Nutrient availability and losses and risk of micro-pollutant contamination from land spreading of chemically precipitated sewage sludge

(NutriSludge 2018-2021)

PROJECT REPORT

Final

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Summary

The treatment of wastewater whereby the removal of contaminants is achieved through chemical reactions is known as chemical treatment. Inorganic metal salts of Al or Fe are normally used as they are cheap, easily applied and effective. Pre-hydrolysed Al products are now the coagulants of choice in most wastewater treatment plants. However, there are some disadvantages associated with the use of inorganic coagulants (IC) e.g., the production of large sludge volumes that incur high management and disposal costs, etc. The use of IC can also restrict the use of sludge as a soil amendment, as Al- or Fe based-coagulants react with P, precipitating it as stable metal phosphates and thus lowering its availability for plant uptake. Organic polymers (synthetic and natural) have been tested as the sole coagulant for the purification of several wastewater sources with benefits such as lower required dosages and lower sludge production. The utilization of OC can slightly increase the organic and nitrogen concentrations of sludge while significantly decreasing its Fe and Al content. In this study we investigated the effectivity of OC as the sole precipitation agent in primary and secondary sedimentation stages of municipal wastewater treatment in comparison to commonly used IC. Special attention was allocated to the characteristics of the sludge produced.

Resource's recovery in municipal wastewater treatment is critical for achieving sustainable sanitation. Among other sludge utilization options, such as the production of energy, recycling to land is still considered the most economical and beneficial way for sludge management. There are many benefits of land application of sludge, e.g., it is a cheap organic alternative to mineral fertilizers. However, there are also concerns and challenges. Among the concerns are the uncertain risks of soil, crop and water courses contamination by pathogens, heavy metals and micro-organic pollutants such as those derived from pharmaceuticals and personal care products etc. Among the challenges are the low nutrient availability and the risk of nutrient and contaminants leaching.

The NutriSludge project evaluated if the use of OC as alternatives to IC could result in a possible increase in nutrient concentration and availably in sewage sludge. In addition, the risk of nutrient losses in runoff from sludge amended soils as well as the possibility of soil contamination by pharmaceutical and their losses in runoff due to land application were studied. The main project objectives were:

- to access the effectiveness of organic coagulants (synthetic and natural) as solo precipitation agents in sewage treatment in comparison to the inorganic coagulants.
- to investigate the effect of replacing inorganic coagulants by organic coagulants in the biological stabilization (composting and digestion) of sludge.
- to identify and quantify the risks of soil contamination by micro-pollutants as well as risks of micro-pollutant losses in runoff from sludge amended soils.
- to identify and quantify the risks of incidental and medium-term nutrient losses in run-off from sludge amended soils.
- to qualitatively assess the acceptance of land spreading of sludge by farmers and general public in Finland.

Overall, the project achieved all its objectives. The effectiveness of OC (synthetic and semi-natural) was compared to that of the IC in the treatment of secondary and primary municipal wastewater. Based on the results obtained, OC products with high molecular weight and high cationic charge have the potential to act as the sole coagulants in both primary and secondary stages of municipal wastewater treatment. In regard to the management of the sludge produced by OC and IC, the type of coagulant used was found to have a clear effect on the biological stabilization processes. The type of coagulant affect gas yield, process temperature as well as the characteristics of the stabilized product. The type of coagulant used had also a significant effect on the leaching of contaminants from sludge-fertilized soils. The effect of the coagulant used was larger than the effect of the biological stabilization method used for sludge treatment. Leaching of N, P and organic

compounds was higher after the first rain than after second rain event after the sludge application to land. Microplots fertilized by synthetic OC (tested) derived sludge presented the highest overall leaching of nutrients and organic compounds.

The opinions and concerns of Finnish stakeholders on the use of stabilized sewage sludge as a soil amendment product was evaluated. The general public was, in general, more positive towards the use of sewage sludge with the majority stating that they would consume products grown in sewage amended soils, including food crops. The farmers stated possible loss of product value and practical issues with the application of the sludge to land as concerns regarding the use of sewage sludge.

Content

1. Background and objectives

The treatment of wastewater whereby the removal of contaminants is achieved through chemical reactions is known as chemical treatment (Metcalf & Eddy, 2014). Inorganic metal salts of Al or Fe are normally used in water and wastewater treatment as they are cheap, easily applied and effective (Bratby, 2016). Controlled hydrolysis of Fe- and Al-based coagulants led to the development of pre-hydrolysed products such as polyaluminium chloride (PAC), which have been found to work more efficiently than non-hydrolysed products such as ferric sulphate and aluminium chloride (Jiang and Wang, 2009; Wei et al., 2015, Sillanpää et al., 2018). Pre-hydrolysed products are now the coagulants of choice in most wastewater treatment plants. However, there are some disadvantages associated with the use of inorganic coagulants (IC) e.g., the production of large sludge volumes that incur high management and disposal costs, high alkalinity consumption which might increase the need for pH adjustment chemicals, and high residual Al or Fe concentrations in the treated water (Liu et al., 2011; Chen et al., 2012). Use of IC can also restrict the use of sludge as a soil amendment, as Al- or Fe based-coagulants are known to react with P, precipitating it as stable metal phosphates and thus lowering its availability for plant uptake (Krogstad et al., 2005; Kirchmann et al., 2017). This decreases the fertiliser potential of the resulting sludge.

Organic polymers (synthetic and natural) have been successfully tested as the sole coagulant for the purification of several wastewater sources with benefits such as lower required dosages, lower sludge production with better dewatering characteristics (Nozaic et al., 2001; Oladoia, 2015; Heiderscheidt et al., 2016). Natural organic coagulants (OC) are naturally produced or extracted from animals, plant tissues or microorganisms and have other benefits such as non-toxicity and high biodegradability in comparison to their synthetic counterparts (Oladoia, 2015). In general, synthetic and natural OC are composed of polymeric organic molecules containing amine or quaternary ammonium groups which provide them cationic surface charge enabling the coagulation/flocculation process (Oladoia, 2015). The utilization of OC can thus slightly increase the organic and nitrogen concentrations of sludge while significantly decreasing its Fe and Al content. During the last decade a number of natural coagulants have been introduced to the market and although these natural materials as well as synthetic products are more expensive than IC, if overall costs of e.g., transport, sludge management, etc. are taken into consideration their application can became cost-effective (Nozaic et al., 2001) as well as environmentally justified. **In this study we investigated the effectivity of OC as the sole precipitation agent in primary and secondary sedimentation stages of municipal wastewater treatment in comparison to commonly used IC.** Special attention was allocated to the characteristics of the sludge produced.

Resource's recovery in municipal wastewater treatment is critical for achieving sustainable sanitation. Among other sludge utilization options, such as the production of energy, recycling to land is still considered the most economical and beneficial way for sewage sludge management (Kirchmann et al., 2017). There are many benefits of land application of sludge, e.g., it is a cheap organic alternative to mineral fertilizers, its use as a soil conditioner improves the soil physical, chemical and biological properties, and reduces the possibility of soil erosion (Kirchmann et al., 2017), etc. However, there are also concerns and challenges regarding the land spread of sludge. Among the concerns are the uncertain risks of soil, crop and water courses contamination by pathogens, heavy metals and micro-organic pollutants such as those derived from pharmaceuticals and personal care products etc. (European Commission, 2010) Among the challenges are the low nutrient availability (stable metal-bounded P and low inorganic N concentration when IC are NutriSludge **project proposed to evaluate the use of organic coagulant as alternatives to inorganic coagulants and to study a possible increase in nutrient concentration and availably in the sludge due to the use of OC.** Process wise, the hypotheses was that by replacing the stable metal-P bounds resulting from the use of inorganic coagulants by organic-P-N bounds from organic coagulants the availability and concentration of nutrients in the sludge could increase. In addition, **we proposed to investigate the risk of nutrient losses in runoff from sludge amended soils and to investigate the occurrence of selected micro-pollutants in sludge as well as the possibility of soil contamination and losses in runoff due to land application.**

The main project objectives were:

- to access the effectiveness of organic coagulants (synthetic and natural) as solo precipitation agents in sewage treatment in comparison to the inorganic coagulants normally used,
- to investigate the effect of replacing inorganic coagulants by organic coagulants in the biological stabilization (composting and digestion) of chemically precipitated sludge as well as in the nutrient availability on resulting bio-solids,
- to identify and quantify the risks of soil contamination by micro-pollutants (pharmaceuticals and personal care products) as well as risks of micro-pollutant losses in runoff from (inorganic and organic coagulants) sludge amended soils,
- to identify and quantify the risks of incidental and medium-term nutrient losses in run-off from (inorganic and organic coagulants) sludge amended soils,
- to qualitatively assess the acceptance of land spreading of sludge by farmers and general public in Finland.

2. Project implementation and collaborations

The project was implemented by the Water, Energy and Environmental Engineering research unit at the University in collaboration with Engineering and Technology research unit at Savonia University of Applied Sciences, Kuopio, Finland and University of Oulu- Botanical gardens with the support of stakeholders such as Oulun Vesi Oy, ProAgria, etc. The project was founded by Maa-ja Vesitekniikan tuki ry (11-6553-51), Vesihuoltolaitosten kehittämisrahasto, University of Oulu, Lakeuden Keskuspuhdistamo, Pohjois-Suomen Vesivaliokunta.

