A shift from chemical oxygen demand to total organic carbon for stringent industrial wastewater regulations

Utilization of organic matter characteristics

Park, Ji Won; Kim, Sang Yeob; Noh, Jin Hyung; Bae, Young Ho; Lee, Jae Woo; Maeng, Sung Kyu

DOI
10.1016/j.jenvman.2021.114412

Publication date
2022

Document Version
Final published version

Published in
Journal of Environmental Management

Citation (APA)
Park, J. W., Kim, S. Y., Noh, J. H., Bae, Y. H., Lee, J. W., & Maeng, S. K. (2022). A shift from chemical oxygen demand to total organic carbon for stringent industrial wastewater regulations: Utilization of organic matter characteristics. *Journal of Environmental Management*, *305*, Article 114412. https://doi.org/10.1016/j.jenvman.2021.114412

Journal of Environmental Management 305 (2022) 114412

Contents lists available at ScienceDirect

Journal of Environmental Management

journal homepage: www.elsevier.com/locate/jenvman

A shift from chemical oxygen demand to total organic carbon for stringent industrial wastewater regulations: Utilization of organic matter characteristics

Ji Won Park[a], Sang Yeob Kim[a,b,c], Jin Hyung Noh[a], Young Ho Bae[d], Jae Woo Lee[e], Sung Kyu Maeng[a,*]

[a] Department of Civil and Environmental Engineering, Sejong University, 209 Neungdong-ro, Gwangjin-gu, Seoul, 05006, Republic of Korea
[b] Department of Water Supply, Sanitation and Environmental Engineering, IHE Delft Institute for Water Education, Westvest 7, 2611AX, Delft, the Netherlands
[c] Department of Biotechnology, Delft University of Technology, Van der Maasweg 9, 2629 HZ, Delft, the Netherlands
[d] Department of Water Environment Management, Effluent Toxicity Management Division, Korea Environment Corporation (KECO), 42 Hwangyeong-ro, Seo-gu, Incheon, 22689, Republic of Korea
[e] Department of Environmental Engineering, Korea University, Sejong, 30019, Republic of Korea

ARTICLE INFO

Keywords:
Chemical oxygen demand
Dissolved organic matter characteristics
Discharge regulation
Industrial wastewater
Total organic carbon

ABSTRACT

From 2022, industrial wastewater discharge regulations in South Korea will replace chemical oxygen demand (COD_{Mn}) with total organic carbon (TOC). A shift from COD_{Mn} to TOC is a pioneering change in protecting water bodies from organic contaminants. However, several industries are struggling to meet these TOC requirements even though their effluents met the COD_{Mn} limits. Effluent COD_{Mn}/TOC ratios (1.28 ± 0.64) found in our study were lower than the COD_{Mn}/TOC coefficients (1.33–1.80) suggested by the Ministry of Environment in South Korea. Aliphatic and particulate organic matter contents in effluents likely influenced the COD_{Mn}/TOC ratio. Regardless of the industrial category, dissolved organic carbon often consists of low molecular weight neutrals, hydrophobic organic carbon, and protein-like substances in raw and treated industrial wastewaters. The present study also revealed that TOC and COD_{Mn} represented different organic matter fractions in the paper mill and oil refinery wastewater, whereas the industrial park wastewater showed similar dissolved organic matter characteristics. Specifically, COD_{Mn} was effective in the determination of humic content in paper mill wastewater but was underestimated in oil refinery wastewater. Additionally, only paper mill effluents exceeded the TOC requirements (4 of 6 samples) and required an additional post-treatment process owing to higher organic loads.

1. Introduction

To protect water bodies from anthropogenic organic carbon contaminants in municipal and industrial wastewaters, the Ministry of Environment (MOE) in South Korea decided to shift from chemical oxygen demand (COD_{Mn}) (permanganate method) to total organic carbon (TOC) as the parameter determining the discharge limits of organic compounds. From 2020, the municipal wastewater discharge limits include TOC as a bulk organic matter parameter, replacing COD_{Mn} (Fig. 1). Korean municipal wastewater treatment plants (WWTPs) should meet the TOC requirements according to the amendment of the Water Environment Conservation Act (Fig. 1). All industrial wastewater effluents should comply with the respective TOC requirements from 2022 (Table 1). In 2023, online TOC measurement and telemonitoring systems will become a regulatory requirement for both municipal and industrial WWTPs.

The main advantages of the shift from COD to TOC are: avoiding the use of toxic chemicals, which subsequently leads to hazardous waste, and providing a more accurate estimation of bulk organic matter present in wastewater. The dichromate method (COD_{Cr}) uses chemicals, including heavy metals, which leads to toxic wastes (Dubber and Gray, 2010; Christian et al., 2017). Thus, TOC is considered a more environment-friendly parameter with respect to the use of chemicals and is more accurate for water bodies and wastewater effluents. The high-temperature combustion TOC method has been reported to be reliable with higher oxidation rates of various types of organic matter

---

* Corresponding author.
E-mail address: smaeng@sejong.ac.kr (S.K. Maeng).

https://doi.org/10.1016/j.jenvman.2021.114412
Received 18 September 2021; Received in revised form 12 December 2021; Accepted 28 December 2021

(Aiken et al. 2002). In particular, COD_{Mn}, which underestimates the organic carbon levels in municipal and industrial wastewaters, has been used for wastewater standards in several countries, including South Korea. There have been attempts to replace COD_{Mn} with either COD_{Cr} or TOC because of the low oxidation efficiency of the permanganate method. COD_{Mn} is known to oxidize less than 30–60% of single organic surrogates, whereas COD_{Cr} and TOC can oxidize 80–100% of the organic compounds (Aiken et al., 2002; NIER, 2014; UBA, 2017).

Previously, TOC has been suggested as a substitute for effluent criteria in some cases. For example, US EPA allows TOC to replace biochemical oxygen demand (BOD) owing to long-term site-specific relationship (Assmann et al., 2017; Christian et al., 2017), but BOD is often not correlated with TOC in municipal and domestic effluents (Dubber and Gray, 2010). As member states in Europe, Germany, and Sweden also suggested that COD_{Cr} can be replaced with TOC using conversion coefficients (i.e., $TOC \geq COD_{Cr}/4$ or $TOC = COD_{Cr}/3$, the ratio for Germany and Sweden, respectively) (UBA, 2017; NVV, 2019) (Table S1). Meanwhile, Switzerland has started using dissolved organic carbon (DOC) for municipal (plants over 2000 population equivalents) and some industrial wastewater discharge (e.g., paper, cardboard mill, and waste incineration plant) (SFC, 2021). Those TOC replacements are often optional, but all WWTPs in South Korea are required to meet the TOC standards by law to accurately measure organic loadings in aquatic environments and prevent organic contaminants that are hard to degrade.

