Excessive greenhouse gas emissions from wastewater treatment plants by using the chemical oxygen demand standard

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Abstract Chemical oxygen demand (COD) is widely used as an organic pollution indicator in wastewater treatment plants. Large amounts of organic matter are removed during treatment processes to meet environmental standards, and consequently, substantial greenhouse gases (GHGs) such as methane (CH₄) are released. However, the COD indicator covers a great amount of refractory organic matter that is not a pollutant and could be a potential carbon sink. Here, we collected and analysed COD data from 86 worldwide municipal wastewater treatment plants (WWTPs) and applied a model published by the Intergovernmental Panel on Climate Change to estimate the emission of CH₄ due to recalcitrant organic compound processing in China's municipal wastewater treatment systems. Our results showed that the average contribution of refractory COD to total COD removal was 55% in 86 WWTPs. The amount of CH₄ released from the treatment of recalcitrant organic matter in 2018 could have been as high as 38.22 million tons of carbon dioxide equivalent, which amounts to the annual carbon sequestered by China's wetlands. This suggests that the use of COD as an indicator for organic pollution is undue and needs to be revised to reduce the emission of GHG. In fact, leaving nontoxic recalcitrant organic matter in the wastewater may create a significant carbon sink and will save energy during the treatment process, aiming at carbon neutrality in the wastewater treatment industry.

Keywords Chemical oxygen demand, Wastewater treatment, Recalcitrant dissolved organic matter, Greenhouse gas emission

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1. Introduction

The driving force for climate change has been the emission of greenhouse gases (GHGs) since the industrial revolution (Hansen and Lacis, 1990; Lashof and Ahuja, 1990; Montzka et al., 2011), and wastewater treatment plants (WWTPs) are known to significantly contribute to these emissions (Koutsou et al., 2018; Nguyen et al., 2019). Since the environmental protection departments have established strict water quality standards for effluent from WWTPs (Union and

Parliament, 2013), to satisfy the environmental standards, organic matter and nutrients are removed from the wastewater (Ra et al., 2000; Zhang et al., 2020). This process produces methane (CH₄), carbon dioxide (CO₂), and nitrous oxide (N₂O), which are then emitted to the atmosphere and contribute to climate change (Gupta and Singh, 2012; Poulsen and Hansen, 2009).

Direct CO₂ emission comes from the mineralization of organics by microorganisms in the biological treatment process (Bao et al., 2015). CH₄ is produced by anaerobic digestion as a consequence of sequential hydrolysis, acetogenesis, and methanogenesis of organic matter (Ziemiński

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and Frac, 2012). The most commonly used biological nutrient removal techniques, such as anaerobic/anoxic/oxic (A₂O) processes and sequencing batch reactor (SBR), have been found to generate large amounts of CH₄ (Bao et al., 2016; Nguyen et al., 2019). Previous experiments have shown that CH₄ emissions occur in all processing units of wastewater treatment (Liu et al., 2014), including both anaerobic and oxic tanks (Wang et al., 2011). The concentration of CH₄ in the global atmosphere has increased from approximately 715 parts per billion (ppb, 1 ppb=1 nL L⁻¹) before the industrial era to 1872 ppb in 2020 (<https://www.esrl.noaa.gov>). Furthermore, CH₄ is equivalent to 28 times the global warming potential (GWP) of CO₂ over a 100-year time scale (IPCC, 2014). It has been reported that WWTPs can contribute up to 5% of global CH₄ emissions (Chai et al., 2015). The GWP of N₂O is much higher than that of CH₄, and is 265 times that of CO₂ (IPCC, 2014). It can be emitted as an intermediate product of denitrification, in which nitrate or nitrite is reduced by organic matter in wastewater (Hanaki et al., 1992; Wunderlin et al., 2012). It is estimated that the global emissions of CH₄ and N₂O from WWTPs will exceed 600 million tons and 100 million tons of CO₂ equivalent (CO₂e) by 2030, respectively (Ragnauth et al., 2015). This indicates the urgency of reducing GHG emissions from wastewater treatment.

