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Biodegradable dissolved organic carbon for indicating wastewater reclamation plant performance and treated wastewater quality

Eakalak Khan, Roger W. Babcock, Jr., Sarunyu Viriyavejakul, Irwin (Mel) H. Suffet, Michael K. Stenstrom

ABSTRACT: Various methods for measuring biodegradable dissolved organic carbon (BDOC) in water have been introduced in the last decade. Applications of the methods have been limited to drinking water. The measure of BDOC has been used mainly to indicate the quality of raw and finished waters and evaluate the performance of biological activated carbon (ozone/granular activated carbon) systems in water treatment plants. Recently, a modified BDOC protocol was developed for examining reclaimed and secondary-treated wastewaters. Use of the new BDOC method can be extended to the wastewater treatment and reclamation fields. Samples collected from a wastewater reuse pilot facility were tested for BDOC. The modified BDOC method was able to detect the increase in biodegradability of ozonated tertiary-treated wastewater. Good relationships among BDOC, dissolved organic carbon (DOC), and soluble biochemical oxygen demand were obtained. The modified protocol was later used to measure BDOC in secondary-effluent samples from 13 municipal wastewater treatment plants. The results show that BDOC can also be used as an indicator of secondary-effluent quality. Likewise, strong and significant correlations were found among BDOC, DOC, and soluble chemical oxygen demand in secondary effluents. *Water Environ. Res.*, **70,** 1033 (1998).

KEYWORDS: biodegradable dissolved organic carbon, wastewater reclamation, ozonation, secondary-treated wastewaters.

Introduction

Within the last few years, there has been an increasing interest in assessing the biodegradability of dissolved aquatic organic matter. Dissolved organic carbon (DOC) is the parameter most commonly used to represent the amount of dissolved organic matter in water. As a result, several methods for determining biodegradable dissolved organic carbon (BDOC) have been proposed in the last decade.

Methods for analyzing BDOC can be categorized into two main groups: batch (Joret *et al.*, 1988; Joret and Levi, 1986; and Servais *et al.*, 1987 and 1989) and biofilm reactor (Frias *et al.*, 1992; Kaplan and Newbold, 1995; Lucena *et al.*, 1990; Mogren *et al.*, 1990; and Ribas *et al.*, 1991), sometimes referred to as static methods and dynamic methods, respectively. Most of the batch methods and all of the biofilm reactor methods share the same concept, which involves measuring DOC concentrations before and after a period of controlled biochemical reaction. All BDOC methods have provided good and statistically identical results for all types of drinking water samples (Frias *et al.*, 1995). Applications of BDOC methods have included examination of raw and finished waters and evaluation of biological activated carbon (BAC) (ozone/granular activated carbon [GAC]) system performance.

Methods for BDOC analysis have been widely accepted in the drinking-water industry, but none of the methods has been proven to be applicable to reclaimed and secondary-treated wastewaters. This is because the characteristics of reclaimed and secondary-treated wastewaters are very different from those of drinking water. The DOC in reclaimed and secondary-treated wastewater typically is of higher concentration and is more recalcitrant than that in drinking water. Several techniques must be added to the batch methods. Biofilm BDOC methods resemble the trickling filter process in wastewater treatment. The methods may perform well with reclaimed wastewater containing more readily degradable BDOC, such as ozonated wastewater. Although not yet tested, application of the methods to secondary effluent might result in insignificant DOC reduction or no BDOC detection.

Khan *et al.* (1998) developed a batch BDOC protocol specifically for reclaimed and secondary-treated wastewaters by combining an existing batch protocol (Servais *et al.*, 1989) with the biochemical oxygen demand (BOD) test. Dilution and seed control techniques are included in the protocol to avoid dissolved oxygen (DO) depletion and to produce more accurate results. The protocol is capable of determining DOC, BDOC, and ultimate soluble BOD ($SBOD_u$) of reclaimed wastewater samples simultaneously. It uses a 2-mL acclimated inoculum (unfiltered sample) and follows both the DOC and DO decreases in reclaimed-wastewater samples during an incubation period of 28 days, in the dark, at 20°C. The BDOC is estimated by multiplying the difference between DOC reductions in the sample and in the seed control by the dilution factor. Soluble BOD is calculated in the same way using DO reduction instead of DOC reduction. For secondary effluent samples, the procedure is the same except that the incubation period for SBOD is 5 days. However, the protocol cannot determine $SBOD_5$ of secondary effluents simultaneously with DOC and BDOC because the inoculum is inadequate.

The objective of this paper is to show that the recently developed BDOC protocol (Khan *et al.*, 1998) can be useful to the wastewater treatment and reclamation industries. The utility of this new method is demonstrated by an evaluation of the performance of a BAC system at a wastewater reuse facility. Application of the method is further demonstrated by showing how it can be used to characterize secondary-treatment effluents.

Background

The first BDOC method (Servais *et al.*, 1987) was developed specifically for testing raw-water quality and for designing, monitoring, and optimizing operating conditions of BAC systems. Occasionally, BDOC has been used to measure the effects of other treatment processes. Interest in the BDOC of finished water grew when BDOC was linked to microbial regrowth in distribution systems.

Use of Biodegradable Dissolved Organic Carbon for Indicating Raw-Water Quality. Hascoet *et al.* (1986) applied a batch BDOC method (Servais *et al.*, 1987) to test river water in France and presented the idea of using BDOC as another parameter for examining raw water. Servais *et al.* (1989) measured BDOC in three Belgian rivers using a revised batch protocol. Two of the rivers were more contaminated by domestic and industrial wastewater than the other. The BDOC concentrations in the more contaminated rivers (2.0 to 6.1 mg/L) were approximately two to nine times higher than that of the less contaminated river (0.7 to 1.2 mg/L).