TOC conversion coefficients have been designated and suggested, and are legally enforced in all wastewater treatment facilities in Korea from 2021 (Water Environment Conservation Act amendment) (Table 1). Before the legal amendment, the coefficient for converting COD_{Mn} into TOC was studied in detail (NIER, 2002, 2014). However, the coefficient was derived by the average COD_{Mn}/TOC ratio, and thus could not be applied universally. Therefore, some concerns have emerged. Even though treatment facilities have met the COD_{Mn} level before the legal amendment, some treatment plants may not meet the new TOC regulation standard. These plants can thus be fined unless they retrofit the facility or revise the operational methods of their existing treatment systems. The discrepancies between COD_{Mn} and TOC could probably be linked to the organic matter oxidation rates that are different for target organic matter characteristics, particularly in industrial wastewater. Therefore, understanding the differences in organic matter characteristics between COD_{Mn} and TOC is helpful in determining the treatment strategy of TOC. This study compared the criteria analytes (TOC, COD_{Mn}, COD_{Cr}, and BOD) and organic matter sub-components (e.g., using size exclusion and excitation-emission matrix) to identify labile and refractory organic matters in different industrial wastewaters. Previous studies have characterized the various types of effluent organic matter (EfOM) from municipal and industrial WWTPs (Table S2). However, the significance of organic matter characteristics in terms of removal of TOC and its regulatory compliance was first documented in this study. The present study has also suggested current limitations and take-home lessons throughout the shift from COD_{Mn} to TOC in wastewater effluent standards in South Korea, and could provide better management strategies when other countries replace COD with TOC.

Table 1
Revision in municipal and industrial wastewater discharge standards from COD_{Mn} to TOC in Korea.

Category	Watershed code	COD_{Mn}, mg L^{-1}	TOC, mg L^{-1}	COD_{Mn}/TOC
Municipal wastewater	I	20	15	1.33
	II	20	15	1.33
	III	40	25	1.60
	IV	40	25	1.60
Industrial wastewater	A	40 (50)	25 (30)	1.60 (1.66)
	B	70 (90)	40 (50)	1.75 (1.80)
	C	90 (130)	50 (75)	1.80 (1.73)
	Special	40 (40)	25 (25)	1.60 (1.60)

Criteria for the facilities discharging less than 2000 m^3 per day are in parenthesis.

2. Materials and methods

2.1. Sampling locations

The influent and effluent wastewater samples were collected from seven industrial WWTPs, including paper mills, oil refineries, and industrial park WWTPs. Sampling campaigns were conducted from May 2020 to October 2020 in the respective industrial facilities. Briefly, the influents and effluents from wastewater treatment steps, including primary, secondary (biological), media filtration, and final effluent, were collected twice during the sampling campaign (Supplementary Fig. S1). The three selected paper mills (i.e., KP, MP, and NP) mainly produce whiteboard paper, toilet paper, newspaper, and other miscellaneous paper products (Table 2). Paper mill wastewater treatment process consists of coagulation/sedimentation/flotation, followed by aerobic biological treatment and media filtration (sand or granular activated carbon (GAC)). Notably, the paper and pulp industry accounts for 10% of the total industrial discharge and organic loads to the aquatic environment (MOE, 2019). In the present study locations, the effluent discharges were 17.2, 18.3, and 11.0 m^3 per day for KP, MP, and NP, respectively. The TOC requirements were 40, 50, and 40 mg C L^{-1} for KP, MP, and NP, respectively (Table 2).

Two crude oil refineries (i.e., HO and SO), producing gasoline, diesel, kerosene, and other byproducts, were also investigated. Oil refinery wastewater quality may vary depending on the source and types of crude oil, but this was not in the scope of our study. The wastewater treatment process typically consists of coagulation, flotation, oil-water separator (grease interceptor), biological treatment, and media filtration. The daily effluent discharges were 22.7 and 46.4 m^3 per day for HO and SO, respectively. The TOC criteria were 50 and 25 mg C L^{-1} for the HO and

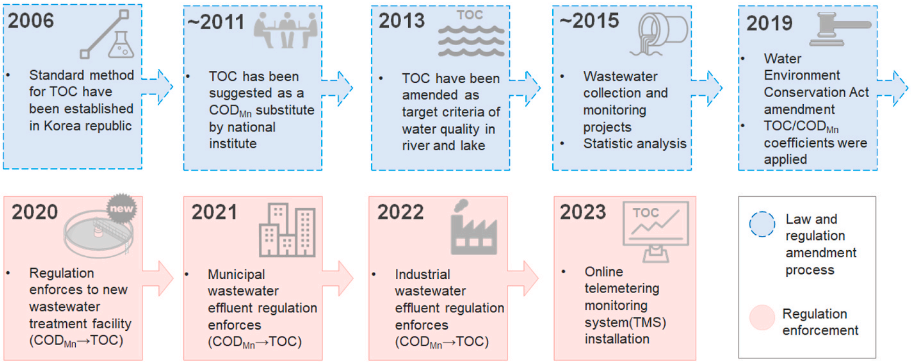


Fig. 1. Schematic of timeline for including total organic carbon in the regulations for wastewater effluents in South Korea.

Table 2
Information on study locations, and sample codes.

Category	Site code	Main products/sources	Discharge, m^3 day^{-1}	TOC limit, mg L^{-1}
Paper mill	KP	Whiteboard, toilet paper, others	17.2	40
	NP	Newspaper	11.0	40
	MP	Matt coated paper, gloss coated paper	18.3	50
Oil refinery	HO	Gasoline, diesel, kerosene	22.7	50
	SO	Gasoline, diesel	46.4	25
Industrial park wastewater	SM	Organic, inorganic chemicals, resin industry effluent	3.9	25
	CM	Paper mill, chemicals, metal industry effluent, urban sewage	44.0	15

SO effluents, respectively (Table 2). In addition, samples from two industrial park WWTPs (SM and CM) were collected. The influent for the SM plant mainly originated from the discharges of resin, organic, inorganic chemical, and plastic manufacturers. Meanwhile, the CM treatment plant influent comprised a mixture of the paper mill, chemical, non-ferric metal, and urban sewage discharges. The SM treatment plant discharges 3.9 m^3 of effluents per day, whereas the CM plant discharges 44.0 m^3 per day. The TOC criteria were 25 and 15 mg C L^{-1} for the SM and CM effluents, respectively (Table 2).

2.2. *Wastewater parameter analysis*

Temperature, pH, dissolved oxygen, conductivity, and total dissolved solids were measured at field locations (Table S3). All wastewater samples were collected in sterile polypropylene 2 L bottles, titrated to pH 2, and kept at 4 °C in an ice cooler storage box before analysis, in accordance with the Korean standard sampling campaign. TOC was analyzed based on the Korean Standard Method for Examination of Water Pollution, ES 04311.1c (high-temperature combustion method) (MOE, 2020). We homogenized the samples using an ultrasonic bath and then meshed the samples with a 300 μm filter. Then, TOC was determined by triplicate measurement using the Multi N/C 3100 system (Analytik Jena GmbH, Germany) (non-purgeable organic carbon method). The detection limit for TOC was 0.5 mg L^{-1}, and method variation coefficient was below 2%. COD_{Mn} (permanganate method, ES 04315.1b), COD_{Cr} (dichromate method, ES 04315.3c), BOD_5 (electrode method, ES 04305.1b), and suspended solids (SS) (ES 04303.1b) were also determined according to the Korean standard methods (MOE, 2020).

