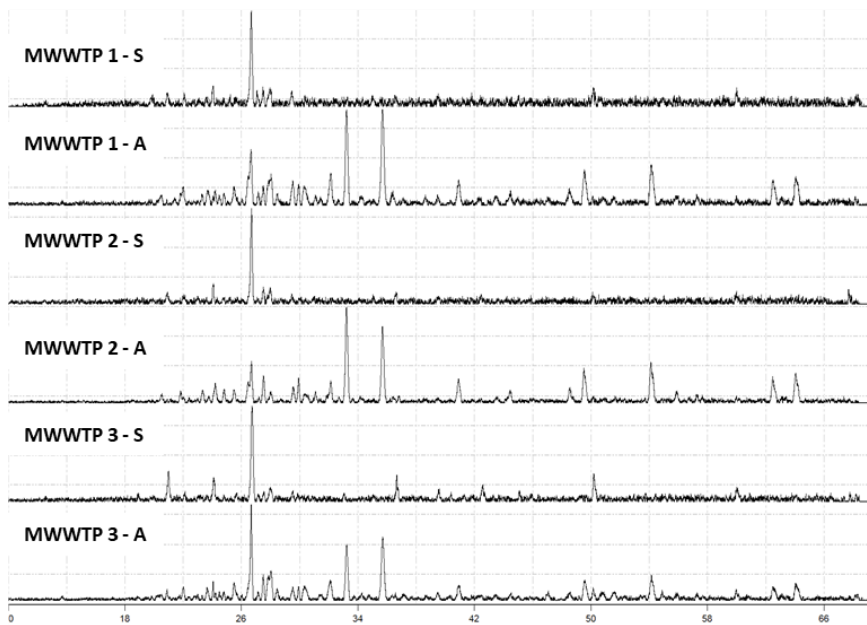
In addition, the samples from MWWTP 2 and 3 included in Paper III were not collected at the same time as those included in paper I and II, why there may be differences in the chemical composition due to temporal changes. This theory is supported by the similarity in concentrations of Al, Ca and Fe in sludge and ash samples from MWWTP 1 by the two methods. Aqua regia digestion shows that the concentrations of Al, Ca and Fe in the sludge from this facility is  $43\pm 5$ ,  $29\pm 2$  and  $58\pm 6$ , respectively, with corresponding results from XRF of 43, 26 and 55 g kg<sup>-1</sup> for Al, Ca and Fe in the sludge. Hence, the consistency in the results indicates that XRF could be a reliable method given the conditions presented in here. As can be seen from the results presented in **Table 13**, the extractable fractions following the Tessier protocol are lower compared to the total concentrations, measured after digestion with *Aqua regia*. This is especially pronounced for the principal elements (Al, Ca and Fe). In the sludge samples this protocol released an average of 21, 79 and 30% of the total content of Al, Ca and Fe, respectively. Corresponding numbers for the ashes are 2, 59 and 29% for Al, Ca and Fe, respectively, thus indicating a substantial decrease in extraction following incineration. The reason for this decrease is most likely related to the redistribution to more ordered phases, especially with regards to aluminium and iron. However, despite the rather low extractability, the redistribution of the extractable fractions following incineration still provide valuable insights in the change in speciation for the selected elements. It is evident that iron is the dominating element in all samples (**Table 13**), which is reasonable considering that all of the facilities use iron in their treatment processes (**Table 9**). The second most abundant metal is aluminium, followed by calcium. Results from the *Aqua regia* digestion indicate that most (Al, Ca, Fe, Mg, Mn) of the metals were quantitatively retained in the ashes (**Table 13**). However, the incineration process did have a clear impact on the chemical speciation of them (**Figure 10**), and consequently also their extractability (**Table 13**). There is an evident decrease in extractability after incineration according to the Tessier protocol, which strongly suggest that more ordered species are formed. This is also in agreement with the results from XRD analysis, presented in **Table 14** (sludge samples), **Table 15** (ash samples) and **Figure 11**.

**Table 14.** Ordered phases reported in the literature and detected in sludge samples with XRD related to the signal to noise ratio (S/N > 0.9 major; 0.9 > S/N > 0.1 present; S/N < 0.1 trace; S/N < 0.01 b.d. (below detection)).

Phase		Plant 1	Plant 2	Plant 3
Albite	$\text{NaAlSi}_3\text{O}_8$	Present	b.d.	b.d.
Berlinite	$\text{AlPO}_4$	b.d.	Trace	Trace
$\text{AlPO}_4$ -1-Hydrate	$\text{AlPO}_4 \cdot \text{H}_2\text{O}$	Trace	b.d.	b.d.
Strontium hydrogen phosphate	$\alpha\text{-SrHPO}_4$	b.d.	b.d.	b.d.
Belite	$\text{Ca}_2\text{SiO}_4$	Trace	b.d.	b.d.
Calcium metaphosphate	$\beta\text{-CaP}_2\text{O}_6$	Trace	b.d.	b.d.
$\text{Ca}_2\text{O}_{11}\text{P}_3\text{V}$		b.d.	b.d.	b.d.
Chopinite	$(\text{Mg,Fe})_3(\text{PO}_4)_2$	b.d.	b.d.	Trace
Crystobalite	$\text{SiO}_2$	b.d.	b.d.	b.d.
Dickitedis	$\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$	b.d.	b.d.	b.d.
Graphite3r	C	Trace	Trace	b.d.
Kaolinite	$\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$	Major	b.d.	b.d.
Struvite	$(\text{NH}_4)\text{MgPO}_4 \cdot 6(\text{H}_2\text{O})$	b.d.	b.d.	b.d.
Muscovite2m1	$\text{KAl}_2(\text{Si}_2\text{Al})\text{O}_{10}(\text{OH,F})_2$	Major	b.d.	b.d.
Nahpoite	$\text{Na}_2\text{HPO}_4$	b.d.	Major	Trace
Quartz	$\text{SiO}_2$	b.d.	b.d.	b.d.
low-T, $\alpha$ -quartz	$\text{SiO}_2$ p3221	b.d.	Major	b.d.
Strontium phosphate	$\text{SrP}_2\text{O}_6$	b.d.	b.d.	b.d.
Vivianite	$\text{Fe}_3(\text{PO}_4)_2$	b.d.	b.d.	b.d.

**Table 15.** Ordered phases reported in the literature and detected in ash samples with XRD related to the signal to noise ratio (S/N > 0.9 major; 0.9 > S/N > 0.1 present; S/N < 0.1 trace; S/N < 0.01 b.d. (below detection)).

Phase		Plant 1	Plant 2	Plant 3
Akermanite	$\text{Ca}_2\text{Mg}(\text{Si}_2\text{O}_7)$	b.d.	b.d.	Trace
Berlinite	$\text{AlPO}_4$	b.d.	b.d.	Trace
Anhydrite	$\text{CaSO}_4$	b.d.	b.d.	Trace
Anorthite	$\text{CaAl}_2\text{Si}_2\text{O}_8$	Present	Trace	b.d.
Augite	$(\text{Si},\text{Al})_2\text{O}_6$	b.d.	b.d.	Trace
Calcium metaphosphate	$\beta\text{-CaP}_2\text{O}_6$	Trace	b.d.	b.d.
Lime	$\text{CaO}$	Present	b.d.	b.d.
Cerussite	$\text{PbCO}_3$	Trace	b.d.	b.d.
Corundum	$\text{Al}_2\text{O}_3$	b.d.	b.d.	Trace
Crandallite	$\text{CaAl}_3(\text{PO}_4)_2(\text{OH})_5$	b.d.	b.d.	Trace
Crystobalite	$\text{SiO}_2$	Trace	b.d.	b.d.
Dickitedis	$\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$	Trace	Major	Trace
Goethite	$\text{FeO}(\text{OH})$	Trace	b.d.	b.d.
Graphite3r	$\text{C}$	b.d.	b.d.	Trace
Hematite	$\text{Fe}_2\text{O}_3$	Major	Major	Major
Kaolinite	$\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$	b.d.	b.d.	Major
Magnetite	$\text{Fe}_3\text{O}_4$	Trace	b.d.	b.d.
Musc1md		b.d.	b.d.	b.d.
Nahpoite	$\text{Na}_2\text{HPO}_4$	Major	b.d.	b.d.
Silicate feldspar	Plag50c1	Present	b.d.	Major
Silicate feldspar	Plag85an	Trace	Present	Trace
Quartz	$\text{SiO}_2$ p3221	Present	Trace	b.d.
Smectite	Smectite di2w fix	Trace	b.d.	b.d.
Strontium phosphate	$\text{SrP}_2\text{O}_6$	b.d.	b.d.	b.d.
Vivianite	$\text{Fe}_3(\text{PO}_4)_2$	b.d.	b.d.	b.d.



**Figure 11.** Example of XRD diffractograms of sludge (S) and ash (A) samples from the three MWWTPs 1, 2 and 3

No ordered iron phases were identifiable in the sludge (**Table 14**) while there is a predominance of hematite ( $\text{Fe}_2\text{O}_3$ ), as well as detectable levels of magnetite ( $\text{Fe}_3\text{O}_4$ ), in all ash samples (**Table 15**). In similarity with results reported by Boudraa *et al.* (2020), no ordered Fe(III)phosphate solids were detected in the XRD spectra for any of the samples, despite the fact that iron is used for phosphorus removal at all three facilities. One possible explanation for the absence of these signals could be that the formed iron phosphates are amorphous in nature, and therefore not detectable using XRD, as exemplified in a previous study reported by Wang *et al.* (2022). Another possibility is that the iron acts as a scavenger and removes phosphorus through coprecipitation upon sludge formation. This is well in line with the formation of hematite and magnetite from the amorphous hydrous oxide phase during incineration. The decrease of extractable amounts of iron according to the Tessier protocol (**Table 13**), from 30% in the sludge samples to 1% in the ashes, further

support the formation of less soluble species during incineration. Approximately 80% of the leachable iron in the sludge samples is released in the reducible fraction, which is a strong indication of amorphous iron(III) hydrous oxides. After incineration, this fraction exceeds 95%, which agrees well with the XRD data, i.e., formation of ordered iron oxides. There is a distinct decrease in the amount of oxidizable iron following incineration, from 10-25% in the sludge to less than 5% in the ashes (**Figure 10**). These results are not surprising since the treatment in this extraction is based on oxidation of organic matter under acid conditions. However, a higher amount organic species was expected to have been removed in the incineration. It is also interesting to note that detectable amounts of iron were released also from the ashes in the oxidative treatment. Although this behaviour could indicate the presence of amorphous sulphides, i.e., oxygen deficiency in the water phase, it suggests that organic species survived the thermal treatment, as previously discussed with respect to phosphorus. The amounts of iron released in fraction 2 only reach a few percent in all samples, except in the sludge from plant 3, where this fraction accounts for some 30% of the extractable amount. This general observation supports formation of hydrous oxides upon addition of iron(II) in the treatment process, since the amounts released in this fraction otherwise would be higher. This also presents a plausible explanation for the high release seen for sludge from plant 3, which could be a result of high dosing of iron (**Table 9**), possibly in combination with oxygen deficiency.

