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Process water properties from hydrothermal carbonization of chemical sludge from a pulp and board mill

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Abstract

Hydrothermal carbonization (HTC) can be used to break down sludge structure and generate carbonaceous hydrochar suitable for solid fuel or value-added material applications. The separation of char and the reaction medium however generates a filtrate, which needs to treated before potential discharge. Thus, this work determined filtrate properties based on HTC temperature and sludge moisture content and estimated the discharge emissions and the potential increase in analyte loads to an industrial wastewater treatment plant based on derived regression models. Direct discharge of HTC filtrate would significantly increase effluent emissions at the mill, indicating the filtrate treatment is crucial for the future implementation of HTC at pulp and paper mills. Recycling the HTC filtrate to the wastewater plant would lead to only a nominal increase in effluent flow, but would increase the suspended solids, BOD, COD and total nitrogen loads by 0.1-0.8%, 3.8-5.3%, 2.7-3.1% and 42-67%, respectively, depending on HTC temperature.

Keywords: biosolids; experimental design; hydrothermal treatment; multiple linear regression; principal component analysis; wastewater treatment.

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1. Introduction

Sludge management represents a significant challenge for the forest industry. Sludge residues from wastewater treatment plants are currently the most important solid waste streams produced at pulp and paper mills. Wastewater treatment within the industry is generally performed through mechanical, biological or chemical methods generating sludge residues with different properties. The low solids content and the physical form of sludge however makes their handling generally problematic. Primary sludge from mechanical clarification or biosludge from activated sludge plants can in some installations be incinerated in the solid fuel or recovery boilers after mechanical dewatering or evaporation. Chemical sludge from the treatment of coating effluents, addition of chemicals or separate tertiary treatment is more difficult to dewater, pump or handle at treatment or final disposal sites (Hynninen et al., 2008). In Sweden, approximately 22,000 tons of dry chemical sludge was produced within pulp and paper mills in 2016. One third was incinerated while the rest was used in material applications such as landfill construction (Swedish Forest Industries Federation, 2017).

Hydrothermal carbonization (HTC) can be used to break down sludge structure and generate carbonaceous hydrochar more suitable for solid fuel or value-added material applications (Alatalo et al., 2013; Danso-Boateng et al., 2015a; Xu & Jiang, 2017). The use of subcritical water under elevated temperature and pressure does not require prior drying of sludge and improves respective drying properties and destroys potential pathogens (Mäkelä et al., 2016; Peterson et al., 2008; Wang et al., 2014). Partial dissolution of organic compounds during HTC however requires further treatment of the subsequently separated filtrate or condensate before potential discharge. Laboratory hydrothermal experiments are generally performed with electrically heated autoclaves, as both external heating with auxiliary fuels or internal heating with steam is being used in continuous or batch-type industrial installations (Hitzl et al., 2015; Prawisudha et al., 2012). The use of steam can enable partial drying of the carbonized feed but will generate a condensate which will need to be further considered.

One of the challenges for the application of HTC is respective integration to existing industrial environments and the management of generated process water. Several research groups have thus determined the effects of process water utilization in various applications. Recycling the separated filtrate back to the reactor can increase char mass and energy yields with feedstocks where additional water for HTC is required (Catalkopru et al., 2017; Kambo et al., 2017). The decomposition of organic compounds during HTC generates organic acids, which lower liquid pH and can further catalyse hydrolysis and decarboxylation reactions upon recycling. The separated filtrate also contains hydrolysed sugars and can be used for methane production by anaerobic digestion (Danso-Boateng et al., 2015a; Erdogan et al., 2015; Villamil et al., 2017). Wirth et al. reported no significant differences between mesophilic and thermophilic digestion and suggested co-digestion of condensate due to increased phenol concentrations and comparatively lower gas production (Wirth & Reza, 2016; Wirth et al., 2015). Wet oxidation of separated filtrate for destruction of chlorinated aromatics not degraded by HTC, and use in acidification of animal slurries have also been reported (Keskinen et al., 2017; Riedel et al., 2015).

