Use of Biodegradable Dissolved Organic Carbon to Assess Treatment Process Performance in Relation to Solids Retention Time

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ABSTRACT: A biodegradable dissolved organic carbon (BDOC) method has been developed and used to analyze secondary- and advanced-treated wastewater effluents and to investigate correlations between residual organic content and the solids retention time (SRT). Conventional biochemical oxygen demand (BOD) bottles and a 28-day incubation period were used. Secondary wastewater effluents from Hawaii were found to contain between 9.0 and 14.0 mg/L of dissolved organic carbon (DOC), of which 23 to 35% was biodegradable in the 28-day BDOC test (from a survey of nine treatment plants). Bench-scale, continuous-flow activated-sludge biological reactors treating synthetic wastewater were operated at SRTs between 2 and 15 days, and effluent BDOCs were determined. A good BDOC prediction equation was developed that incorporates the initial DOC, the DOC remaining after 5 days, and the SRT of the system from which the sample originated. This equation can be used to determine the BDOC value using data that can be obtained during a conventional 5-day BOD test. The determined equation was found to be appropriate for some of the full-scale wastewater effluent survey data. *Water Environ. Res.,* **73,** 517 (2001).

KEYWORDS: wastewater, secondary treatment, organic carbon, biodegradable dissolved organic carbon, solids retention time.

Introduction

Various measurements of the organic content of water and wastewater are available, including biochemical oxygen demand (BOD), chemical oxygen demand (COD), total and dissolved organic carbon (TOC/DOC), and the relatively new biodegradable dissolved organic carbon (BDOC). Similarly, various measures of the biodegradability of organic contents of water are available, including BOD, assimilable organic carbon (AOC), and BDOC. The BOD method is capable of measuring either the total carbonaceous and nitrogenous oxygen demand (BOD) or just the carbonaceous oxygen demand (CBOD). The nitrogenous demand (NBOD) can be obtained by subtraction. The 5-day BOD (BOD_5) method is useful for measuring the organic content of wastewater influents and effluents; however, its accuracy begins to suffer at values less than 4 to 5 mg/L and the detection limit is approximately 2 mg/L (APHA et al., 1995). The conventional Lawrence and McCarty (1970) mass-balance approach to analysis and design of activated sludge (and other biological secondary wastewater processes) using Monod-type kinetics allows calculation of effluent soluble BOD_5 ($SBOD_5$) values that are barely detectable for relatively large ranges of the accepted process control parameter, solids retention time (SRT). Because the BOD_5 method is not highly accurate for the low concentrations expected from modern secondary treatment systems, correlations between effluent BOD_5 and operating parameters such as SRT often are not satisfactory. If the BDOC method is more accurate for treated effluents, it may be more responsive to changes in SRT. The BDOC method is also useful for other purposes such as characterization of tertiary and advanced treatment plant process waters and effluents destined for reclamation and reuse (Khan, Stenstrom, Babcock, Viriyavejakul, and Suffet, 1998). This characterization may be useful in terms of the potential for the water to support the proliferation of microorganisms during distribution, storage, and use. The proliferation can include regrowth of nuisance organisms, opportunistic pathogens, or regulated indicator organisms.

The AOC and BDOC measurements were developed in the context of the potable water industry for characterizing the potential for microorganisms to regrow in water distribution systems following treatment including disinfection (Ribas et al., 1991; Servais et al., 1989; and Van der Kooji et al., 1982). Good correlations have been obtained such that it is now considered highly desirable to limit the amount of BDOC in treated drinking water (Prevost et al., 1998, and Trussell, 1999). In addition, these measures are used to characterize individual water treatment process performance, particularly biological activated carbon adsorption following ozonation (Laurent et al., 1999). Distribution system regrowth causes several problems, including promotion of corrosion; production of taste, odor, and color; introduction of opportunistic pathogens such as Klebsiella and Enterobacter; and interference with regulatory compliance with coliform testing (Rittmann and Snoeyink, 1984). Recently, Prevost et al. (1998) monitored bacterial regrowth associated with water produced at two different drinking water treatment plants in Canada. They found that bacterial production is correlated with BDOC concentrations in plant effluent. Using a pilot distribution system in the laboratory for calibration, Bois et al. (1997) developed a simulation model of bacterial dynamics in distribution systems. They found that BDOC was the main factor determining the growth and numbers of free and biofilm-associated bacteria. Even a large disinfectant residual can only minimize the formation of distribution system biofilms provided there is substantial removal of dissolved organic matter (Trussell, 1999). In one case, the steady-state chlorine demand of distribution system biofilms was found to be linearly related to BDOC concentration in the water (Lu et al., 1999). Biologically stable water is water that is free of biologically

available substances; however, no water can practically meet this definition and some regrowth is virtually unavoidable (LeChevallier et al., 1999). Regrowth of coliforms is a frequent cause of noncompliance with drinking water regulations (Van der Kooji et al., 1999), and this will likely be an even larger problem for reclaimed water distribution. Currently, and to a likely increasing extent in the future, the needs of these two different industries (potable water and wastewater) are becoming one and the same because of the need to reclaim treated wastewater effluents for blending with other waters for potable supply (indirect potable reuse) (Crook et al., 1999; Madireddi et al., 1997; and McEwen, 1998). The main objectives of this work were to investigate the use of a simple BDOC method for characterization of wastewater effluents in Hawaii, to compare the results to those obtained previously in Southern California, and to investigate possible correlations between BDOC and other parameters such as COD, $SBOD_5$, DOC, and SRT.