The low amounts of aluminium released in the first three steps of the Tessier protocol is a clear indication that ordered aluminium species, are formed already in the sludge, and remain after incineration. Based on the XRD results (**Table 14** and **Table 15**), one possible candidate is Berlinite. From the rather high amounts released in the reducible fraction (**Figure 10**) it can be concluded that iron has a clear impact on the aluminium speciation, most likely related to co-precipitation with ferric hydrous oxides. The highest amount of aluminium was released in the oxidative extraction, which strongly supports the theory that organic species survived the incineration process. From the phase analysis it is evident that several aluminium silicates (besides Berlinite) are formed during incineration, probably as a

result of reactions between silica-containing compounds and clay minerals, which were present in all sludge samples (**Table 15**).

Although there is a notable decrease in the extractability of calcium following incineration, this trend is less pronounced compared to iron and aluminium (**Table 13**), especially according to the SMT protocol. This suggests that the accumulation of calcium in the sludge is controlled by other mechanisms than just co-precipitation with ferric hydrous oxides. According to the sequential extraction (**Figure 10**) calcium in the sludge is mainly present as adsorbed ion-exchangeable species in combination with carbonates. After incineration, there is a pronounced shift towards the water-soluble fraction. This phase shift is most likely related to a redistribution of amorphous species to CaO in the ashes. In addition, XRD analysis (**Table 15**) also indicates formation of ordered calcium containing aluminium silicates, which would contribute to the decreased leachability (**Table 13**).

As for calcium, the incineration process also induced an increased fraction of water-soluble species of magnesium and manganese (**Figure 10**). However, only one ordered phase of magnesium was identified in one of the ash samples, while no ordered solids were found for manganese (**Table 15**). Therefore, it is likely that the decrease in leachability following incineration is caused by inclusion in other phases. Also potassium shows a shift towards water soluble species after incineration, although less pronounced compared to calcium and magnesium (**Figure 10**). XRD analysis did, however, identify several ordered phases which contain potassium, mainly phosphate and aluminium silicates (**Table 15**).

### **Impact of incineration on chemical speciation (paper I, II and III)**

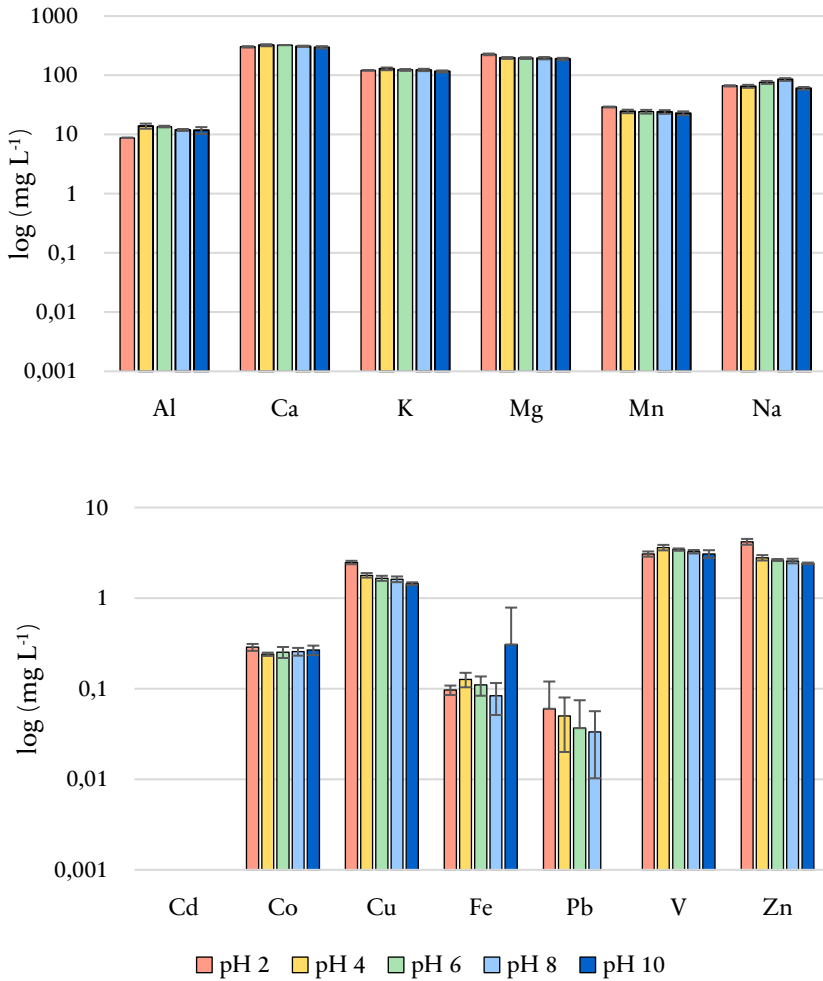
The results from chemical characterization of sludge and ashes, presented in this thesis show that incineration has a clear impact on the speciation of both phosphorus and metals. Although there are substantial differences in the origin of the sludge, in terms of wastewater composition, treatment processes, inclusion of external fractions etc., incineration seems to have a homogenizing effect of the material. In addition, the decomposition of organic material during

the incineration process entails an increase in metal and phosphorus concentration in the ashes, as well as a re-distribution in the speciation of the elements. The low extraction of iron and aluminium from sludge in the three first steps of the Tessier protocol (**Figure 10**) indicate that consolidated species are formed already in the sludge phase.

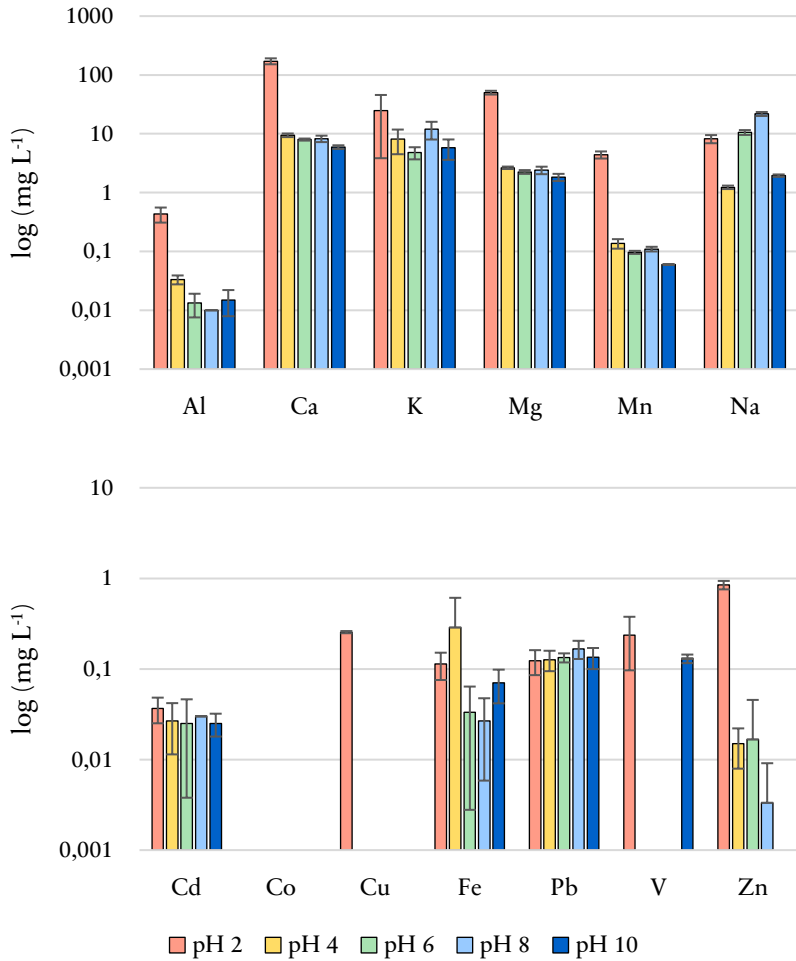
Since the phosphorus concentration in the produced ISSA (**Table 12**) is comparable to that of phosphate rock (65-130 mg g<sup>-1</sup>), which is used for fertilizer production (Kumar Haldar, 2018), this material could be a viable option as phosphorus resource. However, for the ashes to be usable in the existing industrial processes, it would be beneficial if the phosphorus speciation is similar to that in phosphate rock (e.g., associated to calcium). Although all of the facilities included in this thesis use iron to remove phosphorus, no ordered iron-phosphates could be detected through XRD analysis (**Table 14** and **Table 15**). This further supports the theory on co-precipitation with ferric hydrous oxides, or that amorphous phases are present. The presence of aluminium-phosphate in sludge and ash samples indicate that the formation of these takes place already in the sludge phase, or in the sewage water, and remain after incineration. This is also in agreement with the results on phosphorus association to principal elements (Paper I), which clearly show that the redistribution of NAIP to AP is mainly related to a decrease in Fe-P, while the Al-P fraction is unaltered. Given that Fe-P react at temperatures in the range of 600-850 °C, while Al-P is stable at least at temperatures up to 850 °C (Li *et al.*, 2015), this is a clear indication that the temperature during incineration was too low for quantitative transformation to Ca-P. This could also be a contributing factor in explaining the presence of OP in the ashes (Paper I), as well as the substantial fraction of aluminium released in the oxidative extraction following the Tessier protocol (Paper II). Another possibility is potential encapsulation of organic material by ordered oxides that are formed during the incineration. When the resulting ashes are crushed as a part of the sample preparation process, the content of organically associated elements would be exposed and thereby available for extraction.

## Stability of ISSA (paper IV)

Concentrations of elements (Al, As, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Na, Pb, V and Zn) in the filtered solutions after 24 hours equilibration tests of original and washed ashes are presented in **Figure 12** and **Figure 13**, respectively. It can be concluded that the metal concentrations are considerably lower in leachates from washed ashes, with iron at the lower pH values (2 and 4) as the only exception, probably related to poorly ordered ferric hydrous oxides. This observation is attributed to removal of soluble salts in the pre-washing, thereby decreasing the amounts of metals available for extraction. The observation for iron may be explained by a lower proportion of adsorption sites for hydrogen ions, which would lead to lower pH and a more pronounced dissolution of iron-carbonates (Golubev *et al.*, 2009). For the remaining metals, the concentrations in the leachates from washed ashes, compared to the original, are considerably higher for (one or both of) the extremes (pH 2 and 10), as compared to the intermediate pH-interval. This is expected since most soluble metals have been removed in the washing procedure, thereby leading to a limited amount available for extraction at neutral pH. Moreover, the effect of pH on this process is seemingly higher for the washed ashes, although statistical evaluation suggests a significant ( $p < 0.05$ ) effect of pH on the release of metals in both of the setups.



**Figure 12.** Equilibrium concentrations of selected metals as a function of pH for ISSA, after extraction with deionized water (18.2 M $\Omega$ ) for 24 hours at room temperature and a liquid:solid ratio of 5.



