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30 COUNTRIES

March 5, 2002

Ms. Dorothy M. Gunn
Clerk
Illinois Pollution Control Board
100 West Randolph St.
Suite 11-500
Chicago, IL 60601

RE:	IN THE MATTER OF :		
	WATER QUALITY AMENDMENTS TO	)	
	35 Ill. Adm. Code 302.208(e)-(g), 302.504(a)	)	R02-11
	302.575(d), 303.444, 309.141(h); and	)	Rulemaking-Water
	PROPOSED 35 Ill. Adm. Code 301.267	)	
	301.313, 301.413, 304.120, and 309.157.	)	

Dear Ms. Gunn:

Enclosed please find three exhibits to the written testimony of Michael Callahan on behalf of the Illinois Association of Wastewater Agencies that were inadvertently omitted from the filing in the above referenced proceedings.

Very truly yours,

Sheila H. Deely

Sheila H. Deely

Enclosures
CH01/12212127.1

Attachment A

Nitrification in BOD_5 test increases POTW noncompliance

John C. Hall, Robert J. Foxen

The Clean Water Act requires that municipal wastewater treatment facilities achieve limitations based on secondary treatment. The U. S. Environmental Protection Agency (EPA) has defined secondary treatment as an effluent containing no more than 30 mg/L of 5-day biochemical oxygen demand (BOD_5), and 30 mg/L total suspended solids (TSS), or 85% removal of these pollutants, whichever is more stringent. Presently, about 7 900 out of a total of 15 200 municipal treatment plants have facilities designed to provide secondary treatment levels. EPA estimates about 20 to 30% of all secondary plants have significant violations of their BOD_5 permit limitations.

Noncompliance may be caused by a variety of design and operational problems. However, a significant contributing factor that may account for a large percentage of the BOD_5 violations involves the BOD_5 testing procedure itself.[1,2] Recent data analyses by the Office of Water Program Operations (OWPO) indicate that more than 60% of the BOD_5 violations may be caused by nitrification in the BOD_5 test, rather than by improper facility design or operation.

Revisions to the biochemical oxygen demand test procedures to inhibit nitrification would provide a more accurate measure of plant efficiency.

This paper evaluates the treatment capabilities of municipal secondary treatment facilities and examines the extent to which nitrification in the BOD_5 test may be contributing to compliance violations. First, the theoretical basis and origin of the 30-mg/L BOD_5 standard are reviewed. Data from 40 municipal treatment facilities are analyzed to determine actual carbonaceous BOD_5 ($CBOD_5$) treatment capabilities, and to estimate the amount of nitrogenous oxygen demand (NOD) exerted in the BOD_5 test. This information is then used to estimate the overall extent to which nitrification occurring in the BOD_5 test contributes to violations of secondary permit limitations.

STATEMENT OF PROBLEM

Populations of nitrifying bacteria in untreated wastewater are usually too small to impact BOD_5 test results. Therefore, the BOD_5 test typically measures only $CBOD_5$ in untreated wastewaters. However, the impact of nitrifying bacteria on BOD_5 tests of biologically treated wastewaters has long been recognized,[3] because substantial populations of nitrifying bacteria may exist in the effluents. Sawyer[4] states that effluents from secondary facilities "often contain populations of nitrifying organisms sufficient to utilize a *significant* (emphasis added) amount of oxygen during the regular 5-day incubation period. It is important to know the amount of residual carbonaceous BOD in such cases in order to be able to measure plant efficiency."

Interpreting the results of the standard BOD_5 test for secondary effluents is further complicated because populations of nitrifying bacteria vary significantly depending on environmental conditions. For example, during cold weather it is unlikely that large populations of nitrifying bacteria would be present in an effluent from a conventionally designed secondary treatment plant because the low water temperatures minimize their growth rate. However, during warm weather this same facility may develop populations of nitrifying bacteria that are capable of exerting significant amounts of NOD in the BOD_5 test. Because significant populations of nitrifying bacteria may be present in a facility during warm weather conditions, but absent at other times, BOD_5 results measured under different temperature conditions cannot be compared with any certainty of uniform test conditions. The usefulness of BOD_5 data that include varying degrees of NOD in addition to $CBOD_5$ is questionable, therefore the 15th edition of "Standard Methods" recommends inhibiting nitrogenous oxidation for all samples from secondary effluents or polluted waters.[5]

The types of secondary facilities most conducive to development of nitrifying bacteria are underloaded or overdesigned activated sludge facilities and most trickling filters. During warm weather, activated sludge facilities with lower loading rates may provide sufficient mean cell residence time (MCRT) to develop a significant population of nitrifying bacteria. This could occur intermittently or continuously, depending on the characteristics of a particular facility.