Pulp and paper mills represent a special case for the application of HTC as a wastewater treatment plant already exists on-site. The easiest way to treat the separated filtrate would thus be to recycle it back to wastewater treatment plant, generating a circulating carbon load between wastewater treatment and the HTC reactor. However, no research has been published on the effects of HTC conditions on filtrate properties that are important for industrial wastewater treatment. HTC conditions govern char and filtrate properties and affect potential filtrate recycling. The objective of this work was to determine filtrate properties based on HTC of chemical sludge from a pulp and board mill. Laboratory experiments were performed to systematically determine the effects of HTC conditions on filtrate properties based on multivariate and multiple linear regression models. The attained results are important for evaluating the potential of filtrate recycling to a wastewater treatment plant and the overall feasibility of sludge carbonization at pulp and paper mills.

2. Materials and methods

2.1 Sludge sampling and preparation

Chemical sludge was sampled from a Swedish pulp and board mill producing chemical pulp and paper board. The wastewater treatment plant included a large aerated settling pond to which all effluent streams were directed regardless of prior treatment. The effluent from the aerated lagoon was partially or entirely led to chemical treatment where aluminum sulphate was used as the main flocculating agent. After sampling, sludge samples with different moisture contents were prepared by dilution with deionized water to determine the effects of sludge moisture content on filtrate properties.

2.2 Sludge carbonization

The experiments were performed in a 0.28 L Büchi Limbo (Büchi AG) reactor fitted with a magnetic stirrer. Prepared sludge samples of 200 g were heated to 180-260 °C with a PID controlled electrical heating block after flushing with nitrogen. The approximate heating rate was 2.5-4.0 C min^{-1} depending on target temperature. Reactor pressure was observed from a pressure gauge and was approximately equal to the saturated vapour pressure of water at respective temperatures. After an isothermal holding time of 1 hour the reactor was cooled to 100 °C and placed in a cold-water bath. After cooling to 40 °C, the non-condensable gases were vented and the char and filtrate were separated by vacuum filtration through a Whatman 25 μm filter paper. The individual experiments were organized according to a central composite design in which carbonization temperature and sludge moisture content were varied on three different levels (Table

1). The final design was composed of 11 experiments including three repeated experiments in the design center.

Table 1: The carbonization experiments.

Experiment n:o	Reactor temperature (°C)	Moisture content (kg H_2O kg^{-1} db)	Dry solids (%)
1	180	10.2	8.9
2	260	10.2	8.9
3	180	4.4	18.5
4	260	4.4	18.5
5	180	7.3	12.0
6	260	7.3	12.0
7	220	10.2	8.9
8	220	4.4	18.5
9	220	7.3	12.0
10	220	7.3	12.0
11	220	7.3	12.0

db = dry basis.

2.3 Analyses

After solid and liquid separation, the filtrate pH values were measured with a Mettler-Toledo EL20 instrument (Metler-Toledo LLC). The filtrate samples were then sent to an external laboratory certified by the national accreditation body SWEDAC. The total nitrogen and phosphorus contents were determined according to international standards SS-EN ISO 11905-1:1998 and SS-EN ISO 6878:2004, respectively. The seven-day biological oxygen demand (BOD) was determined according SS-EN 1899-1:1998 and the total organic carbon according to EN 1484:1997. The suspended solids in the filtrate were determined according to SS-EN 872:2005 based on filtration. For calculating the carbon and nitrogen yields in the filtrates, the CHN contents of the untreated sludge and dried chars were \determined according to SS-EN 15407:2011 after the char samples were dried at 105 °C overnight and manually ground in a mortar. For determining sample properties on a dry-ash free (daf) basis, the respective ash contents were measured by loss on ignition at 550 °C according to SS-EN-14775. The above-mentioned filtrate analyses were chosen as they are commonly used within the pulp and paper industry to estimate effluent properties before and after wastewater treatment.