Methodology

Biodegradable Dissolved Organic Carbon Protocol. The BDOC protocol was similar to that published elsewhere by the authors (Khan et al., 1999, and Khan, Stenstrom, Babcock, and Suffet, 1998). Samples were filtered through a 0.7-μm glass-fiber filter (GF/F, Whatman, Fisher Scientific, Pittsburgh, Pennsylvania) previously rinsed with 300-mL deionized water containing less than 0.4 mg/L TOC. The TOC of filtrate was measured and reported as the sample DOC. A dilution factor, *F*, was determined to ensure that adequate dissolved oxygen (DO) (> 1 mg/L) remained at the end of the 5-day SBOD test. Dilutions were prepared (2 to 6 times) with deionized water to produce at least 300 mL of combined volume and placed in a washed container (filtrate flask) with at least 20% gas volume. The mixture was saturated with DO by shaking, and a 20-mL sample was collected. The TOC of this sample was measured and recorded as DOC_i. The diluted sample was transferred into a BOD bottle to almost full, and the DO was measured with a washed probe and recorded as DO_i. The probe was removed and 3 mL of unfiltered sample was added as an inoculum containing microorganisms present in the sample environment (autochthonous). The inoculum was mixed with the sample and the bottle was filled to the top with diluted sample. The BOD bottle was capped, water sealed with sample, and incubated in the dark without shaking for 5 days at 20 ± 0.5 °C. After 5 days, the DO was measured and recorded as DO_5. Next, 100 mL of the mixture was discarded and the remaining mixture was resaturated with DO by shaking. The remaining mixture was then incubated under the same conditions stated previously for an additional 23 days. During the incubation, the DO in the mixture was recharged daily by opening and shaking the bottle. At the end of incubation (28th day), a 20-mL sample of the unfiltered mixture was collected. The TOC of this sample was measured and recorded as DOC_{28}. A blank consisting of 300-mL of dilution water and 3 mL seed (from any sample) was carried through the entire procedure. The blank values were recorded as DO_{bi}, DOC_{bi}, DO_{b5}, and DOC_{b28}, respectively. The glucose–glutamic acid solution as specified by the BOD protocol (method 5210 B, APHA et al., 1995) was prepared and analyzed regularly for quality control. The DO and DOC data were used to calculate $SBOD_5$ and BDOC using the following equations:

$$SBOD_5 = [(DO_i - DO_5) - (DO_{bi} - DO_{b5})]F \quad (1)$$

$$BDOC\ (mg/L) = [(DOC_i - DOC_{28}) - (DOC_{bi} - DOC_{b28})]F \quad (2)$$

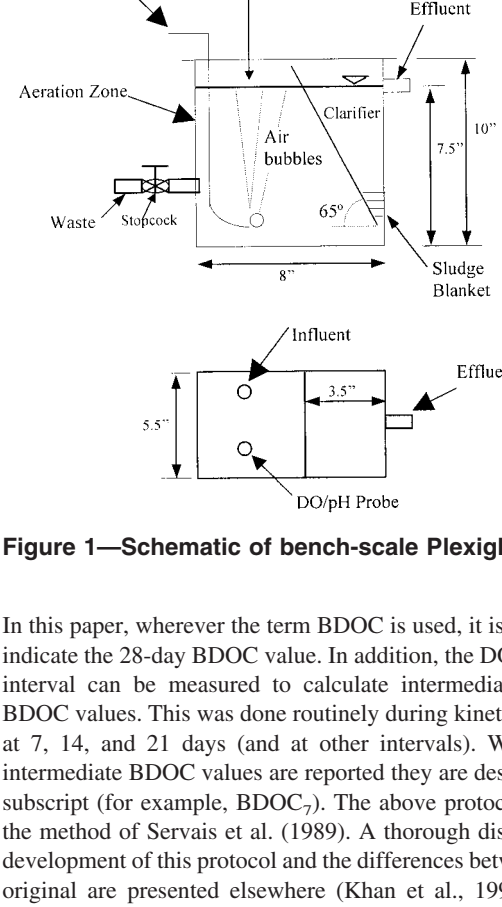

Figure 1—Schematic of bench-scale Plexiglas CFSTR

In this paper, wherever the term BDOC is used, it is understood indicate the 28-day BDOC value. In addition, the DOC at any ti interval can be measured to calculate intermediate (or parti BDOC values. This was done routinely during kinetic experime at 7, 14, and 21 days (and at other intervals). Wherever the intermediate BDOC values are reported they are designated wit subscript (for example, $BDOC_7$). The above protocol is based the method of Servais et al. (1989). A thorough discussion of t development of this protocol and the differences between it and t original are presented elsewhere (Khan et al., 1999; and Kha Stenstrom, Babcock, and Suffet, 1998).

Dissolved oxygen was measured using a YSI model 58 D meter and model 5905 DO probe (Yellow Springs Instruments C Yellow Springs, Ohio). The TOC was measured by a Shimad total organic carbon analyzer model 5000 A with autosamp (Shimadzu Scientific Instruments, Inc., Columbia, Md.) using t combustion–nondispersive infrared gas analysis method (meth 5310 B, APHA et al., 1995). The useful range of the analyzer w 0.05 to 20.00 mg/L for a sample size of 7 mL. The mean value three TOC measurements was used for all data reported herein

Bench-Scale Activated-Sludge Reactors. Five bench-sca continuous-flow stirred tank activated-sludge reactors (CFSTR were operated. The black Plexiglas reactors (Figure 1) had 3.9 completely mixed aeration zones and 1.1-L internal clarifie Aeration was provided by sparging air (2.4 L/min) through fi bubble ceramic stones that maintained the DO at more than mg/L. Synthetic wastewater was continuously pumped into t CFSTR aeration zone, and solids were continuously recycled fr the internal clarifier. The CFSTRs were operated with a hydrau retention time (HRT) of 12 hours. To control the nominal SR sludge was manually wasted daily by removing sufficient mix liquor from the CFSTR aeration zones. One CFSTR each w operated at SRTs of 2, 5, 7, 10, and 15 days. Daily maintenan included scraping to remove wall growth. The CFSTRs we inoculated with actively respiring activated sludge (AS) from conventional AS wastewater treatment plant (WWTP). The sy thetic wastewater consisted of (in mg/L); Bacto peptone (25 yeast extract (50), monobasic potassium phosphate (39.7), diba

Table 1—Steady-state data from bench-scale CFSTRs.

SRT (d)	HRT (d)	Operation time (d)	S_o (mg/L SCOD)	S (mg/L SCOD)	X (mg/L VSS)
2	0.5	15	344	40.5	287
5	0.5	30	344	33.5	422
7	0.5	37	344	30.5	526
10	0.5	58	344	29.5	614
15	0.5	61	344	25.5	683