Trickling filters are particularly conducive to growth of nitrifying bacteria during warm weather because the filter media provides an ideal base for nitrifier growth. Young[1] states that nitrification in the BOD_5 test is a particularly significant problem for "trickling filter plants where nitrification takes place rapidly as compared to effluents from conventional high-rate activated sludge plants where nitrification proceeds more slowly." Thus, trickling filter effluents may contain higher concentrations of nitrifying bacteria than effluents from conventional activated sludge facilities.

ORIGIN AND INTENT OF THE BOD_5 SECONDARY TREATMENT STANDARD

Although significant nitrification can occur in the BOD_5 test for secondary effluents, much debate centers on whether the 30-mg/L BOD_5 standard, as defined by EPA, was *intended* to include only carbonaceous oxidation, or also any nitrogenous oxidation that might be exerted in the BOD_5 test. This distinction is critical, because it would not be appropriate to change the current BOD_5 test requirement to a $CBOD_5$ test without a corresponding change in the effluent standard if the original BOD_5 standard was intended to include both $CBOD_5$ and NOD. On the other hand, if the original 30-mg/L BOD_5 standard was intended to include only $CBOD_5$, the BOD_5 test could be modified to measure only $CBOD_5$, without any corresponding change in the effluent standard.

The position that BOD_5 was intended to include both $CBOD_5$ and NOD is basically as follows:

> The 30-mg/L BOD_5 standard was based on an evaluation of BOD_5 effluent quality from a representative population of secondary treatment facilities. Because the effluents from these treatment plants would presumably contain "typical" amounts of NOD_5, the 30-mg/L BOD_5 standard based on this sample population also accounts for this same "typical" amount of NOD. Use of the $CBOD_5$ test without a corresponding change in the standard would essentially constitute a relaxation of standards that could, in turn, degrade water quality.

Although an evaluation of secondary treatment facilities may indicate that 30 mg/L BOD_5 is a reasonable secondary effluent standard, review of EPA documents leading to the establishment of the secondary treatment standard indicate that the figure of 30 mg/L was not originally derived through an analysis of effluent data. The 30-mg/L BOD_5 standard was based primarily on an 85% BOD_5 removal requirement contained in a superseded regulation.[6]

Development documents concerning the proposed secondary treatment regulation (40 CFR Part 133) state that EPA found "the level of effluent quality proposed is roughly equivalent to the former 18 CFR 601.25 requirement of 85% BOD_5 removal."[7] Other documents also indicate that the 30-mg/L limitation was derived from plant efficiency based on a *percentage* removal (that is, 85% removal assuming a typical influent BOD_5 of 200 mg/L), and was not originally based on an empirical analysis of effluent data.[8] As discussed previously, the BOD_5 test for untreated wastewater typically measures only $CBOD_5$ because nitrifying populations are usually too small to exert any appreciable oxygen demand in the first 5 days. Because the influent test typically measures only $CBOD_5$, the effluent test should also measure only $CBOD_5$ to accurately calculate percent removal. Therefore, the 30-mg/L effluent standard should include only $CBOD_5$.

After making the preliminary determination that 85% removal of BOD_5 was an appropriate measure of efficiency for a well-operated secondary treatment facility[9] and that 30 mg/L was roughly its equivalent (assuming a 200 mg/L influent concentration), EPA completed a study of secondary treatment facilities to verify this finding. The unpublished study[10] evaluated effluent data from 33 secondary activated sludge and trickling filter facilities that were "well operated" and "operated at or near design flow." However, these selection criteria tended to minimize the probability of nitrification occurring in the BOD_5 test. The amount of NOD_5 for these plants should be significantly lower than if a truly representative sample population (that is, including underloaded plants) had been selected. Secondary facilities "at or near design flow" are less likely to have sufficient MCRT for significant numbers of nitrifiers to develop compared to facilities that operate below their design flows. Therefore, effluents from the facilities in the sample population would not exhibit NOD_5 concentrations representative of all secondary facilities. This may be true for newer facilities that are well below their design flow and thus more likely to have adequate MCRTs for significant nitrifier development.

The final EPA document defining best practicable waste treatment technology (BPWTT) for municipal dischargers published in October 1975[11] further clarifies the intent of the BOD_5 test and the secondary standard. This document states that "the BOD_5 test essentially measures the oxygen demand of only the carbonaceous organic material in the wastewater effluent." The document also presents a table summarizing the pollutant removal ca-

Table 1—Typical values of ultimate oxygen demand (UOD).[a]

Treatment type	Carbonaceous	Nitrogenous	Total	% Removal
Raw	300	100	400	0
Primary	180	95	275	31
Secondary (high-rate)	45	90	135	69
Secondary (conventional)				
(winter)	23	90	113	74
(summer)	23	23	46	88
Two-stage nitrification	23	23	46	88
Advanced waste treatment	8	12	20	95

[a] Reprinted from "Alternative Waste Management Techniques for Best Practicable Waste Treatment," EPA-430/9-75-013, 16 (Oct. 1975).

