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Experimental and statistical modeling of the effect of process modification and wastewater characterization on greenhouse gas emissions for a dairy industry wastewater treatment plant: A minimization approach

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ABSTRACT

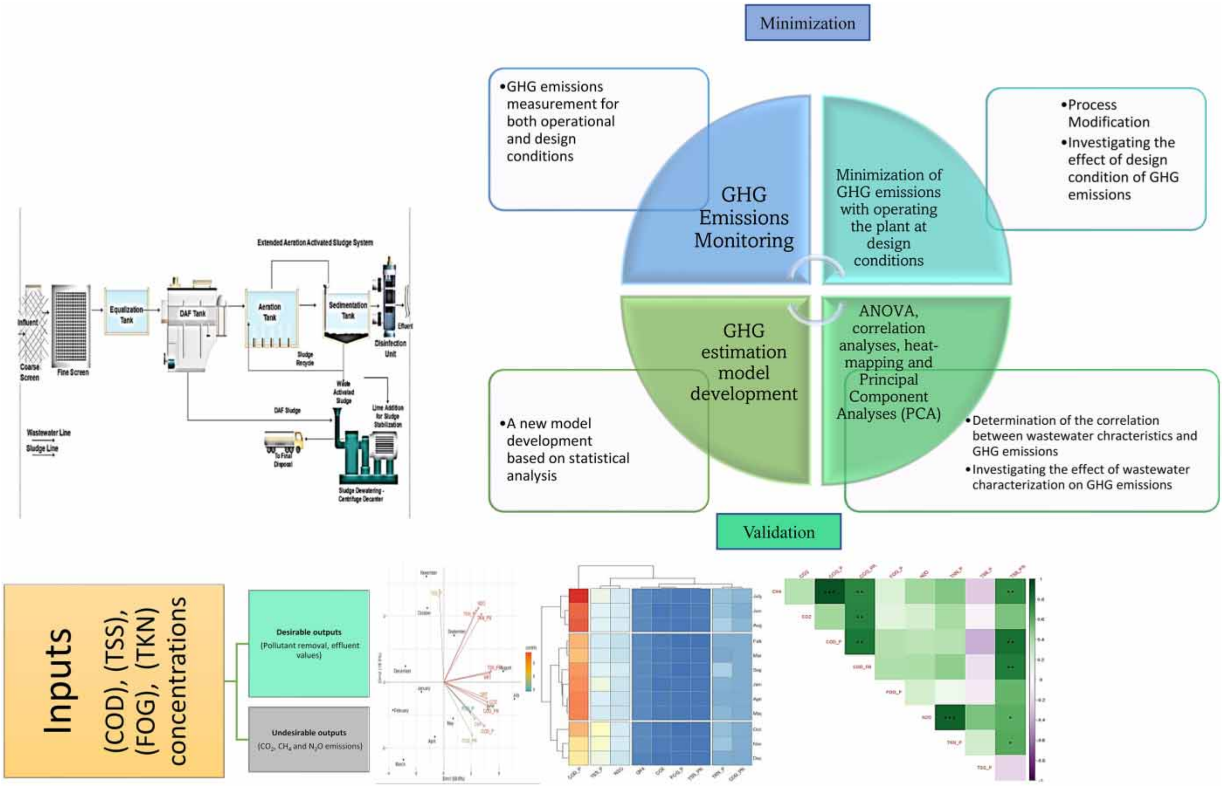
This study aimed to determine the effect of design conditions and wastewater characterization on greenhouse gas (GHG) emissions from an industrial wastewater treatment plant. Analysis of variance, correlation analyses, heat-mapping, and principal component analyses (PCA) were performed to determine the correspondence between GHG emissions and wastewater characterization. Then, a new empirical model based on the correlation of wastewater characterization has been developed. This study has concentrated on using process modification to mitigate GHG emissions. If an aeration tank is operated at 36 h of hydraulic retention time and 20 days of solid retention time at design conditions, an average reduction of 45.4, 45.3, and 45.2% in carbon dioxide (CO_2), methane (CH_4), and nitrous oxide (N_2O) emissions, respectively, have been ensured. According to correlation analysis, a moderately significant positive correlation was found between effluent chemical oxygen demand values and CO_2 and CH_4 values ($r = 0.909$, $r = 0.937$). N_2O emissions were closely related to Total Kjeldahl Nitrogen input values ($r = 0.876$). GHG emissions have been calculated using this correlation, and the results overlapped with the monitoring values. The estimated results of GHG emissions based on wastewater characterization have converged to in situ monitoring results, by an average of 82%.

Key words: design conditions, greenhouse gas, industrial wastewater treatment, process modification, reduction

HIGHLIGHTS

- The mitigation of GHG emissions was aimed at using process modification in terms of the European Green Deal.
- Analysis of variance, correlation analyses, heat-mapping, and principal component analyses (PCA) were performed to determine the correspondence between GHG emissions and wastewater characterization.
- A new empirical model based on the correlation of wastewater characterization has been developed.

GRAPHICAL ABSTRACT



1. INTRODUCTION

In recent years, corrective preventions and policies have been applied to develop system performance by mitigating greenhouse gas (GHG) emissions due to raising attention on the sustainable operation of wastewater treatment plants (WWTPs) (Yapıcıoğlu 2018). The management of WWTPs has concentrated on mitigating operating costs while obtaining effluent discharge limits and minimum GHG emissions (Metcalf & Eddy 2014). The effluent quality and GHG emissions of WWTPs have been mainly influenced by operating conditions, which are hydraulic retention time (HRT) and solid retention time (SRT) for WWTPs. This topic had significant attention worldwide in the last decades. GHG emission generator points have critical importance in determining economic performance in terms of GHG emissions. According to the European (EU) Green Deal, GHG emissions should be reduced in considerable amounts, and this reduction of GHG emissions would lead to economic wealth in the world (EU 2018). WWTPs should obtain incentives to enhance and carry out climate-neutral process management to align with the Green Deal objectives. Especially, industrial WWTPs are an essential element of the EU Green Deal and circular economy (EU 2018). According to the EU Green Deal, there will be a 55% reduction in total GHG emissions by 2030. Within the scope of the Green Deal, the EU envisages reducing the GHG emission value from water treatment by 30% in the next 10 years. From this perspective, GHG emissions should be taken under control and reduced for these types of plants (Adebayo *et al.* 2021; Moretti *et al.* 2021; Pahunang *et al.* 2021; Udemba *et al.* 2021; Voss *et al.* 2021).

Industrial WWTPs can be regarded as one of the GHG emission resources due to high organic wastewater content and high energy consumption (Galve *et al.* 2021; Hashem *et al.* 2021; Kumar *et al.* 2021; Pata & Kumar 2021; Asmal *et al.* 2022; Raji & Packialakshmi 2022). From this perspective, this study mainly aimed to mitigate GHG emissions from a dairy industry WWTP in terms of the EU Green Deal. There are several GHG emission mitigation techniques such as carbon capture systems, innovative wastewater treatment technologies (biochar, microbial fuel (MFC) cell, and microbial electric synthesis (MES) applications), microalgal technology, carbon-neutral processes, as well as process and operational conditions' modification (Qambrani *et al.* 2017). Industrial WWTPs have high first investment and operating costs. Due to this reason, process modification or optimization for available treatment processes is the best alternative for reducing GHG emissions, rather than carbon capture systems or innovative wastewater treatment processes, if the discharge standards are obtained with the available treatment systems. In this context, process modification has been fulfilled in order to obtain possible reductions in GHG emissions of a dairy WWTP, in this study. Operational conditions (HRT and SRT) of the aeration tank have been modified to design conditions with the aim of reducing GHG emissions.