The project tasks were shared among four work packages (WP): 1) **WP1** Coagulants evaluation, 2) **WP2** Effect of coagulant used on sludge stabilization, 3) **WP3** Nutrient plant availability and risks of nutrient and micro-pollutant losses in runoff, 4) **WP4** Qualitative evaluation of the acceptance of land spreading of sludge.

3. Methodology used in different work packages and results obtained

3.1 Effectivity of different coagulants in municipal wastewater treatment- WP1

Methods and results are summarized here. Complete description of the methodology and findings can be found in:

1) Cainglet et al., 2020. Organic polyelectrolytes as the sole precipitation agent in municipal wastewater treatment (https://doi.org/10.1016/j.jenvman.2020.111002)
2) Tesfamariam, A., 2019. Organic polymers as solo coagulants in municipal wastewater treatment. Master Thesis, University of Oulu, Faculty of Technology, Environmental Engineering http://urn.fi/URN:NBN:fi:oulu-201907312715

3.1.1 Methods

Commercially available OC were tested against IC for their effectivity in the treatment of sewage water (primary and secondary sedimentation) under laboratory conditions. The jar-test methodology was used, literature survey and results of previous studies were utilized for the selection of coagulants (Table 1). Laboratory experiments were performed in 2 phases: Phase 1: Determination of optimum dosage range of coagulants and purification efficiency using wastewater samples from secondary sedimentation; Phase 2: Determination of optimum dosage range of coagulants and purification efficiency using wastewater samples from primary sedimentation stage of treatment. Characteristics of the primary and secondary stages wastewater samples are presented in Table 2. The coagulants were tested on real municipal wastewater collected from Taskila wastewater treatment plant (WWTP) in Oulu. In the jar-tester equipment the coagulants were added to 1 L samples and fast mixing (200 rpm, 30 s) was applied. This was followed by 5 min slow mixing (40 rpm) and 60 min sedimentation. Supernatant water was collected, and the volume of settled sludge was recorded. Turbidity and pH of collected samples were measured. Optimum coagulant dosages were determined based on turbidity removal. Samples treated with the optimum dosage were sent to a certified laboratory for analysis of total N, NH4+, NO3-, total P, PO4, BOD, SS, Fe and Al.

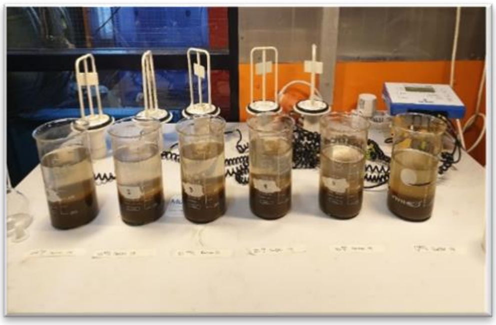
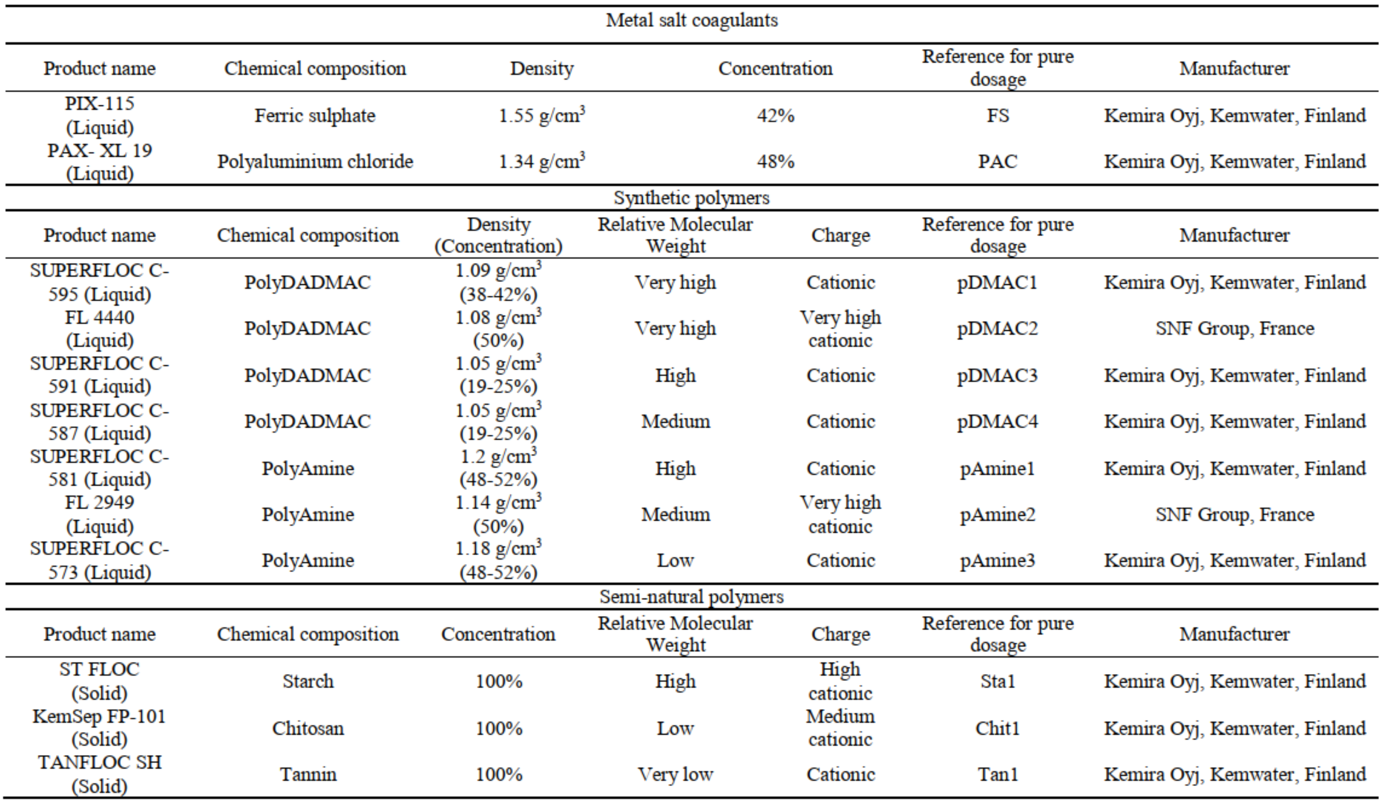


Figure 1 - Jar-test experiment (Photo Cainglet A., 2019)

Table 1 – Characteristics of the coagulants tested.



Metal salt coagulants

Product name	Chemical composition	Density	Concentration	Reference for pure dosage	Manufacturer
PIX-115 (Liquid)	Ferric sulphate	1.55 g/cm^3	42%	FS	Kemira Oyj, Kemwater, Finland
PAX- XL 19 (Liquid)	Polyaluminium chloride	1.34 g/cm^3	48%	PAC	Kemira Oyj, Kemwater, Finland

Synthetic polymers

Product name	Chemical composition	Density (Concentration)	Relative Molecular Weight	Charge	Reference for pure dosage	Manufacturer
SUPERFLOC C-595 (Liquid)	PolyDADMAC	1.09 g/cm^3 (38-42%)	Very high	Cationic	pDMAC1	Kemira Oyj, Kemwater, Finland
FL 4440 (Liquid)	PolyDADMAC	1.08 g/cm^3 (50%)	Very high	Very high cationic	pDMAC2	SNF Group, France
SUPERFLOC C-591 (Liquid)	PolyDADMAC	1.05 g/cm^3 (19-25%)	High	Cationic	pDMAC3	Kemira Oyj, Kemwater, Finland
SUPERFLOC C-587 (Liquid)	PolyDADMAC	1.05 g/cm^3 (19-25%)	Medium	Cationic	pDMAC4	Kemira Oyj, Kemwater, Finland
SUPERFLOC C-581 (Liquid)	PolyAmine	1.2 g/cm^3 (48-52%)	High	Cationic	pAmine1	Kemira Oyj, Kemwater, Finland
FL 2949 (Liquid)	PolyAmine	1.14 g/cm^3 (50%)	Medium	Very high cationic	pAmine2	SNF Group, France
SUPERFLOC C-573 (Liquid)	PolyAmine	1.18 g/cm^3 (48-52%)	Low	Cationic	pAmine3	Kemira Oyj, Kemwater, Finland

Semi-natural polymers

Product name	Chemical composition	Concentration	Relative Molecular Weight	Charge	Reference for pure dosage	Manufacturer
ST FLOC (Solid)	Starch	100%	High	High cationic	Sta1	Kemira Oyj, Kemwater, Finland
KemSep FP-101 (Solid)	Chitosan	100%	Low	Medium cationic	Chit1	Kemira Oyj, Kemwater, Finland
TANFLOC SH (Solid)	Tannin	100%	Very low	Cationic	Tan1	Kemira Oyj, Kemwater, Finland

Table 2- Wastewater characteristics in experiments with primary and secondary samples (average ± standard deviation)