potassium phosphate (25), ammonium sulfate (50), calcium chloride (0.658), magnesium chloride (1.025), ferric chloride (0.078), manganese chloride (0.019), zinc chloride (0.013), cobaltous chloride (0.012), ammonium hepta-molybdate (0.0084), cupric chloride (0.0082), borax (0.0048), 0.000 15 mg/L pyridoxamine dihydrochloride, 0.000 10 mg/L nicotinic acid, 0.000 10 mg/L thiamine hydrochloride, 0.000 05 mg/L Ca-D(+)-pantothenate, 0.000 04 mg/L 4-aminobenzoic acid, and 0.000 01 mg/L D(+)-biotin in tap water. Yeast extract and Bacto peptone were obtained from Difco Laboratories (Detroit, Mich.); all inorganic salts and all vitamins except biotin and pyridoxamine were obtained from Fisher Scientific Co. (Pittsburg, Pa.). Biotin and pyridoxamine were obtained from Sigma Chemical Co. (St. Louis, Mo.). The synthetic wastewater was prepared daily by dilution (1000 times) of a concentrated solution stored at 4 ℃. This resulted in a synthetic wastewater with an SCOD of approximately 350 mg/L, which was stored at room temperature (approximately 25 ℃) and pumped into the bench-scale AS units. Additional analyses were conducted according to *Standard Methods* (APHA et al., 1995). The influent was monitored weekly for SCOD (method 5220 D), $SBOD_5$ (method 5210 B), TOC (method 5310 B), ammonia-nitrogen (NH_3–N, method 4500-NH_3 D), nitrate-nitrogen (NO_3^-–N, method 4500-NO_3^- D), and pH (method 4500-H^+ B). Mixed liquor was monitored weekly for DO (method 4500-O G), total suspended solids (TSS, method 2540 D), and volatile suspended solids (VSS, method 2540 E). Effluent samples were monitored twice weekly for TSS, VSS, NH_3–N, NO_3^-–N, SCOD, and $SBOD_5$. Effluent samples were monitored for BDOC weekly.

Secondary Effluent Samples. Three to five discrete unchlorinated secondary effluent samples were collected at one-week or greater intervals between June and October, 1996, from nine WWTPs on Oahu, Hawaii. Samples were analyzed for BDOC, SCOD, $SBOD_5$, DOC, TSS, pH, NO_3^-–N, nitrite-nitrogen (NO_2^-–N), and orthophosphate.

Results and Discussion

Bench-Scale Activated-Sludge Units. The five bench-scale AS units were initially seeded with actively respiring AS and operated continuously for a total of 15 to 61 days, depending on the SRT. The average SCOD concentration of the influent synthetic wastewater (S_o)was 344 mg/L (12 measurements), which gives an average loading rate of 0.64 kg/m^3 · d (0.040 lb/d/cu ft). As each CFSTR approached steady state, effluent SCOD values (S) and mixed liquor VSS values (X) stabilized to 25 to 40 mg/L and 287 to 683 mg/L, respectively, depending on SRT (Table 1). Longer SRTs resulted in lower effluent SCODs and larger VSS values. It is typical to assume that biological steady state (that is, having relatively constant values of effluent substrate and mixed liquor biomass concentration) is achieved after approximately 3 SRTs. The bench-scale AS units used in this work were operated, and the effluent substrate and mixed liquor suspended solids data were monitored, until the values became steady. The effluent SCOD and mixed liquor VSS data collected on the last day of operation (after 4 to 7.5 SRTs) were used for each AS unit to determine the kinetic coefficients (Table 2). The Lawrence and McCarty (1970) mass-balance approach was used along with Monod kinetics to write mass-balance equations for a completely mixed AS unit with cell recycle. These equations can be rearranged and linearized such that experimental data can be used to determine four kinetic coefficients characteristic of the system, including the maximum substrate utilization rate constant (k), the half velocity constant (K_s), the yield coefficient (Y), and the endogenous decay coefficient (k_d).

The steady-state values in Table 1 were used to compute the values plotted in Figure 2 from which the following kinetic coefficient values were determined: $k = 1.7$ mg SCOD/mg VSS; $K_s = 74$ mg/L SCOD; $Y = 0.36$ mg VSS/mg SCOD; and $k_d = 0.28$ d^{-1}. These values are fairly close to typically reported ranges for municipal WWTPs (Metcalf and Eddy, 1991), except for the value of k_d that is much higher than typical values (0.025 to 0.075 d^{-1}). These differences are likely because of the nature of the synthetic wastewater that was quite different than that of municipal wastewater. The regression statistics shown in Figure 2 (i.e., correlation coefficient, R^2, and probability value p for F-test) indicate that the performance of the bench-scale units could be fairly well predicted by the kinetic model and other types of correlations (that is, related to BDOC) may also be possible.

First-Order Rate Model for Biodegradable Dissolved Organic Carbon Method. The BDOC method is similar to the BOD method such that it is logical to assume that a first-order kinetic equation might be a good model of biodegradation during the closed-bottle test. To determine whether this were true, the time-course of DOC depletion was monitored in each BDOC bottle throughout the experimental program. Small samples (7 mL) were obtained for DOC quantification approximately once per week. It is also logical to assume that as each of the bench-scale AS units operate and proceed toward steady-state acclimation, that the BDOC concentration and, therefore, the first-order BDOC degradation rate constant, would decrease in magnitude. Further, because the effluent BDOC from the bench-scale AS units would be expected to decrease with increases in the SRT, it is logical to assume that the magnitude of the BDOC first-order rate constant might decrease in proportion to increases in the SRT. First-order rate constants were determined graphically by plotting the term $-\log(DOC_t/DOC_i)$ versus time, where DOC_i is the initial DOC at the beginning of the BDOC analysis (time = 0) and DOC_t is the DOC measured at any later time, t, during the BDOC analysis (if linear, the slope is equivalent to the first-order rate coefficient, k_1). Figure 3 shows such a plot using DOC data from a set of four BDOC bottles

Table 2—Correlations and significance among BDOC, DOC, $SBOD_5$, and SCOD for effluent from bench-scale CFSTR and nine WWTPs on Oahu, Hawaii.