pabilities of secondary treatment facilities (Table 1). This table shows that secondary treatment as defined by EPA (that is, high rate secondary; conventional secondary actually provides seasonal nitrification) reduces CBOD ultimate from 300 to 45 mg/L. This level of removal is equivalent to the 85% removal requirement discussed previously. Using the CBOD ultimate/$CBOD_5$ ratio of 1.5, as recommended in the document, a BOD_5 standard of 30 mg/L found in the secondary regulation (40 CFR Part 133) can be calculated. The document also indicates that seasonal nitrification is not to be established as secondary treatment. This reiterated the agency position that the oxygen demand from ammonia would not be controlled through secondary treatment and that EPA intended secondary technology only to have the capability to remove carbonaceous material.[12] Thus, it would have been inconsistent with this intent to set a secondary standard that included nitrogenous BOD_5 in addition to carbonaceous BOD_5. It seems that EPA intended to regulate only $CBOD_5$ through secondary treatment.

A final point of concern raised by advocates of the existing BOD_5 testing procedure is the potential water quality impact of changing the BOD_5 test to include onlyb $CBOD_5$. Advocates of the BOD_5 standard state that NOD should be accounted for in the BOD_5 test because NOD will exert an oxygen demand in the receiving water equal to the oxygen demand in the BOD_5 test. Thus, water quality would be adversely impacted if the test measured only $CBOD_5$, because the impacts of NOD would not be considered.

The fallacy of this position is that the amount and rate of oxidation of ammonia occurring in the BOD_5 test bottle usually differ from that in the receiving water. If an effluent with a significant NOD were discharged into a relatively deep river with a sandy bottom, it is unlikely that any nitrification would occur because of the physical characteristics of the receiving stream.[13] Similar examples could occur in any situation where an effluent initially containing nitrifying bacteria is discharged into a stream where the pH, temperature, chemical, or physical properties were not conducive to the growth of nitrifying bacteria. On the other hand, in a stream or river there may be substantial nitrification occurring even though the plant effluent discharged into the receiving water may not exhibit nitrification in the BOD_5 test. Thus, whether or not nitrification occurs in the receiving water is independent from the occurrence of nitrification in the test. In any event, the potential effects of effluent ammonia and the possible need for nitrification facilities should be evaluated in water quality modeling analyses because these areas of concern are not addressed in the technology-based standard.

THEORETICAL IMPACT OF NITROGENOUS OXIDATION

The possible problems with measuring total BOD_5 are illustrated in the following example. Table 2 shows the effluent quality for two hypothetical treatment facilities, one providing secondary treatment with no nitrifiers in the effluent, and the other just beginning to nitrify. The effluent from the secondary facility contains 30 mg/L $CBOD_5$ and 20 mg/L ammonia, and ultimate oxygen demand (UOD) of 136 mg/L. Because there are few nitrifiers present in effluent from this facility, the BOD_5 test would indicate an effluent BOD_5 of 30 mg/L (identical to $CBOD_5$).

Table 2 also shows that the facility in the incipient nitrification stage provides slightly better treatment, and produces an effluent with about 25 mg/L $CBOD_5$, 18 mg/L ammonia, and 120 mg/L UOD. However, in this case, because nitrifiers are present in the effluent, an NOD of 56 mg/L might be exerted in the BOD_5 test. This would yield a BOD_5 of 81 mg/L—nearly three times greater than that of the secondary facility that discharged poorer

Table 2—Theoretical impact of nitrogenous oxidation on BOD_5 test results.[a]

Type	Operating conditions	$CBOD_5$	NH_3	UOD[b]	NOD	BOD_5
Secondary	No nitrifiers	30	20	136	0	30
Secondary/incipient nitrification	Warm weather, below design flow, some nitrifiers present	25	16	120	56	81

[a] All values in mg/L.
[b] UOD: eq 1.5 $CBOD_5$ + 4.57 NH_3.

quality effluent. Although these estimates are only illustrative, they do underscore the severe compliance problems as a result of nitrification in the BOD_5 test. The following sections present and analyze available side-by-side BOD_5/$CBOD_5$ data and show the effects of nitrification on the BOD_5 test. These data provide a basis for estimating the nationwide impact of this problem on treatment plant compliance.

EVALUATION OF BOD_5 AND $CBOD_5$ DATA

Data description. Data were obtained from municipal treatment plant records at 40 facilities where side-by-side BOD_5 and $CBOD_5$ tests were run. It is believed that the data represent a large percentage of the facilities in the U. S. with available side-by-side BOD_5/$CBOD_5$ data. Although a few facilities submitted data to EPA specifically because of nitrification problems in the BOD_5 test, the sample covers a wide range of facility sizes, locations, and design conditions. The data are believed to represent nationwide conditions.

A list of the data for each facility appears in Tables 3a and 3b, and a summary of the data is presented in Table 4. The effluent concentrations listed in both tables are the average warm weather effluent quality (sampled between May and October), except where otherwise specified. The facilities have been classified as either nitrification or secondary treatment processes. The facilities listed as nitrification plants were either designed to nitrify or exhibited at least 75% ammonia removal during the sampling period. The facilities listed as secondary exhibited either partial (10 to 60%) or minimal ammonia removal.