	Primary wastewater		Secondary wastewater	
Water Quality Parameters	Mean ± std.dev.	Number of analysis	Mean ± std.dev.	Number of analysis
BOD_7 (mg/L)	143± 129	5	64.9 ± 53.3	12
COD (mg/L)	360 ± 193	5	308.3 ± 103.9	12
Tot-P (mg/L)	3.7 ± 0.68	5	1.9 ± 0.6	12
PO_4-P (mg/L)	2.8 ± 0.72	5	0.7 ± 0.6	12
Tot-N (mg/L)	52.6 ± 4.72	5	73.7 ± 8.1	12
NO_3 (mg/L)	0.03 ± 0.00	5	21.7 ± 32.7	12
NH_4 (mg/L)	56.0 ± 3.0	5	76.3 ± 6.5	12
Tot-Fe (mg/L)	7.5 ± 1.8	5	4.4 ± 3.2	12
Tot-Al (mg/L)	0.4 ± 0.2	5	0.8 ± 0.4	12
SS (mg/L)	64.7 ± 15.2	5	35.1 ± 13.5	12
Turbidity (NTU)	74.8 ± 12.8	5	33.4 ± 9.7	12
Colour (mgPt/L)	315.0 ± 30	5	6.9 ± 0.1	12
pH	7.5 ± 0.0	5	581.3 ± 149.0	12
Sludge Volume (ml)	40.1 ± 9.3	5	1270.8 ± 82.9	12
EC (µS/cm)	905.3 ± 100.6	5	64.9 ± 53.3	12

3.1.2 Results

In general, OC required significantly lower doses than PAC and FS for effective treatment (i.e., turbidity removal) agreeing with previously reported findings (Nozaic et al., 2001; Heiderscheidt et al., 2016; Tetteh and Rathilal, 2019). Identified optimum dosages for the treatment of primary and secondary wastewater samples are presented (Table 3). In general, it was observed that dosage requirements of coagulants were up to 60% higher in treatment of secondary samples compared with primary samples (Table 3). This is in line with existing reports describing that suspensions containing a large proportion of smaller particles (as in primary samples in our study) normally require lower doses of coagulant to achieve maximum solids removal (Bratby, 2016; Sun et al., 2019).

Table 3 – Identified optimum doses of the coagulants tested for the treatment of primary and secondary wastewater samples.

Treatment of secondary wastewater		Treatment of primary wastewater	
Coagulant	Dosage	Coagulant	Dosage
FS	75.6 mg/L		
PAC	120 mg/L	PAC	48 mg/L
pDMAC1	36 mg/L		
pDMAC2	10 mg/L		
pDMAC3	15.4 mg/L		
pDMAC4	17.6 mg/L		
pAmine1	20 mg/L	pAmine1	10 mg/L
pAmine2	30 mg/L		
pAmine3	55 mg/L	pAmine3	35 mg/L
Sta1	30 mg/L	Sta1	20 mg/L
Chit1	50 mg/L	Chit1	7.5 mg/L
Tan1	80 mg/L		

Purification efficiency: Treatment of secondary wastewater samples

Purification efficiency (removal of target contaminants) achieved by the optimum dose of the coagulants was evaluated. The removal efficiency was calculated as the percentage removal of target contaminants (SS, tot-P, PO_4-P, BOD_7, COD, and tot-N) relative to the concentrations contained in the experimental blanks. In general, synthetic OC achieved higher removal rates among the products tested, specially PolyDADMACs and polyAmines of very high and high MW. The pAmine1 product achieved higher overall removal efficiencies than PAC and FS for all target contaminants, but particularly BOD_7, COD, tot-P, PO_4-P, tot-N, and SS (Fig. 1a-d). Treatment with Chit caused increased organic matter concentration (COD and BOD_7) in the water while pDMAC2, pDMAC3 and FS cause increased Tot-N concentration thus leading to negative removal rates (Fig. 2b and 2c)

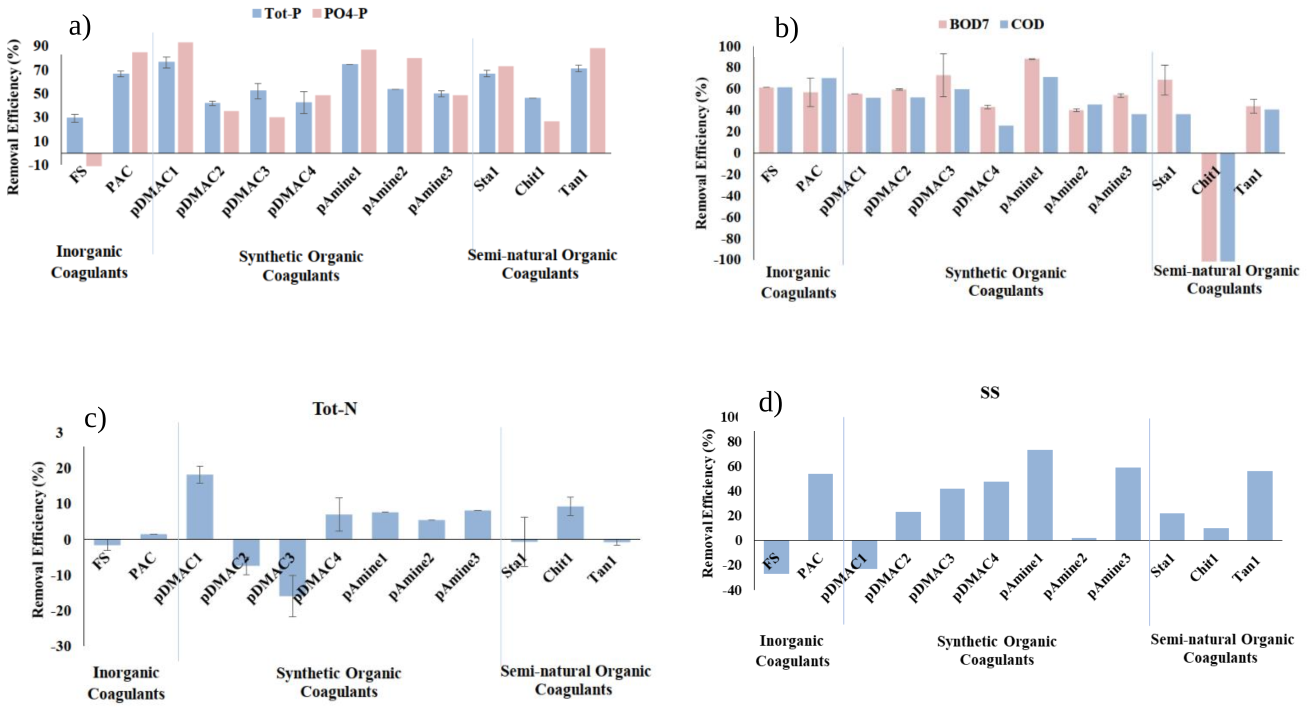


Figure 2 - Removal efficiency (%) of target contaminants achieved by the optimum doses of tested coagulants.

Purification efficiency: Treatment of primary wastewater samples

Five coagulants were tested for the treatment of primary wastewater samples, PAC, pAmine1, pAmine3, Chit1 and Sta1. Overall, the PAC product tested achieved higher removal rates of SS, Tot-P, PO4-P and Tot-N (Fig. 3). The synthetic OC, pAmine1 obtained higher removal rates of BOD_7 and COD (Fig. 3).

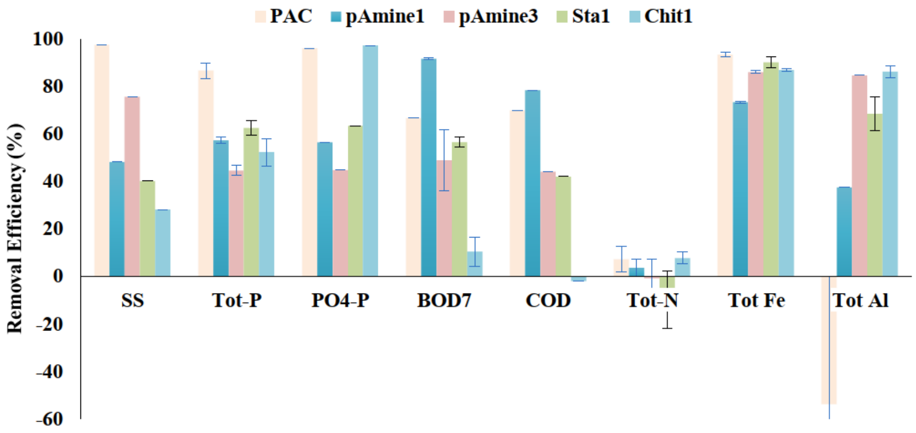


Figure 3 - Removal efficiency (%) of target contaminants achieved by the optimum doses of tested coagulants.

Overview of purification efficiency achieved by different coagulants

The coagulant dose required for treatment and contaminant removal rates are directly dependent on the amount and type of contaminants in the water. As the quality of primary and secondary wastewater samples differed significantly, treatment efficiency and coagulant dose required in purification of primary and secondary samples were very different. In general OC required lower dosages and obtained higher contaminant removal rates. Higher dosage requirements of IC compared with OC have been reported previously (Nozaic et al., 2001; Heiderscheidt et al., 2016; Tetteh and Rathilal, 2019). Based on results obtained with the synthetic OC tested, dosage requirements for OC generally decreased with increasing MW, as also reported by Bolto et al. (1999, 2001) and Wilts et al., 2018. The OC pAmine1 and pDMAC1 were found to produce the lowest residual concentrations of organic matter (BOD7 and COD) achieved similar or better removal of SS, PO_4-P, and tot-P than PAC. Observations made during treatment (Cainglet et al., 2020) highlighted the fact that high-MW and (very) high-CD OC (e.g., pAmine1, PDMAC3, starch) reduced the volume of sludge produced compared with blank samples and samples treated with PAC and FS. It is important to emphasize that, while variations in wastewater quality may have affected the coagulants performance to a great extent, the type of coagulant used was an extremely important factor influencing the results obtained.

