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# Microplastics degradation through hydrothermal liquefaction of wastewater treatment sludge

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## ABSTRACT

Wastewater treatment plant sludge contains large quantities of microplastics (MPs), which is a problematic substance that impedes sustainability efforts, such as in land management. MPs are resilient to degradation, but extreme conditions, such as high temperature and pressure, can lead to residues that can be used as fertilizers on farmlands. Hydrothermal liquefaction (HTL) creates such conditions, converting sludge into valuable bio-crude. To this end, the current study examined the resilience of MPs in sewage sludge that were treated by continuous HTL operated at supercritical water conditions (400 °C, 30 MPa). MPs were extracted before and after the HTL process and quantified by Fourier Transformation Infrared Spectroscopy (FTIR). Particles of 10–500 μm were quantified using Focal Plane Array (FPA) based micro-FTIR (FPA-μ-FTIR) imaging combined with an automated analysis of the generated spectral image, while Attenuated Total Reflection (ATR)-FTIR was used for MPs >500 μm. The continuous HTL led to an MP reduction of approximately 76% in terms of MP number and 97% in terms of MP mass. The difference in reduction of the number of MPs versus their accumulated mass was the result of MPs being smaller after the HTL process. A total of 18 polymer types were detected in the sludge and slurry entering the continuous HTL while only 11 types were identified in the residual materials. No MPs were detected in the bio-crude, i.e. the most favorable product of the process. The polymer composition changed considerably as a result of the HTL process. Polyurethane, polypropylene, and polyethylene were the dominant polymers in the feedstock, while polypropylene and polyethylene were the most present in the residual products. The findings indicate that HTL can be efficient in reducing MPs in highly polluted sludge from wastewater treatment plants, leaving the byproducts and residuals significantly less polluted, hereby reducing the movement of MPs to the terrestrial environment. Thus the products are better suited for sustainability efforts than the raw material.

## 1. Introduction

As a major by-product stream of wastewater treatment plants, sewage sludge contains problematic pollutants, such as microplastics (MPs) that require further treatment to make the sludge eligible for environment-friendly disposal. The latter has recently gained much attention due to its accumulation in nature (Weinstein et al., 2016), adversely impacting ecosystems (Thompson et al., 2009) and human health (Prata et al., 2020). Although sludge is traditionally reused as fertilizer and soil improver, it may contain high levels of pollutants, such as MPs, that diminish its benefits to nature, leading to a non-sustainable disposal of the sludge. Therefore, future sustainable processes, such as hydrothermal liquefaction (HTL), must be considered when examining the resilience of MPs and its existence in residual products.

Scientists are working on resource recovery from sewage sludge, as it contains a high amount of organic and inorganic materials and nutrients. HTL is capable of treating the wet urban residue at relatively mild temperatures (280–400 °C) and high pressures (10–35 MPa). HTL is gaining popularity among researchers and policy-makers, as it provides a cost- and carbon-efficient way to convert complex feedstocks into sustainable chemicals and biofuels (Kohansal et al., 2021). As a thermochemical process, HTL offers an environment-friendly alternative to crude oil, or so-called 'bio-crude', that results from the thermal breakage and reforming of biomass macromolecules (Yang et al., 2019). This process is considered an up-and-coming technology for converting complex feedstock molecules into value-added products, for instance, polyethylene (PE) plastic waste (Su et al., 2004) and electronic waste (Zhao et al., 2019).

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In recent decades, HTL technology has been extensively studied and used to tackle the ever-growing disposal challenges of sludge from WWTPs. Silva Thomsen et al. (2020) studied the effect of a pilot-scale HTL process conditions on the conversion of micropollutants (pharmaceuticals and biocides) in sewage sludge. They report that HTL effectively decreased the environmental risk of micropollutants being released to farmlands in the case of land fertilization. Some HTL studies targeted the depolymerization of common plastic wastes at various HTL conditions: these studies report the bio-crude derivatives of plastics, solid residues, and the recovery of some chemical components from plastic materials (Seshasayee and Savage, 2020). It has been reported that the component variation of the dark and viscous oil derivatives and chemical products is highly feedstock-dependent (Toor et al., 2011); moreover, there is an expectation that the HTL process may induce a certain degree of change to synthetic polymers as well as natural counterparts (e.g. cellulose and hemicellulose) in sewage sludge. However, the impact of the HTL process on the distribution and degradation of the large quantities of microplastics contained in sewage sludge has yet to be studied.

Sewage sludge is a waste product from wastewater treatment plants (WWTPs). It contains most of the MPs held in wastewater from households, institutions, industries, and urban surface runoff (Xu et al., 2021). Modern WWTPs implementing advanced treatment methods have been reported to retain as much as 99% of MPs from the wastewater stream. Lares et al. (2018), for instance, reported an MP retention capacity of 98.3% by a WWTP with a conventional activated sludge process and a pilot-scale advanced membrane bioreactor. Carr et al. (2016) reported a retainment efficiency of 99.9% by the studied WWTP. Talvitie et al. (2017) reported that the advanced final stage technologies in WWTPs can substantially reduce the MP discharge into nearby water resources.

The MPs are retained at various treatment steps and transferred into the sewage sludge (Sun et al., 2019). Mahon et al. (2017), for instance, found sewage sludge to contain from  $4.2 \times 10^3$  to  $15.4 \times 10^3$  N kg<sup>-1</sup> dry matter (DM). The common trend of using sewage sludge as fertilizer on agricultural fields could therefore be a key source of MPs in the terrestrial environment (Edo et al., 2020). Despite these benefits, the application of sewage sludge on agricultural lands can be a double-edged sword. On the one hand, it is a source of sustainable fertilizer; on the other hand, it leads to environmental pollution. Therefore, alternative processes, such as HTL, are needed to preserve the beneficial outcomes while mitigating the negative consequences.

Quantifying MPs in complex matrices like sewage sludge and HTL products is challenging. A multitude of destructive and non-destructive analytical techniques have been tested and employed (Sun et al., 2019). Existing methods and approaches are in no way standardized, and concentrations obtained on the same or similar matrices vary by several orders of magnitude depending on which analytical approach is applied (Gatidou et al., 2019). The lack of standardization extends to other aspects of research, including sampling techniques, sample amount, and methods used to extract the MPs from samples. Analytical methods range from simple microscopy with visual identification of what counts as an MP to state-of-the-art methods, such as Focal Plane Array (FPA) based Micro Fourier Transformation Infrared Spectroscopy (FPA- $\mu$ -FTIR). The latter technique has been reported to yield reliable data regarding number, size, and composition (Löder et al., 2015). It does so at a low size resolution that also estimates MP mass (Simon et al., 2018). A customized polymer library with a large number of polymer spectra further aids in the identification of a recorded sample spectra (Mintenig et al., 2017).

The present study assesses the sustainability of an HTL process on sewage sludge with respect to MPs. It examines the resilience of MPs through the HTL process by quantifying their presence and distribution in feedstock and products. Further, the study addresses whether there is a significant impact on specific polymers, for instance, the disappearance of some plastic types after the HTL process. The effect on the number of MPs, their size and mass were analyzed. Finally, the study

closes the balance over the HTL reactor based on the number and mass of the identified polymeric particles.