The predominant biological treatment process is activated sludge, though data from several trickling filters and combination trickling filter/activated sludge plants were also obtained. The facilities ranged in size from 78.9 to 52 596 L/s (1.8 to 1 200 mgd). Most of the plants were operating below their design flow capacity.

Nitrification was inhibited with 2-chloro-6 (trichloromethyl) pyridine (TCMP). Investigations by Young[4] indicate that TCMP does not inhibit oxidation of carbonaceous material at recommended dosages,[5] and that when nitrifiers are not present, BOD_5 tests with and without TCMP are equivalent.

Data analysis. For nitrification facilities, data presented in Table 4 show that on the average NOD accounts for 66% of the BOD_5. The NOD ranges from 43 to 86% of the BOD_5. Effluent $CBOD_5$ in these facilities averaged about 4 mg/L, whereas the BOD_5 averaged about 13 mg/L.

For secondary facilities, data presented in Table 4 show that NOD comprised about 52% of the BOD_5. The average BOD_5 was 28 mg/L, whereas the average $CBOD_5$ was 13 mg/L. There is greater variability in the percentage of NOD exertion for secondary slants than for nitrification facilities, with the percentage ranging from 24 to 79%. Analysis of cold weather effluent data (not included in this report) indicated, on the average, significantly less NOD exerted in the BOD_5 test, as would be expected.

The degree of NOD exerted in any BOD_5 test is primarily a function of two parameters: the initial concentration of nitrifying bacteria and the available ammonia. In nitrified effluents, the NOD would be limited by the available ammonia, because sufficient bacteria are already present in the sample for ammonia oxidation to begin immediately. Thus, any residual ammonia (including that

Table 3—Comparison of summertime $CBOD_5$ and BOD_5 effluent data—nitrification facilities.*

Name	Flow (mgd) Existing	Flow (mgd) Design	Process	BOD_5 (mg/L)	$CBOD_5$ (mg/L)	TSS (mg/L)	NOD_5 (%)	NH_3 (mg/L)
Chicago (NS), Ill.	333	333.0	AS	6.0	3.0	7.0	50	0.7
Chicago, (WSW), Ill.	900	900.0	AS	7.0	4.0	7.0	43	0.6
E. Fitchberg, Mass.	7	12.4	AS	25.0	13.0	18.0	47	9.0 (W)
E. Fitchberg, Mass.	7	12.4	AS	16.0	7.0	20.0	57	2.0
Ft. Collins, Colo.	7	6.0	AS	12.6	2.5	—	80	2.5
Grand Island, Nebr.	6	7.0	AS	20.0	5.0	—	75	4.0
Lawrence, Kans.	6	9.0	AS	22.0	6.4	7.0	71	5.0 (W)
Marlborough, Mass.	—	5.5	AS-Phos	—	3.4	6.4	—	0.5
Pittsfield, Mass.	10	17.0	TF-AS	—	3.0	6.0	—	0.5
Washington, D.C.	309	309.0	AS	12.0	4.0	10.0	67	0.5
W. Contra Costa, Calif.	10	12.5	TF-AS	35.0	5.0	6.0	86	11.0 (W)

* Less than 60% NH_3 removal.
(W) = Winter-average.
AS = Activated Sludge.
TF – Trickling Filter.
Phos-Chemical addition TP removal.
Fltr = Filtration.

Table 4—Comparison of summertime $CBOD_5$ and BOD_5 effluent data—secondary facilities.