3.1.3 Conclusions

The effectiveness of OC (synthetic and semi-natural) with varying MW and CD was compared with that of the IC (PAC, FS) in the treatment of secondary and primary municipal wastewater samples. Overall, high purification efficiency was achieved by a number of the coagulants tested (e.g., PAC, pAmine1) in treatment of wastewater samples, despite variations in wastewater characteristics. The following can be stated:

- Significantly higher doses of IC (up to 80%) than of OC were needed for effective treatment.
- In treatment of secondary wastewater samples, high-MW OC (e.g., pAmine1) achieved best removal of target pollutants (e.g., SS, PO_4-P, BOD_7), followed by PAC.
- In treatment of primary wastewater, PAC was the best performing coagulant, closely followed by chitosan and pAmine1.

Based on the results obtained, polyamine products with high MW and (very) high CDs have the potential to act as the sole precipitation agent in both primary and secondary stages of municipal wastewater treatment. Further research is needed on the effect of residual coagulant on downstream water and sludge treatment processes (e.g., activated sludge process, sludge dewatering, etc.).

3.2 Effect of coagulant used on the biological stabilization of sewage sludge – WP2

Methods and results are summarized here. Complete description of the methodology and findings can be found in:

1) Cainglet et al., 2022. The influence of coagulant type on the biological stabilization of sewage sludge. Journal submission on-going.

3.2.1 Methods

The effect of three different types of coagulants (Table 4) on the biological stabilization of produced sludge was evaluated in small-scale pilot bioreactors under controlled conditions. The effectivity of biological stabilization was assessed as well as the quality and stability of resulting bio-solids.

Table 4 – Characteristics of coagulants tested.

Coagulant type	Chemical	Density (g/cm^3)	Charge density (meq/g)	Pure solute content	Supplier	Reference name
Inorganic	Polyaluminium ammonium chloride	1.34	5.10	42%	Kemira Oy, Finland	PAC
Synthetic organic	Polyamine	1.20	8.10	50%	Kemira Oy, Finland	pAmine
Natural organic	Chitosan	---	5.02	98%	Teta Vannrensing, Norway	Chit

A continuous-flow pilot system was designed and built (Fig. 4) to simulate the primary and secondary stages of wastewater treatment (coagulation / flocculation and sedimentation) to produce the sludge needed for the stabilization study. Wastewater was continuously pumped into the pilot system while identified optimum dosages of each coagulant was applied in separate experiments. The sludge produced in the sedimentation tank after 2 hours of retention time was drained, thickened, and subsequently dewatered in a centrifuge (Talpet Oy C46 ES, 1400 rpm for 1-3 mins.).

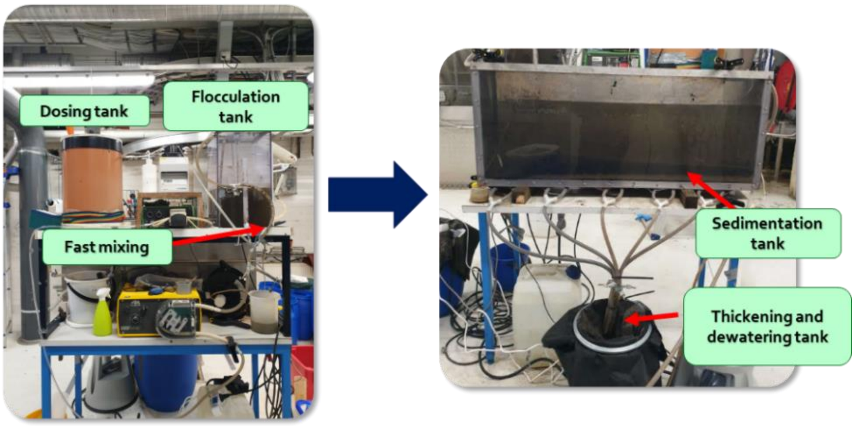


Figure 4 – Sludge production pilot (Photo Cainglet A., 2019)

The sewage sludge produced in the pilot system was divided into 2 parts for different biological stabilization methods; one part of the sewage sludge was sent to Savonia University of Applied Sciences, Kuopio for anaerobic digestion (AD.) and the second part of the sewage sludge was processed in the University of Oulu for aerobic composting (AC). Both methods were performed on mesophilic (36℃ ± 2℃) conditions due to the nature and amount of sludge produced from the pilot system.

Figure 5 – Anaerobic digestion set- up (Photo Savonia UAS, 2020)

Anaerobic digestion was executed in 5L glass bottles which were sealed with plastic caps connected to aluminium gas bags (Fig 5). The tests were initiated with an inoculum of manure-fodder mixture (taking into consideration the initial total solids (TS) and volatile solids (VS) content of the sludges collected (Table 5)) from Kuopio biogas plant. Sodium bicarbonate was added to ensure high buffer capacity. Gas yield measurements of three chemically treated sludge at the end of the batch test include: methane (CH_4), carbon dioxide (CO_2), oxygen (O_2), carbon monoxide (CO), sulphur hydroxide (H_2S), ammonia (NH_3).

Table 5. Initial solids content of coagulant-treated sludge and volatile solids ratio of sample to inoculum.

Coagulant treatment/Inoculum	Total solids (%)	Volatile solids (%)	VS-ratio of Sample: Inoculum added in the reactor
pAmine	17.11	13.62	1.80
PAC	18.64	13.60	1.73
Chit	13.62	11.10	1.71
Inoculum	5.27	4.06	--

The aerobic composting method was performed on chemically precipitated sludges using a modified commercially available PVC Bokashi® kitchen composters with built-in leachate collection port (Fig. 6). Sewage sludge of varying treatments were added to the composters with 30% dried grass (bulking agent) to ensure homogenous addition across all treatments. Constant airflow was provided at 47 l h^{-1} kg^{-1} DM of initial composting mixture for the first week and was reduced to 29 l h^{-1} kg^{-1} DM of initial composting mixture for the 59–118-day period as the microbial activity decreases. Carbon dioxide (CO_2) gas emissions and temperature were constantly measured using Vaisala CARBOCAP® Carbon dioxide probe and laboratory grade thermometer, respectively. Gases were also collected, and gas analysis include CH_4, and N_2O using gas chromatography in an outsourced laboratory.

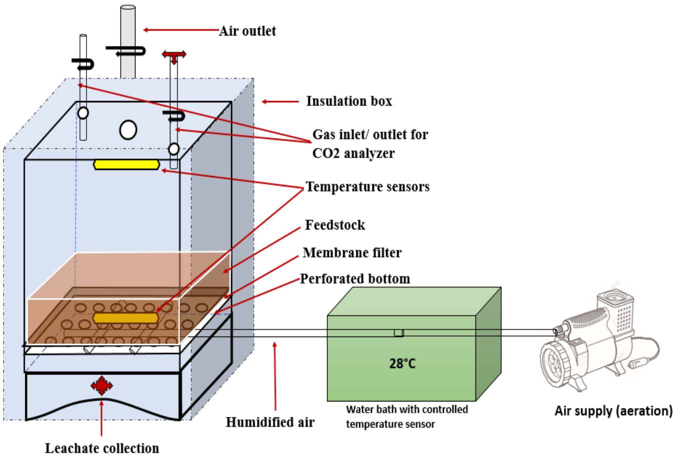


Figure 6 – Aerobic Composting experimental set- up

3.2.2 Results

The effect of the coagulants used on the biological stabilization of sludge produced via anaerobic digestion and composting was evaluated.

Anaerobic digestion

Generally, gas emissions obtained in the anaerobic digestion tests showed that there was no significant difference in maximum CH_4 yield over the incubation period across the different sludge treatments (i.e., coagulant used) and the inoculum (Fig. 6a). However, CH_4 yield over the first 6 days was higher for PAC generated sludge with CH_4 concentrations ca 1.5 times higher than those measured in the gas collected from Chit-derived sludge. Subsequently, CH_4 production decreased in PAC bioreactors 10 days earlier than from other coagulants (Fig. 7a). The effect of the coagulant used can be better described when looking at the CH_4 yield per TS and VS (Table 5, Fig. 7b) concertation of the different materials. It was found that CH_4 yield was higher for chemically precipitated sludges than that of the inoculum when TS and VS of the samples were taken into consideration with the inorganic coagulant PAC showing the highest CH_4 yield followed by the organic coagulants pAmine and Chit (Fig. 7b).

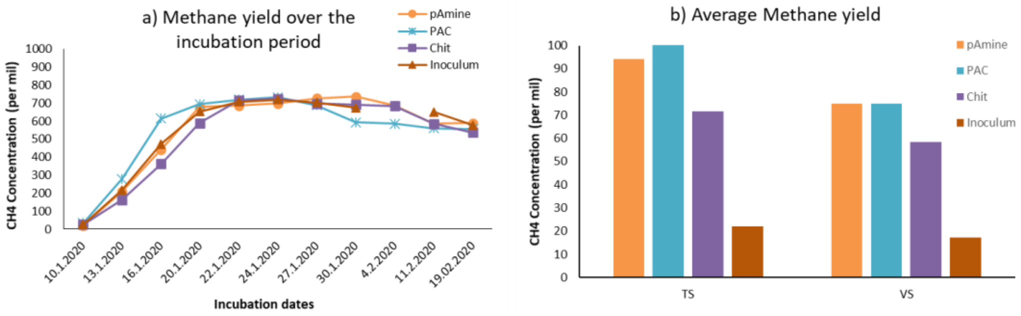


Figure 7- CH_4 emissions over the incubation period (a) and average total CH_4 yield during the anaerobic digestion (b) for the different sludges and the inoculum media.