## 2. Material and methods

### 2.1. Continuous hydrothermal liquefaction (HTL) and separation of the products

Sewage sludge was obtained from Stistrup WWTP, Farsø, Denmark. The WWTP has a capacity of 20,000 Population Equivalents and operates as a one-step aerobic biological process for nitrification-denitrification, removal of organic matter, and simultaneous chemical precipitation of phosphorus. A pilot-scale continuous HTL plant was set up in close collaboration between the Department of Energy, Aalborg University, and Steeper Energy, to handle the wet organic wastes, converting them into a high-quality yield product or so-called bio-crude (Castello et al., 2018). In this project, the feeding material for the HTL process was partially dewatered sewage sludge, which was analyzed for MPs before and after the procedure. The sampled sludge contained 78.5 wt % of moisture and 5.5 wt % of ash content (dry basis). Dry matter (DM) content stands as an essential factor in the continuous processing of biomass. While processing, high DM can potentially cause slurry sedimentation and reactor clogging. In contrast, low DM suppresses the bio-crude yield – known as the most favorable product of the HTL process. To set the dry matter content of the slurry to the highly recommended range of 15–20 wt %, 7.6 kg of freshwater was added to the 50.6 kg of the partially dewatered sludge. Hence, the overall dry matter of the slurry was held at around 18 wt %. Shah et al. (2020) reported a significant increase in bio-crude yield as well as a reduction of solid residue while adding K<sub>2</sub>CO<sub>3</sub> to the sewage sludge HTL reaction medium processing at supercritical conditions.

Moreover, using NaOH in low quantities can potentially increase the conversion of the biomass to the intended products (Posmanik et al., 2017). Therefore, to ease the biomass processability and increase the bio-crude production yield that consequently results in the reduction of solid residue, 2.5 wt % of potassium carbonate (K<sub>2</sub>CO<sub>3</sub>) and 0.5 wt % of sodium hydroxide (NaOH) were subsequently introduced to the slurry. Note that all of the chemicals used in the HTL plant were of industrial grade and as such, potentially containing MPs, reflecting the reality of a future full-scale installation.

For instance, the homogeneous alkali catalysts were stored in the HDPE vessels. Before being fed to the reactor, the slurry was heated to 60 °C in the mixing tank and subsequently pressurized to approximately 30 MPa through a high-pressure piston pump (Pedersen et al., 2016). The well-mixed and pressurized slurry was injected into two sequentially connected induction heaters to increase the slurry's temperature to 400 °C. The slurry was then transmitted to two 5 L serially connected reactors (operated at 390–420 °C) to maintain the residence time of the process. The produced effluent was discharged to a concentric-tube heat exchanger and subsequently passed through two high-pressure filters. Finally, prior to degassing, a series of capillary tubes were used to depressure the product stream. The depressurized products were stored without any phase separation. The single-phase emulsion was called 'as-received products'. A detailed description of the HTL process and phase separation of the as-received products is reported elsewhere (Jensen et al., 2017). No specific steps were taken to avoid MP contamination during the process, reflecting again the reality of a future full-scale system.

In contrast to many lignocellulosic biomasses that can be gravimetrically separated or simply broken down into the different product phases using a separation funnel, the products derived from the continuous HTL of sludge manifest as a single-phase emulsion. Initially, a certain amount of the products was centrifuged (Sigma 6–16 HS) at 3800 min<sup>-1</sup> for 6 min at ambient temperature. The centrifuged effluent was termed 'aqueous phase' and stored for further treatment; the rest was termed 'emulsion'. The aqueous phase obtained from centrifugation

of the as-received product was further concentrated using a semi-pilot scale vacuum evaporator with a total volume of 10 L at 65 °C under a vacuum of 100 to 5 KPa. Due to foaming issues likely resulting from the light nitrogenous compounds dissolved in the aqueous phase, 2 mL of n-octanol was added to the evaporation medium as an anti-foaming agent.

Lab-scale physio-chemical phase separation was carried out by adding 100 g of methyl ethyl ketone (MEK) (VWR International) as a diluent agent to the partially dewatered emulsion. The mixture was continuously stirred using a magnetic stirrer at 1000 min<sup>-1</sup> for 8 h. Thereafter, 100 g of 0.5 M citric acid was added to the mixture to facilitate emulsion breakage. The entire mixture was again centrifuged, and the liquid products were transferred to a decanter funnel, while the solid products that remained at the bottom of the vessel were washed with acetone and filtered through a 2 µm cellulose qualitative filter paper. The water phase and MEK-dissolved bio-crude were appropriately segregated in the decanter funnel. Furthermore, the MEK was evaporated using a lab-scale vacuum rotary evaporator (Büchi R210) at 60 °C for 30 min under a vacuum of 50 KPa. All procedures were carried out without the interference of any plastic material. The approach of liquid product separation is summarized in Fig. 1.

## 2.2. Sampling strategy

Samples were collected from various stages of the HTL process (Fig. 1, green boxes). All products were taken from the same batch experiment. The samples were collected in clean glass bottles and covered with aluminum foil to avoid plastic contamination. From each collected sample, duplicate sub-samples were taken to extract the MPs.

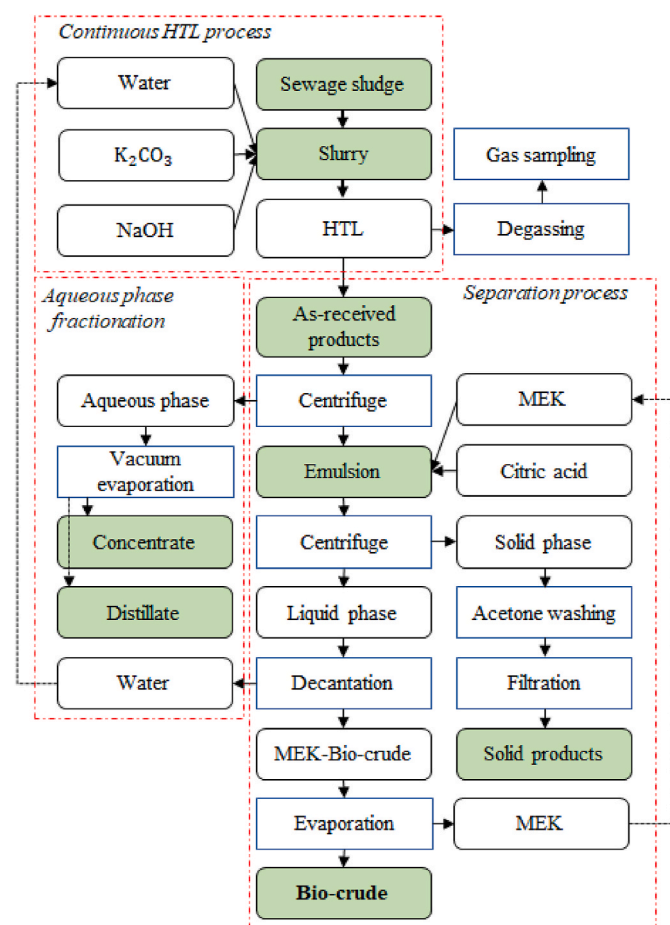


Fig. 1. An overview of the continuous hydrothermal liquefaction (HTL) process, product separation and aqueous phase fractionation.