Name	Flow (mgd) Existing	Flow (mgd) Design	Process	BOD_5 (mg/L)	$CBOD_5$ (mg/L)	TSS (mg/L)	NOD_5 (%)	NH_3 (mg/L)
Akron, Ohio	96.0	76.0	AS	36.0	15.0	—	60	7
Albuquerque, N. Mex.	37.0	37.0	TF-AS	35.0	15.0	15	57	15
Blue Lake, Minn.	14.0	20.0	AS	—	7.0	10	—	—
Chaska, Minn.	—	—	AS	17.0	12.0	10	29	10
Chicago, (CAL), Ill.	220.0	220.0	AS	25.0	7.0	6	72	5
Clearwaters, Fla.	—	—	AS	31.0	12.0	—	61	—
Colorado Springs, Colo.	20.0	30.0	AS	25.0	9.0	15	64	14
Corvallis, Ore.	6.0	9.7	TF-AS	4.3	2.8	5	38	—
Cottage Grove, Minn.	1.9	0.9	AS	56.0	26.0	30	54	18
Dubuque, Iowa	10.0	15.0	AS	30	13	16	57	—
Dunham, Ore.	6.0	20.0	AS-Phos-Filr	12	3	5	75	16
E. Bristol, Conn.	3.0	3.5	TF	63	40	68	35	19
E. Hartford, Conn.	7.8	10.5	AS	19	7	8	63	—
Emporia, Kans.	—	—	TF	29	22	22	24	—
Forestville, Conn.	3.2	5.0	TF	33	22	37	33	12
Hartford, Conn.	44.0	60.0	AS	18	9	12	50	—
Hastings, Minn.	1.3	1.8	AS	—	15	18	—	32
Milwaukee, Wis.	200.0	200.0	AS-Phos	21	9	21	57	10 (W)
Madison, Wis.	35.0	50.0	AS	26	12	19	54	9
Medford, Ore	9.5	15.0	AS	17	5	9	55	—
Minneapolis, Minn.	200.0	250.0	AS	20	14	23	30	6
Oregon City, Ore.	4.5	10.0	AS	17	12	8	29	—
Portland, Me.	16.4	15.0	AS	28	14	20	50	—
Portland, Ore.	5.3	8.3	AS	46	10	12	79	14
Reno, Nev.	20.0	20.0	AS	20	10	17	50	12
Rocky Hill, Conn.	4.3	7.5	AS	23	9	10	61	—
Seattle, Wash.	37.0	—	AS	12	8	10	33	16
Seneca, Minn.	13.0	24.0	AS	27	13	19	53	22
Stillwater, Minn.	2.5	3.0	AS	22	9	11	57	14
Upper Blackstone, Mass.	30.0	57.0	AS	19	5	12	74	13

* Less than 60% NH_3 removal.
(W) = Winter average.
AS = Activated sludge.
TF = Trickling Filter.
Phos = Chemical addition TP removal.
Filr = Filtration.

added to the dilution water used in test) would likely be oxidized during the first 5 days of the test.

Data in Table 3 show relatively little ammonia available in the nitrified effluents (0.5 to 3.0 mg/L, excluding ammonia added to the dilution water). If effluent ammonia levels were increased without a corresponding decrease in nitrifiers, significantly more NOD would be exerted in the BOD_5 test and could cause compliance problems.

Table 5—Summary of individual plant data.*

Type	Number of facilities	BOD_5 (mg/L)	$CBOD_5$ (mg/L)	NOD (%)	TSS (mg/L)
Nitrification	10	13 (7–22)	4 (2.6–7.0)	66 (43–86)	9 (5–20)
Secondary	30	28 (11–63)	13 (5–40)	52 (24–79)	18 (5–68)

* Effluent values listed as average (range).

The problem of increasing ammonia levels without a corresponding decrease in nitrifying bacteria population is represented by West Contra Costa, a seasonal nitrification facility. The effluent data presented in Table 3 were taken after the facility was no longer operating in the full nitrification mode. Effluent ammonia increased to 11 mg/L, and resulted in average BOD_5 values of 35 mg/L (a secondary standard violation). $CBOD_5$ remained low, at only 5 mg/L. Although the facility does not have to remove ammonia all year based on its permit, ammonia removal would be needed to ensure compliance with the secondary treatment standard as a result of the impact of nitrifying bacteria.

For secondary facilities, the degree of nitrification in the BOD_5 test primarily depends on the initial nitrifier population rather than the available ammonia. Because nitrifying bacteria regenerate slowly, the lower MCRT of a typical secondary facility (3 to 6 days) may cause a washout or wide fluctuation in the nitrifying population. As a result, the initial population of nitrifying bacteria in the test sample may vary considerably and may not be sufficient to affect the test results until the population increases. Significant nitrification, if it occurs at all, may be delayed until the last days of the test, so that only a small percentage of the available ammonia is oxidized. A study on the effects of fluctuating MCRT on NOD_5 was conducted at the Colorado Springs facility by Callaway and Young.[14] The study verified that reducing nitrifying population through decreased MCRT results in less NOD_5 exertion in the BOD_5 test.

Although effluent ammonia data were not always available for the secondary facilities, discussions with plant operators indicated that many plants were partially nitrifying (about 10 to 60% ammonia removal). Other plants did not exhibit any ammonia removal. When a facility is partially nitrifying, a sufficient nitrifying population is present to significantly impact the BOD_5 test. However, even facilities where nitrification is not occurring may have sufficient nitrifiers to impact BOD_5 results if the facility is in the incipient nitrification stage. (See Albuquerque N. Mex case study.) Incipient nitrification facilities have loading rates and MCRTs that permit nitrifier populations to be established; however, the detention time in the biological process (usually a few hours) is not adequate for detectable ammonia reduction. During the 5 days of the BOD_5 test, the seed nitrifying population has sufficient time to increase and begin ammonia oxidation. Similarly, seasonally cooler wastewater temperatures reduce plant-scale nitrification, but incubation at 20°C in the test quickly activates the nitrifying population.