This paper aimed to investigate the effect of wastewater characterization and process modification on GHG emissions from an industrial WWTP within the scope of water–energy nexus. The focus of the study is to use process modification in order to reduce GHG emissions and to determine and validate the correspondence between GHG emissions and wastewater quality. The argument of this study is that the mitigation of GHG emissions was aimed at using process modification in terms of the European Green Deal. The major argument of this paper is the validation of the minimization of GHG emissions by applying design conditions with *in situ* GHG monitoring. Statistical and experimental results have been theoretically discussed and modeled at the end of the study. Analysis of variance (ANOVA), correlation analyses, heat mapping, and principal component analyses (PCA) were performed to determine the correspondence between GHG emissions and wastewater characterization. From this point of view, a benchmarked assessment has been applied to define the correspondence of GHG emissions and operational conditions as well as influent and effluent quality. In this context, a new empirical model that depended on the correlation of wastewater characterization has been developed. From this point of view, GHG emissions have been figured out using this correspondence with wastewater characterization and the results have been compared with the *in situ* monitoring values. In this paper, chemical oxygen demand (COD), total suspended solid (TSS), fats, oil, and grease (FOG), and Total Kjeldahl Nitrogen (TKN) were considered as inputs, pollutant removal (effluent values) as desirable outputs, and GHG emissions were regarded as undesirable outputs. These key parameters have been selected for the dairy WWTP. Especially COD, FOG, TSS, and TKN are the main indicator pollutant parameters for dairy industrial plants (Metcalf & Eddy 2014).

This study is unique and novel in that the effect of design conditions on GHG emissions for an industrial WWTP in terms of the EU Green Deal was investigated using various statistical approaches and *in situ* GHG emission monitoring. Also, the other originality of this work is that process modification was investigated as a GHG emission minimization technique. There is a gap in the literature on this topic. So, this study could be a guide for similar industrial WWTPs, which have highly organic content in terms of the reduction of GHG emissions using process modification. This study has dealt with the investigation of the optimal operation of an industrial WWTP in order to mitigate GHG emissions. In this context, process modification could be a GHG emission minimization technique (Sweetapple *et al.* 2014; Barbu *et al.* 2017). For the extended aeration (EA) process, process modification has been fulfilled. First, process conditions were modified in terms of HRT and SRT, and then, CO_2, CH_4, and N_2O emissions were monitored in this plant.

For WWTPs, optimal operating conditions could be defined using optimization methods coupled with an estimative mathematical model of the WWTP (Kim *et al.* 2015). A few studies have investigated optimization solutions that carried out the analysis or operational design of WWTPs. Several researchers have concentrated on model calibration, simulation, and energy efficiency in WWTPs (Kim *et al.* 2015; Kyung *et al.* 2015; Yapıcıoğlu & Demir 2021). Kim *et al.* (2015) studied the optimization of operating conditions in terms of GHG emissions. Another study is related to Kyung *et al.* (2015), in which they used model optimization. Yapıcıoğlu & Demir (2021) investigated the reduction in GHG emissions, and the effects of design and operational conditions on GHG using Monte Carlo simulation. In this study, ANOVA, correlation analyses, heat mapping, and PCA were simultaneously performed to determine the correspondence between wastewater characterization and GHG emissions. Also, this study is unique in that *in situ* GHG emissions were measured under design parameters and operational conditions for a full-scale industrial WWTP. The validation of the proposed model has been ensured by *in situ* monitoring of GHG emissions for design and operational conditions. Also, the effect of wastewater characterization was investigated on GHG emissions. Data interpretation has been done according to correlation analysis. GHG emissions have been also estimated based on this correlation resulting from statistical analysis, which defines the relationship of GHG emissions and wastewater characteristics. In this context, a specific new calculation model has been developed in this paper. Also, this study is original in that model validation has been ensured with *in situ* GHG emission monitoring in the plant. Zhou *et al.* (2022) have used a normalizing method for GHG emission and wastewater characterization in a municipal plant. This study confirms statistical analysis with *in situ* monitoring of GHG emissions using the closed chamber method. Huang *et al.* (2023) have used the correspondence between GHG emissions and pollutant parameters in a municipal

WWTP. They focused on pollutant removal to determine the correspondence with GHG emissions. On the contrary, statistical analyses and *in situ* GHG emission monitoring have been applied in this study.

2. MATERIAL AND METHODS

In this study, a conceptual model has been designed (Figure 1) to define the stages of research. A scope has been defined for GHG emission monitoring and estimation in this paper. First, GHG emissions have been monitored for both EA and dissolved air flotation (DAF) processes, and CO_2, CH_4, and N_2O concentrations for the available operational conditions were determined. DAF and extended aeration tanks have been defined as the GHG emissions resources in this plant. GHG emissions have been figured out using a simple equation based on the IPCC approach. In the second stage of the study, process modification has been carried out for the EA process to investigate the minimization of GHG emissions. The process conditions have been adjusted according to the design conditions, which are 36 h of HRT and 20 days of SRT. Then, statistical analyses that contain correlation analyses, heat mapping, and PCA have been applied in order to determine the correspondence between the GHG emission and wastewater characterization. In this stage, a new GHG emission estimation tool has been developed based on the correlation in the result of statistical analysis. The most effective wastewater parameter has been corresponded with GHG emissions, considering the highest Pearson correlation coefficient in the model. Finally, a benchmarking evaluation has been performed to validate the effect of wastewater characterization on GHG emissions, which has been presented at the end of statistical analyses.

2.1. Process configuration and modification of the plant

An EA-activated sludge system has been performed for the removal of organic and suspended materials. Direct GHG emissions could be originated from the biochemical treatment process. Also, the DAF tank is operated for oil and grease removal. From this perspective, EA and the DAF process were considered as the main GHG emission points, in this study. So, a limitation has been designed for GHG emission monitoring points due to the assumption that

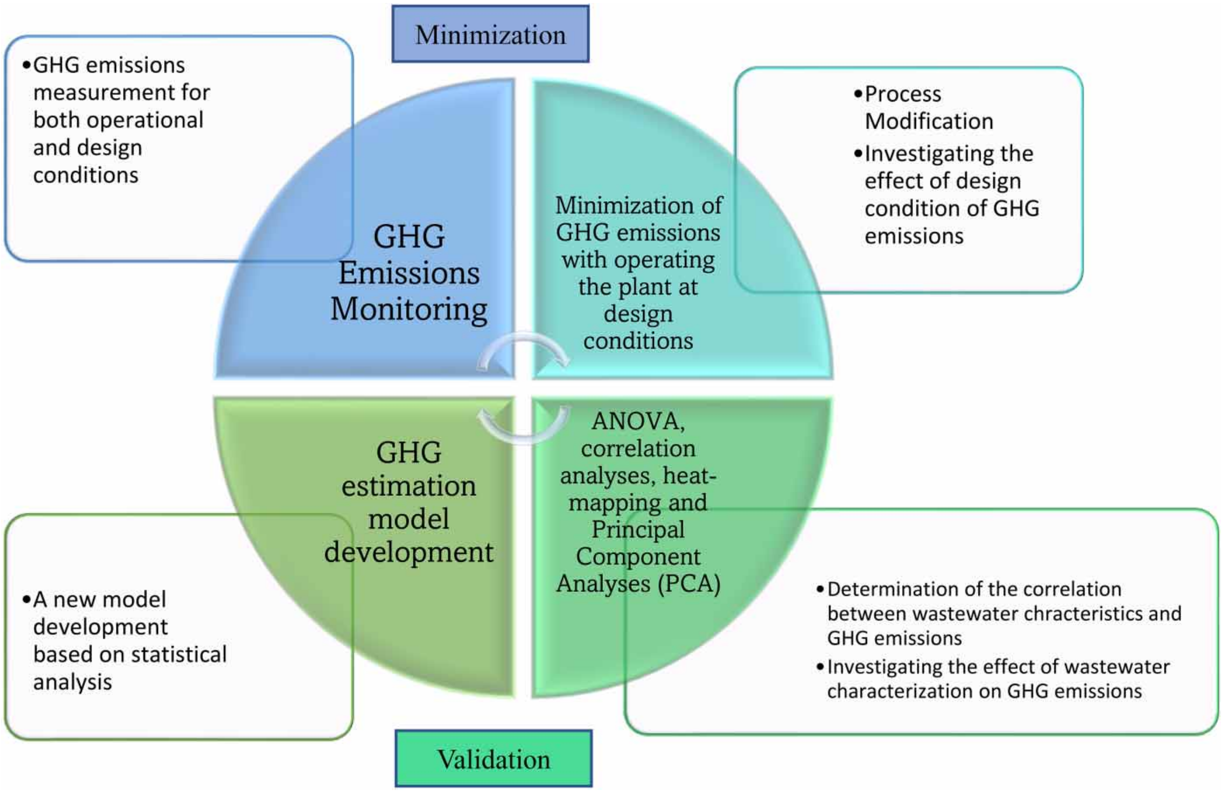


Figure 1 | Conceptual framework of the study.