The concentration of organic matter in wastewater is commonly represented by chemical oxygen demand (COD), which includes biodegradable and nonbiodegradable organic components (Dulekgurgen et al., 2006). Another indicator widely used in water quality monitoring is biochemical oxygen demand (BOD), which represents the readily biodegradable fraction of the organic matter (Samudro and Mangkoedihardjo, 2010; Jouanneau et al., 2014). The minimization of COD and BOD is a major engineering goal to satisfy water quality standards (Cotillas et al., 2018; Freeman et al., 2018; Verma and Suthar, 2018). Biological treatments that rely on the catabolism and anabolism of microbes (including aerobic degradation and anaerobic digestion) are commonly conducted to decrease COD and BOD (de Souza et al., 2010; Mittal, 2011; Zhang et al., 2020). Moreover, anaerobic treatment is more commonly used to treat refractory organic matter (Barker et al., 1999). During anaerobic digestion, it has been reported that 80% of COD organics can be converted to gaseous CH₄ (Foley et al., 2011).

It has been reported that a significant contributor to COD is recalcitrant dissolved organic matter (RDOM) (Jiao et al., 2021), which accounts for the majority of all dissolved organic matter and can act as an important carbon sink (Hansell, 2013; Jiao et al., 2010). RDOM exists in large quantities in influent wastewater, the wastewater treatment processes, and effluent wastewater (Archibald et al., 1998; Bockhorn et al., 2005; Jin et al., 2011; Lu et al., 2018). The relative

contribution of refractory organic matter to the total organic matter has been reported to be as high as 91% in typical WWTPs in Switzerland (Kappeler and Gujer, 1992). This refractory organic matter can be used as a carbon sink in natural water environments; however, the anaerobic digestion process in wastewater treatment has high treatment efficiency for RDOM and thus releases vast amounts of CH₄ (Chelliapan et al., 2012). Sweeping restrictions on COD of effluent from WWTPs will cause a large amount of RDOM to be removed and then release GHG.

BOD reflects the amount of oxygen consumed by biological respiration of organic matter in water bodies (Reynolds, 2002). Therefore, the difference between COD and BOD can be regarded as an approximation of nonbiodegradable RDOM in natural oxygenated waters (Jiao et al., 2021), which is here termed refractory COD (rCOD). The organic matter classified as rCOD can be degraded during anaerobic digestion processes that are usually carried out under severe conditions, such as extremely low pH, high temperature, and high buffering capacity (Ward et al., 2008). To determine the mass of CH₄ emissions by rCOD removal, in this study, we collected operational COD and BOD data from WWTPs across the world to calculate the relative contribution of rCOD to COD removal during municipal wastewater treatment. Furthermore, the annual potential of CH₄ emissions from rCOD removal in wastewater treatment in China was estimated for 2017 and 2018. By investigating the GHG emissions caused by water quality monitoring indicators, this study provides a new perspective on the carbon neutrality of the wastewater treatment industry.

2. Materials and methods

2.1 Data collected from worldwide WWTPs

The Global Water Microbiome Consortium (<http://gwmc.ou.edu>) was launched in 2014 and makes available sample data from municipal wastewater treatment plants around the world (Wu et al., 2019). Using this website, we acquired a dataset from 100 municipal WWTPs, including actual flow rate, influent BOD (BOD_{in}), effluent BOD (BOD_{ef}), influent COD (COD_{in}), and effluent COD (COD_{ef}). Then we ruled out 14 cases where the BOD value was significantly greater than the COD value (data in doubt). The 86 WWTPs were selected from five continents, and the geographic distribution of the WWTPs is shown in Figure 1 and detailed in Appendix Table S1 (<https://link.springer.com>).

