



Precious Data from Tiny Samples: Revealing the Correlation Between Energy Content and the Chemical Oxygen Demand of Municipal Wastewater by Micro-Bomb Combustion Calorimetry

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Wastewater treatment plants (WWTP) are aimed to be transformed from sinks into sources of energy and material. For fostering corresponding engineering efforts and economic assessments, comprehensive knowledge of the energy content of wastewater is required. We show in this proof-of-concept study that these data can be gathered by combining micro-bomb combustion calorimetry with freeze-drying. Thereby, the methodology for measuring the combustion enthalpy ($\Delta_c H$) of wastewater is significantly improved by decreasing the time demand for the drying process as only tiny amounts of samples are required. Here, the effluent of the primary clarifier of a wastewater treatment plant treating low-strength municipal wastewater was sampled on a weekly basis for 1 year, yielding 53 composite samples that were analyzed for $\Delta_c H$ and standard wastewater parameters. A robust correlation between the chemical oxygen demand (COD) and $\Delta_c H$ of $-14.9 \pm 3.5 \text{ kJ gCOD}^{-1}$ ($r = 0.51$) was determined, verifying previous results obtained with more laborious and time-demanding methodologies. The global chemical energy potential of the sampled WWTP is presumably higher as the first treatment steps and losses during sample preparation reduced the amount of energy-rich compounds. A stronger correlation was observed between $\Delta_c H$ and the biochemical oxygen demand (BOD_5 , $r = 0.64$), suggesting its usage for predicting the potential of wastewater as feedstock for biotechnological applications. This demonstrates that micro-bomb combustion calorimetry can be applied for deriving precious information on the energy content of wastewater from simple COD measurements.

Keywords: combustion calorimetry, wastewater, chemical oxygen demand, energy, circular economy

INTRODUCTION

Wastewater treatment plants (WWTPs) belong to the essential infrastructure of modern human societies and contribute to achieving the Sustainable Development Goals (SDGs) postulated by the United Nations General Assembly, especially SDG 6: clean water and sanitation (UN General Assembly, 2015). However, WWTPs consume considerable amounts of electric energy and chemicals for treating wastewater, although wastewater contains 4–6 times more chemical energy than is required for its treatment using conventional technologies (Metcalf & Eddy, Inc et al., 2014; Scherson and Criddle, 2014; Wan et al., 2016; Korth et al., 2017). Thus, reducing energy consumption while increasing energy and resource recovery (e.g., phosphorus and nitrogen) (van der Hoek et al., 2018; Vučić et al., 2021) are necessary improvements for transforming WWTPs from energy sinks to energy-autarkic or even energy-producing facilities.