Treatment[a]	Relationship	Equation	R^2	*P* value *F* test
Bench-scale CFSTRs	BDOC–DOC	BDOC = 0.62 × DOC − 3.80	0.81	0.29
	BDOC–SCOD	SCOD = 2.76 × BDOC + 21.01	0.94	<0.005
	BDOC–$SBOD_5$	$SBOD_5$ = 0.57 × BDOC + 9.35	0.92	0.13
	SCOD–DOC	SCOD = 1.88 × DOC + 8.47	0.92	0.057
	$SBOD_5$–DOC	$SBOD_5$ = 0.39 × DOC_i + 6.73	0.91	0.013
	$SBOD_5$–SCOD	$SBOD_5$ = 0.20 × SCOD + 5.10	0.96	<0.005
CAS (five plants)	BDOC–DOC	BDOC = 0.40 × DOC − 1.28	0.76	<0.005
	BDOC–SCOD	SCOD = 2.57 × BDOC + 25.70	0.44	<0.005
	BDOC–$SBOD_5$	$SBOD_5$ = 1.28 × BDOC + 5.11	0.74	0.02
	SCOD–DOC	SCOD = 1.38 × DOC + 18.55	0.60	<0.005
	$SBOD_5$–DOC	$SBOD_5$ = 0.60 × DOC + 2.53	0.77	0.02
	$SBOD_5$–SCOD	$SBOD_5$ = 0.27 × SCOD − 0.087	0.52	<0.005
TF/SC (two plants)	BDOC–DOC	BDOC = 0.45 × DOC − 2.02	0.76	0.02
	BDOC–SCOD	SCOD = 3.09 × BDOC + 21.66	0.19	<0.005
	BDOC–$SBOD_5$	$SBOD_5$ = 1.09 × BDOC + 5.71	0.35	0.02
	SCOD–DOC	SCOD = 2.79 × DOC + 0.94	0.57	<0.005
	$SBOD_5$–DOC	$SBOD_5$ = 0.74 × DOC + 0.97	0.59	0.88
	$SBOD_5$–SCOD	$SBOD_5$ = 0.16 × SCOD + 3.81	0.39	<0.005
EAS (two plants)	BDOC–DOC	BDOC = 0.34 × DOC − 0.73	0.59	0.003
	BDOC–SCOD	SCOD = 1.50 × BDOC + 16.55	0.093	<0.005
	BDOC–$SBOD_5$	$SBOD_5$ = 0.81 × BDOC + 6.14	0.26	0.08
	SCOD–DOC	SCOD = 1.23 × DOC + 9.04	0.33	<0.005
	$SBOD_5$–DOC	$SBOD_5$ = 0.54 × DOC + 3.17	0.60	0.18
	$SBOD_5$–SCOD	$SBOD_5$ = 0.21 × SCOD + 3.86	0.40	<0.005
Aggregate (CAS, TF/SC, EAS)	BDOC–DOC	BDOC = 0.40 × DOC − 1.32	0.76	<0.05
	BDOC–SCOD	SCOD = 2.60 × BDOC + 20.09	0.15	<0.05
	BDOC–$SBOD_5$	$SBOD_5$ = 1.20 × BDOC + 5.35	0.62	<0.05

[a] CAS = conventional activated sludge; TF/SC = trickling filter–solids contact; EAS = extended aeration activated sludge.

measuring the effluent organic content from the same bench-scale AS unit. Effluent samples were collected from the bench-scale AS unit operated at a 15-day SRT after 14, 30, 43, and 61 days of operation. The sampling intervals correspond approximately to one, two, three, and four SRTs, respectively. Inspection of Figure 3 indicates that the slope of the regression lines and the fraction of DOC remaining after 28 days of incubation both decrease as the AS unit approaches steady state. The first-order rate constants and BDOC values decrease from 0.0080 d^{-1} and 5.96 mg/L after 14 days of operation to 0.0029 d^{-1} and 1.46 mg/L after 61 days of operation.

Similar analyses were conducted for BDOC analyses of effluent samples from each of the other bench-scale AS units. For each unit, the representative BDOC first-order rate constant was determined for the effluent sample corresponding to approximately three SRTs, and the values were plotted in Figure 4. Figure 4 shows an exponential decrease in the BDOC first-order rate constant as a function of SRT. These data indicate that the BDOC test is well represented by the first-order rate model (which could allow extrapolations using only the DOC_i value) and that the DOC degradation rate is related to SRT for effluent from bench-scale AS units treating synthetic wastewater.

Biodegradable Dissolved Organic Carbon Correlations with Other Measures and Operating Parameters. Effluent BDOC values were compared to other measured values such as SCOD, $SBOD_5$, DOC, and SRT to determine any correlations and their significance. Figure 5 shows, for example, the correlation between BDOC and SCOD and between BDOC and $SBOD_5$ (the da points represent duplicate measurements for all SRTs at stea state). These data are fairly well correlated (and the SCOD:BDC relationship is significant, $p < 0.05$) and indicate that BDC (range of values is 1.5 to 9.1 mg/L) is potentially more sensiti than $SBOD_5$ (corresponding range of values is 10.1 to 14.3 mg/ for determination of biodegradable matter present in wastewa effluent. At the tested SRTs and temperatures, the $SBOD_5$ valu were expected to be lower (in the range of 1 to 3 mg/L). The valu are likely higher than expected because of the presence of nitro enous oxygen demand (ammonium). Measured values of efflue NH_3–N were different for each SRT and varied between 4.5 a 10.6 mg/L as N (for the 15-day and 2-day SRT, respectivel Several other such plots were created and the regression lines we calculated as shown in Table 2. Table 2 indicates that only t $SBOD_5$–DOC (in some cases) and $SBOD_5$–SCOD relationshi are significant at the 95% ($p < 0.05$) level according to the F-t for a linear regression model. Figure 6 is a plot of the steady-sta effluent BDOC values (average of duplicate measurements) vers SRT for all of the bench-scale AS units (open circles). A go exponential relationship is indicated. A trial-and-error approa was used to determine a linear relationship between SRT a BDOC. To develop such an equation, the DOC_i and the DO values from the BDOC test were also required. The resulti relationship is given as Equation 3 and values derived from t steady-state bench-scale CFSTR data are plotted in Figure 7. good and significant fit of the data can be observed.

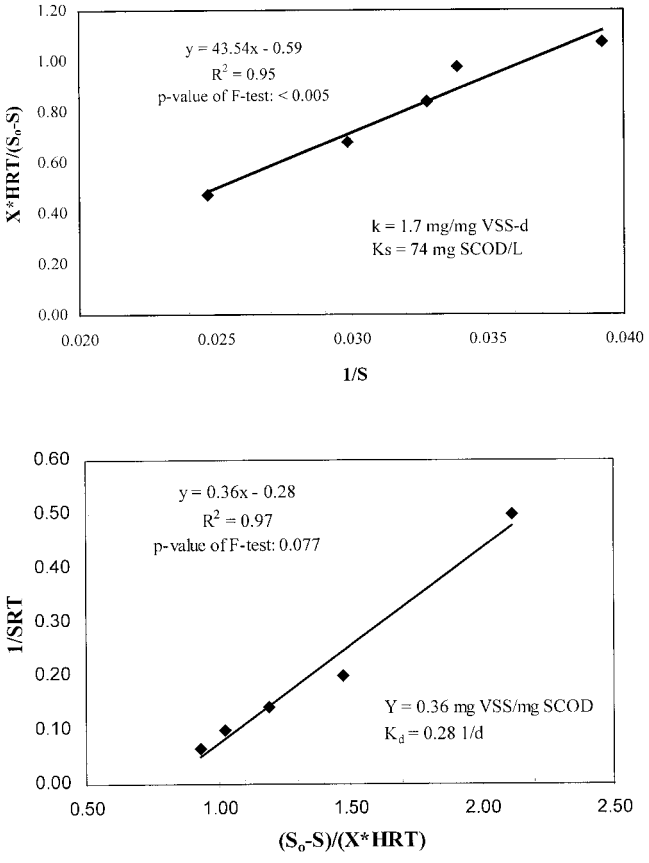

Figure 2—Plots to determine kinetic coefficients for bench-scale CFSTRs.