The results from this survey agree with a similar survey conducted in West Germany by Damieki.[13] Typically, BOD_5 test results for both trickling filters and activated sludge plants in that study were significantly higher than $CBOD_5$ test results. The amount of NOD exerted in the BOD_5 test ranged from greater than 60% for facilities with high MCRTs to about 20% for facilities with low MCRTs. To prevent misleading BOD_5 test results caused by nitrification in the test, West Germany now uses the $CBOD_5$ test.

The following case studies illustrate how the BOD_5 test can provide misleading and contradictory information on plant operations.

Case studies: Fort Collins, Colo., and Albuquerque, N. Mex. Data from Fort Collins, Colo., are presented in Figures 1a, 1b, and 1c. Figures 1a and 1b indicate that there were few nitrifying bacteria in the plant before April, as evidenced by equal BOD_5 and $CBOD_5$ test results, and by high effluent ammonia concentrations. In April, the addition of one activated sludge unit increased the MCRT and the plant began nitrifying. The Figures 1a and 1b show that the monthly average $CBOD_5$ decreased from about 18 to about 3 mg/L and ammonia decreased from about 13 to 3 mg/L. However, the BOD_5 test results

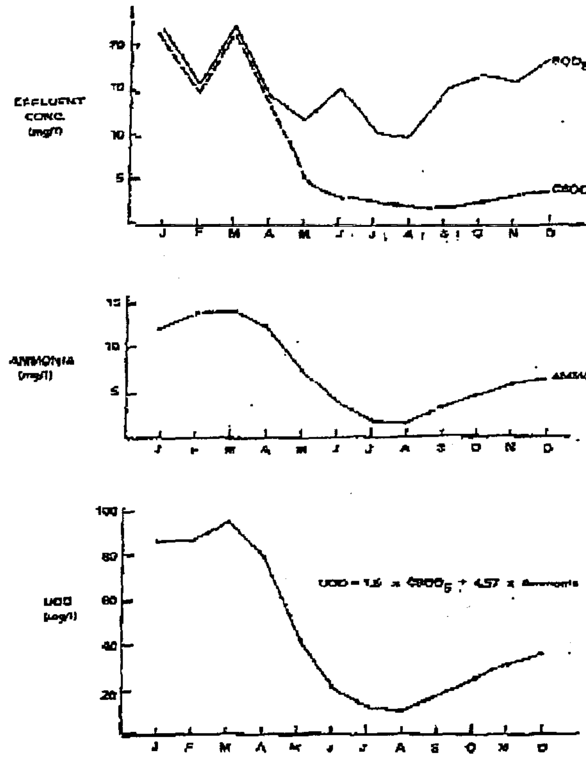

Figure 1—Fort Collins, Colorado: A—effluent BOD_5 and $CBOD_5$; B—effluent ammonia; and C—effluent ultimate oxygen demand.

(Figure 1a) did not reflect the significant improvement in effluent UOD (Figure 1c) because increased ammonia oxidation was occurring in the test. In terms of BOD_5, the additional activated sludge unit seemed to provide little if any improvement, although effluent UOD decreased by about 80%.

$CBOD_5$ and BOD_5 effluent data from Albuquerque, N. Mex., are shown in Figure 2. The data for early March indicated that few nitrifiers were present at this time. $CBOD_5$ and BOD_5 values were roughly equal during this period ($CBOD_5$ ranging 20 to 25 mg/L; BOD_5 ranging 25 to 30 mg/L). In early May, $CBOD_5$ decreased to about 10 to 15 mg/L, but BOD_5 test results increased to between 40 and 90 mg/L. The inflated BOD_5 values occurred even though effluent data did not indicate any significant decrease in ammonia concentrations to indicate increased nitrifier populations. This verifies that even though populations of nitrifiers may not be sufficient to produce plant-scale nitrification, they can still significantly increase BOD_5 test results. The wide swings in the BOD_5 test results also illustrate the problem of using the BOD_5 test to measure treatment efficiency for

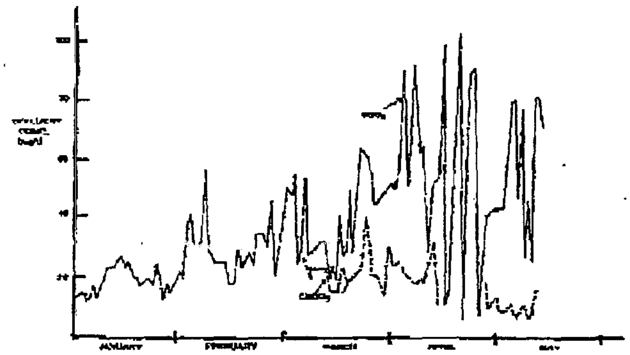

Figure 2—Final effluent BOD_5 and $CBOD_5$ (mg/L) Albuquerque, New Mexico.

facilities operating in the incipient nitrification stage. Because of varying amounts of nitrifying bacteria, significant day-to-day fluctuations occur in the degree of ammonia oxidized during the test. In such cases, the BOD_5 test can not accurately characterize plant performance and operation.