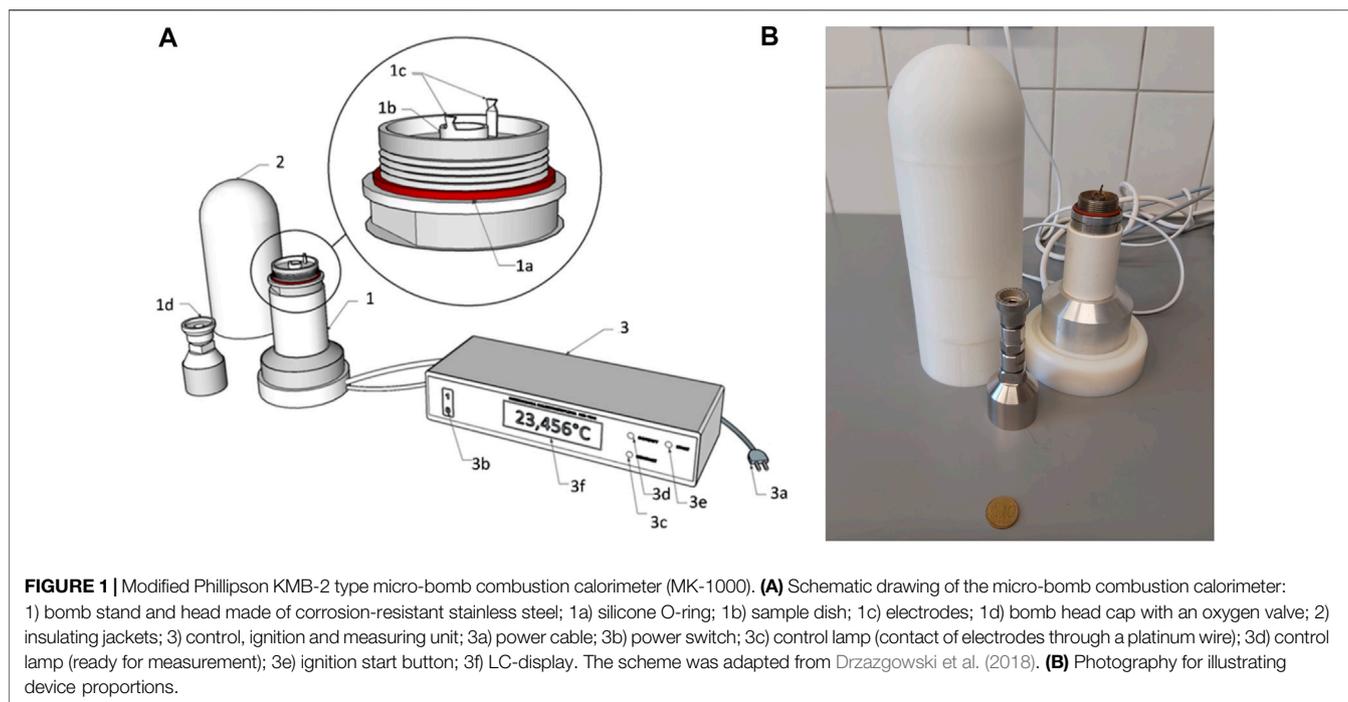
Besides chemical energy, wastewater also contains thermal energy that bears an excellent exploitation potential, even though it represents low-value exergy (i.e., low share of exergy). Approximately 6–8 times more energy than the chemical energy can be recovered using existing technologies like water source heat pumps for, for example, heating of greenhouses and cooling of buildings (Neugebauer et al., 2015; Shen et al., 2018; Hao et al., 2019). As exploiting its thermal energy is an already well-beaten track, the research focuses on extracting chemical energy and materials from wastewater. This extraction or valorization of chemical energy also represents a sustainable strategy with double benefits as it shall make the energy-demanding degradation of energy-rich compounds in WWTPs obsolete. State-of-the-art energetic use of wastewater is anaerobic digestion of the produced sludge (McCarty et al., 2011). Yet, other biotechnological approaches like microbial electrochemical technologies, complete anaerobic treatment, and different microbial conversions of wastewater compounds in valuable products are under research (Schröder et al., 2015; Kehrein et al., 2020; Zha et al., 2021).

A standard parameter in wastewater analysis that is commonly used for assessing the chemical energy content therein is the chemical oxygen demand (COD). Considering a total theoretical energy potential of 1.96 kWh m^{-3} of medium-strength municipal wastewater, it captures the largest energy fractions, that is, biodegradable carbon-rich molecules (63% or 1.24 kWh m^{-3}) and inert nonbiodegradable compounds (22% or 0.42 kWh m^{-3}) (Heidrich et al., 2011; Koch et al., 2014; Metcalf & Eddy, Inc et al., 2014; Scherson and Criddle, 2014). In addition, 0.3 kWh m^{-3} (15%) is based on nitrogen compounds (Scherson and Criddle, 2014). COD measurements are a widespread standard and thus are of particular practical relevance and provide some indications for wastewater's energy content. Yet, from an engineering perspective, COD does not offer comprehensive thermodynamic information as it only reveals the number of electrons (i.e., energy carriers) within a system but not how much work can be performed by these electrons (i.e., the energy level of these energy carriers). However, this is required for assessing the economic

competitiveness of wastewater as a sustainable feedstock for biotechnological processes. Here, the combustion enthalpy (or heat of combustion, $\Delta_c H$) seems an appropriate thermodynamic value. $\Delta_c H$ can be easily converted to the more common enthalpies of formation using the law of Hess (von Stockar, 2013). The enthalpy is a thermodynamic state function and therefore well suited for energetic predictions of wastewater utilization concepts. Thus, a reliable correlation between COD and $\Delta_c H$ would facilitate energetic and thus economic assessments of processes exploiting wastewater as a resource.