Mogren *et al.* (1990) applied a dynamic biofilter BDOC method to three raw-water sources in the U.S.: Ohio River water, Florida groundwater, and Delaware River water. Based on the results from single bioreactor analyses, water from all three sources had low BDOC concentrations: 0.32 mg/L for Ohio River water, 0.75 mg/L for Florida groundwater, and 0.45 mg/L for Delaware River water.

Ribas *et al.* (1992) used their dynamic bioreactor method (Ribas *et al.*, 1991) to monitor BDOC in a Spanish river that served as a water supply for the city of Barcelona. The BDOC and DOC concentrations were influenced by the flow of the river. Two separate monitoring events were performed, in January 1992 and October 1992. The BDOC and DOC concentrations during the first monitoring period were 1.35 ± 0.87 mg/L and 6.80 ± 0.59 mg/L, respectively. The flow of the river during the second monitoring period was 1.5 to 2 times higher, and BDOC and DOC values decreased to 0.48 ± 0.31 mg/L and 4.39 ± 0.62 mg/L, respectively.

Use of Biodegradable Dissolved Organic Carbon for Designing, Monitoring, and Optimizing Operating Conditions of Biological Activated Carbon Systems. Several authors (Hascoet *et al.*, 1986; Mogren *et al.*, 1990; Ribas *et al.*, 1992; and Servais *et al.*, 1987) detected a BDOC increase after ozonating sand filter effluent. Optimum ozone dosage varies with water characteristics, and batch studies are often required (Malley *et al.*, 1993, and Volk *et al.*, 1993). In both pilot- and full-scale BAC systems, the most cost-effective ozone dosages that significantly increase BDOC are chosen (Malley *et al.*, 1993). To reach the optimum BDOC formation, a short contact time and high ozone dose are generally preferred over a long contact time and low ozone dose (Volk *et al.*, 1993).

Hascoet *et al.* (1986) studied a BAC system. They did not specify a backwashing procedure but reported that backwashing had an adverse effect on the biomass in the biological activated-carbon filter (BAF). The BDOC reductions in the filter were 55 to 60% during normal operation. After backwashing, immediately followed by 30 minutes of filtration, only 25% of BDOC was removed in the filter. Nevertheless, Servais *et al.* (1991) monitored bacteria populations in the outlet water from one of the BAFs used in a full-scale drinking water plant in Paris before and after backwashing and learned that only 4 to 8% of the bacterial biomass attached on GAC was released during washing. They later concluded that backwashing the filters has an insignificant effect on microbiological function.

Hascoet *et al.* (1986) and Servais *et al.* (1991) observed BDOC removal only in the first 20 to 40 cm of 100-cm-deep BAFs. The effect of filtration velocity on BDOC removal was briefly studied by Servais *et al.* (1989). A 100-cm-depth BAF was operated at filtration velocities of 6, 12, and 18 m/h. A BDOC removal of approximately 70% was achieved at the filtration velocity of 6 m/h. Dramatic decreases in BDOC removal to approximately 30% and 20% were observed at the filtration velocities of 12 and 18 m/h, respectively. Merlet *et al.* (1991) obtained similar results by studying the relationship between BDOC removal in a BAF and empty bed contact time (EBCT) and concluded that removal of BDOC in a BAF is a function of EBCT. The BDOC reduction in a BAF increases with increasing EBCT and thus decreasing filtration velocity.

Use of Biodegradable Dissolved Organic Carbon for Measuring the Effects of Water Treatment Processes Other Than Biological Activated Carbon. Mogren *et al.* (1990) used their dynamic biofilter BDOC method to evaluate the effect of different drinking water treatment processes on BDOC. Samples from three treatment plants were collected. The first treatment plant drew its raw water from the Ohio River. The effect of chlorination located between coagulation/flocculation/sedimentation and parallel dual-media (anthracite/sand) filtration was examined. Chlorination resulted in a BDOC increase from 0.23 mg/L in the influent to 0.37 mg/L in the effluent and no DOC reduction (2.24 mg/L in the influent and 2.22 mg/L in the effluent). Both BDOC and DOC decreased to less than 0.10 mg/L and 2.06 mg/L when the same influent was fed to the filters without prechlorination. The filter could have been a biologically active filter, therefore leading to biodegradation. The effect of ozonation between lime softening and parallel dual-media (anthracite/sand) filtration was studied for the second plant. The raw water was Florida groundwater. Without preozonation, there was no significant DOC removal in the filter (7.94 to 7.91 mg/L) and BDOC increased from less than 0.10 mg/L to 0.21 mg/L. When the lime softened water was ozonated, BDOC increased to 0.52 mg/L and DOC remained constant (7.85 mg/L). Then, the filter reduced BDOC and DOC to 0.26 mg/L and 7.67 mg/L, respectively. Samples were collected from the following treatment processes of the third plant: ozonation, Superpulsator™ (Infilco Degremont Inc., Richmond, Virginia), and parallel-dual media filters. Raw water for the plant was supplied by the Delaware River. The filters were packed with different combinations of media, anthracite/sand, or GAC/sand, and performance was compared. Unfortunately, the super-pulsator was very effective in removing BDOC (1.16 to 0.10 mg/L) and DOC (3.09 to 1.73 mg/L): the comparison could not be made. The two filters with different combinations of media produced effluents with BDOC and DOC levels similar to those found in effluent of the super-pulsator.