2.4 Data analysis

After the analyses, a 11 × 17 data matrix including individual experiments as row objects and experimental conditions and sample properties as individual columns was compiled. Char solid yield, carbon yield and filtrate carbon yield were calculated as previously described (Mäkelä & Yoshikawa, 2016). Filtrate chemical oxygen demand (COD) was estimated based on measured TOC by calculating the amount of oxygen required to completely oxidize organic carbon:

$$\mathrm{COD} = m_C \frac{O_{2,mw}}{C_{mw}} \tag{1}$$

where m_C denoted the mass equivalent of organic carbon (mg L^{-1}) and $O_{2,mw}$ and C_{mw} the molecular weights of O_2 and carbon (g mol^{-1}), respectively. COD was used for estimating the BOD/COD ratios of the filtrate samples. Correlations between the experimental variables and sample properties were determined based on a principal component model:

$$\mathbf{X} = \sum_{i=1}^{n} \mathbf{t}_i \mathbf{p'}_i + \mathbf{E}_n \tag{2}$$

where $\mathbf{X}$ denoted the preprocessed data matrix, $\mathbf{t}_i$ the score vectors, $\mathbf{p}_i$ the orthonormal loadings and $\mathbf{E}_n$ a residual matrix after n components. The data were preprocessed by subtracting the mean and dividing by the standard deviation of each column to enable comparing variables given in different units.

Individual multiple linear regression models were also determined for selected variables separately by solving the multiple linear regression equation:

$$\mathbf{y} = \mathbf{Zb} + \mathbf{e} \tag{3}$$

by minimizing the sum of squares of model residuals through the least-squares estimate:

$$\mathbf{b} = (\mathbf{Z}'\mathbf{Z})^{-1}\mathbf{Z}'\mathbf{y} \tag{4}$$

where **y** denoted a variable vector of sample properties, **Z** a design matrix of coded experimental conditions including the respective interaction and quadratic columns, **b** a vector of model coefficients and **e** a vector of model residuals (Mäkelä, 2017). Statistically insignificant ($p > 0.10$) model terms were excluded based on an F test. Model fit to the experimental data was assessed through the R^2 value:

$$R^2 = \frac{SS_{mod}}{SS_{tot}} \tag{5}$$

where SS_{mod} denoted the sum of squares, or data variation, explained by the model and SS_{tot} the total sum of squares of **y** around the mean. Data analysis and plotting were performed with the Matlab R2017b (The Mathworks, Inc.), Design-Expert 9 (Stat-Ease Inc.) and OriginPro 2017 (OriginLab Corp.) software packages.

3. Results and Discussion

Carbonization increased the carbon content of chemical sludge from 49% to 55-65% (daf) depending on the experimental conditions. Char solid and carbon yields were in the range 63-77% and 64-81%, respectively, and suggested increased dissolution of organic compounds at higher temperatures and higher sludge moisture contents. Char ash contents were in the range 43-53% with respective ash yields of 75-86%. Filtrate properties were mainly governed by the moisture contents of the sludge feed as a higher moisture content generated a more diluted filtrate. Filtrate carbon yields based on measured TOC were in the range 9-18% and indicated that the dissolution of organic carbon from the sludge feed also increased at higher moisture contents. Respective filtrate COD values were in the range 16,000-47,000 mg L^{-1}.

Suspended solids in the filtrate were in the range 95-2000 mg L^{-1} and decreased with higher temperatures coupled with an increase in BOD (7400-19,000 mg L^{-1}). This increased the BOD/COD ratio (0.4-0.6) of the filtrate and showed that its biological decomposition was improved at higher temperatures. This was an important finding as higher HTC temperatures generally have a negative effect through increased carbon losses to the liquid medium. Higher filtrate BOD also correlated with increased total nitrogen (1200-4300 mg L^{-1}), which can be an advantage for the bacterial activity of aerobic wastewater treatment plants. Filtrate phosphorus contents were in the range 0.6-1.3 mg L^{-1}. Taking into consideration daily sludge generation and effluent emissions at the mill, direct discharge of the HTC filtrate would increase effluent TOC, COD and suspended solids emissions by an average of 2-14%. However, the increase in effluent BOD and total nitrogen emissions would be significantly higher, on average 59% and 106%, respectively. Treatment of the HTC filtrate is thus crucial for implementing sludge HTC at pulp and paper mills.