Few studies have analyzed the $\Delta_c H$ of wastewater to different extents, yielding volumetric and COD-based $\Delta_c H$ values ranging from -5.6 to -20.2 kJ L^{-1} and from -5.9 to $-23.4 \text{ kJ gCOD}^{-1}$, respectively (Shizas and Bagley, 2004; Heidrich et al., 2011; Korth et al., 2017). Whereas the fluctuation of the volumetric $\Delta_c H$ can be caused by different wastewater types, sources, and seasonal and diurnal variations, the variability of $\Delta_c H$ normalized to COD is presumably related to experimental pitfalls and method-inherent limitations. The method of choice used for precisely determining the $\Delta_c H$ of wastewater is combustion calorimetry. Combustion calorimetry requires drying comparable large volumes of wastewater for obtaining sufficient material (i.e., the sample with usually $\approx 1 \text{ g}$ of dry matter) for measurements, in the best-case scenario, without loss of energy-containing matter. While oven-drying of wastewater at ca. 100°C is a fast process, it results in a 40–50% loss of volatile organic substances and thus loss of COD, leading to an apparently lower amount of $\Delta_c H$ (Heidrich et al., 2011; Korth et al., 2017; Dai et al., 2019). In contrast, freeze-drying of wastewater decreases COD loss to ca. 20–25%, but it requires several days to weeks for yielding sufficient samples for conventional combustion calorimetry (Heidrich et al., 2011; Dai et al., 2019). Consequently, although the derived results are much more precise, the application of freeze-drying is limited. Recently, Dai et al. reported that a centrifugal evaporation approach for wastewater drying meets both requirements, decreasing the time needed for drying to less than one day (followed by subsequent drying in a desiccator for two days) and reducing COD loss to ca. 15%. By analyzing 61 composite municipal wastewater samples, the authors revealed a correlation between COD and $\Delta_c H$ of $16.1 \text{ kJ gCOD}^{-1}$ (Dai et al., 2019).

Here, we followed an alternative approach and performed a proof-of-concept study in order to use only small-size wastewater samples for obtaining a reliable correlation between $\Delta_c H$ and COD. Freeze-drying of wastewater is combined with measurements by micro-bomb combustion calorimetry, a small and portable device developed for the calorimetric analysis of small amounts of biological material (Prus, 1975; Drzazgowski et al., 2018). Due to the low quantity of sample required (approx. 30 mg per measurement), the time needed for freeze-drying of wastewater is decreased. The method's suitability is demonstrated by frequent wastewater sampling, drying, and measuring over one year. Thereby, a WWTP treating municipal wastewater with a comparatively low COD, being rather typical for European countries with a centralized WWTP system (Pons et al., 2004), was sampled weekly. The obtained data can be used



for estimating the annual chemical energy potential of WWTPs treating low-strength wastewater and an economic assessment thereof.

MATERIALS AND METHODS

Wastewater Sampling and Analysis

Wastewater from the effluent of the primary clarifier of a municipal WWTP with 55,000 population equivalents treating only domestic wastewater was sampled (S1 in **Supplementary Material**). Once per week (on sequential weekdays), an automated sampling unit collected approximately 800 ml from the primary clarifier effluent every 2 h for 24 h and pooled it. During this procedure, wastewater was stored at 10°C in the sampling system. Approximately 1 h after sampling was finished, 4 × 60 ml were freeze-dried, and standard wastewater parameters were analyzed.

Freeze-Drying of Composite Wastewater Samples

Four pre-dried and weighed serum bottles ($V = 100$ ml) were each filled with 60 ml wastewater and closed with a freeze-drying stopper ($d = 20$ mm, Th. Geyer GmbH & Co. KG, Germany). Serum bottles were deep-frozen at -80°C and transferred to the pre-cooled lyophilizer (ALPHA 1-4 LSC, Martin Christ Gefriertrocknungsanlagen GmbH, Germany). Freeze-drying was performed at -20°C and 0.1 mbar for approximately 40 h. Afterward, serum bottles with dry matter were weighed to obtain the wastewater dry weight (ρ_{WW} in g L^{-1}) and stored at -20°C until samples were measured by micro-bomb combustion calorimetry.

Micro-Bomb Combustion Calorimetry

The energy content was determined using a modified Phillipson KMB-2 type micro-bomb combustion calorimeter (MK-1000) manufactured at the University of Gdansk to study small quantities of biological material (**Figure 1**) (Drzazgowski et al., 2018). The operational principles of this type of micro-bomb combustion calorimeter were described by Prus (1975). The combustion heat is indirectly measured based on the change in amplified voltage determined using a Pt100 resistance sensor (4-core cable, $R_0 = 100 \Omega$). The voltage signal from the sensor (located inside the bomb head) is processed in the A/D converter and digitally transmitted to the microprocessor system. The signal is converted into the temperature value (10 mV per $^{\circ}\text{C}$), leading to a final ΔT value (resolution of $\pm 0.001^{\circ}\text{C}$). Analyses of the studied material were performed according to the procedures described before (Lamprecht, 1999; Normant et al., 2002). A portion of the dried and homogenized sample (30 ± 18 mg) was mixed with benzoic acid (ratio of wastewater sample to benzoic acid = 1:3) for ensuring complete combustion. This mixture was formed into a pellet of a known mass (50 ± 7 mg, m). Subsequently, combustion was conducted using oxygen (20 atm, purity 3.5, Eurogaz-Gdynia Sp. z o.o., Poland) pressurization. Depending on the sample's quantity and quality, the measurement lasted for several minutes until the maximum temperature value was reached. The difference between the final and initial temperatures of the bomb head (ΔT) was recorded. Before measurements, the micro-bomb combustion calorimeter was calibrated using five pellets of benzoic acid, resulting in a calibration factor (K) of 201.7 J K^{-1} . Four replicates of every wastewater composite sample were analyzed. However, probably due to differences in sample quality, a few samples could not be successfully measured