Regarding the CO_2 yield as a product of anaerobic digestion across different treatments, there was higher yield from chemically precipitated sludge compared to the inoculum after the first week of incubation. But a gradual decrease was observed as incubation period progressed in which inoculum CO_2 yield remained almost constant throughout the experiment (Fig. 8a). The organic coagulant- pAmine showed the highest average CO_2 yield compared to PAC and Chit while the inoculum obtained the lowest yield when TS and VS content are taken under consideration (Fig. 8b)

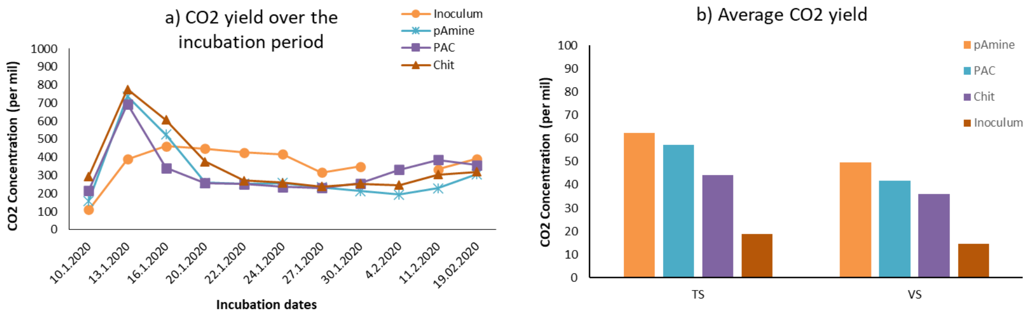


Figure 8- CO$_2$ emissions over the incubation period (a) and average total CO$_2$ yield during the anaerobic digestion (b) for the different sludges and the inoculum media.

Aerobic composting

The preliminary results of the composting processes are available. Production of CO$_2$ gas varied significantly among the sludge produced by different coagulants. At the onset of composting process, the synthetic organic coagulant pAmine presented the highest CO$_2$ concentration (3100 ppm) in the collected gases followed by the natural organic product Chit (2200 ppm) and the inorganic PAC (1600 ppm) (Fig. 9b). The ambient CO$_2$ concentrations remained constant throughout whole composting process at approximately 400 ppm. Temperature inside all composters increase significantly to ca 35 °C within the first two days of the process and remained at this level for about one week. After the material was mixed and humidified the temperature stabilized at about 30 °C for another week and subsequently decreased to 25 °C and stabilized at this level for the rest of the experiment (Fig. 9a). The sudden increase in temperature across treatments show the active microbial community in the composting experiments which helps the stabilization of sludge (Fig. 9a).

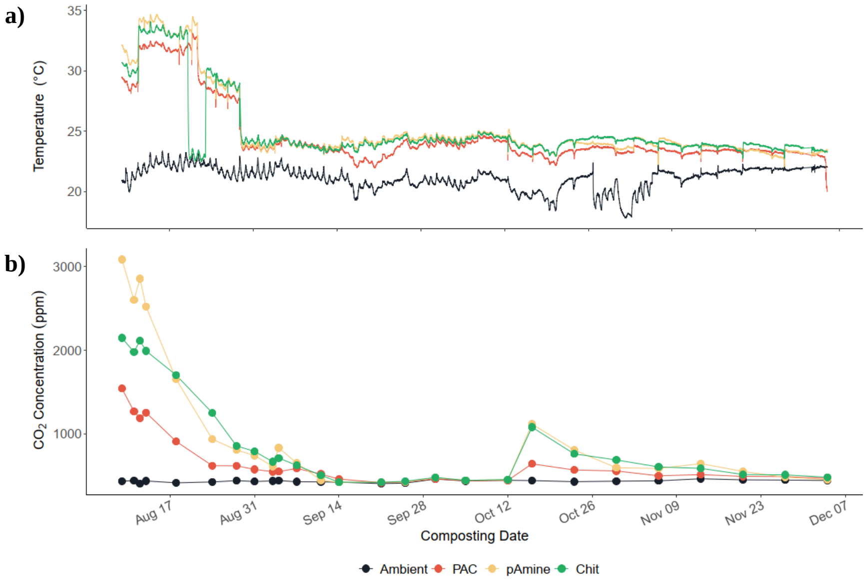


Figure 9- Temperature profile and CO$_2$ gas yield during aerobic composting process of sludge produced by the inorganic coagulant PAC and the organic coagulants pAmine and Chit.

The pAmine sludge achieved the highest temperatures throughout the composting process while PAC sludge achieved the lowest. Similar trends were observed in the CO2 production with pAmine achieving the highest CO_2 concentration in the collected gases and PAC the lowest (Fig. 9b). These point out to a clear effect of the coagulant used on the biological activity throughout the aerobic composting process.

Characteristics of stabilized sludge

Charactiristics of the aerobic composted and anaerobic digested sludge are presented (Table 6). Overall, higher dry matter content was achieved for composted products compared to that of the digestates (Table 6). Nutrients (i.e., P and N) and metal content were greatly reduced on all sludge treatments for both biological stabilization methods. Anaerboc digested and compost sludge metal content are in agreement with Finish linits for land application according to Collivignarelli et al. (2019), except for Hg which is slighty higher for digested sludges across all treatments and fo the composted Chit sludge.

Table 6. Characteristics of composted and digestate sludge products and metal concentration limit values for Finland (Collivignarelli et al., 2019).

	Limit Finland	**Raw sludge**			**Composts**			**Digestates**		
		PAC	**pAmine**	**Chit**	**PAC**	**pAmine**	**Chit**	**PAC**	**pAmine**	**Chit**
Dry matter (%)		1.12	0.94	0.23	52.7	83.8	64.9	3.9	4.2	3.85
TOC (% DM)					49.36	39.38	53.93	30.5	35.5	36
PO_4-P (g/kg DM)		18.75	28.72	652.17	---	---	---	5.5	9.1	9.65
P (kg/kg DM)		2.14	1.70	11.30	0.059	0.035	0.040	0.023	0.021	0.021
N (kg/kg DM)		4.82	5.32	41.74	0.05	0.05	0.06	0.16	0.13	0.09
Al (kg/kg DM)		4.46	0.59	2.48	0.176	0.014	0.011	0.044	0.006	0.004
Fe (kg/kg DM)		4.91	5.74	24.35	0.074	0.078	0.106	0.028	0.034	0.034
Cd (mg/kg DM)	***1.5***	40.18	50	243.48	1.23	0.87	1.20	0.51	0.52	0.55
Cr (g/kg DM)	***0.3***	1.88	1.38	14.35	0.112	0.088	0.088	0.018	0.028	0.027
Cu (g/kg DM)	***0.6***	16.07	22.34	913.04	0.49	0.35	0.51	0.18	0.19	0.30
Hg (mg/kg DM)	***1***	32.14	30.85	695.65	0.59	0.62	**1.51**	**6.55**	**4.95**	**3.50**
Ni (g/kg DM)	***0.1***	1.25	1.596	16.522	0.053	0.045	0.043	0.0105	0.0165	0.015
Pb (g/kg DM)	***0.1***	0.50	0.94	3.74	0.0080	0.0101	0.0137	0.0059	0.0064	0.0060
Zn (g/kg DM)	***1.5***	34.82	48.94	278.26	0.80	0.56	0.76	0.41	0.43	0.43

Complete analysis of results is on-going including gas yield, microbial community assay and biodegradability analysis of digested and composted sludge material. These will be reported on the manuscript.

3.2.3 Conclusions

The effect of used coagulant in wastewater treatment on the biological stabilization the sludge produced was investigated.

- The type of coagulant use had a clear effect on the CH_4 and CO_2 gas yeild produced during anaerboc stabilization of the sludge. Inorganic coagulant (PAC) produced sludge obtained higher average CH_4 yield followed by synthetic organic (pAmine) and semi-natural organic product (Chit). While pAmine obtained the highest average CO_2 yield followed by PAC and Chit.
- The coagulant use also had a measurable effect on the aerobic composting of the sludge. The pAmine sludge achieved the highest temperatures throughout the composting process while PAC sludge achieved the lowest. Similar trends were observed in the CO_2 production with pAmine achieving the highest CO_2 concentration in the collected gases and PAC the lowest. These point out to a clear effect of the coagulant used on the biological activity throughout the aerobic composting process.

3.3 Risks of contaminant losses in runoff and nutrient plant availability in sludge – WP3

Methods and results are summarized here. Complete description of the methodology and findings can be found in:

1) Cainglet et al., 2022. Nutrient plant availability and losses, and risks of micropollutant leaching in surface and groundwater runoff from chemically treated sewage sludge application in soil following growth of *Poa pratensis*. Manuscript writing on-going.