The determined PCA model was useful for illustrating correlations between carbonization conditions and obtained char and filtrate properties. The first two principal components explained 88% of variation in the data matrix and illustrated the effects of reactor temperature and the initial moisture content of chemical sludge on char and filtrate properties. In general, variables which have similar loadings in principal component space show a positive correlation. As illustrated in Fig. 1a, higher reactor temperatures increased char carbon content, filtrate pH and BOD/COD ratio. Although HTC initially lowers liquid pH due to the generation of organic acids, similar effects on increasing pH with higher reactor temperatures have also been reported during HTC of municipal sludge (Xu & Jiang, 2017). Higher temperatures also resulted in decreased char solid and carbon yields and lower suspended solids in the filtrate (Fig. 1a). The moisture content of sludge mainly increased filtrate mass and carbon yields and decreased BOD and total nitrogen due to sample dilution. Filtrate BOD and nitrogen contents expressed as mg g^{-1} daf sludge however showed that both reactor temperature and sludge moisture content had an effect on the decomposition of the sludge feed and resulting filtrate properties (Fig. 1a). The third principal component explained an additional 6% of the remaining data variation and mainly seemed to separate increasing suspended solids of the filtrate (Fig. 1b). A correlation matrix useful for data interpretation is given in the Supplementary material.

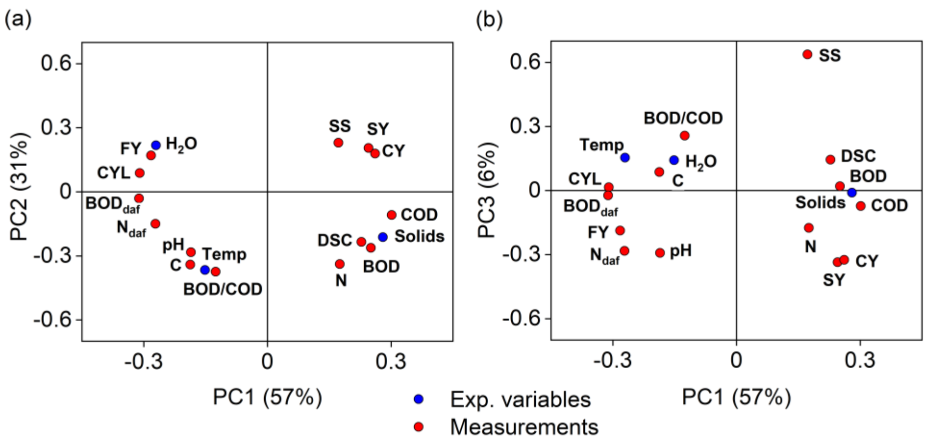

Fig. 1: Loadings of (a) the first and the second and (b) the first and the third principal components illustrate correlations between carbonization conditions and sample properties. Abbreviations: Temp, reactor temperature (°C); H_2O, sludge moisture content (kg H_2O kg^{-1} db); Solids, sludge dry solids (%); SY, char solid mass yield (% db); DSC, char dry solids content (%, wb); C, char carbon content (% daf); CY, char carbon yield (%); FY, filtrate mass yield (%, wb); CYL; filtrate carbon yield (%); SS, filtrate suspended solids (mg L^{-1}); BOD, filtrate BOD (mg L^{-1}); BOD_{daf}, filtrate BOD (mg g^{-1} daf); BOD/COD, filtrate BOD/COD ratio (-); N, filtrate nitrogen content (mg L-1); N_{daf}, filtrate nitrogen content (mg g^{-1} daf).

Individual regression models for selected sample properties were also determined based on carbonization conditions. The final models fit the data relatively well and explained 79-100% of the experimental data. Only the model for total nitrogen content showed indications of potential lack of fit ($p < 0.10$) (Supplementary material). Reactor temperature was found statistically insignificant only for the dry solids content of char ($p = 0.32$), as sludge moisture content was statistically insignificant only for the determined suspended solids ($p = 0.27$) and BOD/COD ratios ($p = 0.40$). One experiment was identified as an outlier based on an abnormal suspended solids content and was subsequently removed from the final suspended solids model. This increased the R^2 value from 0.63 to 0.96 and resulted in a statistically significant model. It should be noted that a limited volume of filtrate was available for the determination of suspended solids, which led to low solids recoveries after filtration and created a level of uncertainty to the suspended solids results. The final regression models were used for predicting sample properties as a function of carbonization conditions within the experimental design range.