## 2.3. Extraction of MPs

### 2.3.1. Sewage sludge and slurry

About 500 g of sewage sludge was homogenized, and 20.08 g of duplicate sub-samples equivalent to 5 g dry matter (each) were taken. Likewise, 23.8 g of duplicate sub-samples were taken from 500 g of homogenized slurry. The samples were pre-oxidized in 1 L beakers by gradually mixing 200 mL of 50% hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) and 250 mL of Milli-Q into the sample. The sample was left for 48 h and then filtered through a 10 µm stainless steel filter. The particles from the filter were detached by ultra-sonication into 500 mL sodium dodecyl sulfate solution (SDS, 5% w/vol). The sample was incubated for 48 h at 50 °C by continuously mixing with a glass-coated magnet. The filtered particles were transferred into 300 mL of acetate buffer (pH 4.8), then 500 µL of cellulase (Cellulase enzyme blend®, Sigma-Aldrich) and 500 µL of cellulolytic enzyme mixture (Viscozyme®, Sigma-Aldrich) were added. The mixture was incubated at 50 °C for 48 h. The filtered particles were transferred to 300 mL of tris buffer (pH 8.2) where 500 µL of protease solution (Protease from Bacillus sp.®, Sigma-Aldrich) was added and incubated at 50 °C for 48 h. The solution was filtered and the particles were transferred into 200 mL of Milli-Q water. A Fenton oxidation was conducted by adding 145 mL of 50% H<sub>2</sub>O<sub>2</sub>, 65 mL of 0.1M NaOH, and 62 mL of 0.1M FeSO<sub>4</sub> while maintaining a temperature of 15–30 °C. After this step, the larger MPs (major dimension >500 µm) were separated from the smaller MPs (major dimension between 500 and 10 µm) using a 500 µm mesh sized sieve and a 10 µm stainless steel filter. The larger particles were removed from the sieve by backflushing with particle-free water, which were then stored in an aluminum tray. The water was evaporated in an oven at 50–60 °C. The cleaned and dried particles were stored for later analysis. The smaller particles were transferred into a 250 mL pear-shaped separation funnel containing a sodium polytungstate (SPT) solution of density 1.7 g cm<sup>-3</sup>. The particles were mixed using compressed air bubbling from the bottom of the funnel for 30 min. The mixture was left to settle for 24 h. Three-fourth of the bottom part was removed: the process was repeated up to 3 times. The top floating particles were filtered using a 10 µm steel filter and washed with Milli-Q water to remove SPT. The filtered particles were removed using an ultra-sonicating bath and transferred into ultra-pure HPLC quality 50% ethanol. The particles were moved to 10 mL vials, and the ethanol evaporated in an evaporation bath (TurboVap® LV, Biotage) at 50 °C. Finally, the particles were suspended into 5 mL of ultra-pure HPLC quality 50% ethanol.

### 2.3.2. Continuous HTL products

Approximately 500 g of as-received product, 500 g of emulsion, 500 g of solid residue, and 200 g of bio-crude were taken as samples and homogenized. Duplicate sub-samples of each product (55 g of as-received product, 10 g emulsion, 10 g solid residue, 10 g bio-crude) were taken. The samples were initially treated with SDS solution and incubated for 24 h at 50 °C. Afterward, 1 mL of lipase (Lipozyme® TL 100 L, Strem Chemicals Inc.) was added to the sample and incubated for 48 h at 50 °C. The particles were filtered and transferred to 200 mL of Milli-Q water. A Fenton reaction was carried out following the aforementioned procedure. Particles were separated using a 500 µm sieve and a 10 µm steel filter. Density separation was carried out for the small MPs as described for sludge and slurry. The cleaned particles from the supernatant were transferred to 50% ethanol, resulting in a total volume of approximately 25 mL, which was later evaporated. The particles from the as-received product and emulsion were suspended in 15 mL of 50% ethanol; solid residue and bio-crude were suspended in 10 mL of 50% ethanol.

Approximately 500 g of concentrate and 2 L of distillate were collected and homogenized. Duplicate sub-samples were taken (13 g concentrate and 1 L distillate for each), filtered through a 10 µm steel filter, and flushed with Milli-Q water and 50% ethanol. The particles from the filter were diluted in 1 L of Milli-Q water and filtered through a

500  $\mu\text{m}$  sieve and a 10  $\mu\text{m}$  steel filter. The small MPs were transferred to 25 mL of 50% ethanol, which was later evaporated. Similarly, the small MPs from the concentrate were transferred to 10 mL of 50% ethanol, and those from the distillate samples were transferred to 5 mL of 50% ethanol.

#### 2.4. Analytic techniques for MPs with ATR-FTIR and FPA- $\mu$ FTIR

The extracted particles  $>500 \mu\text{m}$  were handpicked and imaged using a stereomicroscope (ZEISS, SteREO Discovery.V8) equipped with an Axiocam 105 color camera with a maximum magnification of  $8 \times$ . ZenCore (Zen2Core SP1 from ZEISS) software coupled to the microscope was used to measure particle dimensions, including area, minimum, and maximum Feret diameter. The particles' IR spectra were obtained with an Attenuated Total Reflection: ATR-FTIR (Agilent Cary 630 FTIR with a diamond ATR). Upon obtaining the background, the sample spectrum of the particle was recorded by 64 co-added scans in the spectral range of  $650\text{--}4000 \text{ cm}^{-1}$ . OMNIC software (Thermo Fisher Scientific Inc., 8.2.0.387 version 1) and its library were used to identify the material of the recorded IR spectra.

Particles between 10 and 500  $\mu\text{m}$  were analyzed using FPA- $\mu$ FTIR: Agilent Cary 620 FTIR microscope equipped with a  $128 \times 128$  pixel FPA (Mercury Cadmium Telluride detector) and coupled to an Agilent 670 IR spectroscope. The particles suspended in 50% ethanol were homogenized with a vortex, and sample aliquots were taken with a glass pipette of 25  $\mu\text{L}$ , 50/100  $\mu\text{L}$ , and 200  $\mu\text{L}$ . The sub-sample was deposited on a  $13 \times 2 \text{ mm}$  zinc selenide window (Crystran, UK) held in a compression cell (Pike Technologies, USA), leaving a 10 mm diameter free area. The windows were left to dry for some hours on a heating plate at 50  $^\circ\text{C}$ . If needed, the process was repeated until the window was adequately covered by particles. The volume deposited on the window for each scanning of sludge and slurry was 100  $\mu\text{L}$ . The deposited volumes for as-received products were 25  $\mu\text{L}$ , concentrate 100–200  $\mu\text{L}$ , solid residue 200  $\mu\text{L}$ , distillate 600  $\mu\text{L}$ , and bio-crude 50  $\mu\text{L}$ . Three windows were scanned for each sample. Details of the technology are described in Simon et al. (2018), Vianello et al. (2019), and Kirstein et al. (2021). The background was acquired by 120 co-added scans, while the sample was obtained by 30 co-added scans at the wavenumber range  $3750\text{--}850 \text{ cm}^{-1}$ . The scan was done in transmission mode with a  $15 \times$  Cassegrain IR objective, producing a pixel resolution of 5.5  $\mu\text{m}$ .