Use of Biodegradable Dissolved Organic Carbon for Indicating Finished Water Quality and Controlling Microbial Regrowth. The use of BDOC has been related to regrowth of microorganisms. High BDOC in finished water indicates poor quality and a potential for microbial multiplication. Maintaining a free chlorine residual to prevent the regrowth along the distribution system is a common solution; however, a large amount of chlorine is required. Also, chlorine residual cannot completely inactivate fixed bacteria (Le Chevallier *et al.*, 1988). Controlling

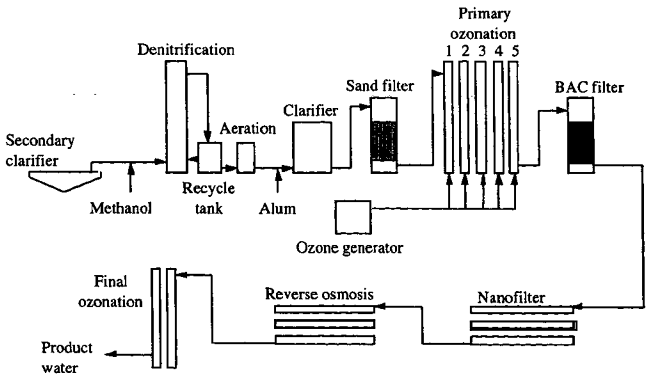

Figure 1—Lake Arrowhead reclamation pilot plant schematic.

microbial dynamics by limiting available substrate (BDOC) is a new and interesting approach. Removal of BDOC to a level that limits microbial growth provides not only a direct control of bacterial population but also an indirect control of protozoan population through a trophic food web (Servais *et al.*, 1993). Servais *et al.* (1993) stated that biologically stable waters should contain less than 0.15 mg/L BDOC. At this threshold level, microbial growth is very limited.

Methodology

Reclaimed Wastewater Samples. Eight reclaimed-wastewater samples were collected weekly from the Lake Arrowhead wastewater reclamation pilot plant, Lake Arrowhead, California. The pilot plant had a capacity of 20 L/min and was operated by the University of California at Los Angeles and the Lake Arrowhead Community Services District (Madireddi *et al.*, 1997). It was designed to repurify secondary unchlorinated effluent from the Grass Valley trickling filter municipal wastewater treatment plant (WWTP) and to use the product water to replenish Lake Arrowhead during drought periods. According to the plan, the product water would be stored for 1 year in a small lake adjoining Lake Arrowhead and then allowed to overflow into Lake Arrowhead, the sole drinking-water source in the community. The treatment scheme of the pilot plant included denitrification, alum coagulation/flocculation/sedimentation, sand filtration, primary ozonation (5 columns), BAF, nanofiltration, reverse osmosis, and final ozone disinfection. A schematic diagram of the pilot plant is shown in Figure 1. The samples were taken from the effluent of the sand filter, each of the primary ozonation columns, the BAF, and the nanofilter.

Secondary Effluent Samples. Unchlorinated secondary effluent samples were collected daily for 10 consecutive working days from each of 13 municipal WWTPs listed as follow:

- The regional plant (RP) 1 WWTP, Ontario, California, 36 mgd, operated by the Chino Basin Municipal Water District;
- The RP 2 WWTP, Chino, California, 5 mgd, operated by the Chino Basin Municipal Water District;
- Carbon Canyon WWTP, Chino, California, 7 mgd, operated by the Chino Basin Municipal Water District;
- Tapia WWTP, Calabasas, California, 9 mgd, operated by the Las Virgenes Municipal Water District;
- Glendale WWTP, Glendale, California, 20 mgd, operated by the Los Angeles Bureau of Sanitation (LABS);
- Tillman WWTP, Van Nuys, California, 65 mgd, operated by the LABS;
- Orange County WWTP No. 1, Fountain Valley, California, 40 mgd, operated by the County Sanitation Districts of Orange County (CSDOC);
- Union Sanitary District (USD) WWTP, Union City, California, 30 mgd, operated by USD;