$$BDOC = -3.51 \ln[(DOC_5/DOC_i) \times SRT] + 10.48 \quad (3)$$

The potential utility of this relationship is that it could be used for prediction of the effluent BDOC given data that can be obtained during a 5-day SBOD test either for a known SRT or any other potential SRT. The slope and intercept coefficients for such an equation would most likely only be applicable to the individual wastewater and treatment process for which they are determined and only within the SRT range examined. In addition, this relationship is expected to be temperature dependent. In this study, a constant temperature, *T*, was used; however, in the general case temperature effects could be considered by adding an Arrhenius-type relationship (Θ^{T-20}) to the derived equation. Further tests are recommended to determine appropriate values of Θ. It is possible that a typical value used to correct kinetic coefficients (1.024) could be applicable (Metcalf and Eddy, 1991). Having discovered this relationship during controlled laboratory conditions, it was desired to determine whether it could fit the data obtained from a survey of full-scale treatment plant effluents.

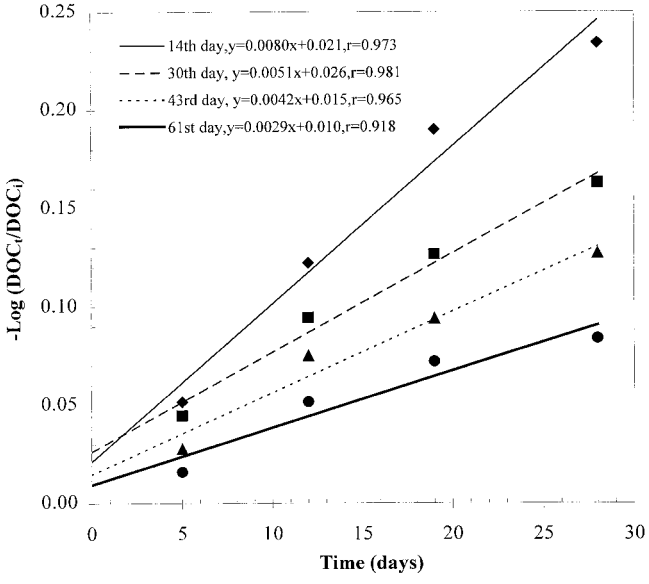

Figure 3—Determination of the first-order BDOC rate constant for the 15-day SRT reactor.

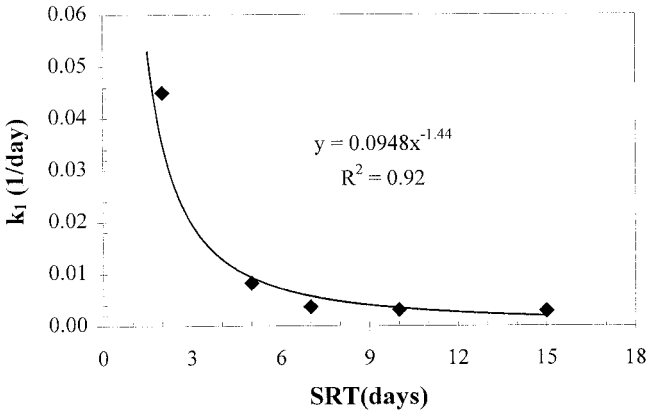

Figure 4—Relationship between first-order BDOC rate constant and SRT for bench-scale CFSTRs at steady state.

Secondary Effluent Survey. Unchlorinated secondary effluent samples were collected once a week for 4 weeks from each of nine municipal WWTPs on Oahu. For each plant surveyed, the SRT was greater than 5 days (5 to 20 days), the secondary effluent was mostly nitrified, and $SBOD_5$ and TSS concentrations were all less than 30 mg/L (data not shown). These data are compared to a

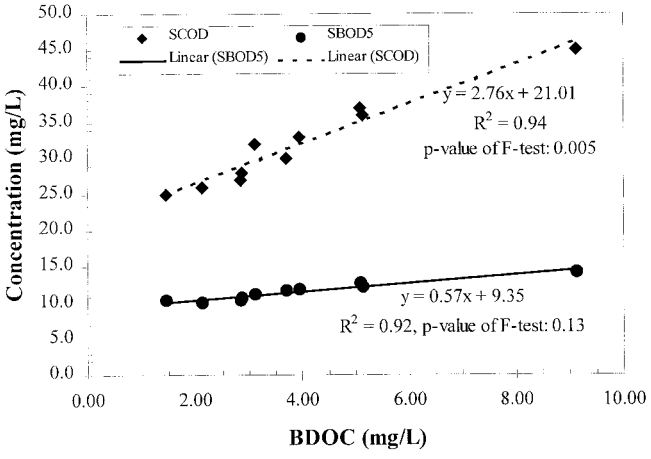

Figure 5—Relationships between BDOC and $SBOD_5$ and SCOD for effluent from bench-scale CFSTRs.