The resulting chemical images were analyzed with siMPle, which is an automated software program that provides particle dimensions, area, volume, and mass estimates of MPs (Primpke et al., 2020). To this end, the MPs were mapped by matching each pixel of the scan to a custom-built reference database, containing more than 110 spectra of different materials by a Pearson's correlation (Liu et al., 2019). Only particles consisting of at least two pixels were included as MPs.

#### 2.5. Quality control and analysis of contamination

To remove traces of organic and synthetic contaminants, all glassware and the stainless steel filters were muffled at 500  $^\circ\text{C}$  before use. Filters were sonicated for 5 min in Milli-Q water to remove ash content and subsequently thoroughly flushed with particle-free water. The filter used for the first treatment was used throughout the sample preparation and was preserved in a clean Petri dish with Milli-Q water. All equipment was rinsed three times before use. Chemicals were filtered through 0.7  $\mu\text{m}$  glass fiber filters prior to use. The sample preparation was performed inside a clean fume hood. Researchers wore cotton clothes (such as top and lab coat) throughout sample preparation and analysis. The deposition of samples for analysis on  $\mu$ FTIR was done inside a clean laminar flow bench, and windows were covered with a muffled beaker. The air in the FTIR and microscope lab room was continuously filtered with a Dustbox® (HochleistungsLuftreiner, Germany) housed with a HEPA filter (H14, 7.5  $\text{m}^2$ ) with over 99.99% filtration efficiency for particles  $<0.2 \mu\text{m}$  (Tan et al., 2021).

Contamination cannot be fully avoided despite the many protocols followed during sample preparation. Duplicate blank samples were prepared in parallel to sample preparation to quantify the possibility of contamination. For each blank sample, 1 L of Milli-Q water was filtered through a 10  $\mu\text{m}$  stainless steel filter and sonicated in Milli-Q water; the final volume was adjusted to 250 mL after removing the filters. The blank control samples were processed and analyzed following the processing steps for sludge and slurry samples, i.e. the matrices requiring the most treatment prior to analysis.

#### 2.6. Statistical analysis

R (version 3.5.2) was used for univariate analysis of datasets, and data visualization was done with the add-on ggplot2 package. The normality of the data was tested by a Shapiro-Wilk's test. Particle size and mass was verified with non-parametric tests, Wilcoxon rank-sum test between the sample matrices, and for prior and after HTL process at a significance level of 0.05.

### 3. Results and discussion

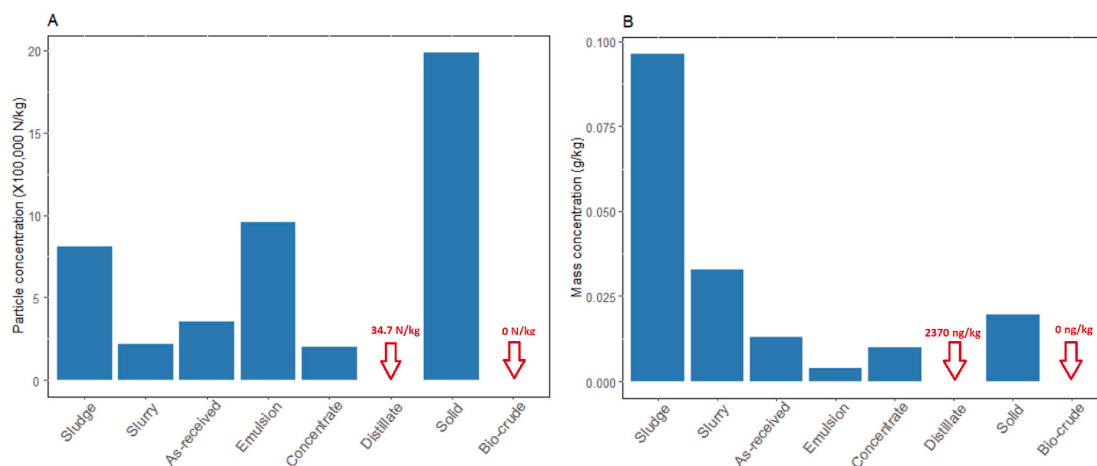
#### 3.1. Continuous HTL products distribution

A sample (1.164 kg) of as-received products was extracted from the HTL storing tank. Centrifugation separated 1.020 kg of the aqueous phase without the intervention of chemicals. As expected, more aqueous phase mass was recovered than the input water content of the slurry 79 wt% (936 g) in the slurry, which is due to the dissolved polar organics in the aqueous phase. Hence, the aqueous phase yield was calculated to be 34 wt%. On the other hand, bio-crude and solid residue yielded around 25 wt% and 33 wt%, respectively. Approximately 92 wt% of the organics present in the as-received products got separated into the three mentioned phases, revealing the efficiency of the separation procedure.