GHG emissions could be originated from organic material removal. This study has been focused on direct emission due to the treatment process to reveal the effect of process conditions, so these main two treatment units have been selected. Chemical and energy consumption of the plant has led to indirect GHG emissions. It is ignored because the focus is on the main treatment process. Figure 2 presents the industrial wastewater treatment process flow scheme in the plant. Table 1 shows the inputs and desirable outputs of the system for the current operating conditions. Figure 3 shows the schematic representation of an industrial WWTP to determine the correspondence between GHG emissions and wastewater characterization.

Process modification could be a GHG emission mitigation technique (Rodríguez-Caballero *et al.* 2014; Sweetapple *et al.* 2014; Barbu *et al.* 2017). For the EA process, process modification was applied. First, process conditions were modified according to Table 2. The inputs and desirable outputs of the modified process condition for the aeration tank are given in Table 1. Many researchers proposed the operation of WWTPs under design conditions for minimum energy consumption (Castellet-Viciano *et al.* 2018). The design conditions are 36 h of HRT and 20 days of SRT. From this perspective, the operating conditions have been adjusted to the design conditions. A limitation has been defined for HRT and SRT in this specific range to define GHG emissions not to disrupt the effluent quality and discharge standards in this industrial WWTP. As well, a jar test has been performed before monitoring to detect the optimum operating conditions. GHG emissions have been measured for both design and operation and modified conditions in the plant. Table 1 presents the inputs and desirable outputs of the design conditions.

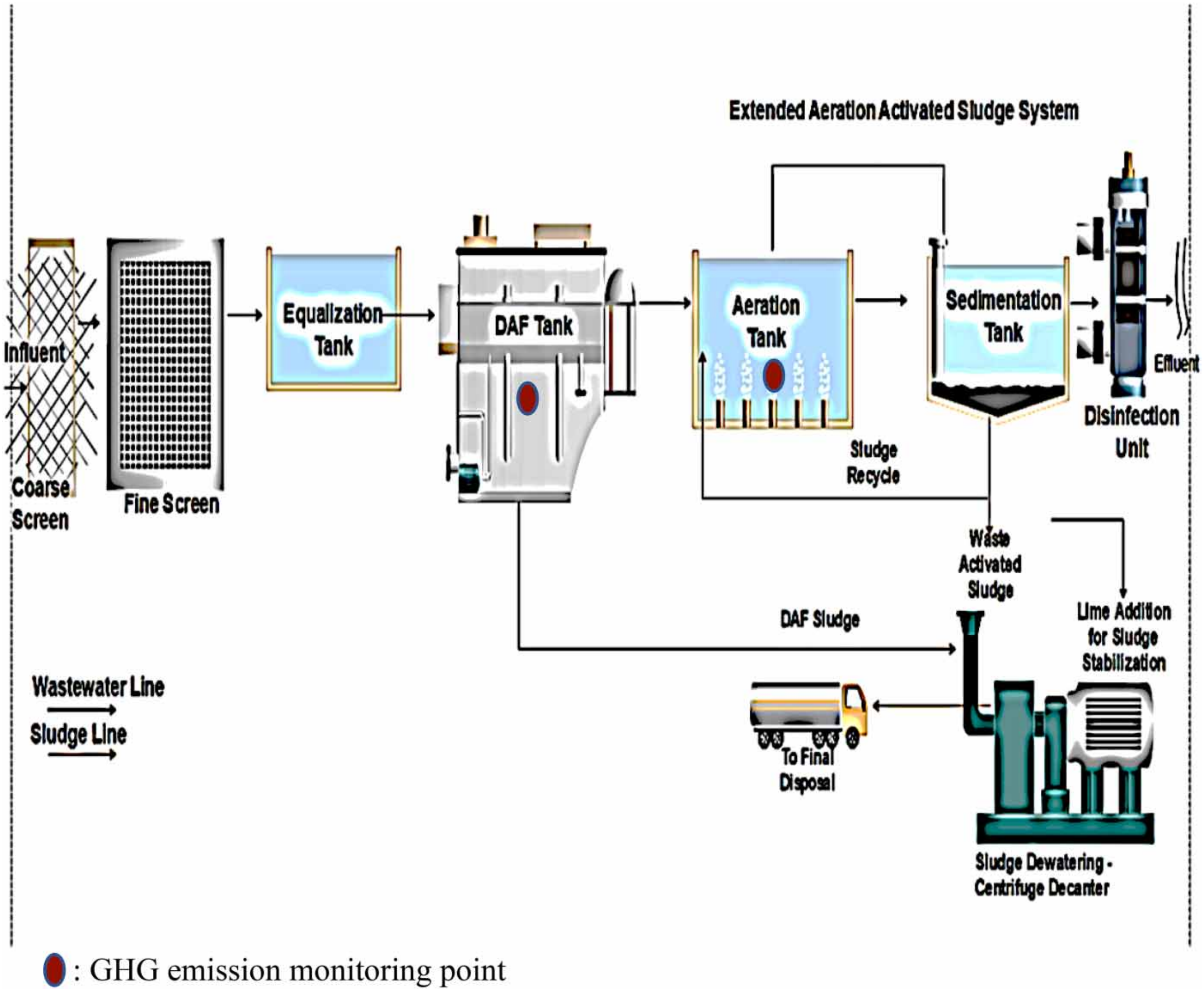


Figure 2 | Wastewater treatment process configuration.

Table 1 | Inputs and desirable outputs of the industrial wastewater system

DAF process

	June	July	August	September	October	November	December	January	February	March	April	May
Inputs (pollutant parameters)												
COD	5,293	5,875	5,410	4,789	4,443	3,789	3,650	4,878	4,424	4,310	4,985	5,000
TSS (mg/L)	2,122	2,456	2,178	2,144	3,022	2,878	2,536	2,501	1,987	2,001	2,078	2,011
TKN (mg/L)	1,245	1,255	1,500	1,478	1,225	1,350	1,001	1,045	989	925	1,013	1,113
FOG (mg/L)	329	335	320	278	258	301	325	299	225	311	315	318
Desirable output (pollutant removal, effluent value) (mg/L)												
COD	1,310	1,425	1,500	1,022	1,009	1,000	1,003	1,025	1,020	1,019	1,121	1,125
TSS (mg/L)	502	500	495	425	400	390	362	355	332	335	389	420
TKN (mg/L)	26	27,5	28	25,5	25	27	24	23	22	20	22,5	24,5
FOG (mg/L)	16	17	15	11	10	12	15,5	12,5	10	14	14,5	14,75

EA process – available operational conditions

	June	July	August	September	October	November	December	January	February	March	April	May
Inputs (pollutant parameters)												
COD	5,293	5,875	5,410	4,789	4,443	3,789	3,650	4,878	4,424	4,310	4,985	5,000
TSS (mg/L)	2,122	2,456	2,178	2,144	3,022	2,878	2,536	2,501	1,987	2,001	2,078	2,011
TKN (mg/L)	1,245	1,255	1,500	1,478	1,225	1,350	1,001	1,045	989	925	1,013	1,113
FOG (mg/L)	329	335	320	278	258	301	325	299	225	311	315	318
Desirable output (pollutant removal, effluent value) (mg/L)												
COD	1,252	1,400	1,425	1,011	1,005	998	977	1,018	1,014	1,009	1,098	1,110
TSS (mg/L)	487	495	490	400	395	387	358	350	325	328	385	410
TKN (mg/L)	25	25	25	25	25	25	25	25	25	25	25	25
FOG (mg/L)	10	10	10	10	10	10	10	10	10	10	10	10