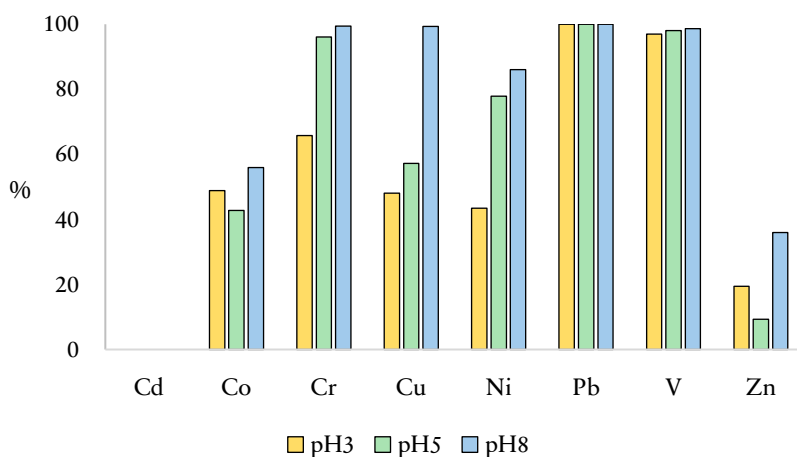
**Figure 13.** Equilibrium concentrations of selected metals as a function of pH for washed ISSA, after extraction with deionized water (18.2 MΩ) for 24 hours at room temperature and a liquid:solid ratio of 5

## ISSA as a sorbent (paper IV and V)

### Metals

Results from the study on metal sorption to ISSA from spiked ARD, performed at different pH (3, 5 and 8) are shown as percentage removal ratios in **Figure 14**. The sorption of several of the metals (Cr, Cu, Ni, Zn) increases with increasing pH, which is consistent with previous results on removal of heavy metals using waste gas sludge (Jafaripour *et al.*, 2015), and is attributed to a combination of adsorption and co-precipitation.

According to the XRD-data (**Table 15**), the main constituent in the produced ISSA was hematite which has been extensively studied for its applicability for removal of a wide range of elements from different kinds of water (c.f. Saharan *et al.*, 2014; Tao *et al.*, 2021).

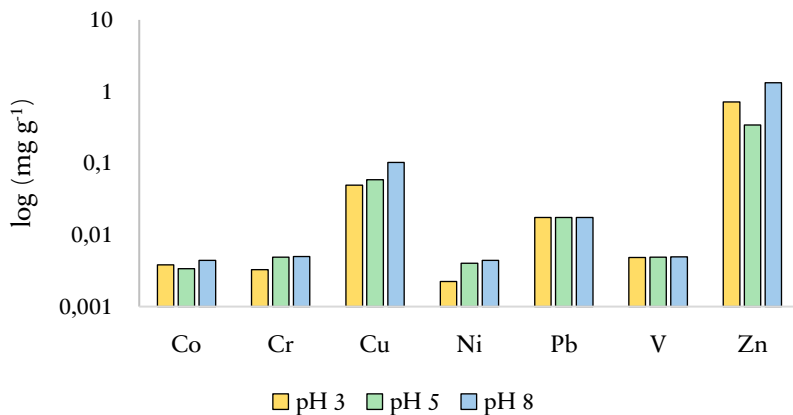


**Figure 14.** Adsorption of metals to ISSA as a function of pH, calculated as the difference between initial and final concentrations of ARD after 24 hours equilibration, presented as percentage removal rate.

Adsorption of metal ions to hematite is related to the concentration of hydroxyl species on the surface (Venema *et al.*, 1998), which in turn is a function of the physical nature of the surface (porosity, exposure of facets etc.), as well as the pH. There are three different types of hydroxyl sites present on hematite surfaces, which differs in their inclination to be protonated (Barrón and Torrent, 1996). As a result, an increase in solution pH will decrease the positive charge of the surface through dissociation of the surface hydroxyls, and therefore increase the adsorption of cations (Tan *et al.*, 2022). It should, however, be mentioned that an increase in pH also imposes changes in the metal speciation in the solution phase. This is especially notable for chromium and vanadium through their formation of oxy-ions. Geochemical modelling identified that both are mainly present as positively charged ions at pH 3 (i.e.,  $\text{Cr}^{3+}$  and  $\text{VO}_2^+$ ). At pH 5, however, approximately 85% of the chromium is present in cationic form, while virtually all vanadium is found as negatively charged ions ( $\text{H}_2\text{VO}_4^-$ ,  $\text{H}_2\text{V}_2\text{O}_7^{2-}$ ,  $\text{HVO}_4^{2-}$ ). As pH is further increased to 8, the oxidation state for chromium is prone to change, from Cr(III) to Cr(VI), and the latter is predominantly pre-sent as anions. Thus, the removal of chromium at pH 8 is most likely related to retention of chromium species associated with cationic ions, such as calcium. This may also be the mechanism responsible for removal of vanadium, since geochemical modelling indicates a quantitative precipitation, predominantly with lead, as  $\text{Pb}_2\text{V}_2\text{O}_7$ , of the anionic species at pH 5 and 8. The removal of zinc was low compared to other metals (**Figure 14**), which is related to its initially high concentration in relation to available specific adsorption sites (Stumm, 1992; Shipley *et al.*, 2013). Although no physical characterization was done on the ash matrices, it is reasonable to assume that the material is rather porous due to decomposition of organic matter during the incineration process (Cheeseman *et al.*, 2003). As organic matter is decomposed, gaseous phases are formed (i.e.,  $\text{CO}_2$ ), which would result in voids (pores) in the solid material.

Based on the experimental results, the accompanied sorption capacities were calculated as a function of pH (**Figure 15**). As can be seen from Figure 14, ISSA has high potential to sorb all of the metals tested in this study. This is especially noticeable for zinc, although the

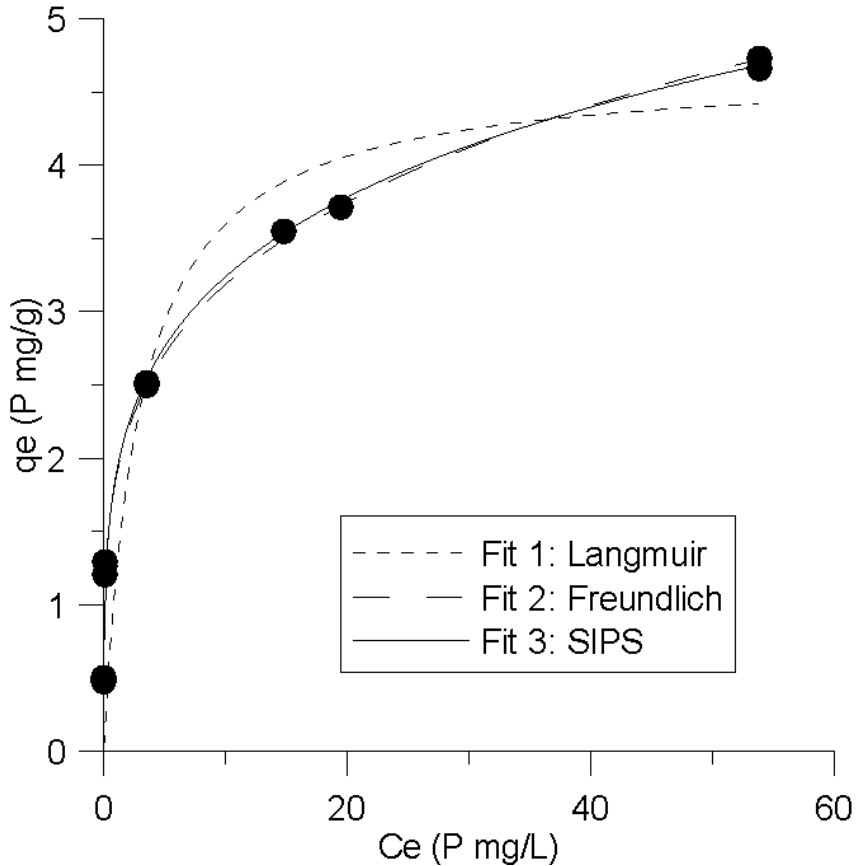
significantly higher concentration of this element in the ARD (Table 7) must be taken into account. Considering the overall high removal efficiencies, it is reasonable to assume the process to be element, or solution species, dependent, which would implicate minor competition between the ions. However, in order to properly assess the sorption capacities more refined studies on the mechanisms are needed.



**Figure 15.** Estimated sorption capacity of ISSA as a function of pH

## Phosphorus

Final concentrations of phosphate in the solution phase were used to calculate the amount removed from the liquid. Based on this mass balance, the adsorption capacity of the material was estimated using three different isotherms (Langmuir, Freundlich and SIPS), as shown in **Figure 16**. Derived parameters for the different models are presented in **Table 16**.



**Figure 16.** Equilibrium concentration on the material ( $\text{mg g}^{-1}$ ) vs final concentrations in the liquid ( $\text{mg L}^{-1}$ ), and visual presentations of the three isotherms.

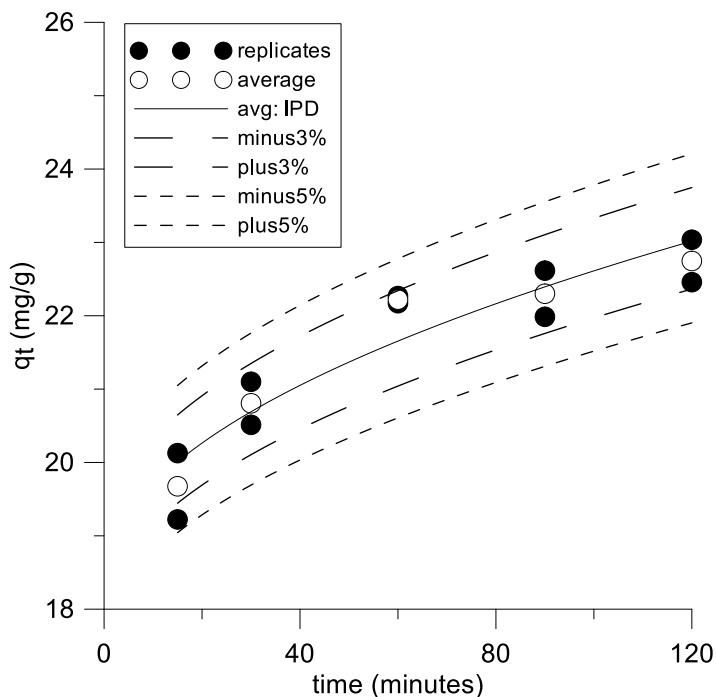
**Table 16.** Adsorption parameters for phosphate sorption to sewage sludge ash, calculated using three different isotherms.

	Langmuir	Freundlich	SIPS
Q (mg g <sup>-1</sup> )	4.66	-	21.9
K	0.339	1.86	1.40*10 <sup>-4</sup>
n	-	4.28	3.75
R2	0.859	0.990	0.991

As can be seen from the results (**Table 16**), the experimental data has a rather poor fit to the Langmuir isotherm, (correlation coefficient,  $R2 = 0.859$ ). This is a clear indication that the surface of the ash does not consist of surface groups with equivalent adsorption affinity, but rather a mixture of different surface groups with different affinities. The data has a better fit to the Freundlich and SIPS isotherms ( $R2 > 0.99$  for both isotherms). Furthermore, the n-values (4.28 and 3.75) indicate that the sorption process is facilitated according to the Freundlich isotherm ( $1/n = 0.23$ ) and that the material has a homogenous distribution of active surface groups according to the SIPS isotherm ( $1/n = 0.27$ ).