The main task of wastewater treatment plants is to remove suspended solids, nutrients and reduce the oxygen demand of the effluent (Bourgin et al., 2018). Wastewater treatment in the pulp and paper industry is often performed through biological methods, where organic matter is broken down by microbes in the presence of oxygen. Both activated sludge processes and aerated lagoons can be used for this purpose, the main difference is whether part of the generated sludge is actively recycled to sustain microbial growth. Nitrogen and phosphorus are often added for biological treatment in the form of urea and phosphoric acid as insufficient nutrient levels lead to sludge with poor settling properties, lower reductions in oxygen demand, and reduced sludge formation (Hynninen et al., 2008). As illustrated in Fig. 2, the results showed that higher HTC temperatures generated a filtrate more suitable for biological treatment based on increased BOD/COD (Fig. 2j). Filtrate BOD:N:P ratios were in the range 100:16-25:0 suggesting that no additional nitrogen would be needed for potential treatment of the filtrate. Nitrogen speciation however depends on the feedstock and carbonization conditions (Kruse et al., 2016; Reza et al., 2016). Reza et al. (2016) reported low ammonium in the total nitrogen content of filtrate samples from HTC of cow manure. Kruse et al. (2016) found both nitrate and ammonium nitrogen in filtrate samples from HTC of carrot green and algae. Nitrate concentrations were higher than those of ammonium as organic nitrogen was significant only in the case of algae. More work is required to determine if the dissolved nitrogen in the filtrate from HTC of chemical sludge can be beneficially utilized by microbes at biological wastewater treatment plants.

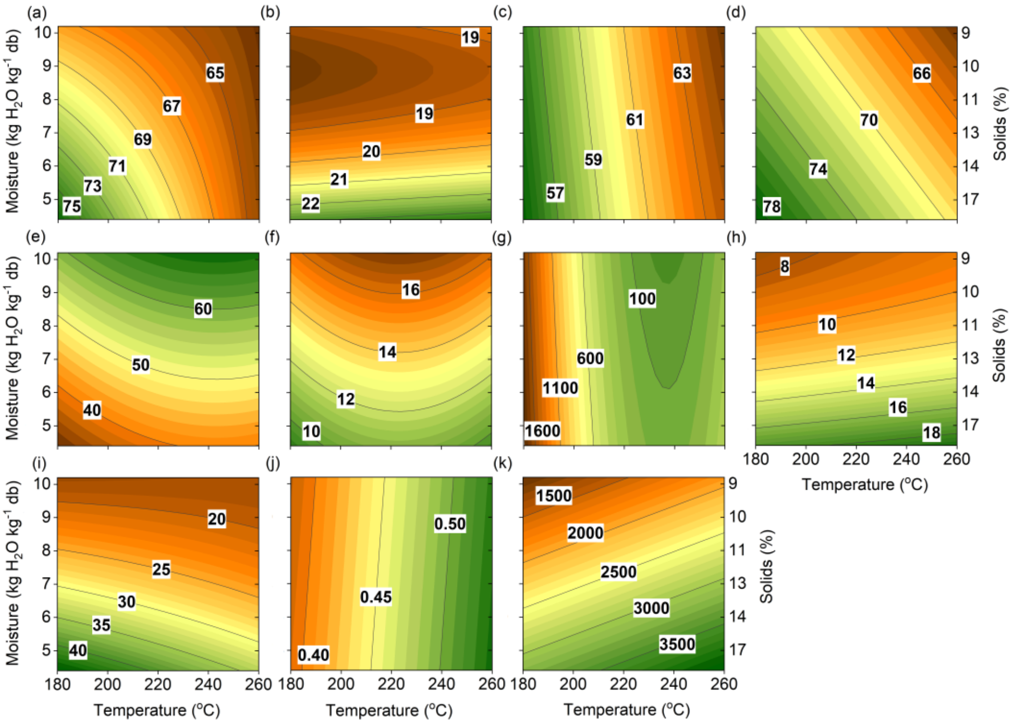

Fig. 2: Response surfaces based on the individual regression models illustrate sample properties based on carbonization conditions: (a) char solid mass yield (%, db); (b) char dry solids content (%,wb); (c) char carbon content (%, daf); (d) char carbon yield (%); (e) filtrate mass yield (%, wb); (f) filtrate carbon yield (%); (g) filtrate suspended solids (mg L^{-1}); (h) filtrate BOD (10^3 mg L^{-1}); (i) filtrate COD (10^3 mg L^{-1}); (j) filtrate BOD/COD ratio; (k) filtrate nitrogen content (mg L^{-1}).