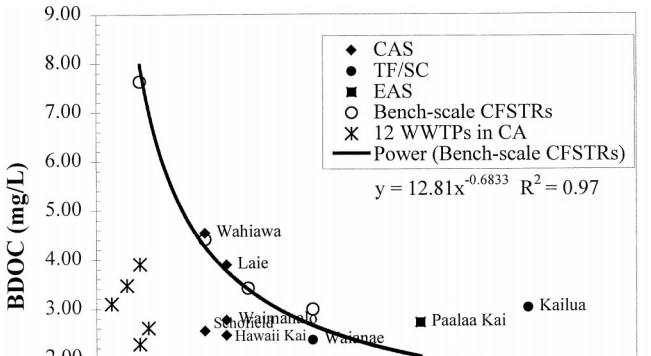

Figure 6—Relationship between BDOC and SRT for effluent from bench-scale CFSTRs at steady state and effluent from nine WWTPs on Oahu, Hawaii, and 12 WWTPs in California.

similar survey of southern California WWTPs (Khan, Stenstrom, Babcock, Viriyavejakul, and Suffet, 1998). Table 3 presents the average measurements and standard deviations of organic-content-related parameters including DOC, BDOC, SCOD, $SBOD_5$, and refractory DOC (RDOC = DOC − BDOC) concentrations and BDOC/DOC ratio during the survey of Hawaiian effluents. The results show that DOC content in secondary-treated effluents ranged from 8.86 ± 1.52 mg/L to 14.22 ± 3.31 mg/L (generally higher than the DOC content of the California WWTPs). The average ratio of BDOC-to-DOC concentrations varied from 20.46 ± 1.57% to 34.26 ± 5.80% (generally higher than ratios for the California WWTPs). Concentrations of RDOC ranged from 6.42 ± 1.18 mg/L to 10.33 ± 1.90 mg/L (similar to RDOC concentrations in the California WWTPs). The BDOC measurements, in nearly all cases, have greater daily variations than DOC, SCOD, and $SBOD_5$, indicating greater sensitivity of the BDOC method (same as in California survey). The data (Table 3) indicate that less than 35% of secondary effluent organic matter is biodegradable. The DOC likely consists of mostly fulvic acids, proteins, carbohydrates, and humic acids, whereas the BDOC is likely the carbohydrates and some fraction of the proteins.

For each type of secondary process surveyed, a series of plots was created to determine relationships between BDOC, DOC, SCOD, and $SBOD_5$ (plots not shown). Linear regressions were performed and the equations obtained are provided in Table 2. The correlation coefficients for CAS plants (0.44 to 0.77) were better than for the TF/SC and EAS plants. This could be because of a smaller number of plants in these categories (two each) than CAS (five). Nearly all of the relationships developed for the CAS plants were significant ($p < 0.05$). Table 2 also shows the overall correlations between BDOC and $SBOD_5$, SCOD, and DOC. The best correlation is between DOC and BDOC (Figure 8), and the correlation with $SBOD_5$ is reasonable (Figure 9). Figure 6 shows average effluent BDOC versus design SRT for all nine WWTPs. Figure 6 indicates that there was no clear trend between the BDOC concentration and the design SRT, and that longer SRT did not always equate to lower effluent BDOC. In contrast, the CA surv found the predictable asymptotic relationship between BDOC a SRT (Khan, Stenstrom, Babcock, Viriyavejakul, and Suffet, 199 (data plotted in Figure 6).

The first-order rate model was examined for the WWTP efflue survey BDOC samples. It was observed that degradation of DO in any given BDOC sample bottle obeyed first-order kineti Figure 10 shows the data for the four sets of replicate sampl measured for Paalaa Kai WWTP (data for other WWTPS we similar). Figure 10 indicates that for a series of samples from t same WWTP, and even for sample replicates, the calculated fir order coefficient was not a constant (the overall regression equ tion for Paalaa Kai WWTP was $y = 0.0036x + 0.040$, $R^2 = 0.7$ $p < 0.05$, data not shown). Therefore, it will likely not be possib to determine a kinetic coefficient that can be used to calcula BDOC given only the sample DOC for any individual WWTP

There are two methods to examine the correlation of BDO with DOC–SRT (equation 3) derived from the bench-sca CFSTRs with respect to the WWTP survey data. First, all of t data can be plotted to examine the overall trend (Figure 1 However, one might expect this correlation to be weak because t origin of the correlation equation was from a single treatment pla treating a single uniform wastewater and operated with a wi range of SRTs. In contrast, the WWTP survey data involves ni different WWTPs with different treatment operating modes a different wastewater characteristics. Figure 11 indicates a statis cally significant relationship; however, there is considerable scat of the data. The second examination method is to determine t BDOC to DOC–SRT correlation equation for each of the ni WWTPs individually. In this case, the wastewater characteristi are relatively uniform and the SRTs are assumed constant. Plo similar to Figure 11 were created (not shown) and regressions (a F-tests) were determined (Table 4). The regressions and signi cance levels in Table 4 are related to the variability of the BDO method for a given WWTP operated at a constant (assumed) SR Therefore, these regressions would not be expected to mirror t correlations obtained for the bench-scale CFSTRs (Figure Table 4 indicates a wide range of statistical significance, and f some WWTPs (namely, Wahiawa, Laie, Hawaii Kai, Waianae, a Kailua), a significant correlation is established. For these WWTI

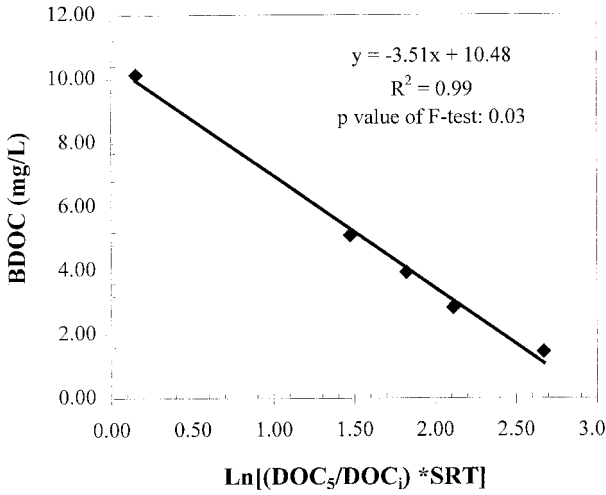

Figure 7—Relationship between BDOC, DOC, and SR for effluent from bench-scale CFSTRs at steady state

Table 3—Dissolved organic carbon, BDOC, SCOD, $SBOD_5$, and RDOC concentrations and BDOC/DOC of secondary wastewater effluent.