The calculated sorption capacity of 21.9 mg g<sup>-1</sup> is well in line other studies of similar materials (c.f. Xia et al. 2020). From their results, the authors identified goethite (FeO(OH)) to be the key component in the material, while the ashes in this study are characterized by hematite (Fe<sub>2</sub>O<sub>3</sub>), as shown in **Table 15**. The obtained results in here are, however, much higher compared to other studies on phosphorus sorption on hematite (Fang *et al.*, 2017; Dimirkou *et al.*, 2002). One possible reason for this is a higher specific surface area in the ISSA. Synthetic hematite is formed under controlled conditions and should therefore have a crystallinity close to optimal, with very low porosity, while ISSA is likely to be less structured.

The adsorption process was further evaluated using the intra particle diffusion model (IPD model), as shown in **Figure 17**, derived parameters are presented in **Table 17**.

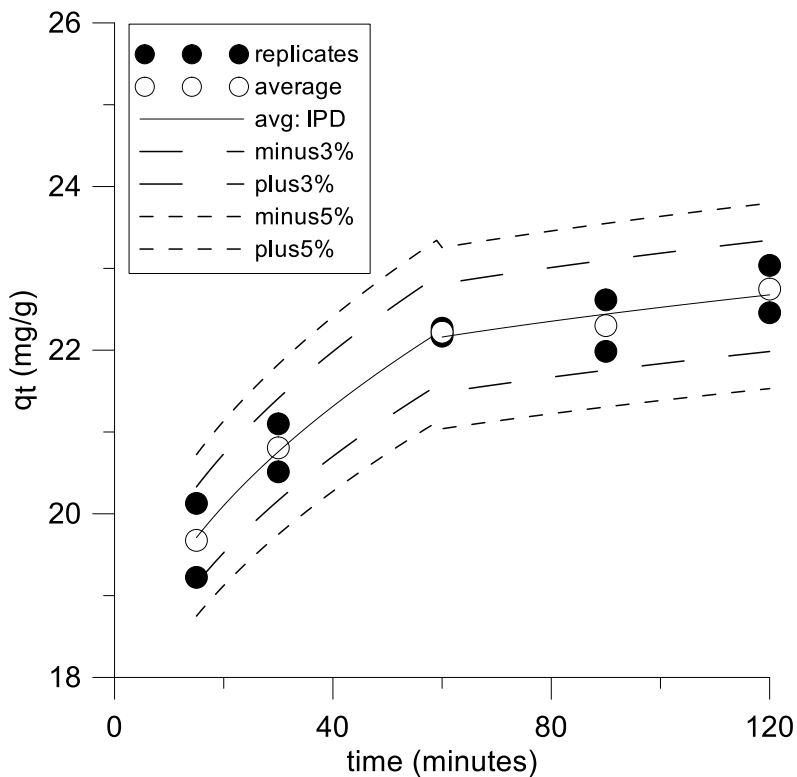


**Figure 17.** Plot of IPD model for adsorption of P to sewage sludge ash assuming one single process.

**Table 17.** Derived parameters for IPD modelling of phosphorus sorption following a one step process ( $X_A$ ) or a twostep process ( $X_B$ ), where the first phase takes place between 15-60 minutes, and the second between 60-120 minutes).

	$X_A$ (15-120 min)	$X_B$ (15-60 min)	$X_B$ (60-120 min)
K	0.425	0.655	0.161
M (mg g <sup>-1</sup> )	18.4	17.2	20.9
R <sup>2</sup>	0.919	0.999	0.826

The first model ( $X_A$ ) was based on the entire timespan, from 15-120 minutes, and had a rather good fit to the data ( $R^2 = 0.919$ ). However, based on the visual appearance, there was reason to suspect the sorption to be a two stage process. The data was therefore divided into two sub-sets covering the two time intervals 15-60 minutes and 60-120 minutes, after which the model was applied to these, resulting in the two step model  $X_B$  (**Figure 18**).



**Figure 18.** Plot of IPD model for adsorption of P to sewage sludge ash assuming a two-step process.

As can be seen from the graph (**Figure 18**), this model has a better fit to the data as all data points fall within  $\pm 3\%$  from the model, compared to  $\pm 5\%$  for model  $X_A$ . These results would imply that the sorption observed in this study is a combination of two different processes. The initial rapid process is probably governed by surface adsorption, while the second takes place in the pores of the material.

### **Use of ISSA as a sorbent**

From the results presented here it is obvious that ISSA could function as a sorbent for both cations (paper IV) and anions (paper V) from solution. It is, however, difficult to compare the sorption capacities of metals and phosphorus from the two studies, since they differed in terms of experimental setup. The study on metal sorption was performed with constant initial concentrations, why these values might be underestimated. The study on phosphorus sorption is, however, based on tests with increased initial concentrations, which allows for the use of isotherms to estimate the sorption capacity. Therefore, further experiments, using increasing initial concentrations, must be performed in order to obtain proper evaluations of these sorption capacities. This reasoning is supported by the lower adsorption ratio seen for zinc, in comparison to the other metals (**Figure 15**), which is related to its higher initial concentration.

In addition to the difference in experimental set up, the sorption mechanisms should also be different for the elements. In the study of metal sorption from ARD, all of metals were present in cationic form, with the exception of vanadium at pH 5 and 8. Phosphorus is, however, negatively charged when  $\text{pH} > 2$  (**Figure 2**), why the adsorption mechanisms are reverse and the process is favoured by a decrease in pH (Li *et al.*, 2016). Furthermore, phosphorus is known to form insoluble salts with several of the metals in the ISSA (e.g., iron and aluminium), which is also likely for some of the studied metals (e.g., copper and cobalt). Zinc, on the other hand, is most likely retained by cation-exchange, while lead and vanadium are co-precipitated as  $\text{Pb}_3(\text{VO}_4)_2(\text{s})$ , as was indicated by geochemical modelling.

It should also be noted that all of the ashes in this study come from incineration of sludge from facilities where iron is used in the treatment process, why iron-oxides are formed upon incineration (**Table 15**). These have been shown to have good capacity for adsorption of both metals and phosphorus from different kinds of solutions (Shi *et al.*, 2021; Ajamal *et al.*, 2018; Chiang *et al.*, 2012). Therefore, it is likely that ISSA from other types of sludge, in which the iron content is lower, would have lower effect in terms of sorption capacity.

From the study on metal sorption, it is evident that the sorption capacity is pH dependent, and that an increase in pH favours the retention of most of the metals studied in here. This is consistent with previous results on the use of waste materials as metal adsorbents (Jafaripour *et al.*, 2015; Abdulai and Lee, 2016), and is probably related to a combination of effects on the adsorption surface and metal speciation. Consequently, the removal of metals would be governed by both adsorption to the surface, as well as pores in the material, and co-precipitation with other metals. In addition, an increase in pH would entail a decreased protonation of surface hydroxyl groups, and therefore also a decrease in competition for sorption sites by hydrogen ions. Although the study on phosphorus sorption was conducted without controlling the pH in the liquid, the measured pH was approximately 4.5, which is but the measured pH of the ash/liquid mixture was approximately 4.5. Since the phosphate is a negatively charged ion, the sorption process should be favoured by low pH (Liu *et al.*, 2021).

From the results on ISSA stability, it is clear that the release of metals increased with pH, most likely caused by formation of hydroxyl species (Gitari *et al.*, 2006). In addition, the release of metals was effectively decreased by pre-washing of the material. Both of the sorption studies were performed on un-washed ISSA, why also the elements originating from the ashes itself would be present in the solution, thereby increasing the amount of ions available for sorption. It is therefore reasonable to assume that pre-washing of the ISSA, preferable with alkaline solution, would favour sorption of metals, as well as phosphorus, to the material.

## Conclusions

From the results obtained within the scope of this thesis it can be concluded that both phosphorus and metals in sewage sludge undergo significant change in speciation upon incineration. These changes entail formation of metal oxides, as well as a redistribution of NAIP to the more plant-available AP fraction, which would benefit extraction and recovery of phosphorus from the produced ISSA. Furthermore, this redistribution of phosphorus species is caused by transformation of iron-associated species, while aluminium associated phosphorus is unaffected, which is attributed to insufficient temperature in the incineration.

Although the aluminium phosphates remained unaltered during the incineration process, the total concentration of aluminium in the sludge significantly hampered the transformation to AP-species. This correlation strongly suggests that the aluminium content within the sludge should be kept at a minimum to facilitate for total conversion of NAIP species, while reducing reduce the energy consumption during incineration of sewage sludge.

The produced ISSA was shown to function as a sorbing agent for both phosphorus and metals from liquid solution, which is attributed to the high concentration of iron oxides formed during the incineration process. The calculated sorption capacity of phosphorus was in agreement with previously reported results, while the capacities for metal sorption were considerably lower compared to other studies. This is most likely related to the rather low and constant initial concentrations used in this study. The ability to use ISSA as a sorbent entails an interesting possibility to enrich the concentration of valuables (phosphorus and metals), which would increase the economic value of the material and thereby enable for a commercial process. However, further studies are needed in order to identify and evaluate the limiting and dimensioning parameters, as well as to develop a technical solution applicable in large scale.

To summarize, the following conclusions can be drawn in relation to the specified aims:

- Incineration of the sludge rendered a redistribution of the inorganic phosphorus content, from iron- to more easily available calcium-associated species. The fraction associated to aluminium was, however, unaffected, as a result of insufficient thermal treatment (paper I and III).
- In order to provide best possible conditions for phosphorus recovery from ISSA, the concentration of aluminium in the sewage sludge should be kept at a minimum. (paper III).
- Incineration of the sludge also entailed a decrease in extractability for all of the included metals, which is related to redistribution of amorphous species to more ordered structures (paper II). As a result, the incineration process was shown to have a homogenizing effect on the material.
- The produced ISSA was shown to work as sorbent for metals and phosphorus from liquid solution (paper IV and V). This presents an interesting opportunity for enrichment of the material, and thereby increasing its potential value for recovery purposes.

In addition, the following aspects should be investigated further:

- The fate of organic material during the incineration process, and more specifically the potential for ordered inorganic structures to function as thermal insulators for organic material:
- Sewage sludge and their ashes after incineration – simply waste or potential raw materials?
- The useability of ISSA to function as a sorbent for metals and/or phosphorus. This implies evaluation of limiting parameters, such as impact of competitive ions and organic molecules, as well as dimensional parameters for full scale applications.