2.3. *Dissolved organic matter characterization*

To characterize DOC, we analyzed wastewater samples using specific UV absorbance at 254 nm (SUVA), size exclusion chromatography (SEC), and excitation-emission matrix (EEM) spectroscopy. Liquid chromatography - organic carbon detection (Model 8 system, DOC-Labor, Germany) enabled size fractionation and revealed DOC composition in each wastewater sample: biopolymers (20 kDa or higher), humic substances (1–20 kDa), building blocks of humic acids (350–500 Da), low molecular weight (MW) neutrals, and acids (lower than 350 Da). The method variation coefficient for chromatographic DOC using SEC system was below 10%. Huber et al. (2011) referred to the hydrophobic organic carbon (HOC) sub-fraction as the difference between the bypassed DOC and chromatographic DOC. Therefore, HOC is a portion of organic matter adsorbed to the gel media in the chromatography column, likely representing the derivatives from lipids, polyaromatic hydrocarbons, and humins as hydrophobic pools of wastewater (Ciputra et al., 2010; Tong et al., 2016). In the present study, we evaluated HOC as a significant portion of the wastewater matrices. Although we agree that these six sub-fraction categories (based on natural organic matter) might not be suitable for industrial wastewater organic composition (Aghasadeghi et al., 2017), we have used these category names for the readers' convenience.

Numerous studies have identified the fluorescent organic components in various municipal and industrial wastewater effluents (paper mill, oil refinery, coking, leather, slaughterhouse, and others) (Louvet et al., 2013; Yang et al., 2015; Cai et al., 2020; Rodriguez-Vidal et al., 2020; Hao et al., 2021). Although these fluorescent components overlap among industries and cannot be successfully applied as fingerprinting for a specific industrial category (Table 3), EEM can be fast, straightforward, and useful for understanding the similarities of organic matter composition across industries and to evaluate organic removal efficiency (Quaranta et al., 2012). Fluorescent spectroscopy (RF-5301 PC, Shimadzu, Japan) was used to scan the emission wavelength spectra from 280 to 600 nm using an excitation light source (220–400 nm, 10 nm width intervals). The observed EEM peaks were as follows: B (tyrosine-like, ex/em: 220–230/309–321 nm), T_1 (tryptophan-like, 220–240/330–360 nm), T_2 (tryptophan-like, 270–280/330–360 nm), A (fulvic-like, 230–260/400–450 nm), and C (humic-like, 300–340/400–450 nm). We also demonstrated the relative fluorescence intensity (RFI, %) of each peak over the total sum intensities to compare the relative abundance of fluorescent organic moieties.

2.4. *Statistics*

Pearson correlation and hierarchical cluster analysis were used to identify the characteristics of degradable and non-degradable (i.e., refractory) TOC in wastewater samples. To identify the components of TOC removed during the treatment, we compared the differentials of the analyte levels between treatment steps. All datasets were normalized using z-scores. The Pearson correlation matrix was obtained for each industrial category (paper mill, oil refinery, and industrial park WWTPs) using the normalized dataset. The significance level for correlation coefficients is expressed using the asterisk (* and ** for $p < 0.05$ and $p < 0.01$, respectively). For clustering EfOM, the final effluent quality data were used to evaluate the similarities of EfOM characteristics among different industrial wastewater facilities. We conducted hierarchical cluster analysis and extracted a dendrogram using Ward's linkage method.

3. Results and discussions

3.1. *Paper mill wastewater characteristics*

Paper mill industries discharged the highest TOC in raw wastewater (621–1023 mg L^{-1}) as compared to that of oil refineries (33–214 mg L^{-1}) and industrial park WWTPs (32–82 mg L^{-1}) (Table 4). In addition, SS concentrations were relatively higher in paper mill wastewater (513–4090 mg L^{-1}) than in the other types of raw wastewater (21–120 and 67–206 mg L^{-1} for oil refinery and industrial park wastewater, respectively), possibly due to pulp residue and fibers. According to Henderson et al. (2011), humic substances and their building blocks predominate the DOC compositions in paper mill wastewater. Relatively higher humic substances and building blocks (5–44% and 4–30% of DOC, respectively) were found in raw wastewater (Table 4), probably originating from pulp lignins. Fluorescence components, such as T_1 and C peaks, were more predominant than the other components. The T_1 peak represents the protein-like organic component, including phenolic moieties in lignins and low-MW free protein substances (Table 3). A previous study had reported that the A peak consists of fulvic- or low-MW humic-like moieties in lignins, whereas the C peak represents high-MW humic-like components and whitening agents for paper processing (Table 3). The product type or pulp recycling could dramatically

Table 3
Sources of fluorescent dissolved organic components.

Category	T1	T2	B	A	C	References
Municipal	Tryptophan-like	Tryptophan-like	Tyrosine-like	Fulvic-like	Humic-like	Carstea et al. (2016); Cai et al. (2020)
Paper and pulp mill industry	Tryptophan-like, phenolic moieties in lignins	Tryptophan-like, phenolic moieties in lignins	Tyrosine-like	Fulvic-like, lignin-derivatives, whitening agents	Humic-like, lignin-derivatives, whitening agents	Ciputra et al. (2010); Goldman et al. (2012); Poojamnong et al. (2020); Rodríguez-Vidal et al. (2020)
Oil and gas industry	Naphthalene, crude oil, coal tar, shale gas	Gasoline, diesel, kerosene, phenols	Benzene, toluene, ethylene, xylene, cresols	Dispersed oil	Crude oil	Alostaz et al. (2008); Zhou et al. (2013); Riley et al. (2018); Wasswa et al. (2019)

influence wastewater compositions. The highest humic substances, building blocks, EEM-A, and EEM-C peak intensities were found in the coated paper samples (MP) using no recycled pulp fibers (Fig. S2). The coated paper products for high-quality printing (e.g., packaging and magazine) probably require virgin pulps.

Primary treatment versus paper mill wastewater showed removal ranges of 41–68%, 4–60%, and 47–95% for TOC, DOC, and SS, respectively, and the primary treatment reduced loads of particulate and dissolved organic matter in the following biological treatment. No significant changes were found in the size distributions of DOC, except for the humic-replete wastewater from the MP plant. In particular, the MP facility showed better DOC removal (52 ± 10%) than other plants (9 ± 7%). The paper mill wastewater from MP showed the reduction of 94–99% humic substances, 58–90% building blocks, 84–92% EEM-A, and 81–87% EEM-C intensities via primary treatment. Thus, raw wastewater characteristics may affect the efficiency of the subsequent primary treatment.