EA process – modified process conditions

	June	July	August	September	October	November	December	January	February	March	April	May
Inputs (pollutant parameters)												
COD	5,293	5,875	5,410	4,789	4,443	3,789	3,650	4,878	4,424	4,310	4,985	5,000
TSS (mg/L)	2,122	2,456	2,178	2,144	3,022	2,878	2,536	2,501	1,987	2,001	2,078	2,011
TKN (mg/L)	1,245	1,255	1,500	1,478	1,225	1,350	1,001	1,045	989	925	1,013	1,113
FOG (mg/L)	329	335	320	278	258	301	325	299	225	311	315	318
Desirable output (pollutant removal, effluent value) (mg/L)												
COD	1,310	1,425	1,500	1,022	1,009	1,000	1,003	1,025	1,020	1,019	1,121	1,125
TSS (mg/L)	502	500	495	425	400	390	362	355	332	335	389	420
TKN (mg/L)	26	27,5	28	25,5	25	27	24	23	22	20	22,5	24,5
FOG (mg/L)	16	17	15	11	10	12	15,5	12,5	10	14	14,5	14,75

2.2. Monitoring and determination of GHG emissions

For the EA process and the DAF unit, GHGs were collected in a flux chamber and analyzed with gas chromatography for CO_2, CH_4, and N_2O emissions. Equation (1) presents the calculation of *in situ* GHG emissions. It has been derived based on the IPCC approach (IPCC 2014). In Equation (1), global warming potentials of CO_2, CH_4, and N_2O are 1, 28, and 265, respectively (IPCC 2014):

$$\mathrm{GHG} = (\mathrm{C}_{\mathrm{GHG}} \times \mathrm{GWP}_{\mathrm{CH_4,\,CO_2,\,N_2O}}) \times 1000 \tag{1}$$

where GHG is the GHG emission (kg CO_2e/d) ($\mathrm{GHG}_{\mathrm{CO_2}}$, $\mathrm{GHG}_{\mathrm{CH_4}}$, $\mathrm{GHG}_{\mathrm{N_2O}}$), $\mathrm{C}_{\mathrm{GHG}}$ is CO_2, CH_4, or N_2O concentration (mg/L d), and $\mathrm{GWP}_{\mathrm{CH_4,CO_2,N_2O}}$ is the global warming potential of CO_2, CH_4, or N_2O.

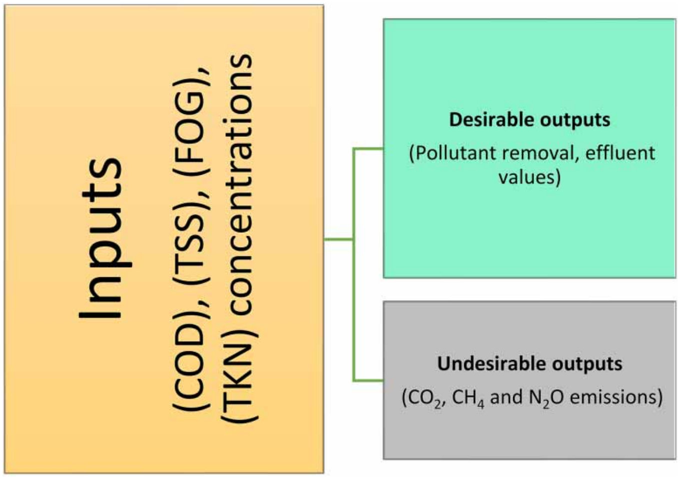


Figure 3 | Schematic representation of the model.

2.3. Statistical analysis and definition of correlation

A sensitivity analysis has been done for all datasets and these parameters. An uncertainty analysis has been performed before statistical analysis. Mean values have been considered and selected in statistical analysis. ANOVA, correlation analyses, heat mapping, and PCA were performed to determine the correspondence between GHG emission and wastewater characterization. R 'pheatmap' (Kolde 2019; İsmail *et al.* 2022), 'Hmisc' (Harrell 2021), 'factoextra' (Kassambara & Mundt 2020) and 'FactoMineR' (Le *et al.* 2008) packages and minitab for all analyses and charts package program (Minitab Inc. 2017) were used. The data were statistically analyzed using Levene's test for variance equality assumption and the Shapiro–Wilk test was applied for normality assumption ($p > 0.05$). For this purpose, two-way ANOVA in repeated measures and Tukey's HSD multiple comparison test were used to determine the differences between the groups and analyzed to determine whether there was a difference between the groups. The Pearson correlation was used to determine the relationships between variables. In addition, multivariate PCA was performed to examine the dimensions of the data. The data are presented as n, mean, and standard deviation. All analyses were performed at $p < 0.05$ significance level.

In order to understand the effect of independent variables on the dependent variable, linear multiple regression analysis was applied. The outputs have been divided into GHG emissions and pollutant removal, and the relevant variables for the EA process, DAF, and GHG emissions (GHG) are included in the analysis separately. In this way, it is thought that the causal properties of the variables will be examined in more detail. In this paper, COD, TSS, FOG, and TKN were considered as inputs, pollutant removal (effluent values) was considered as the desirable output, and GHG emissions were regarded as undesirable outputs. A mass balance that contains carbon and nitrogen content and removal has been performed before the assays.

PCA is a multivariate statistical method that is widely used for pattern identification and variable reduction (Şahin & İşler 2021). The purpose of PCA is to minimize the dimensionality of the data while preserving the variation of the original dataset. PCA decomposes the highly correlated variables of a dataset into smaller unrelated variables known as principal components. They are linear combinations of weighted original variables. In general, the first few principal components are responsible for almost all the variability in the data, and the rest is explained by the later components. The first principal component tends to account for most of the variability of the data. The first step in using PCA to select variables is to look for PCAs with eigenvalues greater than 1 that show PCs that explain the most variation in the dataset.

2.4. Estimation procedure of GHG emissions using correlation with wastewater characterization

After serious analyses, the correlation between GHG emissions and wastewater characteristics has been determined. A new GHG emission estimation tool based on the correlation has been developed. This calculation has been designed specifically

Table 2 | GHG emission monitoring results

DAF process

	June	July	August	September	October	November	December	January	February	March	April	May
Undesirable output (GHG) CO_2, CH_4, N_2O emission (mg/L)												
CO_2 emission	0	0	0	0	0	0	0	0	0	0	0	0
CH_4 emission	525	540	538	521	510	500	425	526	508	515	517	522
N_2O emission	1,010	1,100	1,150	1,145	1,000	1,140	985	990	975	950	985	998
EA–available operational conditions												
Undesirable output (GHG) CO_2, CH_4, N_2O emission (mg/L)												
CO_2 emission	375	410	395	360	357	355	350	378	357	356	362	368
CH_4 emission	600	610,5	608	596	586	525	505	601	578	569,5	584	596
N_2O emission	2,025	2,083	2,100	2,099	2,001	2,095	1,950	1,978	1,825	1,803	1,925	1988,5
Inputs (pollutant parameters)												
HRT (h)	32	36	30	28	25	24	20	19	19	20	23	26
SRT (d)	18	20	19	18	15	13	12	10	11	14	16	17
EA–modified process conditions												
Desirable output (pollutant removal, effluent value) (mg/L)												
COD	1,310	1,425	1,500	1,022	1,009	1,000	1,003	1,025	1,020	1,019	1,121	1,125
TSS (mg/L)	502	500	495	425	400	390	362	355	332	335	389	420
TKN (mg/L)	26	27,5	28	25,5	25	27	24	23	22	20	22,5	24,5
FOG (mg/L)	16	17	15	11	10	12	15,5	12,5	10	14	14,5	14,75
Undesirable output (GHG) CO_2, CH_4, N_2O emission (mg/L)												
CO_2 emission	410	415	400	374	363	358	352	380	360	359	363	370
CH_4 emission	618	620	617	608	590	535	514	607	581	572	587	599
N_2O emission	2,038	2,099	2,112	2,125	2,017	2,103	1,978	1,987	1,845	1,820	1,940	1,999
EA–design conditions												
Undesirable output (GHG) CO_2, CH_4, N_2O emission (mg/L)												
CO_2 emission	300	400	390	350	345	340	335	303	344	340	351	354
CH_4 emission	544	555	553	540	530	520	499	545	527	520	535	541
N_2O emission	2,000	2,007	2,010	2,009	1,980	2,007	1,900	1,905	1,800	1,755	1,840	1,860
Inputs (pollutant parameters)												
HRT (h)	36	36	36	36	36	36	36	36	36	36	36	36
SRT (days)	20	20	20	20	20	20	20	20	20	20	20	20