## Implications for the future

Given the need for recovery of phosphorus, it is obvious that sewage sludge is an attractive and viable source. While direct application is a cost-efficient solution, it also introduces possible pathways for undesired contaminants to the environment, as well as to animals and humans. Although up-stream efforts can decrease the contaminants in the sludge to levels acceptable for agricultural soil, this disposal route is highly questioned in the societal community. As a consequence, several food producers are hesitant to accept crops grown on sludge-fertilized soil, while soil for production of fodder remain a viable option for direct sludge application. Thus, a sustainable phosphorus management will, at least to a certain extent, require active and selective recovery from sewage sludge.

Chemical extraction of phosphorus can be done directly from the sludge, or after thermal treatment (e.g., incineration). A large number of countries have already regulations stating that sewage sludge has to be incinerated, and that the phosphorus should be recovered, why it is reasonable to assume that similar requirements will be introduced also in Sweden, as well as other Nordic countries. In addition to decomposing organic contaminants, the incineration also entails a decrease in mass to be chemically treated for recovery purposes, thus presenting a more cost-efficient extraction process. If the thermal treatment (in full or partly, such as pre-drying) is performed locally at the MWWTPS, or in semi-centralized facilities, un-necessary transportation of water can be avoided. Both of these aspects present opportunities in which the net-cost of the over-all process can be significantly decreased, thereby reducing the economic impact associated by incineration of the sludge. In addition to recover phosphorus from the produced ISSA, its content of metals presents an opportunity to also extract and recover these, thereby contributing to a further decrease the net-costs associated with the process. There are today several commercial processes in which fly ashes from WtE incineration are extracted, in order to remove toxic elements prior to deposit or recirculation, as well as to recover metals of value. The gate fee for accepting ashes for these processes is approximate 90 EUR per metric tonne. Since the extraction processes for ISSA would be

similar to these, it is reasonable to assume that also the costs associated with treatment would be in that range. Thus, in order to create a cost-efficient solution for extraction of phosphorus and other values from ISSA, the value of the output products has to be increased. The results from this thesis indicate that sorption of phosphorus and metals to ISSA, especially from incineration of sewage sludge with high concentration of iron, would be a viable option to increase its concentration of these elements, and thereby also increase the potential values in recovered products. However, although the initial results on metal recovery (paper IV) indicate that the retention processes are element (or species) dependent, the potential to utilize ISSA for treatment of real wastewaters has to be thoroughly examined. This is especially true for waters with concentrations of BOD or humic substances, since these are known to have a limiting effect on the retention capacity (Nilsson *et al.*, 2013; Di Iorio *et al.*, 2022). In addition, since the change in speciation of phosphorus seems to be dependent on the concentration of aluminium (paper III), it is likely that also the concentration of other metals (i.e., copper, magnesium, manganese, nickel) may affect this process. Other aspects that have to be further evaluated include the conditions during incineration (presence of oxygen, temperature, mixing of the material), as well as potential benefits of co-incineration with other substrates. Attention should also be put on how to optimize the sorption capacity of the ISSA, both in terms of optimizing its physical and chemical properties (i.e., surface area optimization, chemical characterization etc.), as well as development of technical solutions for practical utilization of the material.

## **Ethical Considerations**

The design of the studies, data handling and publication policies according to the principle of publicity for Swedish authorities were agreed upon with the stakeholders. After anonymization of the data the principles of the Directive (EU) 2019/1024 of the European Parliament and of the Council of 20 June 2019 on open data and the re-use of public sector information (European Union, 2019) were followed. Authorship and other principles for publications follow the recommendations in the Vancouver Convention (ICMJE, 2022).

The research time for Ms Charlotte Nilsson has been funded by Fortum Waste Solutions AB. The time for supervisor prof Stefan Karlsson was funded by the Faculty of Business, Science and Engineering at Örebro University. Assistant supervisors Prof Bert Allard and Dr Thomas von Kronhelm were financed by Remedy by Sweden AB and the research department at Fortum Waste Solutions AB (project HWSE130003), respectively. None of the projects had commercial interests and experimental costs were granted by Fortum Waste Solutions AB.

## References

- Abdulai, P.J., Lee, S., 2016. Potential use of incineration fly ash as a sustainable low cost material for heavy metals removal from acid mine drainage. *Journal of Korea Society of Waste Management* 33(1): 46-55. doi:10.9786/kswm.2016.33.1.46
- Adam, C., Peplinski, B., Michaelis, M., Kley, G., Simon, F-G., 2009. Thermochemical treatment of sewage sludge ashes for phosphorus recovery. *Waste Management* 29(3): 122-1128. doi:10.1016/j.wasman.2008.09.011
- Ajamal, Z., Muhmood, A., Usman, M., Kizito, S., Lu, J., Dong, R., Wu, S., 2018. Phosphate removal from aqueous solution using iron oxides: Adsorption, desorption and regeneration characteristics. *Journal of Colloid and Interface Science* 528: 145-155. doi:10.1016/j.jcis.2018.05.084
- Al-Ghouti M.A., Da'ana D.A., 2020. Guidelines for the use and interpretation of adsorption isotherm models: A review. *Journal of Hazardous Materials* 393: 122353. doi:10.1016/j.jhazmat.2020.122383
- Angin, I., Aslantas, R., Gunes, A., Kose, M., Ozkan, G., 2017. Effects of sewage sludge amendment on some soil properties, growth, yield and nutrient content of raspberry (*Rubus idaeus* L.). *Erwerbs-Obstbau* 59(2): 93-99. doi: 10.1007/s10341-016-0303-9
- American Public Health Association (APHA), 1992. Method 4500-P: *Standard methods for the examination of water and wastewater*. ISBN: 0-87556-207-1
- Aquastat 2018. Food and Agriculture Organization of the United Nations Statistical Database, <https://www.fao.org/aquastat/en/databases/>. Data collected in October 2018
- Ashley, K., Cordell, D., Mavinic, D., 2011. A brief history of phosphorus: From the philosopher's stone to nutrient recovery and reuse. *Chemosphere*, 84(6): 737-746. doi:10.1016/j.chemosphere.2011.03.001

- Barrón, V., Torrent, J., 1996. Surface hydroxyl configuration of various crystal faces of hematite and goethite. *Journal of Colloid and Interface Science* 177(2): 407-410. doi:10.1006/jcis.1996.0051
- Becidan, M., Johansson, I., 2020. Waste-to-Energy fly ash valorisation. *Workshop report from IEA Bioenergy Webinar* on October 7th, 2020. Retrieved from: [https://task36.ieabioenergy.com/wp-content/uploads/sites/4/2020/12/IEABioT36-workshop-report-Waste-to-Energy-WtE-fly-ash-valorisation-webinar\\_final.pdf](https://task36.ieabioenergy.com/wp-content/uploads/sites/4/2020/12/IEABioT36-workshop-report-Waste-to-Energy-WtE-fly-ash-valorisation-webinar_final.pdf) in October 2022
- BIO Intelligence Service, 2013. Study on the environmental risks of medicinal products, Final Report prepared for Executive Agency for Health and Consumers
- Brownlie, W.J., Sutton, M.A., Heal, K.V., Reay, D.S., Spears, B.M. (eds), 2022. *Our phosphorus future*. UL Centre for Ecology & Hydrology, Edinburgh. doi:10.13140/RG.2.2.17834.08645
- Carliell-Marquet, C., Smith, J., Oikonomidis, I., Wheatley, A., 2010. Inorganic profiles of chemical phosphorus removal sludge. *Proceedings of the Institution of Civil Engineers: Water Management*; 163(2): 65-77. doi:10.1680/wama.2010.163.2.65
- Chang, S.C., Jackson, M.L., 1957. Fractionation of soil phosphorus. *Soil Science* 84 (2): 133-144. doi:10.1097/00010694-195708000-00005
- Cheeseman, C.R., Sollars, C.J., McEntee, S., 2003. Properties, microstructure and leaching of sintered sewage sludge ash. *Resources, Conservation and Recycling* 40: 13-25. doi:10.1016/S0921-3449(03)00022-3
- Chen, X., Liaw, S.B., Wu, H., 2019. A new method for quantifying phosphorus of various occurrence forms in solid fuels. *Energy & Fuels* 33(4): 3311–3321. doi:10.1021/acs.energyfuels.9b00361
- Chiang, Y.W., Ghyselbrecht, K., Santos, R.M., Martens, J.A., Swennen, R., Cappuyns, V., Meesschaert, B., 2012. Adsorption of multi-heavy metals onto water treatment residuals: Sorption

- capacities and applications. *Chemical Engineering Journal* (200-202): 405-415. doi:0.1016/j.cej.2012.06.070
- Chow, E., Patton, D., 2022. China issues phosphate quotas to rein in fertilizer exports – analysts. *Reuters*. Retrieved from <https://www.reuters.com/article/china-fertilizers-quotas-idUSKBN2OQ0KY> in September 2022
- Collivignarelli, M.C., Abbà, A., Frattarola, A., Miino, M.C., Padovani, S., Katsoyiannis, I., Torretta, V., 2019. Legislation for the reuse of biosolids on agricultural land in Europe: Overview. *Sustainability* 11(21): 6015. doi:10.3390/su11216015
- Contin, M., Malev, O., Izosimova, A., De Nobili, M., 2015. Flocculation of sewage sludge with FeCl<sub>3</sub> modifies the bioavailability of potentially toxic elements when added to different soils. *Ecological Engineering* 81: 278-288. doi:10.1016/j.ecoleng.2015.04.033
- Cordell, D., Drangert, J-O., White, S., 2009. The story of phosphorus: Global food security and food for thought. *Global Environmental Change* 19(2): 292-305. doi:10.1016/j.gloenvcha.2008.10.009
- Cornel, P., Schaum, C., 2009. Phosphorus recovery from wastewater needs, technologies and costs. *Water Science & Technology* 59 (6): 1069-1076. doi:10.2166/wst.2009.045
- Corral-Capulin, N.G., Vilchis-Nestor, A.R., Gutiérrez-Segura, E., Solache-Ríos, M., 2019. Comparison of the removal behavior of fluoride by Fe<sup>3+</sup> modified geomaterials from water. *Applied Clay Science* 173(1): 19-28. doi:10.1016/j.clay.2019.03.003
- de-Bashan, L.E., Bashan, Y., 2004. Recent advances in removing phosphorus from wastewater and its use as fertilizer (1997-2003). *Water Research* 38(19): 4222-4246. doi:10.1016/j.watres.2004.07.014
- Derhy, M., Taha, Y., Hakkou, R., Benzaazoua, M., 2020. Review of the main factors affecting the flotation of phosphate ores. *Minerals* 10(12): 1109. doi:10.3390/min10121109
- Desmidt, E., Ghyselbrecht, K., Zhang, Y., Pinoy, L., Van der Bruggen, B., Verstraete, W., Rabaey, K., Meesschaert, B., 2015. Global