The significance of secondary (biological) treatment in organic matter removal has been reported previously (Carstea et al., 2016). In our study, biological treatment substantially removed TOC (70–94%), DOC (65–99%), BOD (78–92%), COD_{Mn} (63–89%), and COD_{Cr} (56–87%). Size exclusion explained that building blocks, low MW acids, and neutrals were readily removed by biological treatment (average removal of 78–97%), while biopolymers, humic substances, and HOC were also moderately removed (62–66%). EEM spectroscopy showed that protein-like organic components (i.e., T_1, T_2, and B peaks) were relatively more biodegradable (59–71%) than humic-like ones (24–38% for A and C peaks), consistent with the findings of Carstea et al. (2016). Hence, peaks A and C likely correspond to the biorefractory or newly transformed substances via microbial decay, lysis, or humification (Carstea et al., 2016; Wang et al., 2017).

Finally, the TOC in the paper mill effluents ranged from 11 to 57 mg L^{-1} (Table 4). It should be noted that the paper mill effluents often exceeded the TOC requirement (4 of 6 samples). Higher organic loading (621–1023 mg L^{-1}, influent TOC) may aggravate the compliance of the criteria. Although humic substances are often regarded as refractory fractions, our data showed that humic substances were significantly removed (average 80%) throughout the treatment process and retained only 13% DOC in the effluent. In contrast, HOC (34%) and low-MW neutrals (28%) were the most abundant DOC fractions in the effluents. Notably, neither sub-fraction was correlated with the removal of TOC and COD_{Mn} (Fig. 2a). Thus, HOC and low-MW neutrals can be regarded as refractory compounds in paper mill wastewater.

3.2. *Oil refinery wastewater characteristics*

Raw wastewater from oil refineries contained 33–214 mg L^{-1} TOC, which is 5-fold lower than that of raw paper mill wastewater (Table 3). However, the relative biodegradability (BOD/TOC = 1.4) was higher than that of paper mill and industrial park wastewater (0.9 and 1.1, respectively). The high BOD loads in raw oil refinery wastewater are well known (US EPA, 1996). Size exclusion revealed that the HOC fraction was the most abundant (46 ± 12%) in DOC, followed by low-MW neutrals (30 ± 13%). Our observations are similar to those of heavy oil wastewater (Tong et al., 2016). HOC probably originated from unsaturated hydrocarbons, heavy alkyl phenols, oil emulsions, and other petroleum derivatives, while low-MW neutrals are naphthalene-like organic carbons (Riley et al., 2018). Meanwhile, biopolymers, humic substances, and building blocks accounted for less than 7% of the DOC. We also observed that protein-like fluorescence components, such as B and T_1 peaks, were predominant (21–39% and 29–35% RFI, respectively) (Fig. S2). Thus, we found similarities between our data and data from wastewater of other oil refineries (Riley et al., 2018) regarding the EEM contour patterns derived from petroleum species.

The primary treatment performance fluctuated from −4% to 67% TOC removal. The removal of HOC ($R^2 = 0.97$) and low-MW neutrals ($R^2 = 0.98$) was highly correlated with that of TOC. In the EEM results, T_1, T_2, B, and C peaks were also correlated with TOC removal in the primary treatment ($R^2 = 0.94$, 0.96, 0.92, and 0.88 for T_1, T_2, B, and C peaks, respectively). Interestingly, UV_{254} absorbance was also an indirect indicator for TOC and HOC removal ($R^2 = 0.68$ and 0.59, respectively), possibly due to light absorbance via unsaturated carbon bonds in oil-derived organic species, such as polycyclic aromatic hydrocarbons (PAHs). A previous study reported that phenolic, heterocyclic, and PAHs can be readily degraded via aerobic/anaerobic/anoxic treatment (Ren et al., 2019).

In the present study area, biological treatment removed 68 ± 32% of TOC (Table 4). In addition, we confirmed that HOC and low-MW neutrals could be biologically degraded (65 ± 17% and 59 ± 19%, respectively). The EEM results also showed a dramatic decrease in B, T_1, and T_2 peaks (71–85%) via biological treatment, which is in agreement with previous studies (Carstea et al. 2016; Ren et al., 2019). Tertiary effluents successfully met the TOC requirements by sieving particulates (e.g., 75% SS removal) and adsorption through sand or GAC filtration before discharge. However, because of the raw wastewater composition, the remaining fractions of oil refinery wastewater did not change substantially, and HOC (41 ± 20%) and low-MW neutrals (39 ± 26%) were predominant. We postulated that HOC and low-MW neutrals were the major components of both TOC and BOD, which are discussed in Section 3.4.

3.3. *Industrial park wastewater characteristics*

Industrial park wastewater contains a mixture of industrial wastewater treatment effluents and municipal wastewater, and its TOC ranges from 32 to 82 mg L^{-1}. The DOC composition in industrial park wastewater consisted of low-MW neutrals (44 ± 24%) and HOC (28 ± 17%). Low-MW neutrals could be the breakdown byproducts throughout biological treatments and relatively refractory organic sub-fractions, regardless of the sources of wastewater. A previous study showed that

Table 4
Changes in organic matter compositions throughout industrial wastewater treatment trains.