2.2 Estimation of rCOD removal ratio in WWTPs

BOD is generally reported as 5-day BOD (BOD₅), 20-day BOD (BOD₂₀), and ultimate BOD (BOD_u) (Bernardo et al., 2011). The obtained dataset is BOD₅. BOD₅ is approximately

Figure 1 Geographic distribution of 86 municipal Wastewater treatment plants (WWTPs) globally sampled. Each circle represents a WWTP, whose flow rate ($\text{m}^3 \text{d}^{-1}$) is proportional to the area of the circle. The sampling WWTPs cover five continents with different circle colours; Asia ($n=46$), Europe ($n=9$), North America ($n=20$), South America ($n=6$) and Australasia ($n=5$). The map is adapted from Wu et al. (2019).

equal to 66% of the oxygen required for complete oxidation and decomposition (according to empirical values), whereas BOD_u measures the amount of oxygen used by micro-organisms over a much longer period of time (Huo et al., 2006; Makinia et al., 2002). Therefore, we estimated the BOD_u of the WWTPs by dividing the reported BOD_5 by 66% (Appendix Table S1). The difference between COD and BOD_5 is defined as rCOD_5 , and the difference between COD and BOD_u is defined as rCOD_u . rCOD_u represents the more recalcitrant organic matter. COD removal can be calculated using the COD of the influent and effluent. The formula for calculating rCOD removal is as follows:

$$\begin{aligned} \text{rCOD}_{\text{Removal}} &= \text{rCOD}_{\text{in}} - \text{rCOD}_{\text{ef}} \\ &= (\text{COD}_{\text{in}} - \text{BOD}_{\text{in}}) - (\text{COD}_{\text{ef}} - \text{BOD}_{\text{ef}}), \end{aligned} \quad (1)$$

where rCOD_{in} is the rCOD of the influent wastewater and rCOD_{ef} is the rCOD of the effluent wastewater.

Then, we performed a cross validation-based intercept-free least square regression of rCOD concentrations against COD concentrations in the influent, effluent, and during removal. For each regression, cross validation was performed 999 times, in which half the samples ($n=43$) were used as the training set and the other half ($n=43$) samples were used as the validation set. The cross-validation R^2 was then calculated as:

$$R^2 = 1 - \frac{\text{RSS}}{\text{TSS}} = 1 - \frac{\sum_{i=1}^n (y_i - \hat{y}_i)^2}{\sum_{i=1}^n (y_i - \bar{y})^2}, \quad (2)$$

where RSS is the residual sum of squares; TSS is the total sum of squares; $\hat{y}_i$ is the fitted value for the i th sample in the validation set; y_i is the observed value for the i th sample in the validation set and $\bar{y}$ is the average of observed values

across all samples in the validation set.

2.3 Calculation model of conversion between COD and CH_4

To estimate the CH_4 emissions by the removal of rCOD in worldwide WWTPs, data from 86 WWTPs were used to establish a model. The data of COD removal and CH_4 emissions from WWTPs released by the Chinese government were used to verify whether the model is applicable. Therefore, we estimated the annual removal of rCOD in Chinese municipal wastewater treatment by obtaining the average proportion of rCOD in COD removal from the 86 WWTPs.

The annual rCOD removal of China's municipal wastewater treatment was estimated using eq. (3):

$$\Delta \text{rCOD} = \Delta \text{COD} \times \text{average removal ratio}, \quad (3)$$

where ΔrCOD is the annual rCOD removal in China's municipal wastewater treatment systems (million tons); ΔCOD is the total COD removal in China's municipal wastewater treatment systems (million tons), which was 11.80 and 12.41 million tons in 2017 and 2018, respectively (<http://www.mee.gov.cn>); the average removal ratio is estimated from section 2.2 ($=\text{rCOD removal}/\text{COD removal from the 86 WWTPs} \times 100\%$).

The maximum potential of CH_4 emissions (ECH_4) by ΔrCOD from wastewater was estimated using eq. (4) (IPCC, 2006):

$$\text{ECH}_4 = \Delta \text{rCOD} \times \text{EF} \times \text{MCF} - R, \quad (4)$$

where ΔrCOD is defined above; EF is the maximum CH_4 production/emission factor ($0.25 \text{ kg CH}_4/\text{kg COD}$); MCF is a

CH₄ correction factor for the type of process employed for wastewater treatment (shown in Appendix Table S2); and R is the mass of CH₄ captured for combustion and/or flaring at the plant or transfer out of the plant (kg). Here, only the maximum potential was considered, and subsequent processing (e.g., CH₄ recovery) was not included.