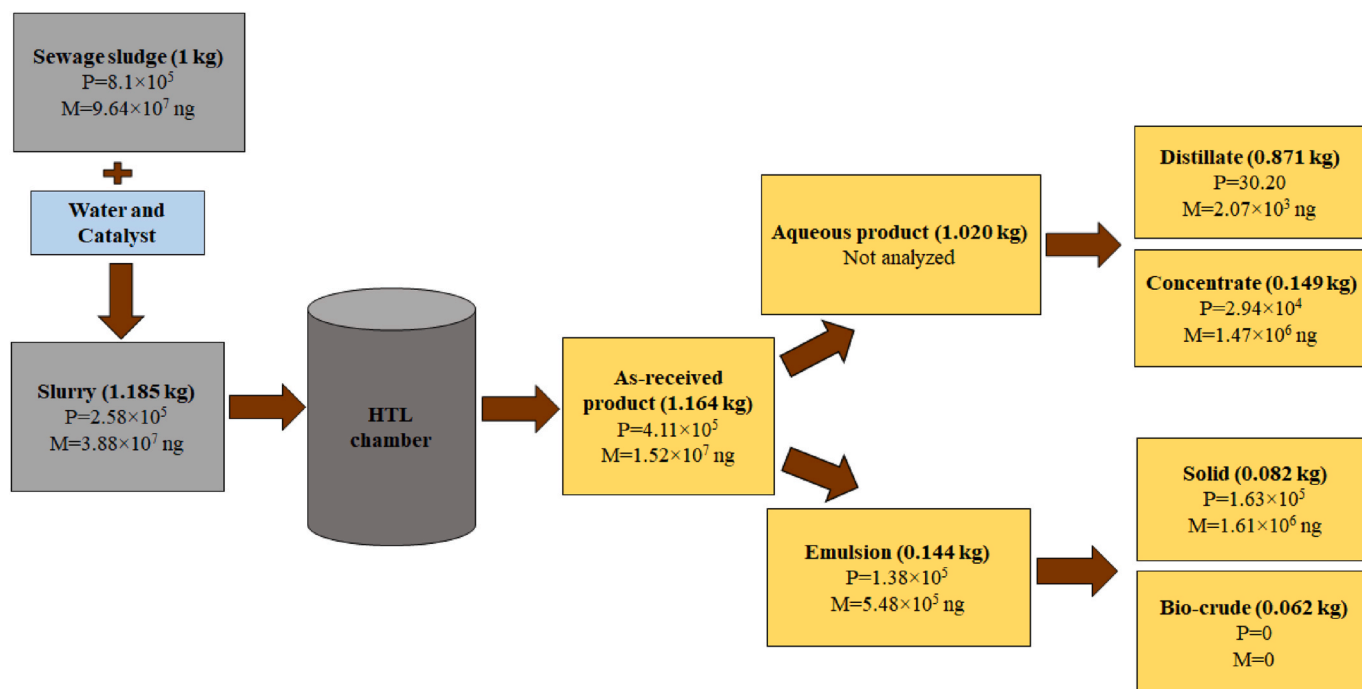
#### 3.2. MPs quantification

MPs were found in all matrices, but not detected in the bio-crude, with contents varying up to four orders of magnitude measured both as number and mass (Fig. 2). During sample preparation, minor contamination was observed compared to the abundance in the samples and the datasets, and thus not corrected for blank values. A detailed description of MP contamination in procedural blanks is given in supplementary materials in the section "MPs in procedural blanks" and in Table S3. In terms of MP numbers, the solid residue held as much as  $5.7 \times 10^4$  times higher concentration than the distillate. The MP mass concentration in sludge was  $0.096 \text{ g kg}^{-1}$ , with ever-decreasing values in the other matrices (Fig. 2). The MP concentration in the slurry was significantly reduced compared to the concentration in the sludge, which was partly due to the latter being diluted by water and catalyst while preparing for HTL. Some variation is also due to uncertainties in sampling the various matrices. Finally, some chemical degradation and stress cracking of the polymers may have resulted because of the added  $\text{K}_2\text{CO}_3$  and NaOH. Gohla et al. (2020) observed that many MP polymers found in beach sediments were resistant to  $\text{K}_2\text{CO}_3$  treatment with the exception of polycarbonate (PC). Teófilo et al. (2010) found that NaOH led to significant surface damage and reduced mechanical properties of poly(ethylene terephthalate) (PET). Similar work by Baah and Baah (2002) revealed a weight loss of polypropylene (PP) upon immersion into a NaOH solution. In the present study, poly(oxyethylene) (POM) and epoxy were not detected in the slurry, which could also be due to degradation or dissolution by the added  $\text{K}_2\text{CO}_3$  and NaOH.

The MP mass in the sewage sludge was reduced significantly by the continuous HTL process, showing that the process was efficient in degrading the plastics in the sludge. A closer look at the MP balance (Fig. 3) shows that approximately 68% of the reduction in terms of MP numbers and 60% in terms of MP mass occurred between the sludge and



**Fig. 2.** The concentration of MPs in analyzed matrices: A) particle concentration and B) estimated mass concentration. The concentration is per wet weight of the sample matrices except for the matrix 'Solid'. Polymer distributions are provided in the supplementary materials [Table S4](#) and [Table S5](#).



**Fig. 3.** MP balance over the continuous HTL process. P = particle numbers (N) and M = mass (as nanogram (ng)). Details of the identified MP polymers in a unit mass of feeding material (1 kg sewage sludge) over the continuous HTL process by number and mass are provided in supplementary materials [Table S6](#) and [Table S7](#).

the slurry. The as-received product held more MPs than the slurry but less MP mass, indicating that particles might have fragmented in the HTL chamber. On the other hand, the sum of emulsion and aqueous product held significantly less MP mass and somewhat fewer MPs than the as-received products. The MP mass, and to a lesser degree, the particle numbers, increased in the sum of the final products. Some discrepancies are likely related to analytical uncertainties and subsampling uncertainties caused by inhomogeneity in the sampled matrices. Nevertheless, it is clear that the continuous HTL process resulted in a significant reduction of the number and mass of MPs in the raw product, the sewage sludge.

The present study is the first to quantify MPs in a continuous HTL process. There, the results cannot be compared to existing research; furthermore, more studies are needed to verify the effects of the process and the analysis used to quantify MP number and MP mass. However, there are several studies that have examined the raw product, the

sewage sludge, in relation to particle numbers, including one investigation that analyzed quantified particle mass ([Chand et al., 2021](#)). The latter study quantified MPs in dry sewage sludge and digested sludge from a Swedish WWTP and found  $4 \times 10^6$  N kg<sup>-1</sup> and  $6.4 \times 10^6$  N kg<sup>-1</sup> MP in terms of particle concentration and 0.23 g kg<sup>-1</sup> and 0.37 g kg<sup>-1</sup> MP in terms of mass concentration, respectively. [Li et al. \(2018\)](#) analyzed 79 sewage sludge samples from 28 different WWTPs in China. They identified MP concentrations from  $1.6 \times 10^3$  to  $56.4 \times 10^3$  N kg<sup>-1</sup> of dry sludge. [Lares et al. \(2018\)](#) investigated a WWTP in Finland and found  $2.3 \times 10^3$  N kg<sup>-1</sup>,  $1.7 \times 10^5$  N kg<sup>-1</sup>, and  $2.7 \times 10^3$  N kg<sup>-1</sup> in dry activated sludge, digested sludge, and sludge from a pilot membrane bioreactor (MBR), respectively. [Xu et al. \(2020\)](#) reported MPs from  $2.9 \times 10^3$  to  $5.3 \times 10^3$  N kg<sup>-1</sup> in dry sludge from a WWTP in Beijing, China. [Edo et al. \(2020\)](#) discovered  $1.8 \times 10^5$  N kg<sup>-1</sup> in mixed sludge and  $1.65 \times 10^5$  N kg<sup>-1</sup> in heat-dried sludge from a WWTP in Madrid, Spain. It is difficult to compare the findings of said past studies with each other, as

well as with the present study, as different analytical approaches were applied. The present study, which applied FPA- $\mu$ FTIR imaging with automated MP recognition, was capable of quantifying MPs down to a size of approximately 10  $\mu$ m. Consequently, the present study was able to identify many more MPs than in studies that manually analyzed individual particles where the size limit is at least one order of magnitude above that reported in this paper.

### 3.3. Identification and composition MPs

A total of 5599 MPs were identified in the analyzed samples with an estimated total mass of  $1.09 \times 10^6$  ng. The abundance of MPs identified in the sample matrices are provided in Table S1. The mean abundance values for identified polymers and the standard deviation from the sample matrices are presented in Table S2. The identified polymers were of 18 types: PP, PE, PEsT, PU, cellulose acetate (CA), polyvinyl chloride (PVC), polystyrene (PS), PA, pan acrylic (PAN), POM, PC, polyvinyl acetate (PVaC), acrylonitrile butadiene styrene (ABS), alkyd, acrylic, epoxy, phenoxy resin, and poly(ethyle acrylate). The most diverse polymeric composition was found in the sewage sludge where 17 polymer types were identified. 15 types were identified in the slurry, 3 in the as-received products, 4 in the emulsion, 3 in the concentrate, 8 in the distillate, and 8 in the solid residue.

Fig. 4 shows the polymer composition based on MP number and mass concentration. The polymer composition between samples was markedly heterogeneous with the exception of sewage sludge and slurry, which were comparable in composition. In terms of MP numbers, PP was the dominant polymer in the samples after the HTL process reactor with the exception of distillate. However, it must be noted that the total concentration for the distillate was very low (Figs. 2 and 3), and uncertainty on the polymer composition was therefore correspondingly high. In terms of mass, PP was the dominant polymer in emulsion and

solid phases. Viewing the two polyolefins (PP and PE) under one showed that these were the most resilient to degradation in the HTL reactor. Some polymer types, namely CA, POM, PVaC, PC, alkyd, phenoxy resin, poly(ethyle acrylate) were not detected in as-received and residual products, indicating a considerable or even total degradation in the HTL reactor.