Category	Analyte	Influent	Primary treatment	Secondary treatment	Effluent
Paper mill (n = 6)	BOD, mg L^{-1}	406–1537 (779)	64–1831 (569)	4–52 (17)	3–24 (7)
	COD_{Mn}, mg L^{-1}	662–1722 (959)	251–585 (428)	37–205 (94)	27–80 (55)
	TOC, mg L^{-1}	621–1023 (823)	318–532 (406)	20–160 (69)	11–57 (40)
	COD_{Mn}/TOC	0.8–1.7 (1.2)	0.8–1.7 (1.1)	1.1–1.9 (1.4)	1.0–2.4 (1.5)
	DOC, mg L^{-1}	261–773 (428)	246–425 (312)	14–73 (48)	13–58 (41)
	HOC, %	5–46 (26)	11–33 (23)	15–43 (32)	3–58 (34)
	BP, %	1–18 (6)	0–7 (4)	4–31 (12)	1–36 (10)
	HS, %	5–44 (20)	1–22 (10)	5–18 (12)	5–18 (12)
	BB, %	4–30 (16)	9–23 (15)	11–16 (13)	9–16 (13)
	LMA, %	0–14 (8)	0–32 (13)	0–3 (2)	0–9 (3)
	LMN, %	11–47 (24)	21–53 (35)	21–37 (30)	15–40 (28)
Oil refinery (n = 4)	BOD, mg L^{-1}	67–251 (149)	37–164 (91)	1–215 (58)	0–30 (9)
	COD_{Mn}, mg L^{-1}	41–305 (134)	36–116 (78)	8–328 (96)	8–61 (21)
	TOC, mg L^{-1}	33–214 (105)	34–71 (62)	6–59 (21)	5–24 (11)
	COD_{Mn}/TOC	1.0–1.4 (1.2)	1.0–1.7 (1.2)	1.1–5.9 (2.9)	1.0–2.5 (1.5)
	DOC, mg L^{-1}	27–169 (92)	33–69 (50)	7–20 (14)	6–18 (11)
	HOC, %	17–69 (43)	17–53 (41)	8–58 (41)	12–60 (37)
	BP, %	1–9 (3)	0–2 (1)	0–18 (5)	0–5 (1)
	HS, %	0–6 (2)	0–7 (2)	0–7 (3)	0–6 (3)
	BB, %	2–7 (5)	3–8 (5)	3–17 (10)	3–17 (11)
	LMA, %	0–28 (10)	0–30 (9)	0–9 (4)	0–9 (5)
	LMN, %	17–74 (37)	20–74 (42)	20–82 (40)	26–78 (39)
Industrial park wastewater (n = 4)	BOD, mg L^{-1}	37–109 (64)	10–75 (29)	1–6 (3)	1–3 (1)
	COD_{Mn}, mg L^{-1}	20–99 (60)	42–84 (64)	7–29 (16)	5–17 (11)
	TOC, mg L^{-1}	32–82 (60)	38–81 (52)	16–19 (18)	13–19 (16)
	COD_{Mn}/TOC	0.6–1.8 (1.0)	0.9–1.8 (1.3)	0.3–1.5 (0.9)	0.3–1.2 (0.7)
	DOC, mg L^{-1}	30–58 (41)	40–62 (46)	16–27 (22)	15–25 (19)
	HOC, %	4–45 (28)	10–42 (26)	11–46 (26)	15–37 (24)
	BP, %	1–5 (2)	4–8 (5)	0–3 (1)	0–1 (1)
	HS, %	4–23 (12)	2–21 (11)	1–32 (15)	0–21 (11)
	BB, %	2–18 (10)	6–16 (11)	5–21 (12)	5–22 (12)
	LMA, %	1–5 (3)	1–6 (3)	1–5 (3)	0–3 (2)
	LMN, %	8–60 (44)	12–67 (44)	3–65 (43)	19–68 (50)

BOD, biochemical oxygen demand; COD, chemical oxygen demand; TOC, total organic carbon; DOC, dissolved organic carbon; HOC, hydrophobic organic carbon; BP, biopolymers; HS, humic substances; BB, building blocks; LMA, low molecular weight acids; LMN, low molecular weight neutrals; Average data are in parentheses.

low-MW neutrals in industrial park wastewater exhibited protein-like fluorescence properties (Cai et al., 2020), and our EEM results also showed dominant protein-like peaks (T_1, T_2, and B) (Fig. S2).

Primary treatment of industrial park wastewater resulted in relatively lower TOC removal (−19–37%) than that of other industrial wastewater categories investigated in our study. Generally, removal of organic fractions varied substantially during the sampling campaign, and no significant contribution of the specific organic fraction was found for TOC removal. SS only showed consistent removal (54 ± 4%) via the primary treatment of industrial park wastewater. Meanwhile, the biological treatment achieved 49–63% of TOC removal, along with higher removal rates of SS (72–91%). Based on differentials, we have found that the low-MW neutrals (6.9 ± 5.4 mg L^{-1}) and HOC (4.1 ± 4.3 mg L^{-1}) were the major biodegradable portions after secondary treatment, probably due to an absence of other organic sub-fractions. Finally, the effluents contained 16.0 ± 2.5 mg L^{-1} of TOC, including 11.0 ± 6.3 mg L^{-1} of low-MW neutrals. We observed that the least BOD (1.3 ± 1.3 mg L^{-1}) was found in industrial park wastewater effluents, followed by paper mill and oil refinery effluents (e.g., BOD/TOC = 0.09 ± 0.09, 0.20 ± 0.17, and 0.49 ± 0.56, respectively).

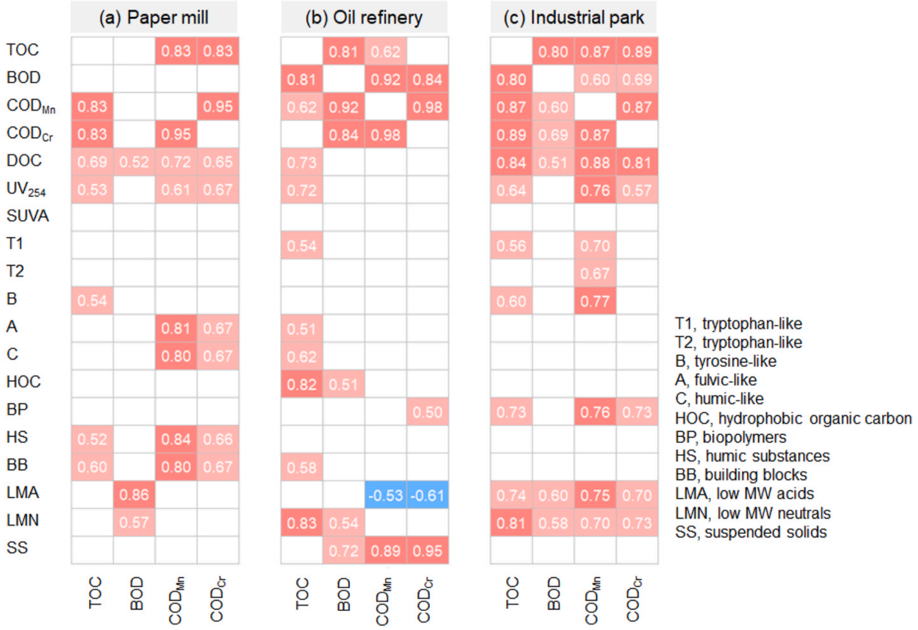
3.4. *Comparison of industrial wastewater*

Fig. 2 shows the relationships among the degradable portions of TOC, COD_{Mn}, and BOD with the dissolved organic matter parameters throughout industrial wastewater treatment trains. The Pearson correlation between COD_{Mn} and TOC was significantly high in the paper mill wastewater ($r = 0.83^{**}$, n = 22). Significant relationships were observed between COD_{Mn}, EEM-A and C peaks, humic substances, building blocks, and UV_{254} absorbance (Fig. 2a). The COD_{Mn} preferentially oxidized fulvic-, humic-, or lignin-like aromatic organic matter. Additionally, TOC was moderately correlated with humic substances, building blocks, UV_{254}, and EEM-B peaks in paper mill wastewater. Therefore, there were some similarities between TOC and COD_{Mn} compositions (i.e., DOC, UV_{254}, humic substances, and building blocks) (Fig. 2a), while TOC was also influenced by proteinaceous organic matter. BOD could not oxidize high-MW or humic substances in paper mill wastewater and was related to only low-MW neutrals and acids (Fig. 2a). Understanding the impact of the new TOC criteria on the paper mill industry is noteworthy as previous COD_{Mn} measurements might have underestimated the extent of refractory organic matter in EfOM, which consists of aliphatic, proteinaceous, and saturated organic carbon bonds. These differences may be one of the causes of compliance failure in paper mill industries. Therefore, it is important to investigate industrial categories where the organic matter in their discharges was underestimated when measuring COD_{Mn}.