- phosphorus scarcity and full-scale P-recovery techniques: A review. *Critical Reviews in Environmental Science and Technology* 45(4): 336-384. doi:10.1080/10643389.2013.866531
- Di Iorio, E., Circelli, L., Angelico, R., Torrent, J., Tan, W., Colombo, C., 2022. Environmental implications of interaction between humic substances and iron oxide nanoparticles: A review. *Chemosphere* 303(SI:2): 135172. doi:10.1016/j.chemosphere.2022.135172
- Dimirkou, A., Ioannou, A., Doula, M., 2002. Preparation, characterization and sorption properties for phosphates of hematite, bentonite and bentonite-hematite systems. *Advances in Colloid and Interface Science* 97: 37-61. doi:10.1016/S0001-8686(01)00046-X
- Driver, J., Lijmbach, D., Steen, I., 1999. Why recover phosphorus for recycling, and how? *Environmental Technology* 20(7): 651-662. doi:10.1080/09593332008616861
- Döbelin, N., Kleeberg, R. 2015. Profex: a graphical user interface for the Rietveld refinement program BGMN. *Journal of Applied Crystallography*, 29(48):1573-1580. doi:10.1107/S1600576715014685
- Ebina J, Tsutsui T and Shirai T (1983) Simultaneous determination of total nitrogen and total phosphorus in water using peroxodisulfate oxidation. *Water Research* 17(12): 1721-1726. doi:10.1016/0043-1354(83)90192-6
- Elbendari, A., Potemkin, V., Aleksandrova, T., Nikolaeva, N., 2019. Mineralogical and technological aspects of phosphate ore processing. *14th International Congress for Applied Mineralogy (ICAM2019)*: 59-65. doi:10.1007/978-3-030-22974-0\_14
- Escudey, M., Galindo, G., Avendaño, K., Borchardt, D., Chang, A.C., Briceño, M., 2004. Distribution of phosphorus form in Chilean soils and sewage sludge by chemical fractionation and <sup>31</sup>P-NMR. *Journal of the Chilean Chemical Society* 49(3): 219-222. doi:10.4067/S0717-97072004000300005
- European Commission, 2020. Communication from the commission to the European parliament, the council, the European economic

- and social committee and the committee of the regions. *Critical Raw Materials Resilience*. Brussels, 3.9.2020
- European Commission, 2018. Commission staff working document. Report on critical raw materials and the circular economy
- European Phosphate Fertilizer Alliance (AEEP), 2022. Information retrieved from the website [www.aEEP.eu](http://www.aEEP.eu) in August 2022.
- European Union, 2019. *Official Journal of the European Union*, 2019, L 172/56. (<https://eur-lex.europa.eu/eli/dir/2019/1024/oj>; accessed 2022-12-21)
- Eurostat, 2022. Statistical office of the European Union. Data retrieved from <https://ec.europa.eu/eurostat> in April 2022
- Fang, H., Cui, Z., He, G., Huang, L., Chen, M., 2017. Phosphorus adsorption onto clay minerals and iron oxide with consideration of heterogeneous particle morphology. *Science of the Total Environment* 605-606: 357-367. doi:10.1016/j.scitotenv.2017.05.133
- Flörke, J., Johnson, R.K., Futter, M.N., Wilander, A., 2014. The Swedish monitoring of surface waters: 50 years of adaptive monitoring. *AMBIO* 43: 3-18. doi:10.1007/s13280-014-0558-z
- Foo K.Y., Hameed B.H., 2010. Insights into the modelling of adsorption isotherm systems. *Chemical Engineering Journal* 156: 2-10. doi: 10.1016/j.cenj.2009.09.013
- Gitari, M.W., Petrik, L.F., Etchebers, O., Key, D.L., Iwuoha, E., Okujeni, C., 2006. Treatment of acid mine drainage with fly ash: Removal of major contaminants and trace elements. *Journal of Environmental Science and Health, Part A* 41(8): 1729-1747. doi:10.1080/10934520600754425
- Golubev, S.V., Bénézeth, P., Schott, J., Dandurand, J.L., Castillo, A., 2009. Siderite dissolution kinetics in acidic aqueous solutions from 25 to 100 °C and 0 to 50 atm pCO<sub>2</sub>. *Chemical Geology* 265(1-2): 13-19. doi:10.1016/j.chemgeo.2008.12.031

- Gustafsson, 2021. Visual MINTEQ chemical equilibrium model. Information and software available for download could be found on <https://vminteq.com> in December 2022.
- Guttormsen, G., Singh, B.R., Jeng, A.S., 1995. Cadmium concentration in vegetable crops grown in a sandy soil as affected by Cd levels in fertilizer and soil pH. *Fertilizer Research* 41:27-32. doi:10.1007/BF00749517
- Harrison, M.L., Johns, M.R., White, E.T., Mehta, C.M., 2011. Growth rate kinetics for struvite crystallization. *Chemical Engineering Transactions*, 25: 309-314
- He, Q.B., Singh, B.R., 1994. Crop uptake of cadmium from phosphorus fertilizers: I. Yield and cadmium content. *Water, Air, and Soil Pollution* 74: 251-265. doi:10.1007/BF00479793
- Herschy, R.W., 1998. River pollution prevention: Historical. In: *Encyclopedia of Hydrology and Lakes*. Encyclopedia of Earth Science. Springer, Dordrecht. doi: 10.1007/1-4020-4497-6\_193
- Hlava, J., Száková, J., Vedlejš, J., Čadková, Z., Balík, J., Tlustoš, P., 2017. Long-term application of organic matter-based fertilizers: Advantages or risk for soil biota? A review. *Environmental Reviews* 25(3): 408-414. doi:10.1139/er-2017-0011
- Hua, M., Zhang, S.J., Pan, B.C., Zhang, W.M., Lv, L., Zhang, Q.X., 2012. Heavy metal removal from water/wastewater by nanosized metal oxides: A review. *Journal of Hazardous Materials* 211: 317-331. doi:10.1016/j.jhazmat.2011.10.016
- Huang W, Cai W, Huang G, Lei Z, Zhang Z, Tay JH and Lee DJ (2015). Identification of inorganic and organic species of phosphorus and its bioavailability in nitrifying aerobic granular sludge. *Water Research* 68(1): 423-431. doi:10.1016/j.watres.2014.09.054
- Hudcová, H., Vymazal, J., Rozkošný, M., 2019. Present restrictions of sewage sludge application in agriculture within the European union. *Soil and Water Research* 14(2): 104-120. doi:10.17221/36/2018-SWR

- IBM, 2016. SPSS 19, product by IBM. Information regarding the software could be found on the website:  
<https://www.ibm.com/spss> in January 2023.
- International Committee of Medical Journal Editors (ICMJE), 2022. Recommendations for the Conduct, Reporting, Editing, and Publication of Scholarly Work in Medical Journals, Updated May 2022. (<https://www.icmje.org/icmje-recommendations.pdf>; accessed 2022-12-22)
- Jafaripour, A., Rowson, N.A., Ghataora, G.S., 2015. Utilization of residue gas sludge (BOS sludge) for removal of heavy metals from acid mine drainage (AMD). *International Journal of Mineral Processing* 144: 90-96. doi:10.1016/j.minpro.2015.10.002
- Jeppu, G.P., Clement, T.P., 2012. A modified Langmuir-Freundlich isotherm model for simulating pH-dependent adsorption effects. *Journal of Contaminant Hydrology* 129-130(15): 46-53. doi:10.1016/j.conhyd.2011.12.001
- Jones, E.R., van Vliet, M.T.H., Qadir, M., Bierkens, M.F.P., 2021. Country-level and gridded estimates of wastewater production, collection, treatment and reuse. *Earth System Science Data* 13: 237-254. doi:10.5194/essd-13-237-2021
- Jones, O.A.H., Voulvoulis, N., Lester, J.N., 2007. Human pharmaceuticals in wastewater treatment processes. *Critical Reviews in Environmental Science and Technology* 35(4): 414-427. doi:10.1080/10643380590956966
- Karlsson, S., Sjöberg, V., Ogar, A., 2015. Comparison of MP AES and ICP-MS for analysis of principal and selected trace elements in nitric acid digests of sunflower (*Helianthus annuus*). *Talanta* 135: 124-132. doi:10.1016/j.talanta.2014.12.015
- Kelling, K.A., Peterson, A.E., Walsh, L.M., Ryan, J.A., Keeney, D.R., 1976. A field study of the agricultural use of sewage sludge: I. Effect on crop yield and uptake of N and P. *Journal of Environmental Quality* 6(4): 339-345. doi:10.2134/jeq1977.00472425000600040002x

- Khan, A., Khan, S., Khan, M.A., Waqas, M., 2015. The uptake and bioaccumulation of heavy metals by food plants, their effects on plant nutrients, and associated health risk: a review. *Environmental Science and Pollutions Research International* 22(18): 13772-13799. doi:10.1007/s11356-015-4881-0
- Kern, O.A., Koutsodendris, A., Mächtle, B., Christianis, K., Schukraft, G., Scholz, C., Kotthoff, U, Pross, J., 2019. XRF core scanning yields reliable semiquantitative data on the elemental composition of highly organic-rich sediments: evidence from Füramoos peat bog (southern Germany). *Science of The Total Environment*, 697: 134110. doi:10.1016/j.scitotenv.2019.134110
- Kidd, P.S., Domínguez-Rodríguez, M.J., Díez, J., Monterroso, C., 2007. Bioavailability and plant accumulation of heavy metals and phosphorus in agricultural soils amended by long-term application of sewage sludge. *Chemosphere* 66(8): 1458-1467. doi:10.1016/j.chemosphere.2006.09.007
- Krogstad, T., Sogn, T.A., Asdal, A., Saebø, A., 2005. Influence of chemically and biologically stabilized sewage sludge on plant-available phosphorus in soil. *Ecological Engineering* 25(1): 51-60. doi:10.1016/j.ecoleng.2005.02.009
- Kumar Haldar S (2018) Chapter 13 – Mineral Processing, in: *Mineral Exploration: Principles and Applications*, Second Edition. ISBN 978-0-12-814022-2
- Kwapinski, W., Kolinovic, I., Leahy, J.J., 2021. Sewage sludge thermal treatment technologies with a focus on phosphorus recovery: A review. *Waste and Biomass Valorization* 12: 5837-5852. doi:10.1007/s12649-020-01280-2
- Lake, D.L., Kirk, P.W.W., Lester, J.N., 1984. Fractionation, characterization, and speciation of heavy metals in sewage sludge and sludge-amended soils: A review. *Journal of Environmental Quality* 13(2): 175-183. doi:10.2134/jeq1984.00472425001300020001x
- Langmuir, D., 1997. Aqueous environmental chemistry. Prentice Hall, Upper Saddle River, New Jersey, pp. 600. ISBN:0-02-367412-1