(see **Supplementary Table 1**). The energy content of the dry wastewater sample (Q , J mg^{-1}) was calculated based on **Eq. 1**:

$$Q = \frac{K \times \Delta T}{m} \quad (1)$$

Subsequently, **Eq. 2** yielded the volumetric heat of combustion of wastewater ($\Delta_c H_{\text{vol}}$):

$$\Delta_c H_{\text{vol}} = \frac{Q - \Delta_c H_{\text{benz}} \times f_{\text{benz}}}{f_{\text{WW}}} \times \rho_{\text{WW}} \quad (2)$$

Here, $\Delta_c H_{\text{benz}}$ is the heat of combustion of benzoic acid (-26.4 kJ g^{-1}), f_{benz} is the fraction of benzoic acid in the pellet, f_{WW} is the fraction of wastewater in the pellet, and ρ_{WW} is the dry weight of composite wastewater samples. According to thermodynamic conventions, a minus sign indicates the release of heat and a plus sign indicates the consumption of heat.

Measuring of Standard Wastewater Parameters

The amount of chemical oxygen demand (COD), nitrate (in $\text{mgNO}_3^- \text{ L}^{-1}$), ammonia (in $\text{mgNH}_4^+ \text{ L}^{-1}$), total nitrogen (TN, in mgN L^{-1}), and phosphate (in $\text{mgPO}_4^{3-} \text{ L}^{-1}$) of composite WW samples were determined using the tests REF 985029, REF 985064, REF 985008, REF 985088, and REF 985055, respectively, of the NANOCOLOR® series (Macherey-Nagel GmbH & Co., KG, Germany) according to the manufacturer's instructions (ftp://ftp.mn-net.com/english/Instruction_leaflets/NANOCOLOR). Three technical replicates were conducted per single composite wastewater sample. By doing so, nitrate measurements always resulted in negligible concentrations or were below the detection limit (**Supplementary Table 1**). The biochemical oxygen demand after five days of incubation was determined using OxiTop® (Xylem Analytics Germany Sales GmbH & Co., KG, Germany) according to the manufacturer's instruction.

Determining Chemical Oxygen Demand Loss During Freeze-Drying

The COD of additional composite wastewater samples were measured as described above, and aliquots of the same wastewater were subjected to the identical drying procedure described in *Freeze-Drying of Composite Wastewater Samples*. Afterward, dry matter was dehydrated with deionized water, and the COD of the suspension was measured. By doing so, five different wastewater samples were analyzed in triplicate, enabling an assessment of the COD losses during freeze-drying of composite wastewater samples.

Data Analysis

Linear regressions were performed according to Pearson using OriginPro 2019 version 9.6.0.172 (OriginLab Corporation, MA, United States). The suitability of Pearson's correlation was verified by testing all analyzed parameters ($\Delta_c H$, COD, BOD_5 , TN, NH_4^+ , and PO_4^{3-}) for normal distribution (Shapiro–Wilk

test, $\alpha < 0.01$), existence of continuous variables and paired observations, homoscedasticity, linearity, and the presence of outliers was excluded by applying the Grubbs test ($\alpha < 0.01$).