In addition to the overall picture outlined above, there were some discrepancies in the measured data, such as only 3 polymer types were identified in the as-received products while up to 8 were identified in the refined products. The discrepancies in the particle numbers and mass quantified in the balance over the reactor are apparently similar (Fig. 3). The true causes are difficult to establish conclusively, but can be partly attributed to sample complexity, particularly for as-received and emulsion samples, which were very difficult to purify and concentrate for analysis. The main reason for this was that they held charred particles, which were challenging to separate from the sample as they frequently entangle and float on the surface of the SPT solution used in the floatation step. Agglomerated particles were broken by using air bubbles passed through the bottom of the funnel, a process which was repeated 3–5 times. This allowed for a proper extraction of MPs, yet some MPs have most likely been lost in this process. Residual charred particles might also have covered MPs while scanning with the  $\mu$ FTIR, which would have led them to be overlooked in the analysis, but the first issue is judged the greater of the two. The other products after the HTL reactor contained less charred materials, and the extraction method was found much more efficient with fewer steps for purifying the particles.

It is finally worth repeating Simon et al.'s (2018) observation that the identification of polymer chemical composition of MPs is not always straightforward, though  $\mu$ FTIR is a powerful tool and routinely used in MP research. Since MPs are exceptionally heterogeneous in size, shape, and structure, such qualities can contribute to some baseline drift and noise, which interferes with the evaluation of the obtained spectra. The

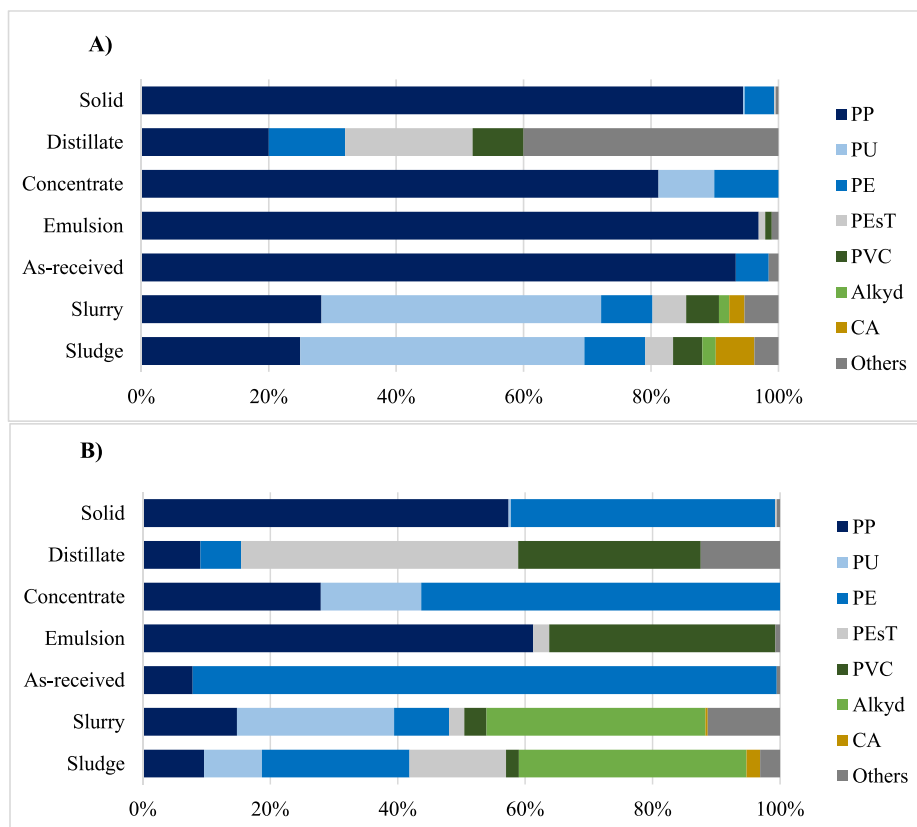


Fig. 4. Distribution of the identified polymers based on: A) particle concentration and B) estimated mass concentration. 'Others' indicates polymer types: acrylic, PS, PA, PAN, POM, epoxy, PC, PVaC, ABS, phenoxy resin and poly (ethyl acrylate).

HTL process might have affected such characteristics and accordingly introduced unknown bias into the analysis.

### 3.4. Effect of the HTL process on MPs size and mass

The size (major dimension) and the corresponding mass of the MPs were also investigated, revealing a change in the size and corresponding mass of the particles before and after the HTL process. In the sludge, approximately 83% of the particles were below 100  $\mu\text{m}$ , whereas in residual products (aqueous phase and solid residue), above 96% were below 100  $\mu\text{m}$ . The corresponding mass showed that approximately 84% and 96% of the identified particles were below 50 ng in sludge and residual products, respectively. A Shapiro-Wilk test showed that the datasets were non-normally distributed for all analyzed matrices. A Wilcoxon rank-sum tests revealed that the sizes of the identified particles were significantly different when comparing the categories before the HTL process (sludge and slurry) to those after the HTL process (as-received, emulsion, concentrate, distillate, and solid). The tests were performed at a 0.05 significance level, and p-values were found to be small ( $<2.2 \times 10^{-16}$ ). Similar low p-values were observed for the mass of the identified particles that showed a significant difference in the mass datasets. However, Wilcoxon rank-sum tests showed non-significant differences for particle size and mass between sludge and slurry with p-values of 0.14 and 0.18, respectively. The same test also showed a non-significant difference between particle size and mass of the as-received and emulsion with p-values of 0.25 and 0.23, respectively. Fig. 5 illustrates the distribution pattern of the major dimension of the identified particles. In sludge and slurry, i.e., the sample matrices before the HTL process, the particle sizes ranged between 11  $\mu\text{m}$  and 2343  $\mu\text{m}$ ; while in the products, i.e., the sample matrices after the HTL process, the sizes were between 11  $\mu\text{m}$  and 515  $\mu\text{m}$ . Likewise, Fig. 6 illustrates the distribution pattern of the estimated mass of the identified particles. In sample matrices before the HTL process, the estimated particle masses varied between 0.16 ng and 148145 ng, while MPs after the HTL process were between 0.13 ng and 2981 ng. For further details,

see supplementary materials Table S8.

### 3.5. Resistant MPs polymers over HTL process

About 76% of the number of MPs and 97% of MP mass was removed by the HTL process. Furthermore, the HTL products had a less rich polymer composition, where some polymer types were completely absent (Table S1). The most resilient polymers seemed to be the polyolefins PE and PP, but also some PU made it through the liquefaction (Fig. 7 and Fig. S1). The solid residue held the largest amount of residual MPs and accounted for approximately 85% by number and 52% by mass of all MPs after HTL.