- Lewis, D.L., Gattie, D.K., 2002. Pathogen risks from applying sewage sludge to land. *Environmental Science and Technology* 36(13): 286-293. doi:10.1021/es0223426. PMID: 12144261.
- Li R, Yin J, Wang W, Li Y and Zhang Z (2014) Transformation of phosphorus during drying and roasting of sewage sludge. *Waste Management* 34(7): 1211-1216. doi:10.1016/j.wasman.2014.03.022
- Li R, Zhang Z, Li Y, Teng W, Wang W and Yang T (2015) Transformation of apatite phosphorus and non-apatite inorganic phosphorus during incineration of sewage sludge. *Chemosphere* 141: 57-61. doi:10.1016/j.chemosphere.2015.05.094
- Li, M., Liu, J., Xu, Y., Qian, G., 2016. Phosphate adsorption on metal oxides and metal hydroxides: A comparative review. *Environmental Reviews* 24: 319-332. doi:10.1139/er-2015-0080
- Linderholm, K., Mattsson, J.E., Tillman, A.M., Phosphorus flows to and from Swedish agriculture and food chain. *AMBIO* 41: 883-893. doi:10.1007/s13280-012-0294-1
- Liu, J., Zhu, R., Ma, L., Fu, H., Lin, X., Parker, S.C., Molinari, M., 2021. Adsorption of phosphate and cadmium on iron (oxyhydr)oxides: A comparative study on ferrihydrite, goethite, and hematite. *Geoderma* 383: 114799. doi: 10.1016/j.geoderma.2020.114799
- Liu, Y., Villalba, G., Ayres, R.U., Schroder, H., 2008. Global phosphorus flows and environmental impacts from a consumption perspective. *Journal of Industrial Ecology* 12(2): 229-247. doi:10.1111/j.1530-9290.2008.00025.x
- Loganathan, P., Vigneswaran, S., Kandasamy, J., Bolan, N.S., 2014. Removal and recovery of phosphate from water using sorption. *Critical Reviews in Environmental Science and Technology* 44(8): 847-907. doi:10.1080/10643389.2012.741311
- Lyngsie, G., Katika, K., Fabricius, I.L., Hansen, H.C.B., Borggaard, O.K., 2019. Phosphate removal by iron oxide-coated diatomite: Laboratory test of a new method for cleaning drainage water. *Chemosphere* 222: 884-890. doi:10.1016/j.chemosphere.2019.01.158

- Ma, W., Tang, Y., Wu, P., Xia, Y., 2019. Sewage sludge incineration ash for co-immobilization of lead, zinc and copper: Mechanisms of metal incorporation and competition. *Waste Management* 99: 102-111. doi:10.1016/j.wasman.2019.08.029
- Mateo-Sagasta, J., Raschid-Sally, L., Thebo, A., 2015. Global wastewater and sludge production, treatment and use. In Drechsel, P., Quadir, M., Wichelns, D. (Eds.). *Wastewater; economic asset in urbanizing world*. Dordrecht, Netherlands, Springer: 15-38. ISBN: 978-94-017-9544-9
- Medeiros, J.J.G., Cid, B.P., Gómez, F., 2005. Analytical phosphorus fractionation in sewage sludge and sediment samples. *Analytical and Bioanalytical Chemistry* 381: 873-878. doi:10.1007/s00216-004-2989-z
- Militaru, B.A., Pode, R., Lupa, L., Schmidt, W., Tekle-Röttering, A., Kazamer, N., 2020 Using sewage sludge ash as an efficient adsorbent for Pb(II) and Cu(II) in single and binary systems. *Molecules* 25(11): 2559. doi:10.3390/molecules25112559
- Morse, G.K., Brett, S.W., Guy, J.A., Lester, J.N., 1998. Review: Phosphorus removal and recovery technologies. *Science of The Total Environment* 212(1): 69-81. doi:10.1016/S0048-9697(97)00332-X
- Mu, T-H., Sun, H-N., 2019. Chapter 22 - Sweet potato leaf polyphenols: preparation, individual phenolic compound composition and antioxidant activity. *Polyphenols in Plants – Isolation, Purification and Extract Preparation*, Second Edition. ISBN: 978-0-12-813768-0
- Muñoz, I., Gómez-Ramos, M.J., Agüera, A., Fernández-Alba, A., García-Reyes, J.F., Molina-Díaz, A., 2009. Chemical evaluation of contaminants in wastewater effluents and the environmental risk of reusing effluents in agriculture. *TrAC Trends in Analytical Chemistry* 28(6): 676-694. doi:10.1016/j.trac.2009.03.007
- Murphy, K., Riley, J., 1962. A modified single solution method for the determination of phosphate in natural waters. *Analytica Chimica Acta* 27: 31-36. doi:10.1016/S0003-2670(00)88444-5

- Naden, P., Bell, V., Carnell, E., Tomlinson, S., Dragosits, U., Chaplow, J., May, L., Tipping, E., 2016. Nutrient fluxes from domestic wastewater: A national-scale historical perspective for the UK 1800-2010. *Science of the Total Environment* 572: 1471-1474. doi:10.1016/j.scitotenv.2016.02.037
- Nilsson, C., Renman, G., Westholm, L.J., Renman, A., Drizo, A., 2013. Effect of organic load on phosphorus and bacteria removal from wastewater using alkaline filter materials. *Water Research* 47(16): 6289-6297. doi:10.1016/j.watres.2013.08.001
- Nunes, N., Ragonezi, C., Gouveia, C.S.S, Pinheiro de Carvalho, M.Â, A., 2021. Review of sewage sludge as a soil amendment in relation to current international guidelines: A heavy metal perspective. *Sustainability* 13(4): 2317. doi:10.3390/su13042317
- Nziguheba, G., Smolders, E., 2008. Inputs of trace elements in agricultural soils via phosphate fertilizers in Euro-pean countries. *Science of the Total Environment* 390: 53-57. doi:10.1016/j.scitotenv.2007.09.031
- Ottosen, L.M., Kirkelund, G.M., Jensen, P.E., 2013. Extracting phosphorus from incinerated sewage sludge ash rich in iron or aluminium. *Chemosphere* 91(7): 963-969. doi:10.1016/j.chemosphere.2013.01.101
- Pan, S.C., Lin, C.C., Tseng, D.H., 2008. Reusing sewage sludge ash as adsorbent for copper removal from wastewater. *Resources, Conservation and Recycling* 39(1): 79-90. doi:10.1016/S0921-3449(02)00122-2
- Pescod, M.B., 1992. Wastewater treatment and use in agriculture. Food and Agriculture Organization of the United Nations, Rome, Italy. ISBN: 92-5-103135-5
- Prosser, R.S., Sibley, P.K., 2015. Human health risk assessment of pharmaceuticals and personal care products in plant tissue due to biosolids and manure amendments, and wastewater irrigation. *Environmental International* 75: 223-233. doi:10.1016/j.envint.2014.11.020

- Puckowski, A., Mioduszewska, K., Łukaszewicz, P., Borecka, M., Caban, M., Maszkowska, J., Stepnowski, P., 2016. Bioaccumulation and analytics of pharmaceutical residues in the environment: A review. *Journal of Pharmaceutical and Biomedical Analysis* 127: 232-255. doi:10.1016/j.jpba.2016.02.049
- Qadir, M., Dreschsel, P., Cosneros, B.J., Kim, Y., Pramantik, A., Mehta, P., Olaniyan, O., 2020. Global and regional potential of wastewater as a water, nutrient and energy source. *Natural Resources Forum* 44(1): 40-51. doi:10.1111/1477-8947.12187
- Raheem, A., Sikarwar, V.S., He, J., Dastyar, W., Dionysiou, D.D., Wang, W., Zhao, M., 2018. Opportunities and challenges in a sustainable treatment and resource reuse of sewage sludge: A review. *Chemical Engineering Journal* 337: 616-641. doi:10.1016/j.cej.2017.12.149
- Ramasahayam, S.K., Guzman, L., Gunawan, G., Viswanathan, T., 2014. A comprehensive review of phosphorus removal technologies and processes. *Journal of Macromolecular Science Part A – Pure and Applied Chemistry* 51(6): 538-545. doi:10.1080/10601325.2014.906271
- Revaq 2021. Regulations for certification (regler för certifieringssystemet), 8th edition. Available at [svensktvatten.se](https://svensktvatten.se) on April 4, 2022 (in Swedish)
- Revaq, 2021b. Yearly report, 2020 (Årsrapport 2020), report 2021-02. Available at [svensktvatten.se](https://svensktvatten.se) on April 4, 2022 (in Swedish)
- Ridder, M., Jong, S., Polchar, J., Lingemann, S., 2012. Risks and opportunities in the global phosphate rock market. *The Hague Centre for Strategic Studies*, report 17:12. ISBN: 978-94-91040-69-6
- Rieuwerts, J.S., 2007. The mobility and bioavailability of trace metals in tropical soils: a review. *Chemical Speciation & Bioavailability* 19(2): 75-85. doi:10.3184/095422907X211918
- Ruban, V., López-Sánchez, J.F., Pardo, P., Rauret, G., Muntau, H., Quevauviller, Ph., 2001. Harmonized protocol and certified reference material for the determination of extractable contents of phosphorus in freshwater sediments – A synthesis of recent works.

- Fresenius' Journal of Analytical Chemistry* 370(2-3): 224-228.  
doi:10.1007/s002160100753
- Saharan, P., Chaudhary, G.R., Mehta, S.K., Umar, A., 2014. Removal of water contaminants by iron oxide nanomaterials. *Journal of Nanoscience and Nanotechnology* 14(1): 627-643.  
doi:10.1166/jnn.2014.9053
- Sato, T., Qadir, M., Yamamoto, S., Endo, T., Zahoor, A., 2013. Global, regional, and country level need for data on wastewater generation, treatment, and use. *Agricultural Water Management* 130: 1-13. doi:10.1016/j.agwat.2013.08.007
- Schneider, F., Haderlein, S., 2016. Potential effects of biochar on the availability of phosphorus: mechanistic in-sight. *Geoderma* 277: 83–90. doi:10.1016/j.geoderma.2016.05.007
- Scholz, R.Z., Wellmer, F.W., 2016. Comment on: “Recent revisions of phosphate rock reserves and resources: a critique” by Edixhoven *et al.* (2014) – clarifying comments and thoughts on key conceptions, conclusions and interpretation to allow for sustainable action. *Earth System Dynamics* 7(1): 103-117.  
doi:10.5194/esd-7-103-2016
- Seleiman, M.F., Santanen, A., Mäkelä, P.S.A., 2020. Recycling sludge on cropland and fertilizer – Advantages and risks. *Resources, Conservation and Recycling* 155: 104647.  
doi:10.1016/j.resconrec.2019.104647
- Shahid, M., Shamshad, S., Rafiq, M., Khalid, S., Bibi, I., Niazi, N.K., Dumat, C., Rashid, M.I., 2017. Chromium speciation, bioavailability, uptake, toxicity and detoxification in soil-plant system: A review. *Chemosphere* 178: 513-533.  
doi:10.1016/j.chemosphere.2017.03.074
- Sharma, A., Kapoor, D., Wang, J., Shahzad, B., Kumar, V., Bali, A.S., Jasrotia, S., Zheng, B., Yuan, H., Yan, D., 2020. Chromium bioaccumulation and its impacts on plants: an overview. *Plants (Basel)* 9(1):100. doi:10.3390/plants9010100