RESULTS AND DISCUSSION

Over 1 year, wastewater from the primary clarifier of one municipal wastewater treatment plant (WWTP, S1) was sampled on a weekly basis, yielding 53 composite samples that were analyzed using standard methods for wastewater characterization. Four aliquots of each sample were freeze-dried. Subsequently, all freeze-dried samples were analyzed by micro-bomb combustion calorimetry, resulting in 158 independent combustion enthalpy ($\Delta_c H$) measurements. The average value of $\Delta_c H$ of all composite wastewater samples ($n = 53$) was $-6.7 \pm 2.9 \text{ kJ L}^{-1}$, and thus, it is in line with previous studies on WWTPs treating mainly municipal wastewater reporting values in the range of -5.6 to -16.8 kJ L^{-1} (Shizas and Bagley, 2004; Heidrich et al., 2011). $\Delta_c H$ exhibited a robust linear correlation with the COD of the respective wastewater composite samples ($-14.9 \pm 3.5 \text{ kJ gCOD}^{-1}$, $r = 0.51$, $p < 0.001$, **Figure 2A**). Applying regression analysis to single combustion measurements of composite samples ($n = 158$) resulted in a smaller and weaker correlation ($-13.3 \pm 2.6 \text{ kJ gCOD}^{-1}$, $r = 0.38$, $p < 0.001$, **Figure 2B**). The results of both approaches are comparable to the correlation factor of $-16.1 \text{ kJ gCOD}^{-1}$ that was recently reported by Dai et al., using centrifugal evaporation for drying wastewater. This clearly demonstrates the general applicability of freeze-drying combined with micro-bomb combustion calorimetry for determining $\Delta_c H$ of municipal wastewater (Dai et al., 2019). In contrast to previous work, linear regressions were not forced through the origin as some compounds likely found in wastewater (e.g., urea) do not contribute to COD but to $\Delta_c H$ (Heidrich et al., 2011). Therefore, it is reasonable to consider a certain offset in the COD– $\Delta_c H$ -correlation. Consequently, the calculated correlation factors are worse than, for example, those from the study by Dai et al., but presumably better reflect reality as wastewater contains compounds that contribute to its energy content but cannot be detected with routine COD measurements (Scherson and Criddle, 2014; Dai et al., 2019). Furthermore, interpretation of linear regression analyses forced through the origin can be challenging as the apparent goodness of fit is biased (Gordon, 1981).

During drying of wastewater for combustion calorimetry, the COD loss is an unavoidable experimental drawback, independent of the drying procedure (e.g., freeze-drying or centrifugal evaporation). This loss is mainly ascribed to the evaporation of volatile organic compounds (e.g., acetate) and leads to a systematic underestimation of wastewater's energy content. Freeze-drying was combined with micro-bomb combustion calorimetry for reducing the residence time of wastewater in the lyophilizer as less than 5% of the sample amount, compared to standard combustion calorimetry, is required for measurements (approx. 30 mg instead of 1 g). Consequently, the loss of volatile organic compounds is also reduced. The COD of composite

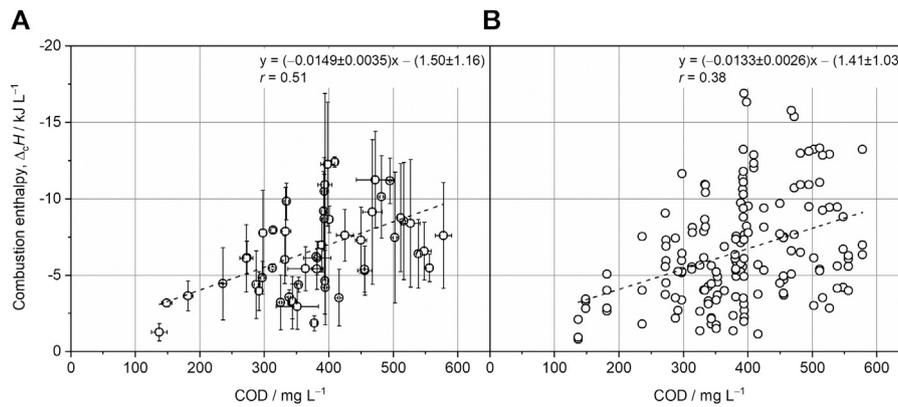


FIGURE 2 | Linear regression analysis with the COD of wastewater samples and the respective combustion enthalpies ($\Delta_c H$) derived from freeze-dried wastewater samples. **(A)** Average values of composite samples ($n = 53$) and **(B)** single combustion measurements thereof ($n = 158$) are shown. Error bars indicate standard deviations.