for this study. The most effective wastewater parameter has been corresponded with GHG emissions with the highest Pearson correlation coefficient. Also, an assumption has been defined that GHG emissions could be figured out from organic material removal from wastewater and wastewater amount:

$$\mathrm{GHG}^{\mathrm{I}} = Qr(\mathrm{WP}_{\mathrm{R}})\mathrm{GWP} \tag{2}$$

where $\mathrm{GHG}^{\mathrm{I}}$ is the estimated GHG emissions based on wastewater characterization (kg CO_2e/d), Q is the wastewater flow rate (m^3/d), r is the Pearson correlation coefficient, WP_{R} is the removal of COD, TSS, TKN or FOG (kg/m^3), and GWP is the global warming potential.

3. RESULTS AND DISCUSSION

3.1. Effect of process modification on GHG emissions

According to the analyses results, process modification has a serious impact on GHG emissions. CO_2 emissions were the lowest direct GHG emission in December. CO_2 emission was not observed at the DAF tank. Table 2 shows the GHG emission monitoring results and operating conditions related to the available process conditions. The highest GHG emission was observed in the EA process in September as N_2O emissions. It could be originated from wastewater nitrogen content and the denitrification process. Caniani *et al.* (2015) similarly reported that N_2O emission had the highest value for the membrane processes for a WWTP. According to the results, GHG emissions were closely correlated with process conditions and operational parameters of the WWTP. Also, Rodríguez-Caballero *et al.* (2014) researched the process conditions on GHG emissions for municipal wastewater treatment. They similarly found that process conditions have a considerable impact on GHG emissions. Also, similar results have been obtained in terms of seasonal variations with this study. They similarly reported the lowest GHG emissions in winter and the highest GHG emissions in summer.

Process modification has been applied to mitigate GHG emissions for the aeration tank. First, GHG emission monitoring was fulfilled on operating conditions for each month. Then, process modification has been applied as shown in Table 2. Finally, process modification has been adjusted to design conditions as 36 h of HRT and 20 days of SRT. Figure 4 shows the variation of GHG emissions applying process modification.

According to the results, lower direct GHG emissions were measured at design conditions for all types of GHG emissions. From these results, it could be said that if the plant is operated at design conditions, lower GHG emissions would be released. Also, process modification has a serious impact on GHG emissions. The results revealed that N_2O emissions had the highest value among GHG emissions due to its global warming potential. The highest GHG emission was related to N_2O emissions in September at operational conditions ($HRT = 26$ h, $SRT = 15$ days). The lowest GHG emission is CO_2 emission in June with a value of 300 mg/L at design conditions ($HRT = 36$ h, $SRT = 20$ days). From this perspective, it could be said that if the plant is operated at design conditions, lower GHG emissions could be monitored. If the aeration tank is operated at 36 h of HRT and 20 days of SRT at design conditions, an average reduction of 45.4, 45.3, and 45.2% in CO_2, CH_4, and N_2O emissions have been ensured, respectively. An average reduction of approximately 46% in overall GHG emissions has been reported in the study. A limitation has been designed for GHG emission monitoring points because the assumption contains that GHG emissions could be originated from organic material removal. If chemical and energy consumption has been considered, then a larger GHG emission has been calculated. Inorganic material removal has been applied in the screens and settling tanks. These units are not monitoring points, so it could be said that they have no effect on this correlation.

There are limited studies on this topic in the literature. Kim *et al.* (2015) studied the optimization of operating conditions in terms of GHG emissions. Similarly, they reported a 31% reduction, while reducing the operating costs by nearly 11%. They recommended an integrated performance index including GHG emissions, operating costs, and effluent quality. The novelty of this paper is that the impact of design conditions within the scope of GHG emissions has been investigated and the possible GHG emission mitigation that was calculated depended on GHG emission measurement. In this study, approximately 46% reduction has been achieved by applying design conditions in the plant. If a WWTP is operated at design conditions, more reduction in GHG emissions has been obtained rather than the optimization of operating conditions. Also, Rodríguez-Caballero *et al.* (2014) investigated process conditions on GHG emissions for municipal wastewater treatment. They reported that similar process conditions have a considerable impact on CO_2, CH_4, and N_2O emissions. They reported that, similarly, various GHG emissions result in various operational conditions. Molinos-Senante *et al.* (2014) investigated the economic and environmental performances of WWTPs in terms of the reduction of GHG emissions. They estimated potential future reductions in GHG emissions using the economic approach in the scope of energy consumption. In this study, the focus has been on process modification. In the literature, some studies recommended energy efficiency and energy consumption reduction for carbon-neutral operations in WWTPs. Badeti *et al.* (2021) revealed that the simulation shows that 33% of energy could be saved, and N_2O and CO_2 emissions could also be minimized by 98 and 25%, respectively, with energy efficiency.

3.2. Results of statistical analyses

ANOVA, correlation analyses, heat mapping, and PCA were performed to define the correspondence between GHG emissions and wastewater characterization. In this section, all statistical analyses are shown in detail.

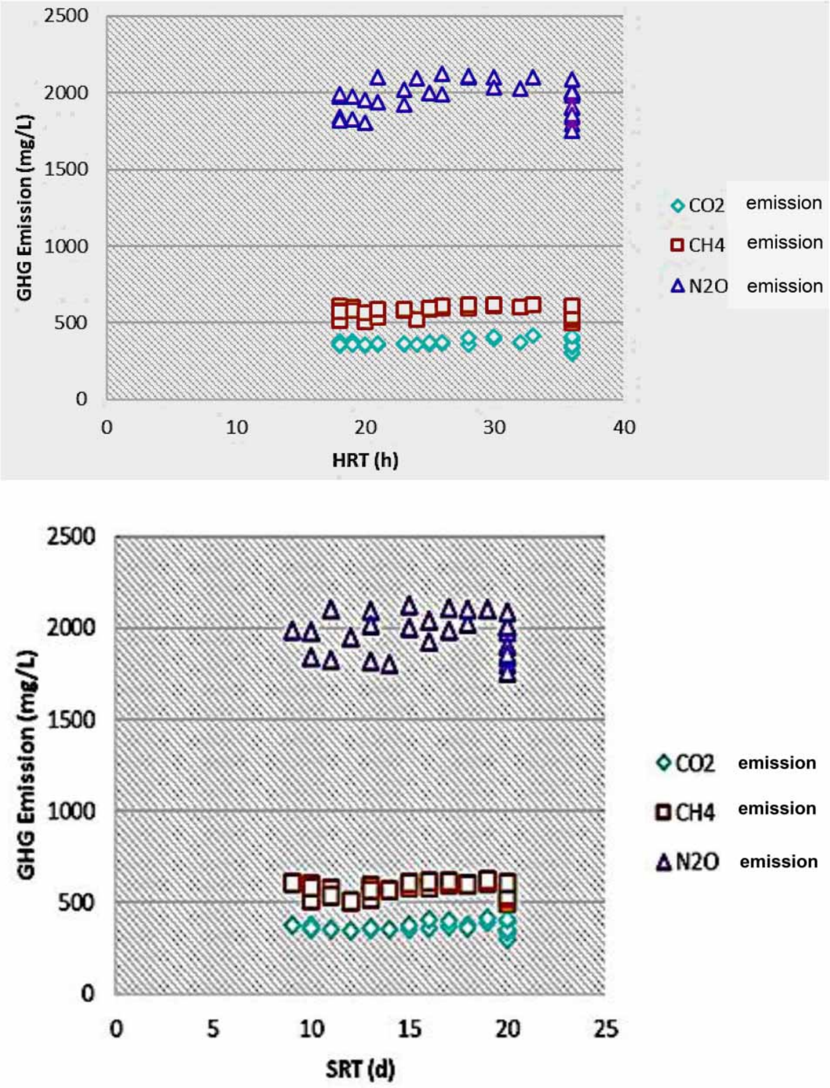


Figure 4 | GHG emission variation based on process modification.