Some studies have raised concerns about the ability of HTL to remove MPs from sludge. Prestigiacomo et al. (2021) reported partial degradation of MPs, arguing that MPs in sludge could also challenge the performance of the HTL process. While the number of studies addressing aspects of MPs in HTL of sludge is limited, several studies have assessed residual products of plastic materials treated at sub/supercritical water conditions, either individually or in combination with organic biomass materials. A co-processing of different polymers, such as PE, PP, PET and nylon with pistachio hull (biomass) was carried out by Hongthong et al. (2020). The study showed that PE and PP were highly resistant toward the specified thermochemical operating conditions. On the other hand, nylon (polyamides) and PET showed significant degradation of 84% and 53%, respectively. Raikova et al. (2019) investigated co-liquefaction of microalgae with commonly used plastics such as PE, PP, and nylon. They reported that 3.7–18% of these were converted to bio-crude, depending on loading rates. However, the remaining was either converted to solid residue (char) or remained as unreacted plastics in the solid phase. Zhao et al. (2019) found an effect of temperature on four types of electronic plastic waste. This included PC and PA, which were susceptible to degradation at lower temperatures and yielded removal rates of 82% and 74% at 250  $^{\circ}\text{C}$ , respectively. Simultaneously, high impact polystyrene (HIPS) and acrylonitrile butadiene styrene (ABS) were degraded by 88.4% and 98.4% at 350  $^{\circ}\text{C}$ , respectively. Jin et al. (2020) identified

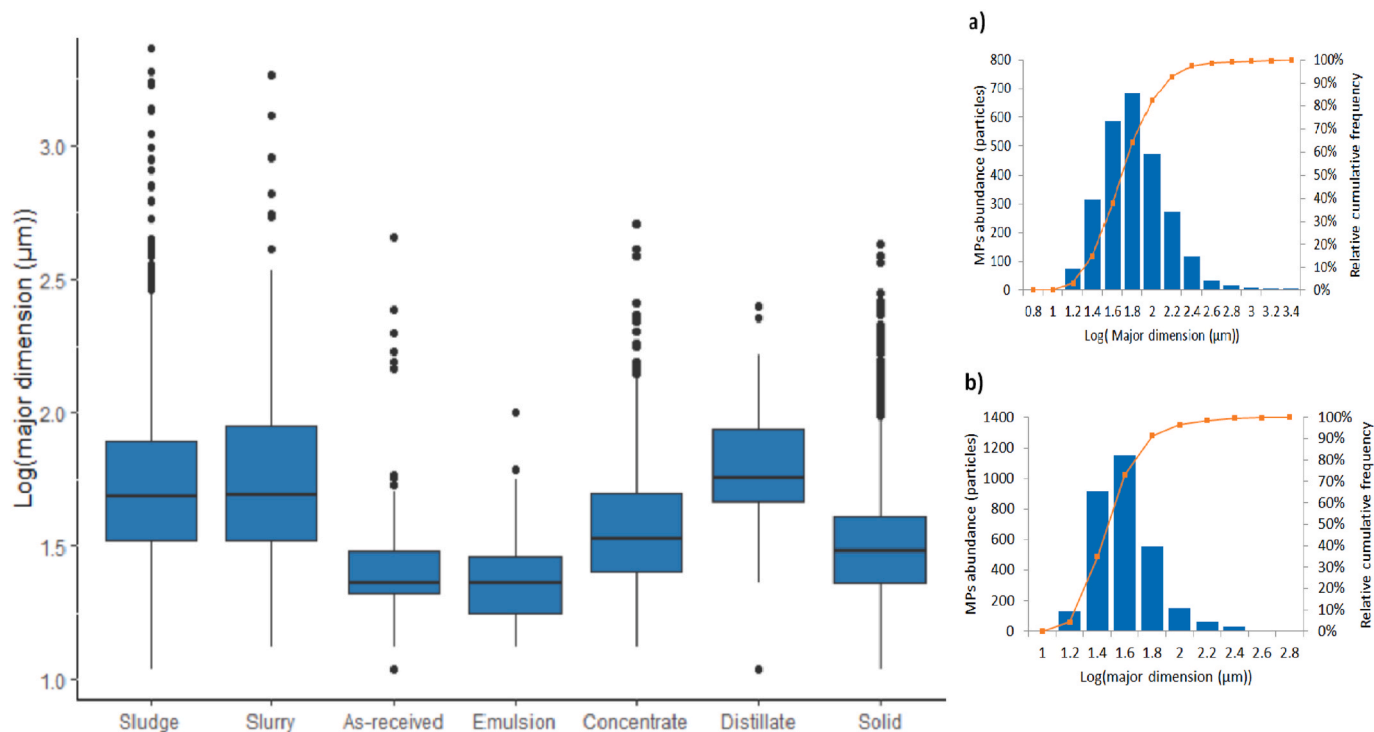


Fig. 5. Box plot for major dimension (as log of the major dimension ( $\mu\text{m}$ )) of identified MPs (a) size distribution and the relative cumulative frequency of the identified particles before HTL (in sludge and slurry) and (b) after HTL (in as-received, emulsion, concentrate, distillate, and solid residues).