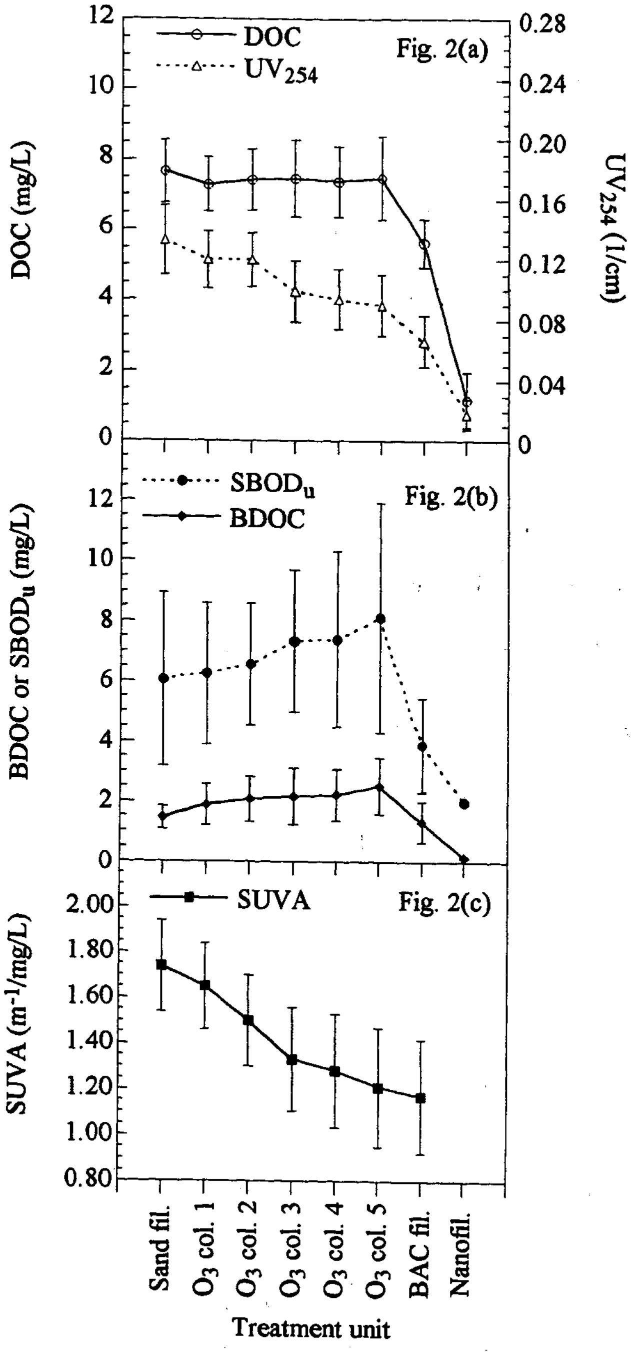

Figure 2—The DOC, UV_{254}, $SBOD_u$, BDOC, and specific UV absorbance (SUVA) profiles of the pilot plant.

- Las Vegas WWTP, Las Vegas, Nevada, 50 mgd, operated by the city of Las Vegas;
- Orange County WWTP No. 2, Huntington Beach, California, 60 mgd, operated by the CSDOC;
- Hyperion WWTP, Playa del Rey, California, 200 mgd, operated by the LABS;
- The Joint Water Pollution Control Plant (JWPCP), Carson, California, 200 mgd, operated by the Sanitation Districts of Los Angeles County; and
- Sacramento Regional WWTP, Elk Grove, California, 170 mgd, operated by the Sacramento Regional County Sanitation District.

All of the plants are conventional activated-sludge (AS) plants except the last four (Orange County No. 2, Hyperion, JWPCP, and Sacramento), which are high-purity-oxygen (HPO) AS plants. The flow rates listed above are approximate actual flow rates, and only the secondary portions of the Orange County No. 1 (only AS), Orange County no. 2, Hyperion, and JWPCP facilities are reported.

Analyses and Measurements. The modified protocol (Khan *et al.*, 1998) was used to determine BDOC. In addition to the application of the modified BDOC protocol to both reclaimed and secondary-treated wastewaters, ultraviolet (UV) absorbance at 254 nm (UV_{254}) was measured for reclaimed-wastewater samples, and soluble chemical oxygen demand (SCOD) was analyzed for secondary-effluent samples. A Hewlett-Packard Diode Array Spectrophotometer, model 8452A (Hewlett-Packard Company, Palo Alto, California), and a 1-cm quartz cell were used to determine UV_{254}. The spectrophotometer was first adjusted to read zero absorbance with a water blank (deionized water containing less than 0.20 mg/L DOC). Each sample was then analyzed three times (three portions), and the mean value was taken as the UV_{254}. The SCOD was analyzed using the open reflux method as specified in *Standard Methods for the Examination of Water and Wastewater* (APHA *et al.*, 1989).

Results and Discussion

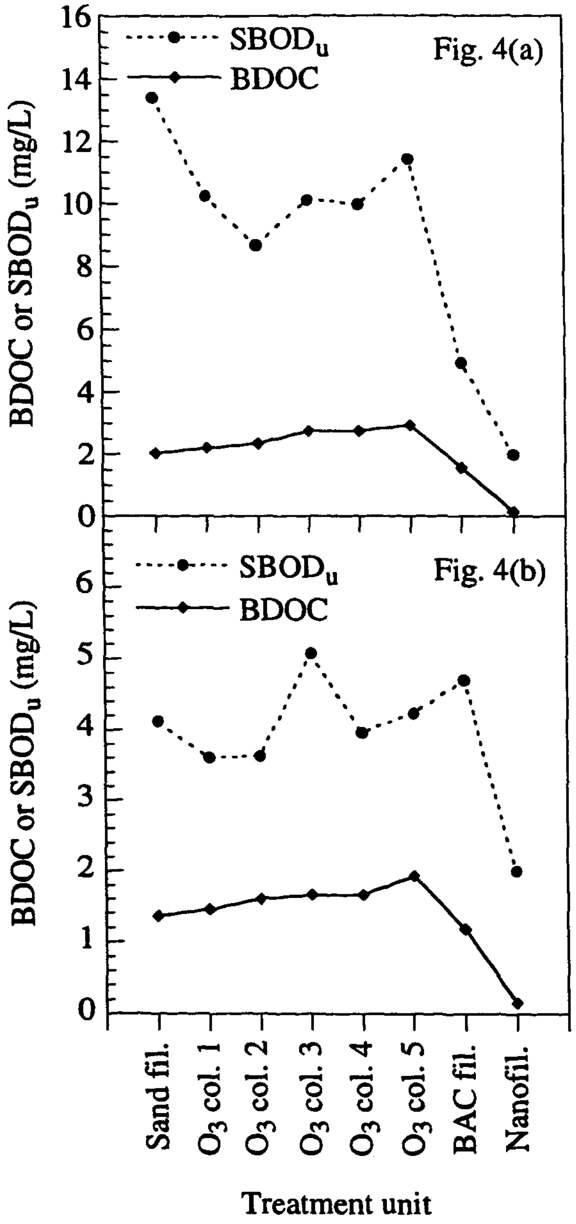

Figure 4—Weekly profiles for $SBOD_u$ and BDOC. Sampling dates (a) October 25, 1994, and (b) November 22, 1994.