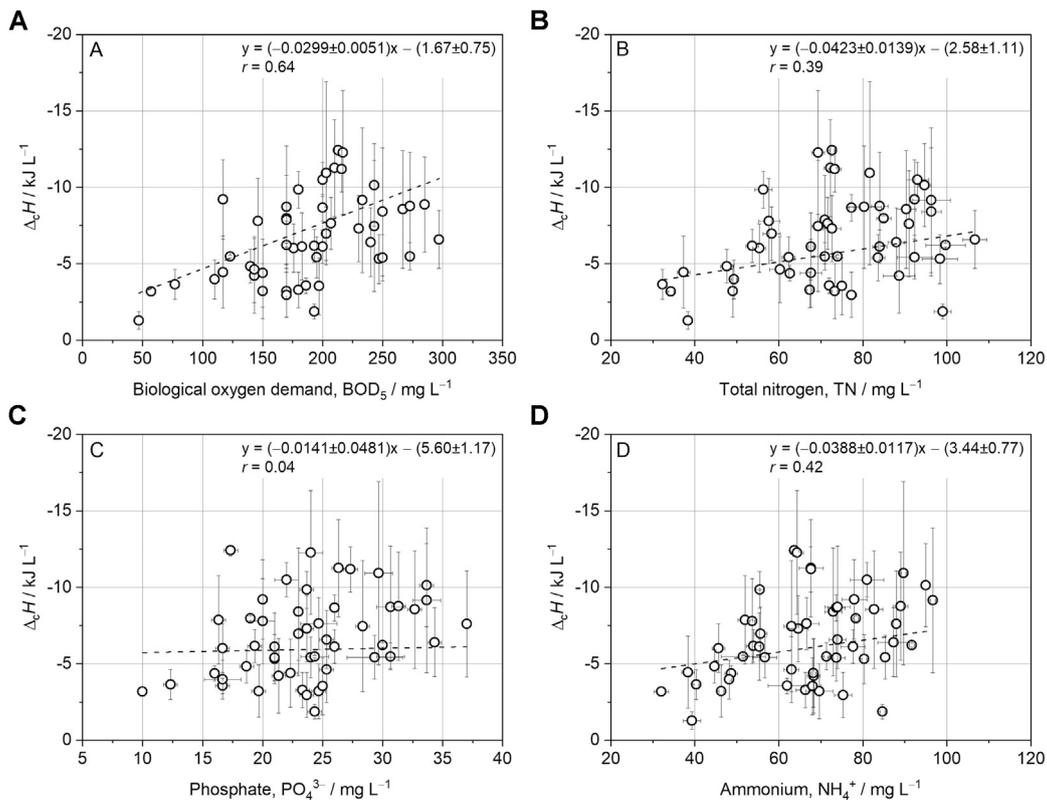


FIGURE 3 | Linear regression analysis with combustion enthalpy ($\Delta_c H$) derived from freeze-dried wastewater samples and **(A)** biochemical oxygen demand after five days of incubation (BOD_5), **(B)** Total nitrogen (TN), **(C)** phosphate (PO_4^{3-}), and **(D)** ammonium (NH_4^+). Analysis was performed using composite samples ($n = 53$), and error bars indicate standard deviations.

wastewater samples and the corresponding resuspended dry matter obtained from freeze-drying was measured for evaluating this experimental approach. By analyzing five composite wastewater samples, a mean COD recovery of $71.2 \pm 6.1\%$ was determined (**Supplementary Material S2**),

which is lower than the reported COD recovery when using centrifugal evaporation (84.8%) but is in the range of previously reported values for freeze-drying (77.8%) (Dai et al., 2019).

Although measures were taken for increasing the statistical robustness of the analysis (e.g., composite wastewater samples

and four technical replicates per composite sample), the measured values of $\Delta_c H$ scattered notably. We hypothesize three main reasons for the variability among replicates: 1) as the sample volume of freeze-dried wastewater used for micro-bomb combustion calorimetry was comparatively small (i.e., 60 ml), it possessed an inherent heterogeneity that is also reflected in $\Delta_c H$. This heterogeneity is in line with those determined for the dry weight of several samples (standard deviation of up to 29.8%, **Supplementary Table 1**). 2) The sampled WWTP treats only domestic wastewater, resulting in a comparatively low average COD ($384 \pm 99 \text{ mg L}^{-1}$, **Supplementary Table 1**). For this low-strength wastewater, the influence of its inherent heterogeneity can be considered high. Thus, it is more affecting combustion calorimetry measurements as it was already observed by Dai et al. for spot samples (Dai et al., 2019). 3) Although micro-bomb combustion calorimetry is advantageous for small sample sizes of biological material, the addition of an ignition material (here, benzoic acid representing $73 \pm 8\%$ (w/w) of combustion samples) is required for ensuring complete combustion of freeze-dried wastewater samples of relatively low energy content. However, the addition of equal-weight amounts of benzoic acid, as often done in calorimetry, could lead to significant errors (Lamprecht, 1999).