For oil refinery wastewater, the correlation between COD_{Mn} and TOC was moderate ($r = 0.62^{**}$, n = 17), and the two parameters were likely related to the biodegradable component, i.e., BOD (Figs. 2b and 3b). BOD removal was correlated with that of HOC, low-MW neutrals, and SS (r = 0.51*, 0.54*, and 0.72**, respectively) in oil refinery wastewater (Fig. 2b). COD_{Mn} was highly correlated to only COD_{Cr}, BOD, and SS, but no relationships were observed with DOC characteristics. On the other hand, TOC covered a wider range of organic matter, and HOC, low-MW neutrals, UV_{254}, EEM-C, T_1, and A peaks were the major sub-components of the TOC matrix in oily wastewater (Fig. 2b), which were likely underestimated by COD_{Mn}. Therefore, the shift from COD_{Mn} to the TOC criteria was the most substantial for oil refinery wastewater.

The industrial park wastewater matrix showed no significant differences between TOC and COD_{Mn} (Figs. 2 and 3). The organic matter composition exhibited low MW and proteinaceous properties. Both TOC and COD_{Mn} were significantly correlated with UV_{254}, low-MW neutrals, low-MW acids, and biopolymers (n = 16, $p < 0.01$). Protein-like EEM peaks (T_1 and B) were also correlated to the fate of both COD_{Mn} and TOC through the treatment steps. These similarities are probably due to the absence of aromatic humic substances, high molar mass, and polymeric organic substances, resulting in lower oxidation rates. BOD removal was correlated with low-MW acids and neutrals (r = 0.60* and 0.58*, respectively) (Fig. 2c). The low-MW neutrals in industrial park wastewater could thus be moderately biodegradable.

The hierarchical cluster analysis showed similarities in the EfOM



	(a) Paper mill				(b) Oil refinery				(c) Industrial park			
	TOC	BOD	COD_{Mn}	COD_{Cr}	TOC	BOD	COD_{Mn}	COD_{Cr}	TOC	BOD	COD_{Mn}	COD_{Cr}
TOC			0.83	0.83		0.81	0.62			0.80	0.87	0.89
BOD					0.81		0.92	0.84	0.80		0.60	0.69
COD_{Mn}	0.83			0.95	0.62	0.92		0.98	0.87	0.60		0.87
COD_{Cr}	0.83		0.95			0.84	0.98		0.89	0.69	0.87	
DOC	0.69	0.52	0.72	0.65	0.73				0.84	0.51	0.88	0.81
UV_{254}	0.53		0.61	0.67	0.72				0.64		0.76	0.57
SUVA												
T1					0.54				0.56		0.70	
T2											0.67	
B	0.54								0.60		0.77	
A			0.81	0.67	0.51							
C			0.80	0.67	0.62							
HOC					0.82	0.51						
BP								0.50	0.73		0.76	0.73
HS	0.52		0.84	0.66								
BB	0.60		0.80	0.67	0.58							
LMA		0.86					-0.53	-0.61	0.74	0.60	0.75	0.70
LMN		0.57			0.83	0.54			0.81	0.58	0.70	0.73
SS						0.72	0.89	0.95				

Fig. 2. Pearson correlation heatmap for relationships between TOC, BOD, COD_{Mn}, COD_{Cr}, SS, and dissolved organic matter characteristics. Insignificant coefficients were blanked in heatmap ($-0.5 < r < 0.5$ and p-value > 0.05).

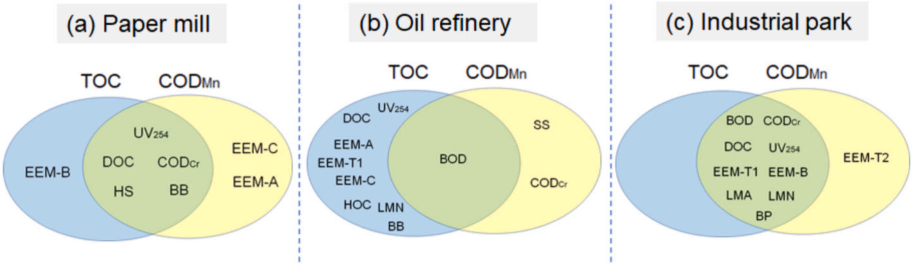


Fig. 3. Venn diagrams demonstrating the overlap in compositions between TOC and COD_{Mn} based on Pearson correlation coefficients ($r > 0.5$ and $p < 0.05$).

among the industrial categories. Two main clusters were found: paper mill effluent samples were grouped together, whereas other wastewater effluents were clustered regardless of the industrial category (Fig. 4). Distinct clustering was possibly due to relatively higher humic content and organic matter residuals in paper mill effluents than in others. In summary, paper mill discharge showed unique characteristics between effluents and may require enhanced treatment techniques to achieve regulatory compliance.

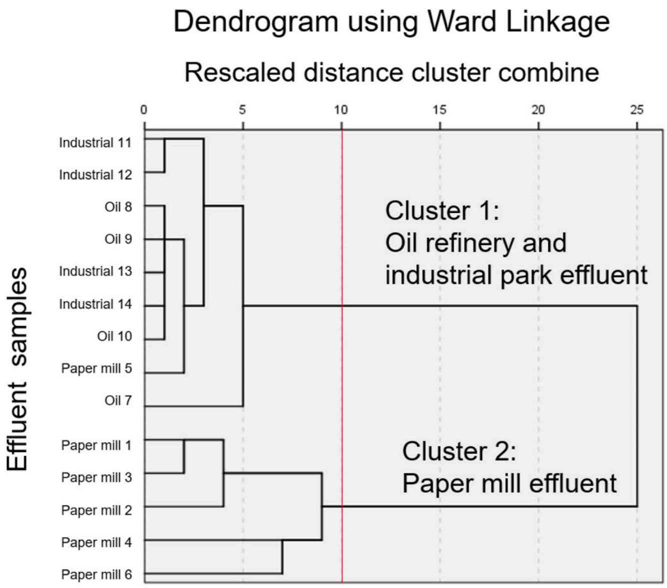


Fig. 4. Hierarchical cluster analysis using the effluent organic matter characteristics.