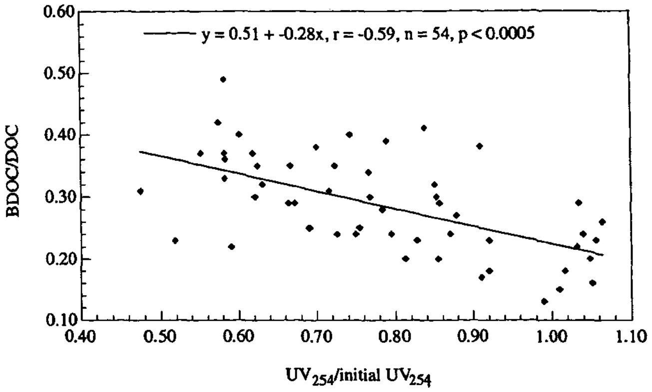

Figure 3—Relationship between biodegradability ratio (BDOC/DOC) and normalized UV_{254} (UV_{254}/initial UV_{254}) for ozonated, reclaimed wastewater.

Use of Biodegradable Dissolved Organic Carbon as an Indicator of Reclamation Plant Performance. The modified BDOC procedure was used to quantify the performance of the Lake Arrowhead reclamation pilot plant. Use of the procedure for this purpose was the original motivation for its development. Although the modified BDOC protocol was developed for samples with 4 to 15 mg/L DOC, it was also tested with the nanofilter effluent, which had only 0.25 to 2.0 mg/L DOC. Figures 2a and 2b show DOC, UV_{254}, $SBOD_u$, and BDOC profiles of the Lake Arrowhead reclamation pilot plant from the sand filter to the nanofilter. The UV_{254} was measured to indicate the relative concentration of organic compounds that are aromatic in structure or that have conjugated double bonds. Each value is an average of the weekly data collected for 11 consecutive weeks. The error bars represent the standard deviations (SDs). The DOC remains fairly constant from the sand filter through the ozonation columns (7.29 to 7.66 mg/L) and drops dramati-

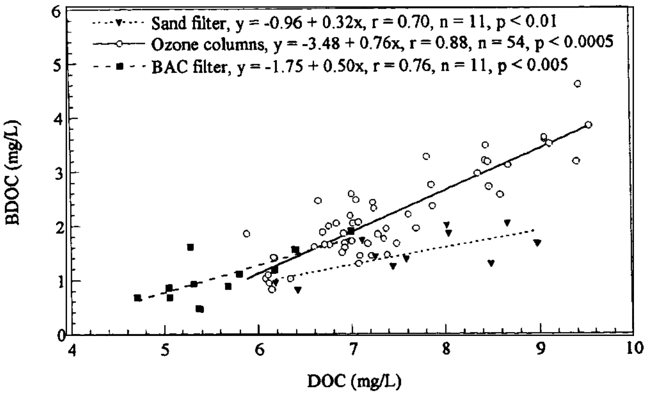

Figure 5—Correlations of DOC and BDOC for reclaimed wastewaters.

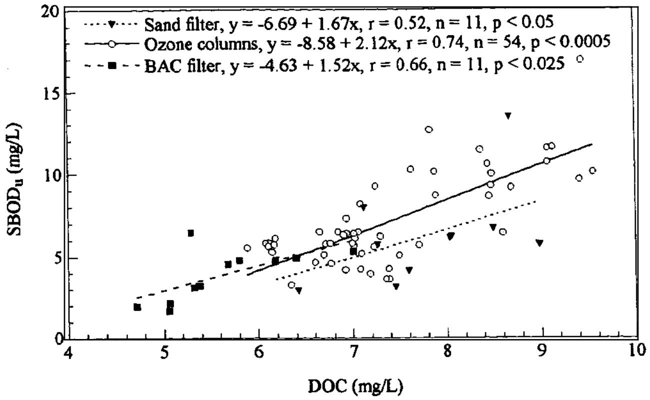

Figure 6—Correlations of DOC and SBOD$_u$ for reclaimed wastewaters.

cally after the BAC and nanofilter. This indicates that DOC is not a good parameter for monitoring the efficiency (biodegradability increase) of the ozonation. An increase in BDOC can be observed after each ozonation column (1.46 to 2.52 mg/L). The BAC filter removes approximately 50% of the BDOC. Eventually, most of the BDOC is removed by the nanofilter. The BDOC data show that the biodegradability is gradually enhanced by the ozonation, and the BDOC increase by ozonation is subsequently removed by the BAC filter. The SBOD$_u$ of nanofilter the effluent was too low to measure. The same problem occurred occasionally with BDOC. Therefore, at the nanofilter position in Figure 2b, the detection limits of BDOC and SBOD$_u$ (0.15 and 2.0 mg/L) were plotted without error bars.

The detection of BDOC increase during ozonation agrees with a specific UV absorbance (UV$_{254}$/DOC, expressed in m^{-1}/mg/L) profile of the pilot plant, shown in Figure 2c. In the drinking water field, the specific UV absorbance (SUVA) value has been used to characterize the DOC of raw waters (Edzwald and Van Benschoten, 1990). The SUVA values of reclaimed-wastewater samples (excluding nanofilter effluent) were 0.80 to 2.00 m^{-1}/mg/L. The SUVA decreases after each ozone column (constant DOC and reduction in UV$_{254}$). Substantial reduction in SUVA was found after each of the first three ozone columns. According to Edzwald and Van Benschoten (1990), this reduction suggests that the DOC of the reclaimed wastewaters is composed largely of nonhumic materials and is very hydrophillic, less aromatic, and of low molecular weight. Also, high-molecular-weight and aromatic compounds presented in the sand filter effluent were transformed to lower-molecular-weight and aliphatic compounds by ozonation (Hascoet *et al.*, 1986; Malley *et al.*, 1993; Mogren *et al.*, 1990; Ribas *et al.*, 1992; Servais *et al.*, 1987; and Volk *et al.*, 1993). The transformation occurred predominantly in the first three ozone columns. As shown in Figure 3, a significant but not strongly negative linear relationship (Pearson $p < 0.000\ 5$ and correlation coefficient $r = -0.59$) was observed between the biodegradability ratio (BDOC/DOC) and normalized UV$_{254}$ (UV$_{254}$/initial UV$_{254}$) for ozonated, reclaimed wastewater (all 5 columns). This also shows that relative BDOC increase is associated with relative UV$_{254}$ decrease.