3.2.1. ANOVA statistics

When the ANOVA results for inputs (pollutant parameters) and desirable outputs (pollutant removal and effluent value) were examined, it was found that, statistically, the DAF process had the highest mean and the EA process had the lowest mean in terms of COD, TSS, TKN, and FOG variables ($p < 0.001$). Table S1 in the Supplementary material shows the results of the ANOVA statistics. In addition, since there were no GHG emission values for FOG, only the difference between EA and DAF processes was examined and it was observed that DAF was significantly higher than EA for this parameter. On the other hand, when undesirable output (GHG) CO_2, CH_4, N_2O emission (mg/L) parameters were examined, it was reported that the EA process for CO_2 was higher in terms of statistical averages; it was observed that the EA process had the highest value. In addition, while data for DAF for HRT and SRT were not available, data for GHG were not included in the analysis because they were obtained the same in all months.

3.2.2. Regression analysis

Regression analysis results overlapped with the results of ANOVA statistics. Table SM3 shows the effects and ratios of independent variables on the dependent variables of CO_2, CH_4, and N_2O. The CO_2 emission model was not significant, while DAF_{PR} was significant for CH_4 emissions. It was observed that the N_2O model was predicted significantly in both. When the regression coefficients in CH_4 models for the DAF process were examined, it was estimated that TKN was above DAF_P, while DAF_{PR} was estimated as FOG. It could be estimated that FOG removal has been applied at the DAF tank. Nitrogen removal could be obtained in the lowest value at the DAF tank. Explanation coefficients for CH_4 (R^2) are DAF_P 44.42% and DAF_{PR} 72.92%. In other words, while DAF_{PR} of the independent variables explains 72.92% of the change in CH_4, DAF_P explains 44.42% of the change in CH_4. In another definition, it means that lower CH_4 emissions are released from the DAF tank rather than the EA process. Similarly, according to the ANOVA statistical results, the highest GHG emission has been reported at the EA tank for all conditions.

3.2.3. Principal component analysisCA

Separately, PCA has been performed to examine the EA and DAF processes and GHG emission dimensions. Analysis results including eigenvalues, total variance, percentage, and cumulative variance percentages are shown in S4 in the Supplementary material. PCA biplots showing the grouping of wells with respective variables and month parameters are shown in Figure 5. It was found that the top three PCs for EA, top three PCs for DAF processes, and two PCs for GHG had significant eigenvalues greater than 1. The total cumulative variance in PC-annotated datasets was 89.7, 85.5, and 82.8% for EA, DAF processes, and GHG emissions, respectively (Table S4). For EA, COD_P, COD_{PR}, TSS_{PR}, HRT, SRT, and CO_2 are included in PC1. Biplot helps to interpret the relationships between variables and PCs and the patterns in the datasets after the data are mirrored on the new PCs. According to PCA, the highest GHG emission has been monitored during the EA process. PCA has confirmed not only ANOVA but also the results of regression analysis.

3.2.4. Heat-mapping analysis

Coloring and clustering analysis were performed on the heatmap graph between the relevant parameters and months (Figure 6). Accordingly, while the parameters in the EA create five clusters (1st Cluster: COD_P; 2nd Cluster: TSS_P, N_2O; 3rd Cluster: TKN_P, CODPR; 4th Cluster: FOG_{PR}, SRT, TKN_{PR}, HRT; 5th Cluster: CH_4), it has been observed that FOG_P, TSS_{PR}, CO_2, and the months form three clusters. All analyses showed that the highest values in related months have dark colors and the lowest values have light colors. Heat mapping analysis showed that when the COD_P parameter is nearly corresponded with CO_2 and CH_4 emissions, the TKN_P parameter is closely related to N_2O emissions. Also, cluster analysis results have represented that COD closely corresponds to CO_2 emissions. Heat mapping and cluster analysis results have confirmed correlation analysis. Similar results have been obtained at the end of all statistical analyses.

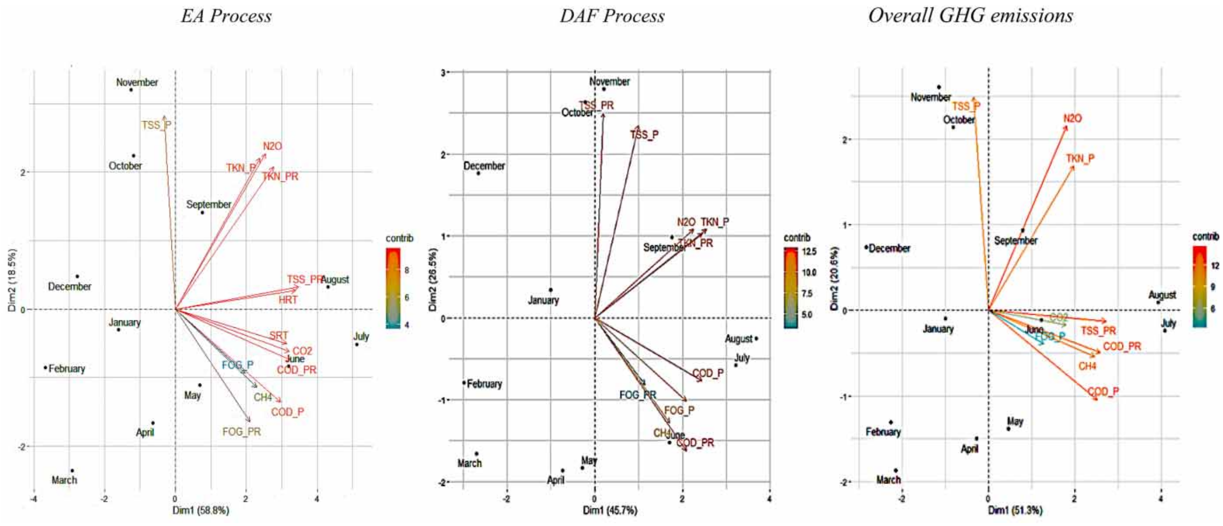


Figure 5 | PCA in terms of GHG emissions and EA and DAF processes.