Regression analysis with further wastewater parameters showed weak correlations of $\Delta_c H$ with total nitrogen (TN, $r = 0.39$, $p < 0.01$, **Figure 3B**) and ammonia concentration (NH_4^+ , $r = 0.42$, $p < 0.01$, **Figure 3D**), indicating their limited but not negligible contribution to the chemical energy content of wastewater (assumed to be $\approx 15\%$) (Scherson and Criddle, 2014). Generally, this slightly contradicts previous results that assigned the contribution of TN and NH_4^+ as inconsequential (Dai et al., 2019). Nevertheless, those conclusions could be influenced by a biased statistical approach (i.e., linear regressions were forced through the origin). The biochemical oxygen demand after 5 days of incubation (BOD_5) exhibited a slightly better correlation with $\Delta_c H$ ($r = 0.64$, $p < 0.001$, **Figure 3A**) than COD, suggesting its applicability in predicting wastewater's chemical energy content, especially under the perspective of the microbial accessibility of wastewater's energy (see discussion below). This stronger correlation compared to the COD- $\Delta_c H$ -correlation is presumably related to the presence of compounds in wastewater that contribute to measurements of $\Delta_c H$ but not COD. For instance, urea is commonly hydrolyzed in water but can hardly be oxidized with an oxidizing agent like potassium dichromate, used in COD measurements. In contrast, numerous microorganisms can contribute to urea degradation in wastewater (Urbańczyk et al., 2016) and thus are likely active in BOD_5 measurements. This could also apply for chlorinated carbon-based compounds. Consequently, all these compounds support the BOD_5 - $\Delta_c H$ -correlation but bias the correlation between $\Delta_c H$ and COD. No correlation with $\Delta_c H$ could be determined for phosphate (PO_4^{3-} , **Figure 3C**), confirming previous results (Korth et al., 2017; Dai et al., 2019).

Combining freeze-drying with micro-bomb combustion calorimetry to determine the chemical energy content of wastewater confirms previous results obtained with different but more laborious methodologies. Korth et al. reported

$-13.0 \pm 1.6 \text{ kJ gCOD}^{-1}$ for few samples by applying freeze-drying and conventional combustion calorimetry (Korth et al., 2017). By using centrifugal evaporation and conventional combustion calorimetry, Dai et al. found a correlation of $-16.1 \text{ kJ gCOD}^{-1}$ (Dai et al., 2019). As the correlations of $-14.9 \pm 3.5 \text{ kJ gCOD}^{-1}$ and $-13.3 \pm 2.6 \text{ kJ gCOD}^{-1}$ revealed here for composite and individual wastewater samples, respectively, are in good accordance with the literature, it can be concluded that micro-bomb combustion calorimetry is an appropriate tool for investigating the energy content of wastewater. This is also reflected by the COD recovery that is comparable to the literature (**Supplementary Material S2**). By decreasing the time needed for freeze-drying due to the smaller sample size required for micro-bomb combustion calorimetry, the COD loss is reduced. Nevertheless, the heterogeneity of wastewater samples and the requirement of adding benzoic acid for ensuring complete combustion resulted in a frequent scattering of $\Delta_c H$. For improving $\Delta_c H$ measurements of wastewater with micro-bomb combustion calorimetry, the following steps should be taken: 1) the dry matter-to-benzoic acid ratio should be optimized, 2) sample homogeneity should be ensured without affecting the sample quality, and 3) the freeze-drying process could be further improved.

Interestingly, the BOD_5 and $\Delta_c H$ exhibited the strongest correlation in this study, suggesting its use for assessing the potential of wastewater as an energy and material resource for microbially catalyzed valorization processes (e.g., fermentation). The BOD_5 -to-COD ratio of 0.49 ± 0.07 determined here is typical for low-strength wastewater (Henze and Comeau, 2008) and shows that at least half of wastewater's chemical energy can be regarded as bioaccessible. Thus, this share of energy could be potentially exploited by biotechnological applications. For instance, the total energy potential of the WWTP sampled here (8050 m^3 wastewater per day, **Supplementary Material S1**) amounts to 5.52 GWh per year. Assuming that biotechnological applications could extract 20% of this energy (considering the BOD_5 -to-COD ratio and biological and technological efficiencies), the annual power production of solar panels located in Germany with a total size of ca. $8,693 \text{ m}^2$ could be provided by this WWTP (see **Supplementary Material S3** for details on calculations). For extrapolating the annual worldwide chemical energy potential with the obtained $\Delta_c H$ -COD correlation, further assumptions are required. Recently, it was estimated that the global wastewater production amounts to 369 billion $\text{m}^3 \text{ y}^{-1}$ (Jones et al., 2021). Assuming that all wastewater has a comparatively low COD (0.4 gCOD L^{-1}), is treated, and that the energy extraction efficiency is 20%, the global chemical energy potential of wastewater amounts to $1.2 \times 10^5 \text{ GWh}$ (see **Supplementary Material S3** for details on calculations). With this energy, the Netherlands' annual electricity consumption ($1.1 \times 10^5 \text{ GWh}$) or 0.5% of the annual worldwide electricity consumption ($2.3 \times 10^7 \text{ GWh}$) could be provided (U.S. Energy Information Administration, 2021). Obviously, these calculations included several uncertainties. For instance, substantial fractions of wastewater could have higher COD (especially industrial wastewaters), and at