3. Results and discussion

3.1 Contribution of rCOD to COD

The concentrations of BOD and rCOD in the influent and effluent of global WWTPs are shown in Figure 2. We found that the removal of BOD was always accompanied by the removal of rCOD. The BOD loss can be easily explained by the catabolism and anabolism of microbes, whereas the accompanying rCOD loss may be explained by excessive sludge digestion or advanced elimination of pollutants to meet strict COD discharge standards. In addition, a small proportion of inorganic ions could contribute to both COD (such as nitrite, sulphate, and ferrous ions) (Kylefors et al., 2003; Samudro and Mangkoedihardjo, 2010) and BOD (such

as sulphide and ferrous ions) (Hudson et al., 2008; Yu et al., 2016).

To quantitatively characterize the relationship between COD and rCOD, we performed an intercept-free linear regression of rCOD (rCOD₅ and rCOD_u) against COD (Figure 3). It was found that influent rCOD₅ contributed 56% of the influent COD (cross-validation $R^2=0.95$, $p<10^{-16}$) (Figure 3a), indicating a predominant proportion of rCOD₅ in the COD of the influent. Effluent rCOD₅ contributed 74% of the effluent COD ($R^2=0.78$, $p<10^{-16}$) (Figure 3c), which supports the notion that the biodegradability of wastewater decreases after treatment. Taking rCOD₅ removal as the difference between influent rCOD₅ and effluent rCOD₅, we found that the overall contribution of rCOD₅ removal to COD removal was 55% ($R^2=0.93$, $p<10^{-16}$) (Figure 3b). This indicates that the per unit concentration of COD removal represented 0.55 units of rCOD₅ removal in these WWTPs. The estimated rCOD_u accounted for 33% ($R^2=0.75$, $p<10^{-16}$) of the influent COD (Figure 3d), 61% ($R^2=0.67$, $p<10^{-16}$) of the effluent COD (Figure 3f), and 32% ($R^2=0.15$, $p<10^{-16}$) of COD removal (Figure 3e). At least 32% of the removed COD originated from organic matter that was resistant to aerobic

Figure 2 The removal of wastewater COD comprises BOD (blue) and rCOD (red), which is defined as COD–BOD. (a) and (b) show the concentration changes of BOD₅ and rCOD₅ and BOD_u and rCOD_u, respectively. Influent and effluent concentrations from the same WWTP are matched by a grey line. Bar plots in the bottom panel show the average influent concentrations (solid line) and effluent concentrations (dashed lines) across all sampled WWTPs. Curves in the top panel show the density distribution of influent and effluent concentrations of BOD and rCOD.

Figure 3 Relationship between COD and $rCOD$ in influent, removal and effluent. An intercept-free least-square regression identifies a strong relationship between COD and $rCOD$ that is robust to cross-validation. (a) $rCOD_s$ contributed to 56% of COD in influent, (c) 74% of COD in effluent, and (b) 55% of COD removal in municipal WWTPs. (d) $rCOD_u$ accounted for 33% of the influent, (f) 61% of the effluent, and (e) 32% of removal COD.

degradation. When applying this regression model to China's annual COD removal, it was estimated that the $\Delta r\text{COD}_5$ and $\Delta r\text{COD}_u$ removed by municipal wastewater treatment in 2017 were 6.49 and 3.78 million tons, and in 2018, they were 6.83 and 3.97 million tons, respectively.