Khan *et al.* (1998) showed that BOD$_5$ is less precise than BDOC. Even though SBOD$_u$ is more precise than BOD$_5$, it was not expected that the SBOD$_u$ profile would show the same trend as the BDOC profile. The similarity between the SBOD$_u$ profile and the BDOC profile may be attributed to the fact that all of the samples were well nitrified; the oxygen demand was, therefore, exerted only from the organic carbon biodegradation (SBOD$_u$ approximately equals SCBOD$_u$). However, some of the weekly profiles shown in Figures 4a and 4b indicate that BDOC is a better parameter, especially when long-term monitoring cannot be performed.

The correlations among DOC, BDOC, and SBOD*u* for the sand filter, ozonation columns (regardless of the column), and BAC filter effluents are illustrated in Figures 5, 6, and 7. Because the BDOC and SBOD$_u$ of the nanofilter effluent were often less than the detection limits, they were not included. All of the correlations are significant ($p < 0.05$). Strong linear relationships were found between DOC and BDOC, and between BDOC and SBOD$_u$ ($r = 0.70$ to 0.88 and 0.70 to 0.85). The linear regressions on the DOC and SBOD$_u$ data show weaker relationships ($r = 0.52$ to 0.74), indicating that BDOC is a more appropriate parameter than SBOD$_u$ for this case. However, all of the correlations support the earlier discussion. They all show that the effluents from the ozonation columns were more biodegradable than those from the sand filter and BAC filter.

For the sand filter effluent, DOC and BDOC have strong and

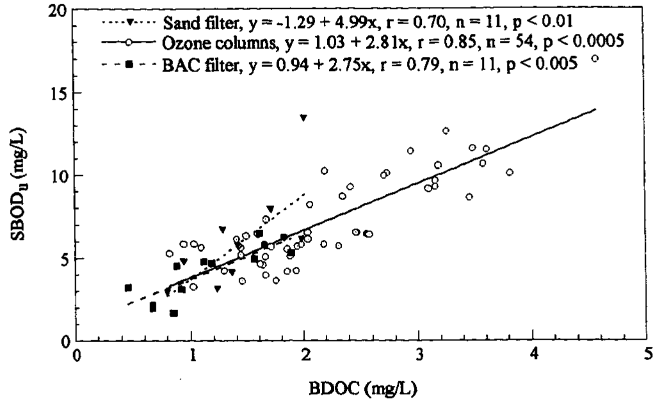

Figure 7—Correlations of BDOC and SBOD$_u$ for reclaimed wastewaters.

Table 1—Concentrations of DOC, BDOC, SCOD, and RDOC and BDOC/DOC of secondary effluents.

WWTP	Approx. SRT,[a] days	Average DOC ± SD, mg/L (% daily variation)	Average BDOC ± SD, mg/L (% daily variation)	Average SCOD ± SD, mg/L (% daily variation)	Average RDOC ± SD, mg/L	Average BDOC/DOC ± SD, %
Orange No. 2[b]	0.7	11.0 ± 0.63 (6)	3.10 ± 0.42 (13)	34.6 ± 2.0 (6)	7.90 ± 0.57	28.20 ± 3.29
Hyperion[b]	1.4	10.96 ± 0.86 (8)	3.47 ± 0.60 (17)	33.5 ± 2.1 (6)	7.49 ± 0.50	31.50 ± 3.83
Sacramento[b]	2.0	8.58 ± 0.50 (6)	2.82 ± 0.38 (13)	24.1 ± 0.9 (4)	5.76 ± 0.20	32.73 ± 2.79
Union[c]	2.0	13.72 ± 0.98 (7)	3.90 ± 0.50 (13)	38.7 ± 1.7 (4)	9.82 ± 0.79	28.43 ± 2.89
Glendale[c]	2.0	9.21 ± 0.43 (5)	1.64 ± 0.29 (18)	28.0 ± 2.1 (8)	7.57 ± 0.20	17.78 ± 2.38
JWPCP[b]	2.4	12.35 ± 0.57 (5)	2.61 ± 0.48 (18)	38.1 ± 1.3 (3)	9.74 ± 0.31	21.04 ± 3.18
Orange No. 1[c]	2.5	8.72 ± 0.43 (5)	1.79 ± 0.39 (22)	28.1 ± 1.8 (6)	6.93 ± 0.39	20.43 ± 3.91
Tillman[c]	4.0	8.74 ± 0.27 (3)	1.72 ± 0.35 (20)	28.0 ± 0.8 (3)	7.01 ± 0.27	19.67 ± 3.60
Tapia[d]	10.0	7.66 ± 0.16 (2)	0.77 ± 0.14 (18)	21.0 ± 0.3 (1)	6.89 ± 0.12	10.03 ± 1.68
RP1[d]	10.0	4.96 ± 0.26 (9)	0.45 ± 0.12 (26)	14.4 ± 2.0 (14)	4.50 ± 0.23	9.07 ± 2.16
RP2[d]	10.0	5.72 ± 0.08 (1)	0.72 ± 0.11 (15)	16.6 ± 0.8 (5)	5.00 ± 0.13	12.60 ± 1.91
Las Vegas[e]	13.6	6.30 ± 0.37 (6)	0.67 ± 0.09 (13)	17.9 ± 0.8 (4)	5.64 ± 0.30	10.52 ± 1.12
Carbon Canyon[d]	80	4.91 ± 0.26 (5)	0.68 ± 0.17 (25)	11.0 ± 1.6 (15)	4.24 ± 0.15	13.66 ± 2.70