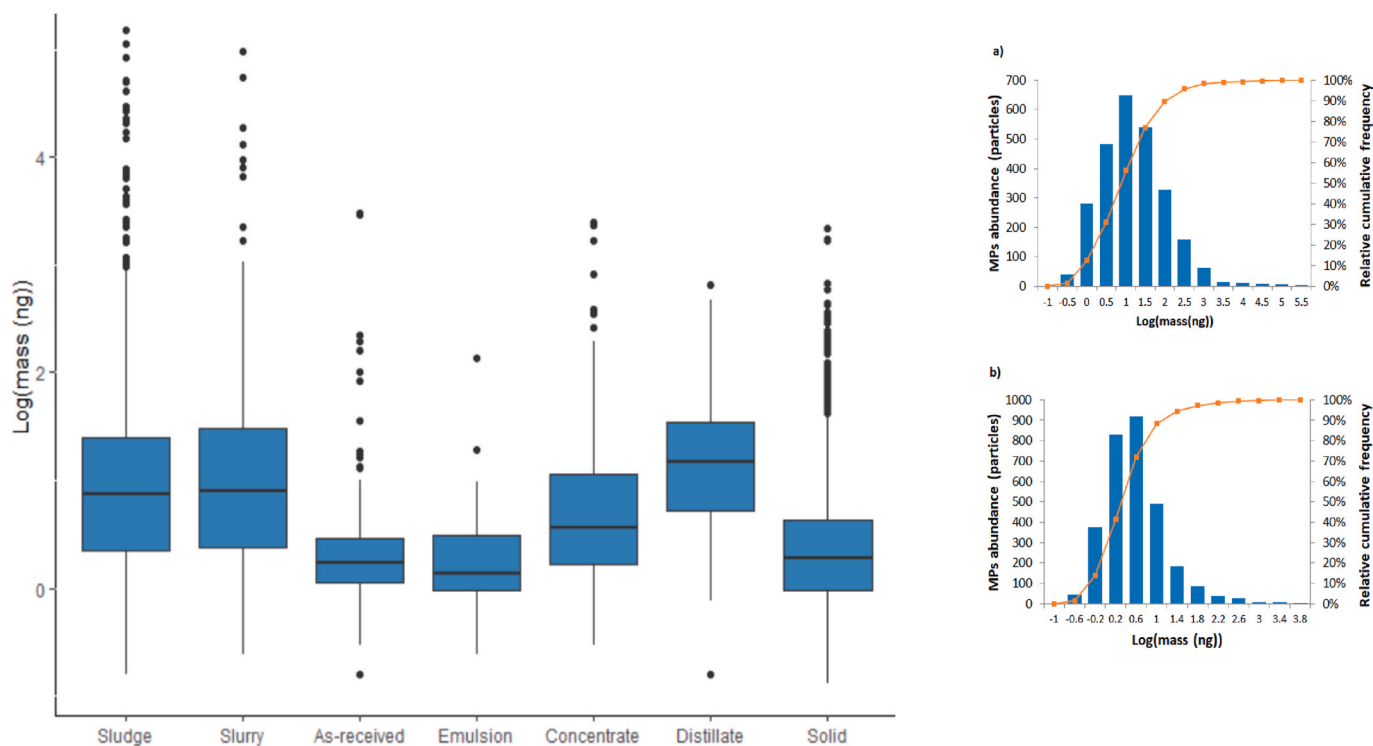


Fig. 6. Box plot for mass (as log of the mass (ng)) of identified MPs (a) mass distribution and the relative cumulative frequency of the identified particles before HTL (in sludge and slurry) and (b) after HTL (in as-received, emulsion, concentrate, distillate and, solid residues).

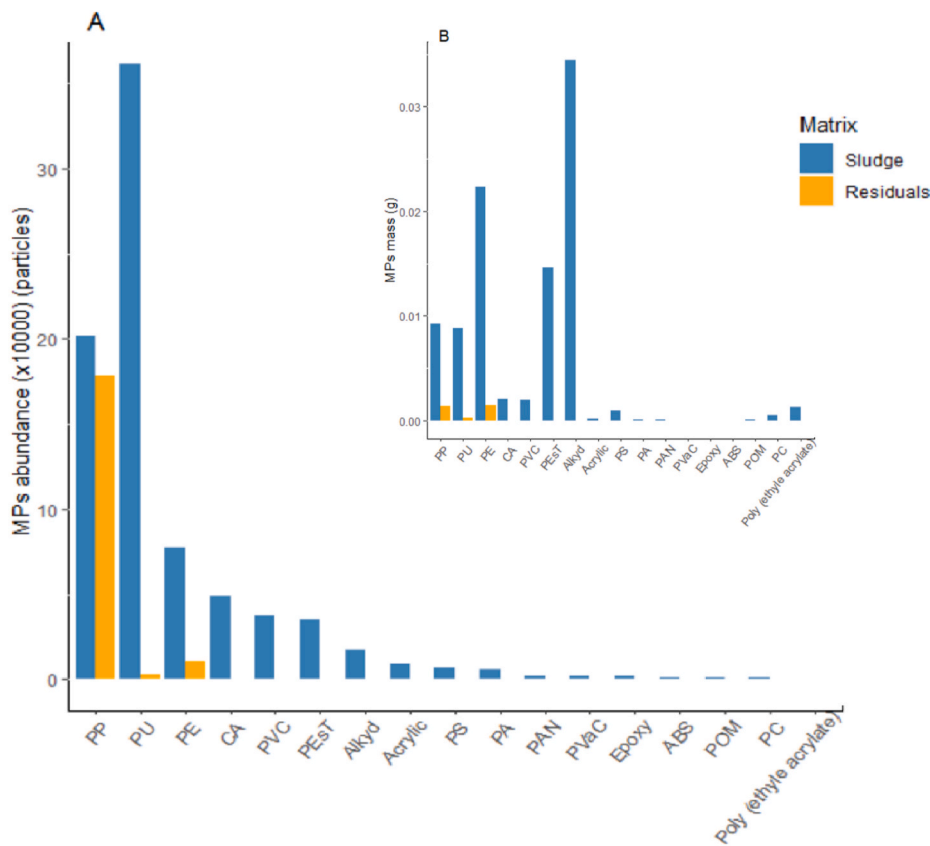


Fig. 7. MPs load reduction over HTL process A) by number and B) by mass.

PC as a temperature-sensitive plastic, which could be depolymerized at temperatures between 350 °C and 450 °C. Pedersen and Conti, (2017) found the solid residue from a HTL process between 1 wt% to 68.5 wt% for styrene-butadiene (SB), poly (vinyl alcohol) (PVA), poly (p-phenylene oxide) (PPO), poly(oxyethylene) (POM), PET, poly (butylene terephthalate) (PBT); while PC, Poly (lactic acid) (PLA), and Poly(methyl methacrylate) (PMMA) were non-detectable in the residue. They presented no information on the plastics, which seemed to be less reactive in their study (PP, PE, and PU). dos Passos et al. (2020) stated that due to the absence of heteroatoms and reactive sites in polyolefins, such as PE (HDPE and LDPE), PP, and PS, these plastic types are highly resistant to HTL processing and remained in their solid residue at over 90%.

The results of the present study, which shows that the HTL process can significantly reduce MPs in sewage sludge, demonstrates that the reported process has the potential to mitigate the MP pollution issue of this material when applying it as fertilizer on agricultural fields. The remaining amount of MPs in residual products would pose a lower environmental risk compared to the original product: sewage sludge. However, there is still room for improvement, and it is essential to further explore the viability of MPs during the HTL process in order to optimize the process.

#### 4. Conclusion

Continuous hydrothermal liquefaction of sewage sludge is an innovative field of study that generally targets the production of bio-crude. This study showed that it also has the potential to significantly reduce microplastics in sludge, adding to its sustainable use for fertilization and soil improvement. It was discovered that the HTL process reduced the amount of MPs significantly, namely by 76% as particle numbers and 97% as plastic mass. Furthermore, it was seen that some polymer types were more resistant than others, but none were unaffected by the process. In addition, the HTL process was found to decrease the particle size of the more resistant polymers, such as the PP, PE, and PU. The HTL process is thus able to not only convert sludge to bio-crude, but also mitigate the issue of the sludge being polluted by MPs, creating residual products with significantly less MP than the original product. This clearly shows that the application of the HTL process significantly reduces the movement of MPs from the sewage sludge into the terrestrial environment. The present study is the first of its kind yet still opens up many unanswered questions. Some questions relate to the analytics involved in the quantification of MPs in the rather difficult matrices of HTL products. Others questions relate to how the HTL process can be optimized to remove as much MP as possible without compromising its main objective: the production of bio-crude. Overall, however, the picture is clear: The HTL process is highly effective in producing cleaner bio-crude and solid product from the highly microplastic-polluted sludge. The process could contribute significantly to mitigate MP pollution, and enhance sustainable reuse of waste products.

#### CRedit authorship contribution statement

**Rupa Chand:** Conceptualization, carried out the experiments, Methodology, Formal analysis, Writing – original draft. **Komeil Kohansal:** Formal analysis, Writing – review & editing, Writing – original draft, Assisted in conducting sampling and sent to the lab for analysis and, contributed in the original. **Saqib Toor:** Writing – original draft, Coordinated the project work, revised the work and reviewed the. **Thomas Helmer Pedersen:** Conceptualization, the project plan, coordinated the project work, revised the work and reviewed the, Writing – original draft. **Jes Vollertsen:** Supervision, Writing – review & editing, Equally, all authors contributed for the final manuscript.

#### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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#### Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jclepro.2022.130383>.

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