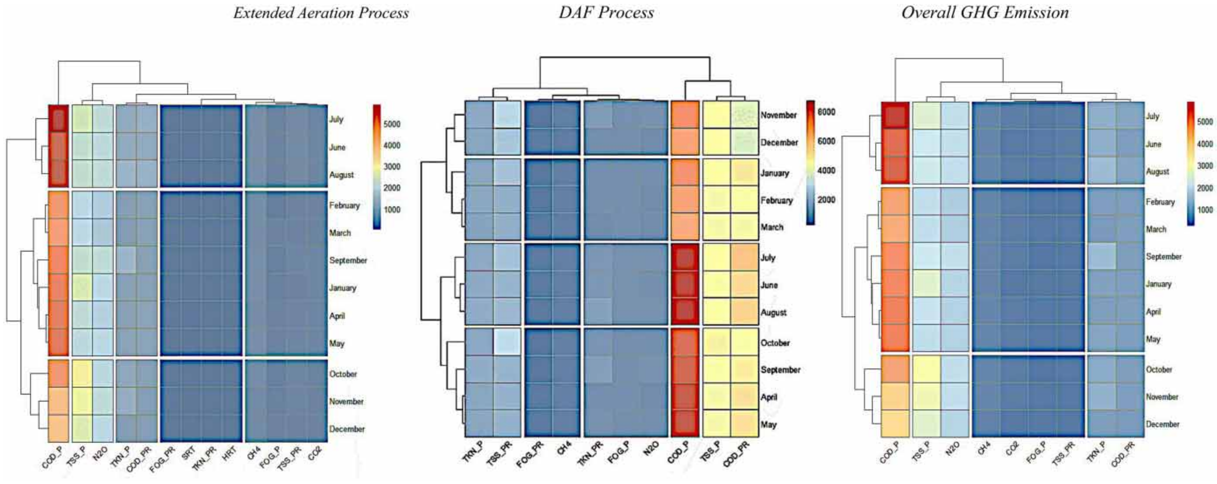


Figure 6 | Heat-mapping analysis for EA and DAF processes and GHG emissions in terms of wastewater characterization.

3.3. Correlations between GHG emissions and wastewater characterization

In this section, data interpretation and correlations between GHG emissions and wastewater characterization have been presented in detail. In the correlation definition, those with one star above the *p*-value are found to be significant at the 0.05 level and two stars at the 0.01 level. The *r* value represents the Pearson correlation coefficient. Correlations between 0.20 and 0.40 are interpreted as weak, between 0.4 and 0.6 as medium, 0.6 and above as strong, and 0.8 and above as very strong. Negative coefficients show an inverse relationship. Tables S5 and S6 (Supplementary material) and Table 3 show the correlation between GHG emissions and wastewater characterization for EA and DAF processes and general GHG emissions, respectively. Also, Figure 7 shows the correlation in a schematic diagram.

According to the findings, there is a very strong positive ($r = 0.823$, $p = 0.001$) correlation between COD_P and COD_{PR} values. A moderately significant positive correlation was found between COD_P (influent) and CH_4 values ($r = 0.907$, $p = 0.000$) for the EA process. Also, COD_{PR} (effluent) and CO_2 emissions were closely correlated with each other ($r = 0.909$, $p = 0.000$) for the EA process. While considering the overall correlation between GHG emission and wastewater characterization, CO_2, CH_4, and N_2O emissions were closely related to COD effluent values ($r = 0.759$, $p = 0.004$), COD influent values ($r = 0.937$, $p = 0.000$), and TKN influent values ($r = 0.876$, $p = 0.000$), respectively. According to the correlation results for the DAF process, COD effluent values and CH_4 emissions had a similar correlation with each other ($r = 0.794$, $p = 0.002$). N_2O emission has a similar high correlation with effluent TKN values ($r = 0.925$, $p = 0.000$). From this point of view, it could be assumed that TKN and COD removal would be considered as pollutant resources of N_2O and CO_2 and CH_4 emissions, respectively. The estimation tools (Equations (3)–(5)) have been derived considering the correlation between GHG emissions and wastewater parameters. Then, GHG emissions have been figured out based on wastewater characterization and their correspondence:

$$\mathrm{GHG^I CO_2} = Qr_1(\mathrm{COD_R})\mathrm{GWP_{CO_2}} \tag{3}$$

$$\mathrm{GHG^I CH_4} = Qr_2(\mathrm{COD_R})\mathrm{GWP_{CH_4}} \tag{4}$$

$$\mathrm{GHG^I N_2O} = Q\,r_3(\mathrm{TKN_R})\,\mathrm{GWP_{N_2O}} \tag{5}$$

In the derivative models (Equations (3)–(5)), GHG^I (kg CO_2e/d) represents the estimated CO_2, CH_4, and N_2O emissions. Q is the wastewater flow rate, and it also means the volume of wastewater (m^3/d). The other variable is the pollutant removal values. Correlation analysis showed that the COD removal (COD_R) value closely corresponded with CO_2 and CH_4 emissions, and nitrogen (TKN) removal (TKN_R) (kg/m^3) nearly corresponded to N_2O emissions. In the calculation tools, r_1, r_2, and r_3 are the Pearson correlation coefficients resulting from statistical analysis and the values of GWP are the global warming potentials of each related GHGs. While considering negative coefficients, TSS_P

Table 3 | Correlations between GHG emissions and wastewater characterization for all systems

		COD_P	TSS_P	TKN_P	FOG_P	COD_PR	TSS_PR	CO_2	CH_4	N_2O
COD_P	*r*	1	−0.360	0.333	0.342	0.799	0.822	0.408	0.937	0.304
	p		0.250	0.291	0.276	0.002	0.001	0.188	0.000	0.336
	n	12	12	12	12	12	12	12	12	12
TSS_P	*r*	−0.360	1	0.225	−0.091	−0.147	−0.196	−0.052	−0.238	0.510
	p	0.250		0.482	0.778	0.649	0.541	0.872	0.456	0.091
	n	12	12	12	12	12	12	12	12	12
TKN_P	*r*	0.333	0.225	1	0.088	0.451	0.610	0.383	0.487	0.876
	p	0.291	0.482		0.785	0.141	0.035	0.219	0.109	0.000
	n	12	12	12	12	12	12	12	12	12
FOG_P	*r*	0.342	−0.091	0.088	1	0.352	0.565	0.141	0.185	0.217
	p	0.276	0.778	0.785		0.262	0.056	0.661	0.566	0.498
	n	12	12	12	12	12	12	12	12	12
COD_PR	*r*	0.799	−0.147	0.451	0.352	1	0.771	0.759	0.749	0.365
	p	0.002	0.649	0.141	0.262		0.003	0.004	0.005	0.244
	n	12	12	12	12	12	12	12	12	12
TSS_PR	*r*	0.822	−0.196	0.610	0.565	0.771	1	0.501	0.727	0.599
	p	0.001	0.541	0.035	0.056	0.003		0.097	0.007	0.040
	n	12	12	12	12	12	12	12	12	12
CO_2	*r*	0.408	−0.052	0.383	0.141	0.759	0.501	1	0.336	0.205
	p	0.188	0.872	0.219	0.661	0.004	0.097		0.286	0.524
	n	12	12	12	12	12	12	12	12	12
CH_4	*r*	0.937	−0.238	0.487	0.185	0.749	0.727	0.336	1	0.409
	p	0.000	0.456	0.109	0.566	0.005	0.007	0.286		0.187
	n	12	12	12	12	12	12	12	12	12
N_2O	*r*	0.304	0.510	0.876	0.217	0.365	0.599	0.205	0.409	1
	p	0.336	0.091	0.000	0.498	0.244	0.040	0.524	0.187	
	n	12	12	12	12	12	12	12	12	12

GHG: greenhouse gas; *r*: correlation; *p*: significance; *n*:sample.

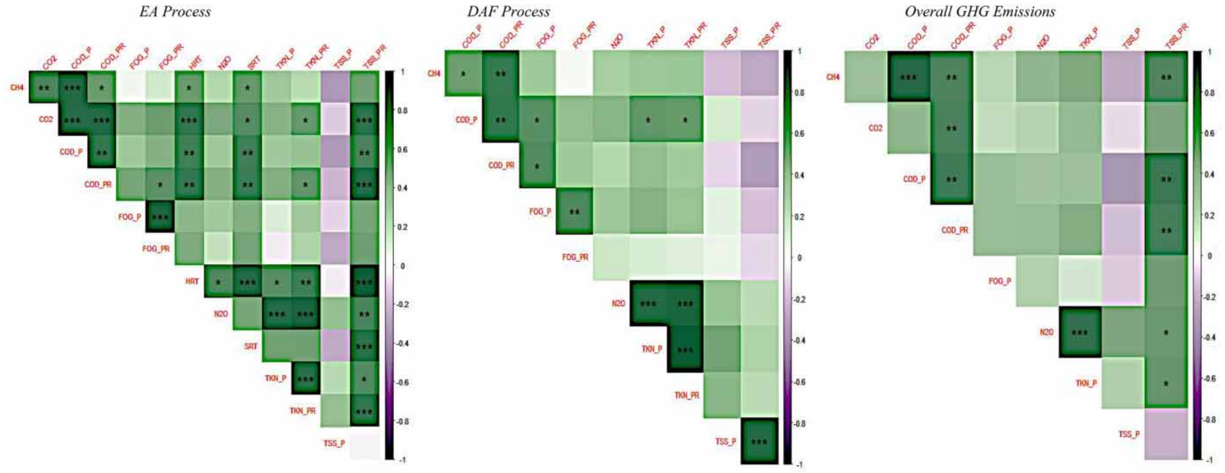


Figure 7 | Schematic diagrams of correlations.