WWTP location	Secondary treatment	Design SRT (d)	Average DOC ± SD[a] (mg/L) (percent daily variation)	Average BDOC ± SD[a] (mg/L) (percent daily variation)	Average SCOD ± SD[a] (mg/L) (percent daily variation)	Average $SBOD_5$ ± SD[a] (mg/L) (percent daily variation)	Average RDOC ± SD[a] (mg/L)	Average BDOC/DOC ± SD[a] (%)
Schofield	CAS	5	8.96 ± 1.19 (13)	2.55 ± 0.61 (24)	25.88 ± 4.43 (17)	7.72 ± 0.80 (10)	6.42 ± 1.18	28.62 ± 6.60
Wahiawa	CAS	5	13.00 ± 3.88 (30)	4.54 ± 1.94 (43)	36.38 ± 6.48 (18)	10.06 ± 3.17 (32)	8.46 ± 2.17	34.26 ± 5.80
Laie	CAS	6	14.22 ± 3.31 (23)	3.89 ± 1.46 (38)	18.33 ± 8.76 (48)	10.44 ± 2.49 (24)	10.33 ± 1.90	26.72 ± 4.16
Waimanalo	CAS	6	10.97 ± 1.32 (12)	2.77 ± 0.33 (12)	34.50 ± 5.58 (16)	9.39 ± 0.37 (4)	8.21 ± 1.07	25.28 ± 1.95
Hawaii Kai	CAS	6	9.45 ± 0.59 (6)	2.46 ± 0.43 (17)	30.17 ± 6.64 (22)	8.69 ± 1.23 (14)	6.99 ± 0.56	25.94 ± 5.60
Waianae	TF/SC	10	10.13 ± 1.16 (11)	2.36 ± 0.80 (34)	30.00 ± 2.62 (9)	8.66 ± 1.20 (14)	7.78 ± 0.44	22.75 ± 5.53
Paalaa Kai	EAS	15	8.93 ± 2.66 (30)	2.71 ± 1.12 (41)	19.75 ± 4.27 (22)	7.90 ± 1.81 (23)	6.22 ± 1.71	29.92 ± 5.76
Kahuku	EAS	16	8.86 ± 1.52 (17)	1.81 ± 0.31 (17)	20.13 ± 9.67 (48)	8.03 ± 1.14 (14)	7.05 ± 1.26	20.46 ± 1.57
Kailua	TF/SC	20	10.69 ± 2.31 (22)	3.01 ± 0.98 (33)	29.88 ± 9.33 (31)	8.48 ± 2.27 (27)	7.68 ± 1.52	27.89 ± 3.68

[a] Standard deviation.

the equations in Table 4 would allow prediction of BDOC from parameters that can be readily obtained in concert with an $SBOD_5$ test.

The poor overall correlation (Figure 11) and the poor correlations for some of the individual WWTPs were not totally unexpected and could be caused by several factors, including a relatively small sample set, differences in treatment process design and operation, differences in wastewater characteristics among plants and among sampling intervals, and inaccurate values of SRT (plant operators reported that the design values were being used and they were assumed to be constant at each sampling event). Temperature effects are not important for these WWTPs where wastewater temperatures are virtually constant year-round (approximately 24 to 27 ℃). It is likely that strong relationships could be obtained for similar plants treating similar wastewaters or for an individual WWTP where routine estimation of the regrowth potential in its reclaimed water distribution system is desired. The BDOC method will be more suitable than BOD for this purpose because it is a direct measurement of biodegradable organic material and could be related to the cell mass of microorganisms that could grow by considering stoichiometric yield (with appropriate considerations of nutrient availability, velocity, and other parameters). Because BOD is a measurement of the oxygen required for oxidation of biodegradable organic matter, it cannot as easily be related to regrowth. Previous studies (Khan, Stenstrom, Babcock, Viriyavejakul, and Suffet, 1998) have shown the utility of the BDOC method for characterizing reclaimed water following advanced treatments (sand filtration, ozonation, activated carbon filtration, and nanofiltration) that have nondetectable quantities of $SBOD_5$. Additional sampling at several full-scale facilities (and accurate measurements of SRT) is recommended to determine the potential accuracy of the laboratory-derived relationship between BDOC and SRT.

Comparisons to Southern California. A comparison of the Hawaii and California survey data indicates some of the same trends and some differences (the same methods were used). In both cases, the WWTPs operated at longer SRTs tend to produce effluents with lower DOC, BDOC, SCOD, and $SBOD_5$ concentrations. The Hawaii treatment plants had SRTs of either 5 to 6 days (mid-SRT) or from 10 to 20 days (high SRT). In contrast, the California plants were either low-SRT (0.7 to 4 days) or high-SRT (10 to 15 days) WWTPs. The data can be grouped by the type of process (EAS, CAS, TF/SC) and by SRT (high: 10 to 20 days or medium: 5 to 6 days). The TF/SC processes seem to have slightly higher effluent DOC, BDOC, SCOD, and $SBOD_5$ concentrations. In general, the BDOC, DOC, SCOD, and BDOC/DOC ratio data show slightly higher values in Hawaii than in California (see Table 3). On Figure 8, the regression equation obtained from the California survey (Khan, Stenstrom, Babcock, Viriyavejakul, and Suf-

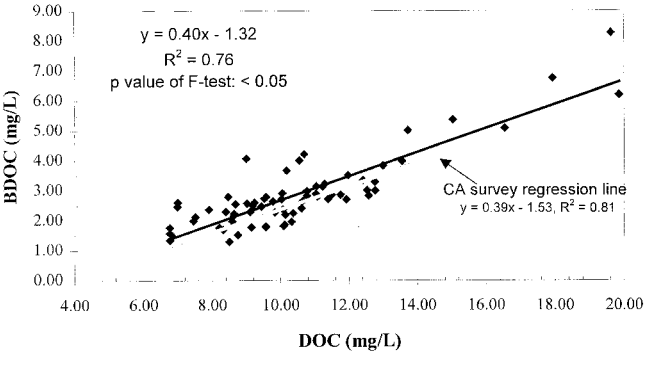

Figure 8—Correlation between BDOC and DOC for secondary effluent from nine WWTPs on Oahu, Hawaii.

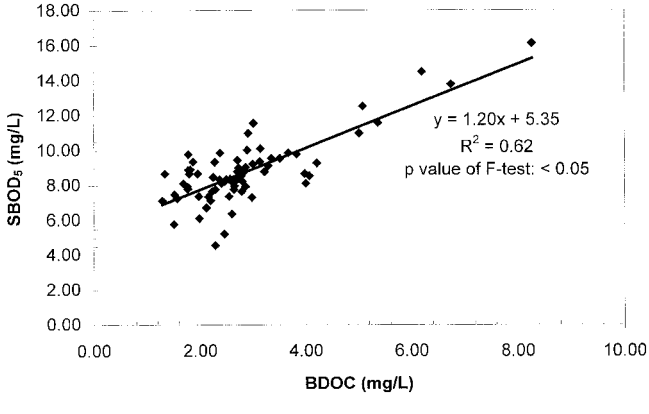

Figure 9—Correlation between BDOC and $SBOD_5$ for secondary effluent from nine WWTPs on Oahu, Hawaii.