3.5. Lessons from the shift from COD_{Mn} to TOC in industrial wastewater discharge regulations

The criteria for the replacement of COD_{Mn} with TOC require more consideration and investigation of pulp mill and oil refinery wastewaters due to different organic matter characteristics, whereas industrial park wastewater showed no differences between COD_{Mn} and TOC. We hypothesized that the organic matter composition of industrial wastewater might shape recalcitrance and determine the success/failure of regulatory requirements. However, low-MW neutrals and HOCs are often the most abundant in all types of wastewater, and any specific components cannot exemplify the refractory nature of industrial wastewater. The observed COD_{Mn}/TOC ratio was generally lower (11 of 14 effluent samples) than the designated coefficients (Table S4), resulting in higher TOC than expected. Compared to a previous study (NIER, 2014), the COD_{Mn}/TOC ratio was lower in paper mill effluent, followed by oil refineries and industrial parks. The main limitations in setting the coefficients were as follows. First, monitoring campaigns required substantial labor, time, and analytic costs for decades. In South Korea, wastewater discharge facilities currently account for over 50,000 sites. However, for instance, monitoring of only 512 of these sites (38 industrial categories) was feasible under national projects from 2012 to 2014 (NIER, 2014). Second, effluent COD_{Mn}/TOC ratios were influenced by industrial category, discharge capacity, treatment train, and sample sizes during the monitoring campaign (NIER, 2014). However, the new TOC regulation only considers the receiving water bodies. Thus, meeting the new regulatory requirements might be challenging for discharge facilities with low COD_{Mn}/TOC ratios in clean watersheds (e.g., municipal or industrial park wastewater). Additionally, as previous projects did not consider advanced organic matter characterization, utilizing the organic matter characteristics for TOC compliance is a significant aspect of this study. We found that BOD, SUVA, and SS (r = 0.62**, 0.57*, and 0.61*, respectively) only marginally influenced the effluent COD_{Mn}/TOC ratio, but further evaluation is needed because of low sample size (n = 14).

Lab-scale studies have suggested the best available treatment options for refractory compounds in wastewater effluents, such as GAC, ion exchange, advanced oxidation, and membrane filtration (Bijan and Mohseni, 2005; Cipurta et al., 2010; Bassandeh et al., 2013; Cai et al., 2020). In particular, several studies have suggested that Fenton-based advanced oxidation processes effectively decrease TOC in paper and pulp mill wastewater (Perez et al., 2002; Klidi et al., 2019). However, further full-scale studies are necessary as industries face limitations in the form of land use, budget, and maintenance skills. TOC removal cannot be completely understood using BOD in biological treatment, possibly due to low accuracy and experimental errors. Thus, we suggest considering an alternative parameter for BOD in the future. For instance, biodegradable dissolved organic carbon (BDOC) measures a biodegradable portion of bulk organic matter and uses a TOC detection system that synchronizes an equivalent organic carbon unit (mg C L^{-1}). Although it has been estimated in treated effluents and reclaimed water (Weinrich et al., 2010), BDOC requires an optimum microbial inoculum and modification for wastewater.

4. Conclusions

The present study demonstrated the experiences of a new effluent standard in South Korea and the role of organic matter characteristics in the criteria shift (from COD_{Mn} to TOC). TOC replacement led to compliance failure in some of the paper mill industry effluents. The target organic matter characteristics in the industrial wastewaters varied between the COD_{Mn} and TOC criteria, except for industrial park wastewater. A careful investigation of the ratio of COD_{Mn} and TOC was conducted for different industries when the regulation of bulk organic matter switches from COD_{Mn} to TOC.

The following highlights can be drawn:

- Low-MW neutrals, HOC, and protein-like fluorescent components are often abundant in raw and treated wastewater.
- Humic content in paper mill wastewater depends on product type and ingredient and is correlated to COD_{Mn}, though TOC covers a wider range of organic compounds.
- Oil refinery wastewater is relatively more biodegradable and consisted of HOC, low-MW neutrals, and proteinaceous and aliphatic components, which were underestimated by COD_{Mn}.
- The COD_{Mn}/TOC ratio was lower than the conversion coefficients and led to higher TOC values than expected, probably due to aliphatic and particulate organic carbon.

Credit author statement

Ji Won Park: Methodology, writing and investigation. Sang Yeob Kim: Experiment and data collection. Jin Hyung Noh: Experiment and data collection. Young Ho Bae: Data collection and supervision. Jae Woo Lee: Revised manuscript preparation and data collection. Sung Kyu Maeng: Supervision and manuscript preparation.

Declaration of competing interest

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

Acknowledgments

This study was supported by a National Research Foundation of Korea (NRF) grant funded by the Korean government (Ministry of Science and ICT, grant no. NRF-2021R1A4A3030924). We also acknowledge Soo Jung Lim, staff in KECO, for her valuable field research and project management.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jenvman.2021.114412.

References

Aghasadeghi, K., Csordas, M., Peldszus, S., Latulippe, D.R., 2017. Combining Lc-Ocd analysis with design-of-experiments methods to optimize an advanced oxidation process for the treatment of industrial wastewater. Can. J. Chem. Eng. 95 (10), 1943–1952.

Aiken, G., Kaplan, L.A., Weishaa, J., 2002. Assessment of relative accuracy in the determination of organic matter concentrations in aquatic systems. J. Environ. Monit. 4 (1), 70–74.

Alostaz, M., Biggar, K., Donahue, R., Hall, G., 2008. Soil type effects on petroleum contamination characterization using ultraviolet induced fluorescence excitation-emission matrices (EEMs) and parallel factor analysis (PARAFAC). J. Environ. Eng. Sci. 7 (6), 661–675.

Assmann, C., Scott, A., Biller, D., 2017. Online total organic carbon (TOC) monitoring for water and wastewater treatment plants processes and operations optimization. Drink. Water Eng. Sci. 10 (2), 61–68.

Bassandeh, M., Antony, A., Le-Clech, P., Richardson, D., Leslie, G., 2013. Evaluation of ion exchange resins for the removal of dissolved organic matter from biologically treated paper mill effluent. Chemosphere 90 (4), 1461–1469.

Bijan, L., Mohseni, M., 2005. Integrated ozone and biotreatment of pulp mill effluent and changes in biodegradability and molecular weight distribution of organic compounds. Water Res. 39 (16), 3763–3772.

Cai, M.H., Wu, Y.P., Ji, W.X., Han, Y.Z., Li, Y., Wu, J.C., Shuang, C.D., Korshin, G.V., Li, A.M., Li, W.T., 2020. Characterizing property and treatability of dissolved effluent organic matter using size exclusion chromatography with an array of absorbance, fluorescence, organic nitrogen and organic carbon detectors. Chemosphere 243.

Carstea, E.M., Bridgeman, J., Baker, A., Reynolds, D.M., 2016. Fluorescence spectroscopy for wastewater monitoring: a review. Water Res. 95, 205–219.

Christian, E., Batista, J.R., Gerrity, D., 2017. Use of COD, TOC, and fluorescence spectroscopy to estimate BOD in wastewater. Water Environ. Res. 89 (2), 168–177.

Ciputra, S., Antony, A., Phillips, R., Richardson, D., Leslie, G., 2010. Comparison of treatment options for removal of recalcitrant dissolved organic matter from paper mill effluent. Chemosphere 81 (1), 86–91.