- Singh, R.P., Agrawal, M., 2008. Potential benefits and risks of land application of sewage sludge. *Waste Management* 28(2): 347-358. doi:10.1016/j.wasman.2006.12.010
- Shi, M.Q., Min, X.B., Ke, Y., Lin, Z., Yang, Z.H., Wang, S., Peng N., Yan, X., Luo, S., Wu, J.H., Wei, Y.J., 2021. Recent progress in understanding the mechanism of heavy metals retention by iron (oxyhydr)oxides. *Science of the Total Environment* 752: 141930. doi:10.1016/j.scitotenv.2020.141930
- Shipley, H.J., Engates, K.E., Grover, V.A., 2013. Removal of Pb(II), Cd(II), Cu(II), and Zn(II) by hematite nanoparticles: effect of sorbent concentration, pH, temperature, and exhaustion. *Environmental Science and Pollution Research International* 20: 1727-1736. doi:10.1007/s11356-012-0984-z
- Singh, R.P., Agrawal, M., 2008. Potential benefits and risks of land application of sewage sludge. *Waste Management* 28 (2): 347-58. doi:10.1016/j.wasman.2006.12.010
- Smit, A.L., Bindraban, P.S., Schröder, J.J., Conijn, J.G., van der Meer, H.G., 2009. Phosphorus in agriculture: global resources, trends and developments. Report 282, Plant Research International B.V., Wageningen, The Netherlands
- Smith, S., Takacs, I., Murthy, S., Daigger, G.T., Szabo, A., 2008. Phosphate complexation model and its implications for chemical phosphorus removal. *Water Environment Research* 80(5): 428-438. doi:10.1002/j.1554-7531.2008.tb00349.x
- Statens Offentliga Utredningar, SOU 2020:3. Hållbar slamhantering (in Swedish). ISBN: 978-91-38-25017-4
- Statistics Sweden, 2020. Discharges to water and sewage sludge production in 2018. Municipal wastewater treatment plants, pulp and paper industry and some other industry. MI 22 SM 2001 (in Swedish)
- Statistics Sweden, 2020b. Sales of fertilizers for agricultural and horticultural purposes in 2018/19. MI 30 SM 2001 (in Swedish)

- Statistics Sweden, 2022. Statistical Database, <https://www.statistikdatabasen.scb.se/pxweb/en/ssd/>. Data collected on March 31 2022
- Suciu, N.A., Vivo, R.D., Rizzati, N., Capri, E., 2022. Cd content in phosphate fertilizer: Which potential risk for the environment and human health? *Current Opinion in Environmental Science and Health* 20: 100392. doi:10.1016/j.coesh.2022.100392
- Swedish Environmental Protection Agency, 2013. Report 6580: Sustainable recycling of phosphorus (Hållbar återföring av fosfor) (in Swedish) ISBN: 978-91-620-6580-5
- Swedish Environmental Protection Agency, 2018. Wastewater treatment in Sweden (Rening av avloppsvatten i Sverige) (in Swedish) ISBN: 978-91-620-8866-8
- Swedish Environmental Protection Agency, 2001. Constitutional assembly (Naturvårdsverkets författningssamling) SNFS 1994:2 MS:72, consolidated version SNFS 1001:5 (in Swedish). ISSN: 0347-5301
- Swedish Water, 2022. Sewage facts, available online <https://www.svenskvatten.se/fakta-om-vatten/avloppsfakta/> in March 2022 (in Swedish)
- Steckenmesser, D., Vogel, C., Adam, C., Steffens, D., 2017. Effect of various types of thermochemical processing of sewage sludges on phosphorus speciation, solubility, and fertilization performance. *Waste Management* 62: 194-203. doi:10.1016/j.wasman.2017.02.019
- Stumm, W., 1992. Chemistry of the solid-water interface: Processes at the mineral-water and particle-water interface in natural systems. *Wiley Interscience*, John Wiley & Sons Inc., New York, pp 428. ISBN: 978-0-471-57672-3
- Swedish Water and Wastewater Association (Svenskt Vatten), 2014. REVAQ – Yearly report 2013 (in Swedish)
- Syed-Hassan, S.S.A., Wang, Y., Hu, S., Su, S., Xiang, J., 2017. Thermochemical processing of sewage sludge to energy and fuel: Fundamentals, challenges and considerations. *Renewable and*

*Sustainable Energy Reviews* 80: 888-913.  
doi:10.1016/j.rser.2017.05.262

Tao, Q.Q., Bi, J.T., Huang, X., Wei, R.L., Wang, T., Zhou, Y.A., Hao, H.X., 2021. Fabrication, application, optimization and working mechanism of Fe<sub>2</sub>O<sub>3</sub> and its composites for contaminants elimination from wastewater. *Chemosphere* 263: 127998. doi:10.1016/j.chemosphere.2020.127889

Tan, W., Liang, Y., Xu, Y., Wang, M., 2022. Structural-controlled formation of nano-particle hematite and their removal performance for heavy metal ions: A review. *Chemosphere* 306: 135540. doi:10.1016/j.chemosphere.2022.135540

Tessier A, Campbell PGC and Bisson M (1979) Sequential extraction procedure for the speciation of particulate trace metals. *Analytical Chemistry* 51(7): 844-850. doi:10.1021/ac50043a017

Toro-Vazquez, J.F., Proctor, A., 2009. Chapter 10 - The Freundlich isotherm in studying adsorption in oil pro-processing. In: *Bleaching and Purifying Fats and Oils. Theory and Practice*, Second Edition. ISBN: 978-1893997912

UN Habitat, 2016. Urbanization and development – emerging futures. *World cities report 2016*. ISBN: 978-92-1-132708-3

United Nation, 1987. Our Common Future. Report of the World Commission on Environment and Development (the Bruntland Commission)

United Nations World Water Development Report 2021. United Nations *World Water Assessment Programme*, Perugia, Italy. ISBN:978-92-3-100434-6

U.S. Geological Survey, 2021. Minerals Yearbook – 2018: Phosphate rock (advanced release). U.S. Department of the Interior, U.S. Geological Survey

U.S. Geological Survey, 2013. Mineral commodity summaries 2013. U.S. Geological Survey. ISBN: 978-4112-3548-6

- Uysal, A., Yilmazel, Y.D., Demirer, G.N., 2010. The determination of fertilizer quality of the formed struvite from effluent of a sewage sludge anaerobic digester. *Journal of Hazardous Materials* 181(1-3): 248-254. doi:10.1016/j.jhazmat.2010.05.004
- van Dijk K, Lesschen JP and Oenema O (2016) Phosphorus flows and balances of the European Union Member States. *Science of the Total Environment* 542(part B): 1078-1093. doi:10.1016/j.scitotenv.2015.08.048
- Venema, P., Hiemestra, T., Weidler, P.G., van Riemsdijk, W.H., 1998. Intrinsic proton affinity of reactive surface groups of metal(hydr)oxides: Application to iron (hydr)oxides. *Journal of Colloid and Interface Science* 198(2): 282-295. doi:10.1006/jcis.1997.5254
- Verlicchi, P., Aukidy, M.A., Zambello, E., 2012. Occurrence of pharmaceutical compounds in urban wastewater: Removal, mass load and environmental risk after secondary treatment – A review. *Science of The Total Environment* 429: 123-155. doi:10.1016/j.scitotenv.2012.04.028
- Wang, J., Liu, W., Mu, H., 2010. Inorganic phosphorus fractions and phosphorus availability in a calcareous soil receiving 21-year superphosphate application. *Pedosphere* 20(3): 304-310. doi:10.1016/S1002-0160(10)60018-5
- Wang, Q., Li, J., Poon, C.S., 2019. Recycling of incinerated sewage sludge ash as an adsorbent for heavy metals removal from aqueous solutions. *Journal of Environmental Management* 247(1): 509-517. doi:10.1016/j.envman.2019.06.115
- Wang J, Guo X. Adsorption isotherm models: Classification, physical meaning, application and solving method. *Chemosphere* 258: 127279. doi:10.1016/j.chemosphere.2020.127279
- Wang, Q., Raju, C.S., Almind-Jørgensen, N., Lastrup, M., Reitzel, K., Nielsen, U.G., 2022. Variation in phosphorus speciation of sewage sludge throughout three wastewater treatment plants: Determined by sequential extraction combined with microscopy,

- NMR spectroscopy, and powder X-ray diffraction. *Environmental Science & Technology* 56: 8975-8983. doi:10.1021/acs.est.2c01815
- Wu, H., Zhang, J., Ngo, H.H., Guo, W., Hu, Z., Liang, Z., Fan, J., Liu, H., 2015. A review on the sustainability of constructed wetlands for wastewater treatment: Design and operation. *Bioresource Technology* 175: 594-601. doi:10.1016/j.biortech.2014.10.068
- Wyrwicka, A., Urbaniak, M., 2018. The biochemical response of willow plants (*Salix viminalis* L.) to the use of sewage sludge from various sizes of wastewater treatment plant. *Science of the Total Environment* 615: 882-894. doi:10.1016/j.scitotenv.2017.10.005
- Xia, W.J., Xu, L.Z.J., Yu, L.Q., Zhang, Q., Zhao, Y.H., Xiong, J.R., Zhu, X.Y., Fan, N.S., Huang, B.C., Jin, R.C., 2020. Conversion of municipal wastewater-derived waste to an adsorbent for phosphorus recovery of secondary effluent. *Science of the Total Environment* 705: 135959. doi:10.1016/j.scitotenv.2019.135959
- Xie, C., Zhao, J., Tang, J., Xu, J., Lin, X., Xu, X., 2011. The phosphorus fractions and alkaline phosphatase activities in sludge. *Bioresource Technology* 102: 2455-2461. doi:10.1016/j.biortech.2010.11.011
- Ye, Z., Shen, Y., Ye, X., Zhang, Z., Chen, S., Shi, J., 2014. Phosphorus recovery from wastewater by struvite crystallization: Property of aggregates. *Journal of Environmental Sciences* 26: 991-1000. doi:10.1016/S1001-0742(13)60536-7
- Yoon, S.Y., Lee, C.G., Park, J.A., Kim, J.H., Kim, S.B., Lee, S.H., Choi, J.W., 2014. Kinetic, equilibrium and thermodynamic studies for phosphate adsorption to magnetic iron oxide nanoparticles. *Chemical Engineering Journal* 236: 341-347. doi:10.1016/j.cej.2013.09.053
- Zhang, Q., Hu, J., Lee, D.-J., Chang, Y., Lee, Y.-J., 2017. Sludge treatment: Current research trends. *Bioresource Technology* 243: 1159-1172. doi:10.1016/j.biortech.2017.07.070
- Zhu, Y., Zhai, Y., Li, S., Liu, X., Wang, B., Liu, X., Fan, Y., Shi, H., Li, C., Zhu, Y., 2018. Thermal treatment of sewage sludge: A

comparative review of the conversion principle, recovery methods and bioavailability-predicting of phosphorus. *Chemosphere* 291(3): 133053. doi:10.1016/j.chemosphere.2021.133053

Zumdahl, S.S., Zumdahl, S.A., 2003. Chemistry . sixth edition. Houghton Mifflin Company, Boston, U.S.A. ISBN: 0-618-22156-5

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ÖREBRO STUDIES IN CHEMISTRY

1. Bäckström, Mattias, *On the Chemical State and Mobility of Lead and Other Trace Elements at the Biogeosphere/Technosphere Interface*. 2002.
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