ESTIMATE OF BOD_5 VIOLATIONS CAUSED BY NITRIFICATION-NATIONAL IMPACT

Given the significant effect that nitrifying bacteria may have on BOD_5 test results, it is apparent that some BOD_5 noncompliance may result solely from NOD exertion. Only 7 of the 40 plants surveyed were out of compliance with the 30-mg/L BOD_5 standard during the sampling period. Of these seven plants, only East Bristol would have been out of compliance with the 30-mg/L standard even if the $CBOD_5$ test had been used. Although this sample is small, these findings suggest that a significant percentage of BOD_5 compliance problems may be due to nitrification in the test and not due to poor plant performance.

Because there are relatively few facilities for which side-by-side BOD_5/$CBOD_5$ data are available, the national significance of this problem had to be estimated by analyzing available data to identify "indicators" of nitrification in the BOD_5 test. From the available data it was observed that in nearly all cases where significant nitrification occurred in the BOD_5 test, BOD_5 concentrations were greater than TSS concentrations (Tables 3a and 4). In every case but one, $CBOD_5$ was less than TSS, regardless of the degree of nitrification occurring. This point is illustrated by Figure 3, which plots the relationship between $CBOD_5$ and TSS for the 40 facilities sampled. Figure 3 shows that $CBOD_5$ was typically 60 to 85% of the TSS value. Analysis of winter effluent TSS and $CBOD_5$ data (not included in this report) also indicated that $CBOD_5$ values are typically less than TSS values, when TSS is above 20 mg/L. A BOD_5 value greater than the TSS value would be a good indicator of significant nitrification in the BOD_5 test.

The empirical relationship between $CBOD_5$ and TSS was used as a basis for estimating the number of cases where noncompliance was caused by nitrification in the BOD_5 test. It was assumed in these estimates that nitrification was the cause of noncompliance if BOD_5 concentration was greater than 30 mg/L but the TSS concentration was less than 30 mg/L. Because the data indicate tht $CBOD_5$ is typically about 60 to 85% of the TSS value, it is conservative to assume that nitrification is responsible only when BOD_5 exceeds TSS.

Effluent monitoring data from 325 secondary treatment facilities in New York state were used to estimate the national extent of BOD_5 test violations caused by nitrification. The sample included all major categories of biological treatment processes (Table 6). Because of the size of the sample and the variety of facility types, a national sample is not likely to produce significantly different results.

The New York data show that 99 of the 325 facilities were in violation of their 30-mg/L BOD_5 permit requirement during the period of record. However, a comparison of BOD_5 and TSS data revealed that in almost 60% of these cases TSS was less than 30 mg/L. Therefore, based on available $CBOD_5$ data indicating that $CBOD_5$ should be less than TSS, it was concluded that about 60% of the BOD_5 permit violations may be caused by nitrification in the test, rather than by improper facility design or operation.

A detailed breakdown of the number of BOD_5 violations caused by nitrification for different categories of facilities appears in Table 5. This table shows that trickling

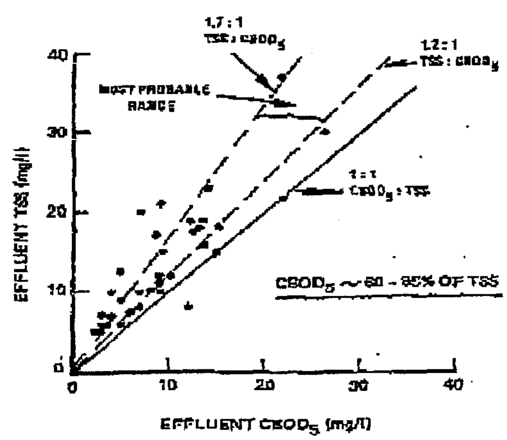

Figure 3—Relationship between $CBOD_5$ and TSS.

Table 6—Prediction of secondary BOD_5 violations caused by nitrification.*

Type of process	Number of facilities	Total violations	Violations owing to nitrification in BOD_5 test	Percentage of violations overestimated
Trickling Filters	133	61	40	65
Activated Sludge	65	15	9	60
Extended Air	64	10	4	40
Contact Stabilization	39	5	2	40
Bio Disc	4	2	0	0
Lagoon	16	5	2	40
Oxidation Ditch	4	1	1	100
Total:	325	99	58	59

* It is assumed that $CBOD_5$ is equal to suspended solids (based on compliance monitoring data from New York state).

filters were most often cited for noncompliance (61 of 133 plants did not meet 30 mg/L BOD_5). However, this table shows that 40 of the 61 violations, or 65%, were probably the result of NOD exertion in the test. Previous discussion indicates that attached growth plants provide an excellent environment for growth of nitrifying bacteria. BOD_5 test results for this type of process may well be significantly inflated as a result of ammonia oxidation. The data in Table 5 show that about 60% of BOD_5 compliance violations for the activated sludge facilities may be caused by NOD exertion.