In general, HTC of chemical sludge at a pulp and paper mill would be best performed after mechanical dewatering. A higher solids content maximizes the quantity of treated solids and provides a higher char yield for a given reactor capacity (Danso-Boateng et al., 2015b; Mäkelä & Yoshikawa, 2016). As illustrated by the results, direct discharge of the HTC filtrate would significantly increase effluent emissions at the mill, indicating that the treatment of the HTC filtrate is crucial for the implementation of sludge HTC at a pulp and paper mill. It is thus useful to estimate the additional load to the wastewater treatment plant if the filtrate would be recycled. If the filtrate properties at different HTC temperatures can be predicted, the additional load to the wastewater treatment plant from filtrate recycling can be estimated given that the current effluent characteristics are known.

The potential increase in effluent loads to the wastewater treatment plant was estimated based on the average mill data from 2016 (data not shown). Filtrate properties were calculated based on the determined regression models assuming that all of the sludge generated within a day would be HTC treated at a dry solids content of 18.5%. This corresponds with the approximate dry solids of dewatered sludge at the mill. Based on the estimations, recycling of the HTC filtrate would lead to a nominal increase in the actual effluent flow (0.04-0.05%). The HTC filtrate is however significantly more concentrated than the average effluent. As illustrated in Fig. 3a, the increase in the respective BOD and COD loads to the wastewater treatment plant would be in the range 3.8-5.3% and 2.7-3.1% depending on HTC temperature. The increase in suspended solids would be lower, in the range 0.1-0.8% (Fig. 3b). The highest increase would be in the load of total nitrogen, estimated as 42-67% (Fig. 3b). This additional nitrogen can affect the total nitrogen emissions in the discharged effluent, which is however difficult to estimate. Future work should take into consideration nitrogen speciation and the removal efficiencies of individual analytes upon recycling of the HTC filtrate.

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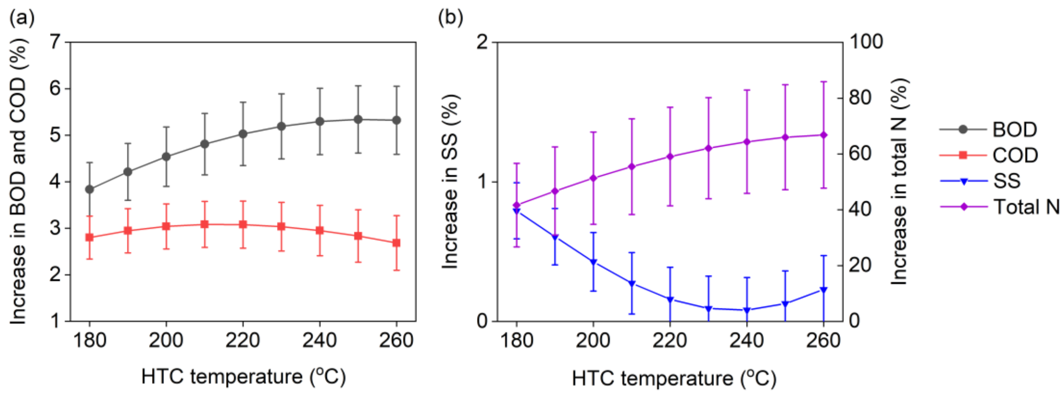

Fig. 3: Estimated increase in (a) BOD and COD and (b) suspended solids (SS) and total nitrogen loads to the wastewater treatment plant with recycling of the HTC filtrate. Error bars denote the 95% confidence intervals of prediction based on the respective regression models. Uncertainties related to the dry solids content of separated char and mass yields of the filtrate were neglected.

Conclusions

Direct discharge of the HTC filtrate would significantly increase effluent emissions, indicating the filtrate treatment is crucial for the future implementation of HTC at pulp and paper mills. Higher HTC temperatures decreased suspended solids and increased the biological decomposition of the filtrate, which is beneficial for biological treatment. BOD also correlated with increased total nitrogen, potentially removing the need for nitrogen additions upon recycling. Recycling the filtrate to the wastewater plant would lead to a nominal increase in effluent flow, but would increase the suspended solids, BOD, COD and total nitrogen loads by 0.1-0.8%, 3.8-5.3%, 2.7-3.1% and 42-67%, respectively.

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