3.3.1 Methods

Sludge produced by different coagulants were stabilized via anaerobic digestion and aerobic composting were applied to different micro-plots as fertilizer material (two replicates of each treatment). In addition, commercially available mineral fertilizer was also applied, and reference (control, soil only) micro-plots were implemented. The aim was to investigate the risks of losses of soil and fertilizer material (nutrients, organic matter, metals and micropollutants) in runoff and drainage water discharging from the microplots at controlled rain events. Additionally, bioaccumulation of nutrients and metals on *Poa pratensis* leaves planted on the micro-plots was studied.

Micro-plots were designed and built as completely isolated (Fig. 10), and weather protected soil compartments with effective drainage systems for runoff and infiltrated water collection. The soil sample used was collected from Tarhapelto, Ruuki, Finland. The area has not been fertilized for at least 10 years ensuring no additional fertilizer contamination. The soil can be described as sandy black loam with rich organic matter content (6 - 11.9%). Approximately 7.5 kg of soil was added to each micro-plot and the total surface area of each microplots (0.15 m^2) was market in a matrix of 15 separated areas of 10 cm x 10 cm to allow for the systematic planting of grass seeds (*Poa pratensis*). Soil and sludge samples

Figure 10 – Micro-plots (picture by Cainglet, 2021).

(composted and digested) were sent for characterization to certified laboratories (nutrient content, metals and selected pharmaceuticals). Characteristics of the anaerobic composted and anaerobic digestated sludge materials can be seen in Table 6. However, results for soil sample characterization have not been received prior the elaboration of this report.

The microplots (16 in total, Fig. 11) were initially implemented in an outdoor tent at the University of Oulu Botanical garden facilities (from August to October 2021). The tent protected the microplots from natural rain events. In total 150 *Poa pratensis* seeds were planted per plot with 10 seeds planted in one spot and the spots have a 10 cm distance from one another. The gemination period was 4 weeks during which the microplots were watered with collected rainwater to maintain soil moisture at 10-15 %. At the on-set of winter (October- December 2021), the microplots were transferred to a climate controlled (temperature and light) room with the Oulu Botanical garden facilities.

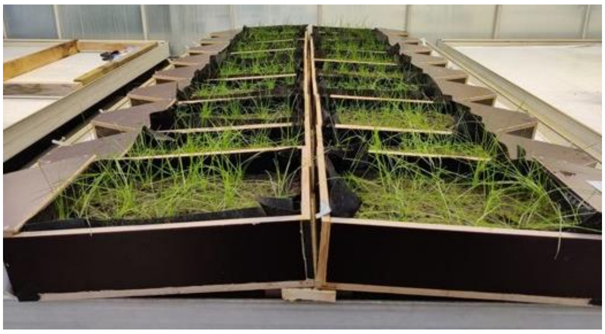


Figure 11 – Micro-plots with germinated *Poa pratensis* (picture by Cainglet, 2021).

The amount of sludge as well as fertilizer to be applied to the different micro-plots was calculated based on Finnish agricultural limit value for sludge applied as soil amendment at 22 kg/ha (Luke, 2021). Prior to the application of sludge, germinated grass leaves were cut to a uniform 7 cm height. The micro-plots were submitted to controlled rain events (sprinklers) using rainwater collected during the previous rain events at the study site. Synthetic rain events intensity and duration were defined according to Finnish climate conditions and the volume required for the generation of runoff/drainage water needed for analysis as follow:

- Rain event 1: November 2 and 3/2021, Duration = 21 min.; Intensity = 120 l/s/ha.
- Rain event 2: November 15 and 16/2021, Duration = 14 min.; Intensity = 120 l/s/ha

Runoff/drainage water was collected according to a carefully elaborated monitoring program and analysed for selected pharmaceuticals, nutrients (i.e., tot-N, tot-P) and metals (i.e., tot-Fe, tot-Al, Ca, Zn, Ni)., grass biomass was collected and biomass production and nutrient content was evaluated in one growth season. Soil samples at the end of the study was characterized by analysing nutrients (i.e., tot-N, tot-P) and metals (i.e., tot-Fe, tot-Al, Ca, Hg, Zn, Cr, Cu) and organic matter content (i.e., TOC). Additionally, *Poa pratensis* leaves after the growth season was harvested and tested for nutrients (i.e, tot-N, tot-P), organic matter (i.e., TOC) and chlorophyll content.

3.3.2 Results

The micro-plot system experiments have been completed on December 10, 2021. Samples collected including soil, grass and drainage/runoff samples have all been dent for analysis to outsourced laboratories but not all results have been received. Preliminary results regarding concentration of different compounds in the drainage/runoff water collected from different microplots is reported. For the first and second rain events, the concentration of organic matter and nutrients contained in the drainage/runoff water showed that there were measurable differences on the loss of these compounds between the aerobic composting and anaerobic digestion treatment (Figs. 12 and 13). In general, composted sludges released more N species while digested sludges released more organics. More significant differences were observed among the concentration of N, and organic substances in the drainage/runoff water discharge from microplots fertilized with sludges from different coagulants and the control unfertilized micro-plots. In general, P leaching was slightly higher from pAmine micro-plots in the first rain event and from the control microplots in the second rain event. During the first rain event, the pAmine-derived sludge fertilized microplots presented the highest concentrations of tot-N, TOC and DOC in the discharging water (both composted and digested) compared to the control and other coagulants (Fig. 12a-d). It is important to note that the concentrations of nutrients and organic matter presented refer to values where from the measured concentration the nutrient and organic matter concentrations found in the rainwater applied in the micro-plots was deducted.

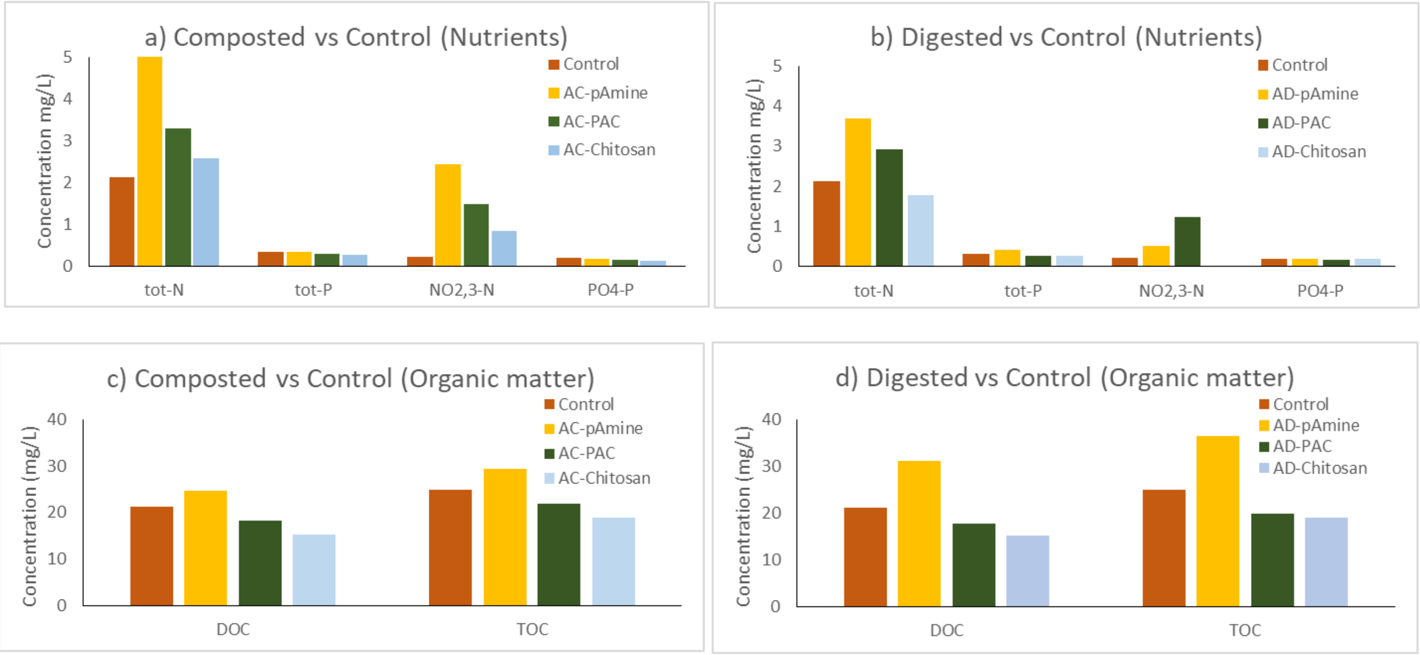


Figure 12 - Concentration of different compounds in the drainage/runoff water collected from microplots with different fertilizer (sludge) treatments and control after the first rain event.

Overall, during the second rain event the concentration of N, P and organic compounds in the collected drainage/runoff water samples were lower than the concentrations found in samples of the first rain event. The composted pAmine treated micro-plots samples had slightly higher tot-N concentrations compared to the control for composted sludges (Fig. 13a). There was high leaching of tot-N however from digested Chitosan treated micro-plots (Fig. 13b).