present, only 51% of the produced wastewater is also treated (Jones et al., 2021).

Considering the COD loss during freeze-drying ($28.1 \pm 5.9\%$, **Supplementary Material S2**), it can be assumed that the combustion enthalpy of wastewater and, consequently, the bioaccessible energy thereof is underestimated, even though the determined correlation factor of $-14.9 \pm 3.5 \text{ kJ gCOD}^{-1}$ seems reasonable as it falls into the range of various carbon-based compounds (Heidrich et al., 2011; Dai et al., 2019). Considering the observed COD loss during sample treatment in this and prior studies, a correction factor of approximately 1.3 could be derived and applied to the COD- $\Delta_c H$ -correlation, resulting in approximately $-19.4 \text{ kJ gCOD}^{-1}$. Moreover, as the wastewater was sampled from the effluent of the primary clarifier, it can be assumed that substantial fractions of particulate BOD and total suspended solids (TSS) are already removed. Thus, an even higher global energy potential of this WWTP seems conceivable. Furthermore, this value also suggests the presence of, for example, chlorinated carbon-based compounds, as they bear a higher $\Delta_c H$ than most carbon-based compounds (Heidrich et al., 2011). The determined energy content of wastewater of $-6.7 \pm 2.9 \text{ MJ m}^{-3}$ corresponds to an average heat value of $6.7 \pm 3.2 \text{ MJ kg}^{-1}$ for the dry matter (see **Supplementary Table**). Thus, it is one order of magnitude lower than common energy carriers like diesel fuel ($42\text{--}46 \text{ MJ kg}^{-1}$) and gasoline ($44\text{--}46 \text{ MJ kg}^{-1}$) but is in the range of low-energy combustibles like fresh wood (6.8 MJ kg^{-1}) and domestic refuse ($2.5\text{--}12.0 \text{ MJ kg}^{-1}$), indicating that wastewater could be used as a reasonable energy and material source (World Nuclear Association, 2021; Brandt, 2000).

CONCLUSION

The novel approach of using micro-bomb combustion calorimetry for analyzing the energy content of wastewater led to an improved sample treatment as only tiny amounts of samples were required for combustion enthalpy measurements. The obtained robust correlation between the combustion enthalpy and COD of wastewater of $-14.9 \pm 3.5 \text{ kJ gCOD}^{-1}$ confirms the findings of previous studies that used more laborious and time-demanding sample preparation methods. The gathered data can be used for estimating the chemical energy potential of WWTPs treating low-strength wastewater, supporting efforts to transform WWTPs into sources for energy and material. Intriguingly, the global chemical energy potential is assumed to be higher as the first treatment steps of the WWTP and losses during sample preparation (i.e., freeze-drying) reduced the amount of energy-rich compounds before

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being measured by micro-bomb combustion calorimetry. Nevertheless, the so far restricted data foundation on thermodynamic parameters of wastewater for supporting efforts to engineer energy balances of WWTPs can be further extended, not only by the precious data set reported here.

DATA AVAILABILITY STATEMENT

The original contributions presented in the study are included in the article/**Supplementary Material**; further inquiries can be directed to the corresponding author.

AUTHOR CONTRIBUTIONS

BK: methodology, data analysis, and writing—original draft and editing. CH: micro-bomb combustion calorimetry and data analysis. MN-S: conceptualization, micro-bomb combustion calorimetry, and writing—review and editing. TM: conceptualization, methodology, and writing—review and editing. FH: conceptualization, methodology, supervision, project administration, and writing—review and editing.

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SUPPLEMENTARY MATERIAL

The Supplementary Material for this article can be found online at: <https://www.frontiersin.org/articles/10.3389/fenrg.2021.705800/full#supplementary-material>

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Conflict of Interest: The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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