Figure 3a shows that BOD accounted for less than half the COD when the COD of the influent was divided into BOD and rCOD. This indicated that approximately half of the organic matter in wastewater cannot be rapidly degraded by aerobic microbes in natural water environments. This refractory organic matters are mainly composed of high-molecular-weight humic substances and low-molecular-weight microbial products (Lu et al., 2018). Specifically, humic substances and fulvic acid compounds are not only present largely in the influent wastewater but are also a major by-product of both aerobic and anaerobic biological treatment of wastewater (Guo et al., 2011). It was estimated that the microbial products measured in terms of COD were an average of 2.2% of the COD_{in} (Ince et al., 2000). These microbial-derived products could resist biodegradation and could be stored in natural environments for a long time (Jiao et al., 2010). However, in wastewater treatment, these products are further removed in the subsequent denitrification and phosphate removal processes, which promotes the production of GHG (Lemaire et al., 2006; Yan et al., 2020). Different from natural conditions, wastewater treatment processes are usually carried out under specific and severe conditions (Ward et al., 2008), resulting in RDOM removal during wastewater treatment.

3.2 Estimated mass of GHG converted by $\Delta r\text{COD}$

It was found that anaerobic processes played an important role in the degradation of refractory compounds (Wang et al., 2012). To estimate the potential maximum emission due to the removal of refractory organic matter, we assumed that the rCOD was removed anaerobically, although the majority of WWTPs (especially in China) do not utilize only anaerobic treatment processes (Fang et al., 2016). The maximum MCF (0.8; Appendix Table S2) was used to estimate CH_4 emissions from Chinese municipal WWTPs (Table 1). For a simpler comparison, CH_4 was converted to CO_2e ($\text{GWP}=28$). If CH_4 recovery was not considered, the maximum potential for the conversion of $\Delta r\text{COD}_5$ to CH_4 (CO_2e) was 1.30 (36.34) and 1.37 (38.22) million tons in 2017 and 2018, respectively. The maximum potential for conversion of $\Delta r\text{COD}_u$ to CH_4 (CO_2e) was 0.76 (21.15) and 0.79 (22.24) million tons in 2017 and 2018, respectively.

The calculated mass of CH_4 could be overestimated since anaerobic treatment (major process) is not the sole treatment process of rCOD and a small part of rCOD was treated by intensive post-treatments with less CH_4 released, such as aerobic polishing, ozonisation, electrocoagulation and elec-

tron beam irradiation (Barker et al., 1999; Deogaonkar et al., 2019; Kallas and Munter, 1994; Makwana and Ahammed, 2017). In addition, we did not take the recovery of CH_4 into account for the estimation of maximal CH_4 emission potential. Previous studies have estimated that energy recovery from CH_4 may compensate for half of the consumed energy in the wastewater treatment process and thus reduce indirect CO_2 emissions by at least 50% (dos Santos et al., 2016; Hao et al., 2014, 2015). This can help approach to its target regarding carbon neutrality in WWTPs.

To confirm the reliability of the model, the estimated data were compared with the official data released by the Chinese government. When the $r\text{COD}_5$ removal ratio (55%) was applied to China's wastewater treatment in 2014, $\Delta r\text{COD}_5$ would have contributed 1.49 million tons of the officially released total CH_4 emission data (2.71 million tons) (<http://www.mee.gov.cn>), which was even higher than the estimated value in 2018 (1.37 million tons). This also reflects, to a certain extent, that the recovery and utilization of CH_4 as an energy source in China is still in urgent need of development.

Table 1 shows that the removal of rCOD in 2018 could result in the emission of approximately 22.24–38.22 million tons of CO_2e . Compared with the energy, transportation, and other carbon-intensive industries, the cost of emission reduction within wastewater treatment is low and the benefit of emission reduction is obvious (Zhang et al., 2015). The wastewater treatment industry has already been listed as a priority sector for reducing emissions and achieving carbon neutrality in many countries (Mo and Zhang, 2012). If measured according to the algorithm of the forestry carbon sink (Li, 2007), the CO_2 emitted from the annual removal of rCOD would require afforestation of approximately 2.5 to 4 million hectares to offset, which would cost 31–53 billion dollars. Furthermore, these GHG emissions could account for 50–86% of the annual carbon sequestered by China's wetlands (44.54 million tons) in 2014 (<http://www.mee.gov.cn>). Wetlands are important carbon sinks in the Earth's ecological system, and they play an important role in absorbing atmospheric GHG and preserving recalcitrant organic matter (Chen et al., 2017; Mitsch et al., 2013).