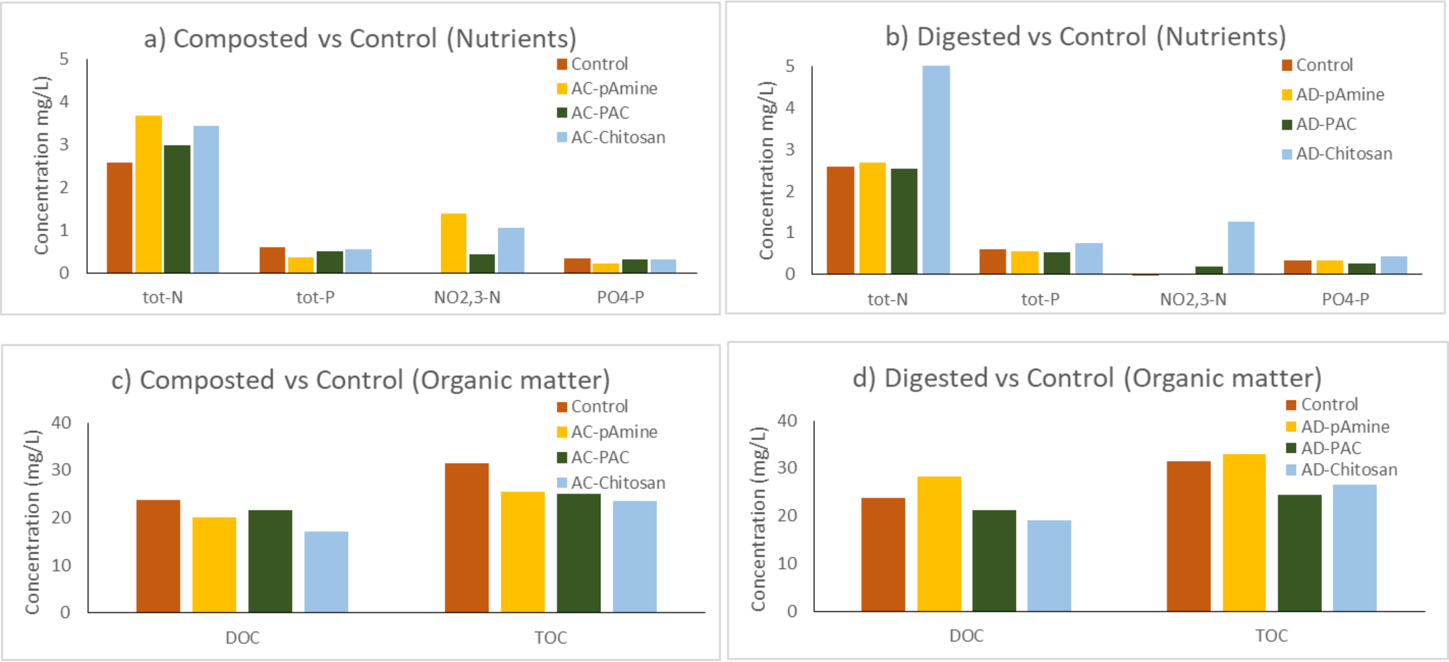


Figure 13- Concentration of different compounds in the drainage water collected from microplots with different sludge treatments and control after the second rain event.

3.3.3 Conclusions

The effect of using chemically precipitated sludge on the growth of *Poa pratensis* as well as risks of contaminant (nutrients, metals and micropollutants) transport to surface and groundwater was evaluated. Due to delays in analyses results from certified laboratories, only nutrients (tot-N, $NO_{2,3}$-N, tot-P, PO_4-P) and organic matter (DOC and TOC) concentration results were presented in this report. However, complete analysis and findings will be presented in the paper with publication set for summer 2022.

Based on the concentration of different compounds found in drainage/runoff water from microplots subjected to two controlled rain events, the following can be stated:

- The coagulant used had a larger effect on the leaching of nutrient and organic matter from the sludge treated microplots than the biological stabilization method used for sludge treatment.
- Larger concentration of N, P and organic compounds were found in drainage/runoff water samples discharge from micro-plots after the first rain event when compared to the second.
- Among the coagulants tested, pAmine-derived sludge (composted and digested) microplots presented the highest leaching of tot-P, tot-N, DOC and TOC during the first rain event.
- Chitosan-derived sludge (composted and digested) microplots presented the highest tot-N and tot-P concentrations after the second rain event.

3.4 Qualitative evaluation of the acceptance of land spreading of sludge – WP4

The purpose of this WP was to evaluate the opinions and concerns of Finnish stakeholders on the use of stabilized sewage sludge in agricultural and recreational areas as a soil amendment product.

3.4.1 Methods

Online questionnaire in Finnish language was elaborated using the Webropol 3.0 program. Due to covid restrictions, face-to-face surveys planned to reach wider audience had to be discarded. The link to the online survey was distributed using University of Oulu employee mailing list and the WE3 research unit website and Facebook channels. In addition, the link was sent to collaborating institutions and agricultural associations and foundations with request to be shared via their mailing lists or via ProAgria Oulu region newsletter as well as during organized meetings and workshops. Suppliers were approached via email (supermarkets and warehouses) but most refuse to share the link among their employers and collaborators. The survey was open for responses from 9th of June 2021 to the 15th of July 2021.

3.4.2 Results

Overall, participation was considered low when compared to the possible number of people reached. A total of 45 respondents completed the survey while another 53 started but never finished. From the 45 respondents, 40 (89%) declare themselves to belong to the "general public" group while 5 (11%) declare to be from the "farmers and other users" group. The category of "suppliers" (supermarkets, retailers, etc. including all potential suppliers of products containing sewage sludge derived biosolids) had no respondents. From all respondents, 51% were male, 47% Female and 2% opted for not disclosing gender. The age range of the respondents can be seen in Fig. 14

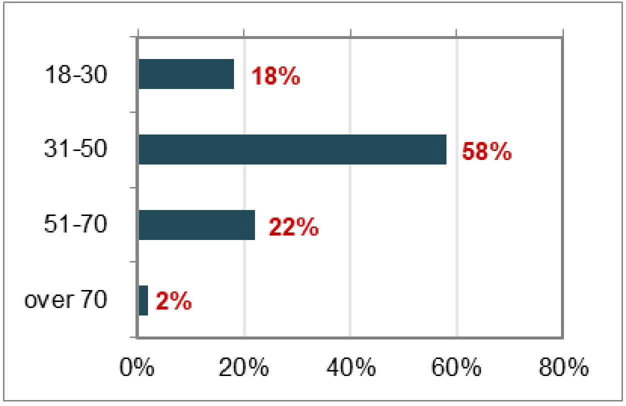


Figure 14 – Age of respondents according to pre-selected categories

Questions asked from the two respondent groups were:

1) <u>In your opinion, is pre-treated or stabilized sewage sludge a suitable material to be used as fertilizers on landscaping or gardening?</u>

Answers from the two groups differed significantly (Fig. 15 a and b). However, it is important to note that number of respondents belonging to the "general public" group is far higher than the "farmers and other users" group. The vast majority of the "general public" group fully agreed that sewage sludge is a suitable fertilizer to be used in landscaping or gardening. While 40% of "farmers and other users" also agreed, 20% disagreed and 40% had other opinion which they described in the comment section. For example, a respondent stated that bad odour could be an issue for application in urban environments while another raised the question of possible overfertilization of these areas.

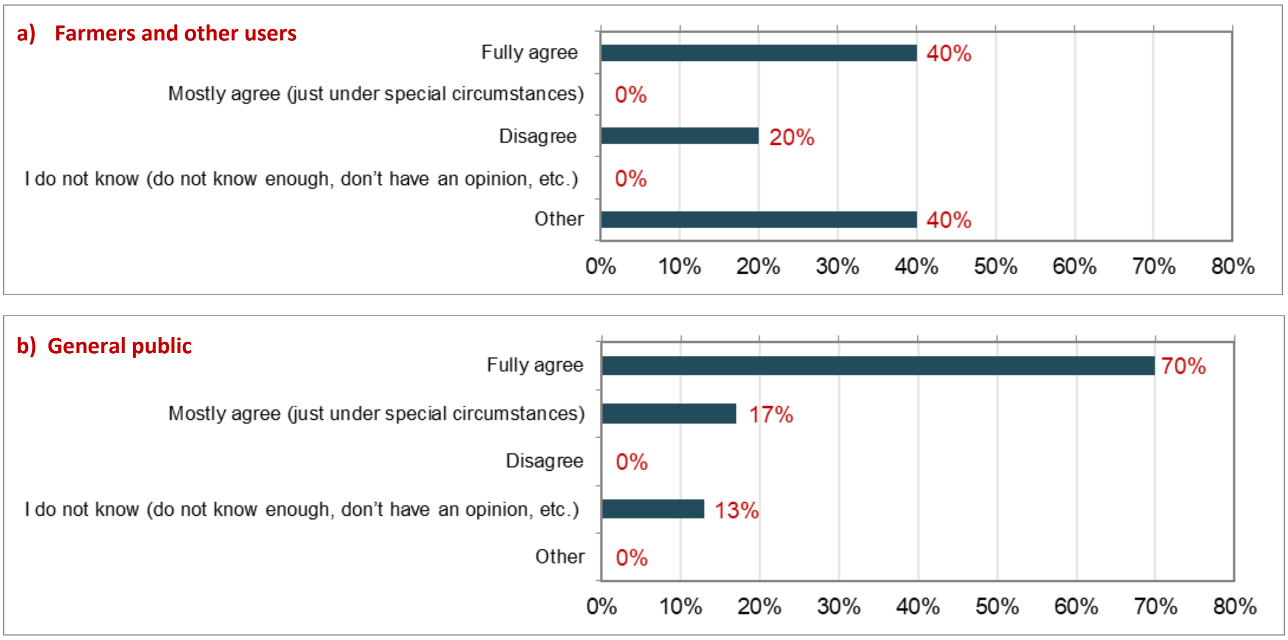


Figure 15 – Opinion of farmers and general public groups regarding the use of pre-treated or stabilized sewage sludge as fertilizers on landscaping or gardening.