[a] Solids retention time; based on aeration tank volume.
[b] High-purity oxygen AS.
[c] Conventional AS.
[d] Conventional AS with nutrient removal.
[e] Trickling filter followed by conventional AS with nutrient removal.

significant positive relationships with UV_{254} (data not shown; $r = 0.73$ and 0.81, and $p < 0.01$ and 0.002 5). As expected, DOC and BDOC correlate weakly with UV_{254} for the effluent samples from the ozonation columns (data not shown; $r < 0.40$) and BAC filter (data not shown; $r < 0.50$). The poor relationships may be attributed to the highly varying and stochastic nature of reclaimed-wastewater composition and the reaction with ozone. Trickling filter performance varies considerably during the course of normal operation. Poor correlation was also found between BDOC increase and UV_{254} decrease after each ozone column (data not shown; $r = 0.16$). The UV_{254} declines dramatically across the ozonation columns but is not well connected to DOC and BDOC.

Use of Biodegradable Dissolved Organic Carbon as an Indicator of Secondary Effluent Quality. Average DOC, BDOC, and SCOD concentrations and SDs of secondary effluents are listed in Table 1. The plants were selected to cover a wide range of solids retention times (SRTs). Most of the plants are typically operated at either low or high SRTs (SRT ≤ 4 days or SRT ≥ 10 days). As a result, the secondary effluents of these plants are either nonnitrified or fully nitrified. In some high-SRT plants (RP1, RP2, and Carbon Canyon), 5-day BOD concentrations of secondary effluents are frequently below the detection limit. Total organic carbon has been used as an indicator of secondary effluent quality as well as a process control parameter.

The relationships between the three parameters and SRT indicate similar trends. The AS plants operated at higher SRTs tend to produce secondary effluents with much less DOC, BDOC, and SCOD. The BDOC concentrations range from 0.47 ± 0.12 to 0.77 ± 0.14 mg/L for the effluent samples from high-SRT plants and from 1.64 ± 0.29 to as high as 3.91 ± 0.52 mg/L for the effluent samples from low-SRT plants. The BDOC concentrations in every plant have much greater daily variation than the other two parameters, indicating higher sensitivity provided by the modified BDOC method. As illustrated in Figure 8, the relationship between BDOC and SRT is nonlinear; BDOC sharply decreases with increasing SRT in the lower SRT range (0 to 4 days) and is stable in the higher SRT range (≥10 days). The plot in Figure 8 agrees with the effluent substrate concentration–SRT relationship theoretically proposed by Lawrence and McCarty (1970). Though the relationship is routinely predicted by models, experimental verification using BOD or COD has not been very successful, probably because of the variability of the BOD and COD procedures. The relationship can be clearly seen using BDOC.

The type of plant has an effect on the effluent BDOC. High

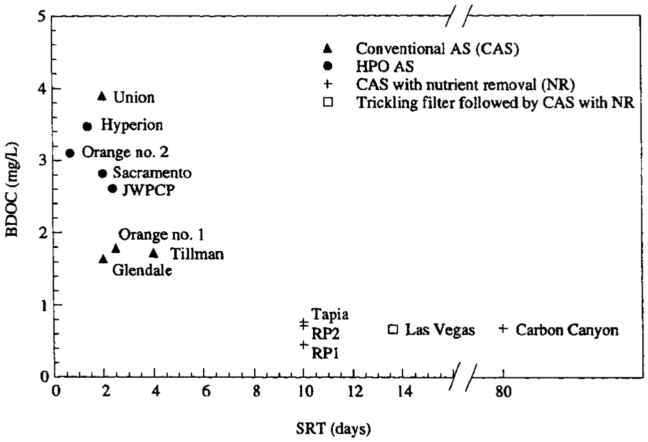

Figure 8—Concentrations of BDOC in secondary effluents versus SRTs of treatment plants.

BDOC was observed in the effluents of the HPO AS plants (SRT = 0.7 to 2.5 days). Medium BDOC was detected in the effluents of conventional (CAS) plants (SRT = 2.0 to 4.0 days). The effluents of CAS plants with nutrient removal (SRT ≥ 10 days) have the lowest BDOC. However, the effluent of one of the CAS plants (Union) has higher BDOC, DOC, and SCOD than the effluents of the HPO AS plants and therefore does not follow the trend. The reason for this difference was not investigated.

Average refractory DOC (RDOC = DOC - BDOC) concentrations and BDOC/DOC values of secondary effluents are also shown in Table 1. Like the first three parameters, RDOC concentrations are lower in high-SRT plants. However, RDOC does not abruptly decrease with increasing SRT in the lower SRT range. The BDOC/DOC ratio could be used to indicate biodegradability. Regardless of the absolute BDOC concentration, samples with higher BDOC/DOC values are more biodegradable than samples with lower BDOC values. As shown in Table 1, DOCs of secondary effluents from low-SRT plants are more biodegradable or have greater BDOC per unit DOC than effluents from high-SRT plants.