Exacerbating GHG emissions is the contribution of N_2O , a significant product of COD removal. N_2O is thought to be an inevitable intermediate product in the process of wastewater nitrogen removal because of incomplete denitrification. Limits on COD have led to more N_2O production (Shannon et al., 2008), and previous studies have found that a low COD/N ratio, which represents a shortage of carbon, will cause denitrifying bacteria to use internal carbon sources for denitrification (Geng et al., 2010; Wu et al., 2009). This can lead to the accumulation of nitrite and then cause more N_2O to be produced, which will exacerbate GHG emissions (Rodriguez-Garcia et al., 2012).

Table 1 Estimation of the annual greenhouse gas (GHG) emission potential stemming from recalcitrant chemical oxygen demand (rCOD) removal in Chinese municipal wastewater treatment in 2017 and 2018

Year	GHG emissions from anaerobic digestion ^{a)} (million tons)			
	ECH ₄ ^{b)}	CO ₂ e ^{b,c)}	CH ₄ ^{d)}	ECO ₂ e ^{c,d)}
2017	1.30	36.34	0.76	21.15
2018	1.37	38.22	0.79	22.24

a) Does not include CH₄ recovery, b) converted from estimated $\Delta rCOD_5$, c) CH₄ was converted to CO₂e (GWP=28) (IPCC, 2014), d) converted from estimated $\Delta rCOD_u$

3.3 The balance between GHG emissions and wastewater treatment efficiency

Future wastewater treatment should pursue not only the goal of reducing organic pollutants but also a balance between organic matter removal efficiency and reduction of GHG emissions. Using the classical COD indicator has disadvantages, and in fact, a high COD value does not necessarily correspond to the poor water quality. There are many natural water environments with a richness of RDOM that are of high water quality, while the COD does not meet the standards (Aoki et al., 2004; Jiao et al., 2021; Raike et al., 2012). It has been reported that effluent wastewater from paper mills contains large amounts of lignin-based recalcitrant organic material that can contribute to COD but is not acutely toxic and is very similar to natural organic matter (Archibald et al., 1998). Additionally, it was reported that a high COD value may not indicate the eutrophication of the water body (Guo et al., 2017).

With the development of human society, the content of DOM in water will inevitably increase (Sepp et al., 2018), and if DOM is removed indiscriminately, carbon will be emitted to the atmosphere, aggravating climate change. With the improvement of wastewater treatment technology, more organic matter will be removed to meet the COD standard. Therefore, if the use of the COD indicator is not revised, a high COD removal ratio will be accompanied by higher levels of direct GHG emissions. The water treatment industry should set up improved water quality monitoring indicators, such as indicators distinguishing the characteristics and biodegradability of wastewater organic matter as well as their fates in natural environments and indicators focusing on inorganic ions and organics that are hazardous to humans and other organisms. The improved water quality monitoring indicators could help preserve nontoxic RDOM as carbon storage, whereby carbon neutrality of the wastewater treatment industry could be achieved in a more economical way.

4. Conclusion

The wastewater treatment industry is an important part of the

global carbon cycle with significant climate change impacts. When organic matter is removed from wastewater, large amounts of CO₂, N₂O, and CH₄ are released, resulting in the greenhouse effect. This study highlights that COD is not a suitable water quality monitoring indicator. Under present regulations for COD in wastewater effluent, a large amount of RDOM is removed, and GHGs are emitted to the atmosphere as a result. The theoretical carbon emission potential of recalcitrant organic matter processed by China's municipal WWTPs in 2018 could be as high as 38.22 million tons of CO₂e, which is equivalent to the annual amount of carbon sequestered in Chinese wetlands. Therefore, the COD indicator standards applied in the wastewater treatment industry should be revised. More work should be done in the future to improve water quality monitoring indicators to achieve a balance between water quality improvement and GHG emission reduction, aiming at carbon neutrality in the wastewater treatment industry.

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