<u>2) In your opinion, is pre-treated or stabilized sewage sludge a suitable material to be used as fertilizers on agricultural land?</u>

Once again, answers obtained from the two groups differed significantly (Fig. 16 a and b). The "farmers and other users" group had a less positive opinion about the suitability of sewage sludge as a fertilizer with 20% disagreeing with its application and another 40% not agreeing or disagreeing with its utilization. Some comments were made by respondents that did not agree or disagree with the provided statements described practical issues with the transport and land application of sludge as a challenge to its suitability. In the other hand, 32% of the "general public" group agreed that sludge is a suitable fertilizer for agricultural use and another 47% agreed that it could be used but only under special circumstances.

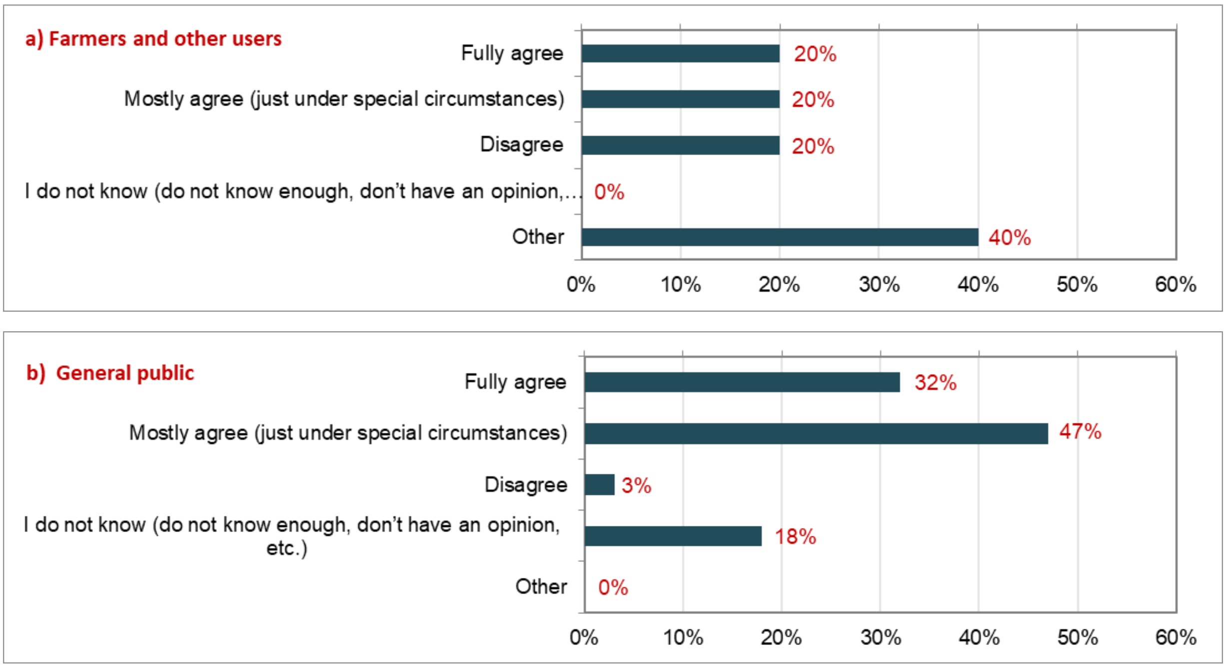


Figure 16 – Opinion of the "farmers and other users" and the "general public" groups regarding the use of pre-treated or stabilized sewage sludge as fertilizers on agricultural land.

The following question was asked from the "farmers and other users" group only

- <u>What are your main concerns about using sewage sludge in land amendment?</u>

Equal share of respondents' (29%) express concerns with loss of product value, land contamination and practical issues regarding sludge application in agricultural land (Fig. 17). Among the respondents that selected the option "other" concerns, one expanded his views by commenting that all the concerns were valid and highlight the need for more information on the impact of pharmaceutical compounds. In addition, the need for long distance transporting and the requirement for additional land work needed during sludge application were practical challenges for sludge application but also (the respondent believed) increase emissions.

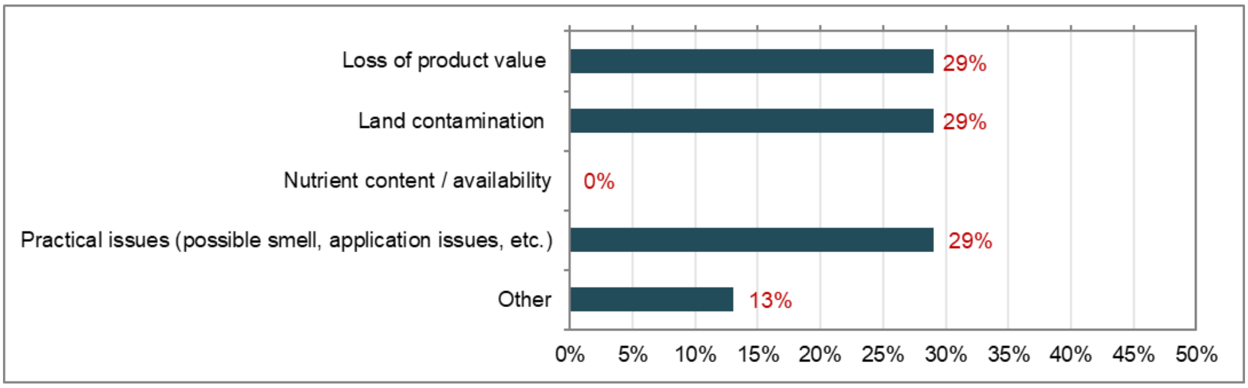


Figure 17 - Opinion of the "farmers and other users" group regarding main concerns about using sewage sludge in land amendment.

The following question was asked from the "general public" group only

- Would you consume/use products grown on sewage amended soils given that it complies to the standard limit of pollutants following EU and Finnish regulations?

The "general public" group view on the use of sewage sludge as a fertilizer was quite positive (Fig. 18). While 25% of respondents agree that they would consume non-food products grown on sewage amended, 40% stated that they would consume different products including food crops. Only 7% of respondents said they would not purchase products grown in sludge fertilized areas.

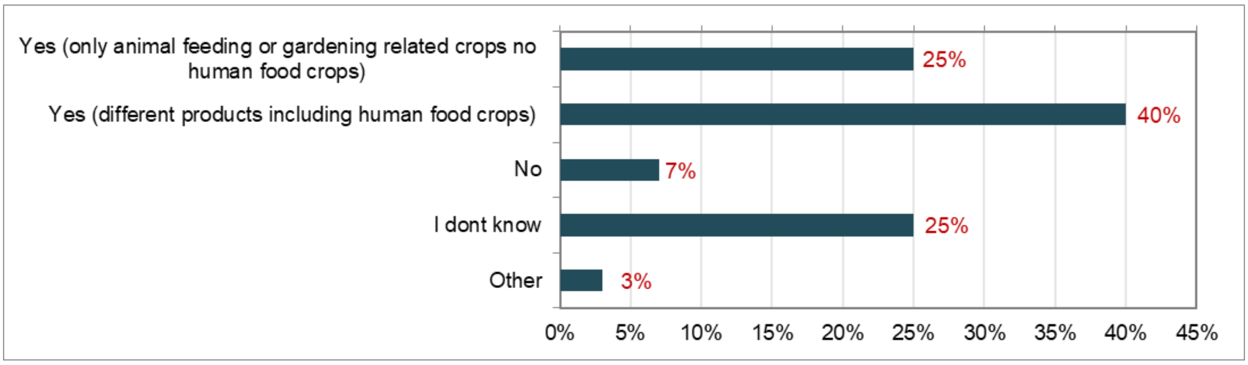


Figure 18 - Opinion of the "general public" group regarding their willingness to consume products grown on sewage amended soils

3.4.3 Conclusions

The opinions and concerns of Finnish stakeholders on the use of stabilized sewage sludge in agricultural and recreational areas as a soil amendment product was evaluated. Overall, participation was considered low when compared to the possible number of people reached. A total of 45 respondents completed the survey with 89% declaring themselves to belong to the "general public" group and 11% declaring to be from the "farmers and other users" group. The small number of respondents, especially of the "farmers and other users" group increase the uncertainty of obtained results and any conclusion or statement based on the provided answers must be made with care. In general, significant differences were observed among answers of the two groups for the common questions. The "general public" group was, in general, more positive towards the use of sewage sludge as a soil amended material in landscaping as well as in agriculture soils. While "farmers and other users" stated possible loss of product value as a concern regarding the use of sewage sludge, the majority of "general public" group stated that they would consume products grown in sewage amended soils, including food crops. The more negative view of "farmers and other users" were clearly linked to their concerns regarding environmental impacts and practical issues regarding the land spread of sludge. In the other hand, possible bios in the answers of the "general public" group might have arisen from the educational background of the respondents. 51% of respondents had a higher education degree while 38% declared to have a post graduate degree.

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