(input) values have a negative impact on CO_2 and CH_4 emissions. It could be said that low TSS inputs could lead to higher CO_2 and CH_4 emissions. It could vary according to the wastewater content and organic load of the plant, although TSS_PR (effluent) values have a significant correlation with CO_2 emission ($r = 0.843$). It could have originated from the degradation of carbonaceous materials to carbon dioxide. FOG is an important wastewater parameter for dairy industry plants. While considering FOG effluent values, it could be said that a moderate correlation is available between CO_2 emissions ($r = 0.571$). Even so, FOG (effluent) has a weak correlation with CH_4 and N_2O emissions with values of 0.111 and 0.172, respectively. SRT and HRT are the main operational parameters of the EA process. Also, these operational parameters could have a great impact on GHG emissions. The results revealed that HRT strongly corresponds with CO_2 and N_2O emissions with values of 0.825 and 0.703, respectively. Also, SRT has a strong correlation with CO_2 emissions ($r = 0.689$).

GHG emission estimation has been performed for the DAF tank and the EA process at available modified process and design conditions, separately. Average GHG emission values have been considered as a benchmark. Finally, the results have been benchmarked with the *in situ* GHG emission monitoring results to determine the effect of wastewater characterization on GHG emissions. The estimative results based on wastewater characterization revealed that validation has been ensured between the estimation and monitoring results of GHG emissions. If obtained results are compared with the monitoring results, it could be said that the results have been overlapping with the monitoring values for the operational conditions. The estimated results that depended on wastewater characterization converged to the measured results by an average of 82%. The estimated results of CO_2, CH_4, and N_2O emissions converged to the measured results by an average of 77, 83, and 84%, respectively. Figure 8 presents the converge pilot of estimated results based on the correlation and monitoring of GHG emissions. So, correlation analysis has been validated for this study. It could be regarded that there is a strong correspondence between GHG emissions and wastewater characterizations. It can be said that COD is closely related to CO_2 and CH_4 emissions, and TKN is strongly related to N_2O emissions. This result, which was revealed by statistical analysis, was calculated with the help of the developed model and it was found that it converged to the real measurement results and was confirmed.

In the literature, several studies have been focused on municipal WWTPs. Zhou *et al.* (2022) analyzed GHG and contaminant parameters resulting from municipal WWTPs applying the normalizing method. Similar to this study, they found that CH_4 and N_2O emissions have been highly corresponded with the COD and TKN parameters, respectively. They have only confirmed using the normalizing approach and calculated GHG emissions from organic pollutant removal. In this study, direct GHG emissions have been monitored using a flux chamber and analyzed with gas chromatography, whereas statistical analysis has been validated with the *in situ* experimental GHG monitoring results. Huang *et al.* (2023) have similarly used the correspondence between GHG emissions and wastewater quality parameters for a municipal WWTP. They reported that COD removal has a major significant effect on GHG emissions. In a study, Yapıcıoğlu (2021) figured out GHG emissions using pollutant removal. Apart from these studies, this study has validated the scientific argument with *in situ* experimental analysis of GHG emissions.

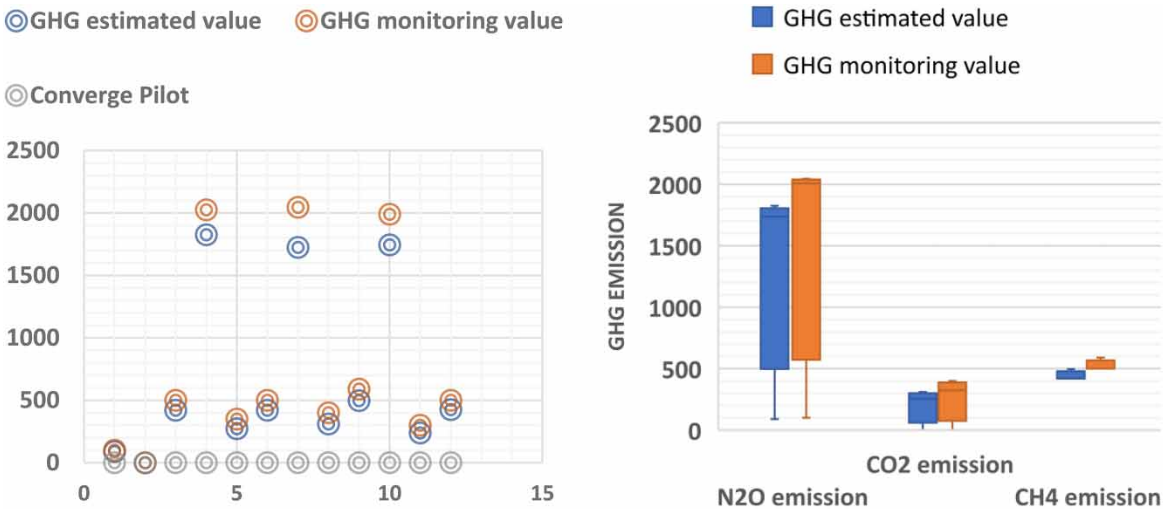


Figure 8 | Results of benchmarking evaluation between the estimation and *in situ* monitoring results of GHG emissions.

4. CONCLUSIONS

In this study, statistical and experimental modeling of the effect of process modification and wastewater characteristics on GHG emissions has been done for an industrial WWTP. This study confirms that process modification could be performed to reduce GHG emissions for the aeration process in WWTPs. If the aeration tank is operated at 36 h of HRT and 20 days of SRT at design conditions, an average reduction of 45.4, 45.3, and 45.2% in CO_2, CH_4, and N_2O emissions have been ensured, respectively. It is obvious that process modification has a significant effect on GHG emissions. According to correlation analysis, a moderately significant positive correlation was found between the COD effluent value and CO_2 and CH_4 values ($r = 0.909$ and $r = 0.937$). N_2O emissions were closely correlated with TKN input values ($r = 0.876$). From this point of view, a new GHG emission estimation tool has been developed based on this correlation. The results revealed that the estimated results have been overlapping with the *in situ* monitoring values. The estimated results of GHG emissions based on wastewater characterization have converged to the monitoring results by an average of 82%. The estimated results of CO_2, CH_4, and N_2O emissions based on statistical analysis have converged to the GHG emission monitoring results by an average of 77, 83, and 84%, respectively. This study focused on direct emission due to the treatment process to reveal the effect of process conditions, so these main two treatment units have been selected. Chemical and energy consumption of the plant has led to indirect GHG emissions. It is ignored because the focus is on the main treatment process. This study has added a scientific contribution to the literature on the reduction of GHG emissions from industrial WWTPs using process modification. Also, the validation of the recommended statistical model has been obtained with *in situ* experimental GHG emission monitoring. More research should be developed for the reduction of GHG emissions from industrial wastewater treatment plants.

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AUTHOR'S CONTRIBUTION

P.Y. carried out GHG emission monitoring and prepared the manuscript and H.Y. verified the analysis work. M.I.Y. compiled the manuscript with proper corrections.

DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

CONFLICT OF INTEREST

The authors declare there is no conflict.

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