Dubber, D., Gray, N.F., 2010. Replacement of chemical oxygen demand (COD) with total organic carbon (TOC) for monitoring wastewater treatment performance to minimize disposal of toxic analytical waste. J. Environ. Sci. Health A Tox. Hazard Subst. Environ. Eng. 45 (12), 1595–1600.

Goldman, J.H., Rounds, S.A., Needoba, J.A., 2012. Applications of fluorescence spectroscopy for predicting percent wastewater in an urban stream. Environ. Sci. Technol. 46 (8), 4374–4381.

Hao, Y.Y., Ma, H.R., Wang, Q., Ge, L.K., Yang, Y.L., Zhu, C., 2021. Refractory DOM in industrial wastewater: formation and selective oxidation of AOPs. Chem. Eng. J. 406.

Henderson, R.K., Subhi, N., Antony, A., Khan, S.J., Murphy, K.R., Leslie, G.L., Chen, V., Stuetz, R.M., Le-Clech, P., 2011. Evaluation of effluent organic matter fouling in ultrafiltration treatment using advanced organic characterisation techniques. J. Membr. Sci. 382, 50–59.

Huber, S.A., Balz, A., Abert, M., Pronk, W., 2011. Characterisation of aquatic humic and non-humic matter with size-exclusion chromatography - organic carbon detection - organic nitrogen detection (LC-OCD-OND). Water Res. 45 (2), 879–885.

Klidi, N., Proietto, F., Vicari, F., Galia, A., Ammar, S., Gadri, A., Scialdone, O., 2019. Electrochemical treatment of paper mill wastewater by electro-Fenton process. J. Electroanal. Chem. 841, 166–171.

Louvet, J.N., Homeky, B., Casellas, M., Pons, M.N., Dagot, C., 2013. Monitoring of slaughterhouse wastewater biodegradation in a SBR using fluorescence and UV-Visible absorbance. Chemosphere 91 (5), 648–655.

MOE, 2019. Standards for Best Available Techniques for Environmental Pollution Prevention and Integrated Management of Pulp, Paper and Paperboard Manufacturing Industry. Ministry of Environment (Korean Literature).

MOE, 2020. Standard Methods for Examination of Water Pollution. Ministry of Environment (MOE).

NIER, 2002. A Study on the Conversion Indicator of Organic Pollutant for Wastewater Effluent - Optimum Conversion Indicator of COD_{Mn} Standard. National Institute of Environmental Research. Project Report (Korean Literature).

NIER, 2014. TOC Monitoring and its Improvement of Regulation Standard in Industry. National Institute of Environmental Research. Project Report (Korean literature).

NVV, 2019. Swedish Pollutant Release and Transfer Register - Total Organic Carbon. Naturvårdsverket (Swedish Environmental Protection Agency). https://utslappisiffror.naturvardsverket.se/en/Substances/Other-organic-substances/Total-organic-carbon/. (Accessed July 2021).

Perez, M., Torrades, F., Garcia-Hortal, J.A., Domenech, X., Peral, J., 2002. Removal of organic contaminants in paper pulp treatment effluents under Fenton and photo-Fenton conditions. Appl. Catal. B Environ. 36 (1), 63–74.

Poojamnong, K., Tungsudjawong, K., Khongnakorn, W., Jutaporn, P., 2020. Characterization of reversible and irreversible foulants in membrane bioreactor (MBR) for eucalyptus pulp and paper mill wastewater treatment using fluorescence regional integration. J. Environ. Chem. Eng. 8 (5).

Quaranta, M.L., Mendes, M.D., MacKay, A.A., 2012. Similarities in effluent organic matter characteristics from Connecticut wastewater treatment plants. Water Res. 46 (2), 284–294.

Ren, J., Li, J.F., Li, J.G., Chen, Z.L., Cheng, F.Q., 2019. Tracking multiple aromatic compounds in a full-scale coking wastewater reclamation plant: interaction with biological and advanced treatments. Chemosphere 222, 431–439.

Riley, S.M., Ahoor, D.C., Regnery, J., Cath, T.Y., 2018. Tracking oil and gas wastewater-derived organic matter in a hybrid biofilter membrane treatment system: a multi-analytical approach. Sci. Total Environ. 613, 208–217.

Rodriguez-Vidal, F.J., Garcia-Valverde, M., Ortega-Azabache, B., Gonzalez-Martinez, A., Bellido-Fernandez, A., 2020. Characterization of urban and industrial wastewaters using excitation-emission matrix (EEM) fluorescence: searching for specific fingerprints. J. Environ. Manag. 263.

SFC, 2021. SR 814.201 - Waters Protection Ordinance (WPO) (Status of 1 January 2021). The Swiss Federal Council. https://www.fedlex.admin.ch/eli/cc/1998/2863_2863_2863/en. (Accessed July 2021).

Tong, K., Lin, A.G., Ji, G.D., Wang, D., Wang, X.H., 2016. The effects of adsorbing organic pollutants from super heavy oil wastewater by lignite activated coke. J. Hazard Mater. 308, 113–119.

UBA, 2017. Final Report - Specific Contract No. 07.0201/2015/SFRA/714792/ENV.C.2 Implementing Framework Service Contract ENV.D2/FRA/2012/0013.

US EPA, 1996. Preliminary Data Summary for the Petroleum Refining Category. EPA 821-R-96-015. DCN PR00158. U.S. Environmental Protection Agency. Office of Water, Engineering and Analysis Division, 401 M Street, SW., Washington, DC 20460.

Wang, L., Li, Y.J., Xiong, Y., Mao, X.H., Zhang, L.Y., Xu, J.F., Tan, W.B., Wang, J.S., Li, T. T., Xi, B.D., Wang, D.H., 2017. Spectroscopic characterization of dissolved organic matter from sludge solubilization treatment by micro-bubble technology. Ecol. Eng. 106, 94–100.

Wasswa, J., Mladenov, N., Pearce, W., 2019. Assessing the potential of fluorescence spectroscopy to monitor contaminants in source waters and water reuse systems. Environ. Sci-Wat Res. 5 (2), 370–382.

Weinrich, L.A., Jjemba, P.K., Giraldo, E., LeChevallier, M.W., 2010. Implications of organic carbon in the deterioration of water quality in reclaimed water distribution systems. Water Res. 44 (18), 5367–5375.

Yang, L., Han, D.H., Lee, B.M., Hur, J., 2015. Characterizing treated wastewaters of different industries using clustered fluorescence EEM-PARAFAC and FT-IR spectroscopy: implications for downstream impact and source identification. Chemosphere 127, 222–228.

Zhou, Z.Z., Guo, L.D., Shiller, A.M., Lohrenz, S.E., Asper, V.L., Osburn, C.L., 2013. Characterization of oil components from the Deepwater Horizon oil spill in the Gulf of Mexico using fluorescence EEM and PARAFAC techniques. Mar. Chem. 148, 10–21.