Figures 9, 10, and 11 illustrate extremely strong and significant relationships ($r > 0.85$ and $p < 0.000\,5$) among DOC, BDOC, and SCOD of the secondary effluents. This suggests that BDOC can be used for indicating the effluent quality as well as or better than DOC and SCOD. The SCOD is less precise, and both DOC and SCOD are unable to indicate the biodegradability.

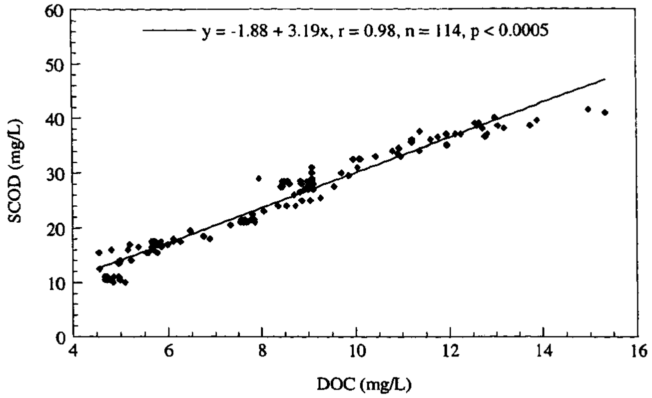

Figure 10—Correlation of DOC and SCOD for secondary effluents.

Conclusions

This paper presents two applications of a modified BDOC protocol exclusively designed for examining reclaimed and secondary-treated wastewaters. The protocol was used to evaluate the performance of a wastewater reclamation system and secondary-effluent quality.

The modified BDOC protocol was used to successfully evaluate the performance of an ozone/GAC system during a municipal wastewater reclamation project at Lake Arrowhead, California. The biodegradability increase during ozonation can be detected using the modified BDOC protocol. The BDOC is a more appropriate parameter than DOC or $SBOD_u$ for indicating plant performance when removal of degradable organic carbon is an objective. The DOC measurements could not distinguish the biodegradability in water samples from primary ozone columns. Although $SBOD_u$ and BDOC measurements along the reclamation pilot plant for 11 consecutive weeks provided similar profiles, $SBOD_u$ was less accurate and less precise. Significant and

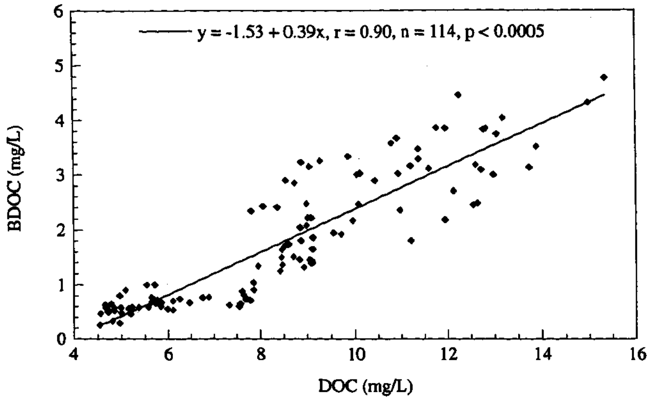

Figure 9—Correlation of DOC and BDOC for secondary effluents.

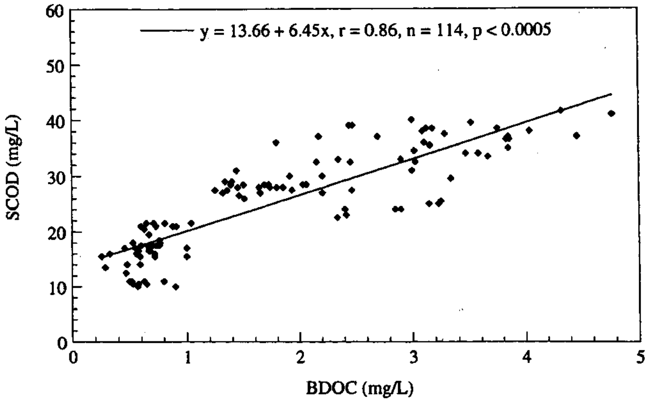

Figure 11—Correlation of BDOC and SCOD for secondary effluents.

strong positive linear correlations among DOC, BDOC, and $SBOD_u$ were obtained.

The BDOC can indicate secondary effluent quality. It provides more sensitivity than DOC and SCOD. The relationship between BDOC and SRT is nonlinear. The effluents of low-SRT treatment plants have higher BDOC concentrations than the effluents of high-SRT treatment plants. The lowest BDOC was detected in the effluents of high-SRT plants with nutrient removal. Excellent correlations were found among DOC, BDOC, and SCOD of secondary-effluent samples. Thus, BDOC can be used as a water quality parameter for secondary effluents as effectively as, or better than, currently existing parameters.

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Authors. At the time of this study, Eakalak Khan was a graduate research assistant and Sarunyu Viriyavejakul was a graduate student in the Department of Civil and Environmental Engineering at the University of California at Los Angeles (UCLA). Currently, Eakalak Khan is a postdoctoral research associate in the Institute of the Environment at UCLA. Sarunyu Viriyavejakul is a lecturer at the Chulachomkao Royal Military Academy, Nakornnayok, Thailand. Michael K. Stenstrom is a professor in the Department of Civil and Environmental Engineering at UCLA. Roger W. Babcock, Jr., is an assistant professor in the Department of Civil Engineering, University of Hawaii at Manoa. Irwin (Mel) H. Suffet is a professor in the Environmental Science and Engineering Program at UCLA. Correspondence should be addressed to Michael K. Stenstrom, 4173 Engineering I, UCLA, Los Angeles, CA 90095-1600.

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