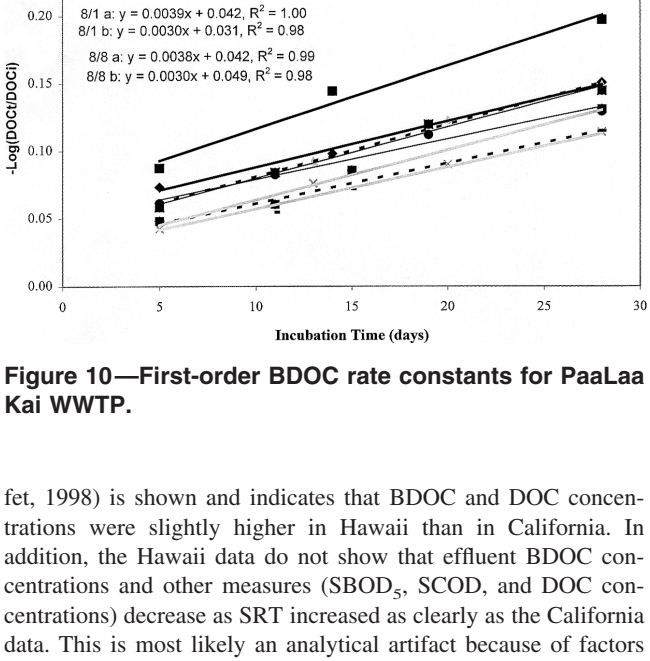

Figure 10—First-order BDOC rate constants for PaaLaa Kai WWTP.

fet, 1998) is shown and indicates that BDOC and DOC concentrations were slightly higher in Hawaii than in California. In addition, the Hawaii data do not show that effluent BDOC concentrations and other measures ($SBOD_5$, SCOD, and DOC concentrations) decrease as SRT increased as clearly as the California data. This is most likely an analytical artifact because of factors discussed in the previous paragraph or different TOC instrument results (this would affect values of DOC, DBOC, RDOC, and BDOC/DOC ratio, but not the values of SCOD or $SBOD_5$).

Conclusions

The use of a simple BDOC method to evaluate wastewater effluent organic content and to derive a relationship between residual degradable organic matter and SRT was examined. The purpose of this examination was to determine whether BDOC data could yield equivalent or better information than either BOD or SCOD data for performance assessment, and to determine whether BDOC values would correlate better than $SBOD_5$ values with SRT. Several notable findings were obtained. A relationship was discovered that enabled the prediction of steady-state effluent BDOC concentration from SRT, initial DOC, and DOC remaining after 5 days for bench-scale CFSTRs treating synthetic wastewater. The same prediction equation was not as successful for prediction of the effluent BDOC concentrations from nine full-scale WWTPs in Hawaii. In a survey of nine WWTP effluents there was no clear

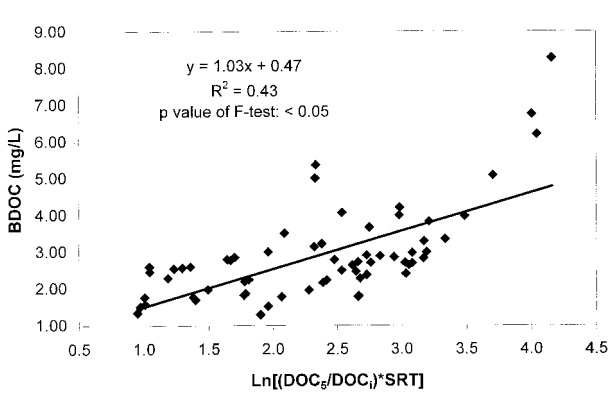

Figure 11—Relationship between BDOC, DOC, and SRT for effluent from nine WWTPs in Hawaii.

Table 4—Relationships between SRT, DOC_i, DOC_5, ar BDOC for effluent from nine WWTPs on Oahu, Hawaii

WWTP location	Equation	R^2	*P* valu of *F* te
CAS			
Schofield	BDOC = −1.98*X** + 8.48	0.45	0.11
Wahiawa	BDOC = 3.03*X* − 5.52	0.77	0.00
Laie	BDOC = 3.51*X* − 7.94	0.96	0.01
Waimanalo	BDOC = 1.26*X* − 0.85	0.68	0.28
Hawaii Kai	BDOC = 2.00*X* − 2.72	0.19	<0.00
EAS			
Paalaa Kai	BDOC = 1.84*X* + 0.02	0.75	0.06
Kahuku	BDOC = 0.75*X* + 0.70	0.77	0.68
TF/SC			
Waianae	BDOC = 3.72*X* − 5.85	0.82	0.00
Kailua	BDOC = 2.11*X* − 0.36	0.76	0.03
Aggregate (all nine plants)	BDOC = 1.03*X* + 0.47	0.43	<0.00

* $X = \ln[(DOC_5/DOC_i) \times SRT]$.

relationship between reported SRT and the measured BDOC co centration. However, there are doubts about the true SRT at ma of the WWTPs, which may be partially responsible for the po correlations and additional, more detailed, testing (including a curate measurements of SRT and temperature) at one or mo full-scale plants is recommended to determine if more reliab equations can be developed. BDOC values were found to correla fairly well to initial DOC, $SBOD_5$, and SCOD values. All BDO test data could be accurately modeled as a first-order kine process; however, the first-order coefficient was not found to be constant. A comparison of secondary wastewater effluent BDO values determined for several Hawaii and California treatme plants found that Hawaii effluents tended to have slightly grea concentrations of BDOC for a given SRT, a trend which was al observed for SCOD and $SBOD_5$. Because the BDOC method relatively easy to use and offers more pertinent information th BOD, effluent BDOC values for wastewaters that are to be reus can be useful in the context of potential for regrowth of microb in reclaimed water distribution systems and other reuse applic tions such as decorative fountains, golf course water features, a water supply reservoirs.

Acknowledgments

Credits. Presented, in part, at WEFTEC '97, the 70th Annu Conference of the Water Environment Federation, Chicago, Il nois, October 20-22, 1997. This work was supported in part by t Directorate of Public Works, U.S. Army Garrison, Hawaii.

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Submitted for publication May 8, 2000; revised manuscript submitted January 22, 2001; accepted for publication April 16, 2001.

The deadline to submit Discussions of this paper is February 15, 2002.

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