Assuming that these estimates are representative of a national cross section of secondary facilities, it is estimated that about 60% of all BOD_5 permit violations may not be caused by poor treatment plant operation or faulty design, but are primarily a result of nitrification in the BOD_5 test.

SUMMARY AND CONCLUSIONS

The 30-mg/L secondary standard defined by EPA was initially derived from the 85% BOD_5 removal requirement in a superceded statute (18 CFR 601.25). Because the BOD_5 test typically measures only $CBOD_5$ in untreated wastewaters, but may also mesure NOD in secondary effluents, treatment efficiency (percent removal) can be determined only if the $CBOD_5$ test is used. The EPA document defining BPWTT reiterated that secondary facilities are required to remove only carbonaceous BOD and stated that the BOD_5 test was primarily a measure of carbonaceous BOD. Therefore, it appears that the 30-mg/L BOD_5 secondary standard was intended to include only $CBOD_5$.

The standard BOD_5 test may measure only $CBOD_5$, or both $CBOD_5$ and NOD. The amount of NOD exerted in the standard BOD_5 test depends on the level and type of treatment and environmental conditions. Available summertime effluent data from 40 facilities show that nitrification in the BOD_5 test accounts for 24 to 86% of the total BOD_5. Summertime carbonaceous removal capabilities of secondary and nitrification facilities are often significantly underestimated by the existing BOD_5 test. At times, nitrification can cause BOD_5 test results to indicate poorer quality effluent when wastewaters have actually received better treatment.

Nitrification can also cause BOD_5 values to exceed effluent limits set for treatment facilities. It is estimated that nearly 60% of the compliance violations nationwide may result from nitrification occurring in the BOD_5 test, rather than from improper design or operation. Revision of the BOD_5 test to include only $CBOD_5$ would reduce improper reporting of compliance violations and provide a more accurate measure of treatment plant efficiency and $CBOD_5$ removal capabilities. EPA is currently in the process of adding the CBOD test to the list of accepted test procedures contained in 40 CFR Part 136. The agency is also proposing changes to 40 CFR Part 133, "Secondary Treatment Information," to allow use of the $CBOD_5$ test.

ACKNOWLEDGMENTS

Credits. Personal thanks are given to all of the regional, state, and municipal authorities who aided in locating the data base reported in this paper. Special appreciation goes to James Young of the University of Arkansas, whose research on the BOD test brought this problem to the attention of EPA. Although the information in this document has been funded wholly or in part by EPA, it does not necessarily reflect the views of the agency and no official endorsement should be inferred.

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Attachment B

30/30 Hindsight

On November 16, 1983, the U.S. Environmental Protection Agency (EPA) proposed a revision to the regulations governing secondary treatment (40 CFR Part 133) to allow, at the discretion of the permitting authorities, substitution of 25 mg/L carbonaceous biochemical oxygen demand (CBOD) for the previous limit of 30 mg/L biochemical oxygen demand (BOD) on effluent discharge permits. The revision is to be selectively applied in those cases where the BOD test does not accurately reflect the degree of treatment achieved by the plant. Although many of the people who campaigned for a regulation addressing this issue feel it is not exactly what they had in mind, the regulation has been so long in coming that they are willing to settle for a compromise.

A BOD bottle will certainly be included in the environmental engineering time capsule. BOD removal, its measurement, its mechanism and kinetics, even the appropriateness of its use in process control, have been the topics of more engineering research studies than any other single characteristic of wastewater. BOD is one of the fundamental criteria on which the design of nearly every wastewater treatment plant in the country is based. Even so, whether or not it is an accurate indicator of the efficiency of biological treatment processes has been the subject of debate for years, especially since the development of other measurements of organic material in water such as chemical oxygen demand (COD) and total organic carbon (TOC). Now BOD has been dissected into two components, carbonaceous oxygen demand (CBOD) and nitrogenous oxygen demand (NOD), for still another controversy.

BOD defined

According to the 15th edition of "Standard Methods for the Examination of Water and Wastewater," BOD is a measurement of the quantity of oxygen utilized in the biochemical oxidation of organic matter in wastewater in a specific time and at a specific temperature. It also measures the oxygen used to oxidize inorganic material such as sulfides and ferrous iron. It can also measure the oxygen used to oxidize reduced nitrogen forms if the organisms that mediate that process (nitrification) are present.

A sample is diluted with water containing appropriate amounts of essential nutrients, a culture of microorganisms capable of degrading the organic material is added, the dissolved oxygen (DO) in the mixture is measured, the sample is incubated for a fixed period (5 days) at 20°C, the DO in the incubated sample is measured, and the difference between the two measurements, corrected for the dilution, is the 5-day BOD, BOD_5. Simple, right?

The analysis is actually fairly simple in comparison with some of the chemical analyses for wastewater, but interpreting the results and maintaining the strict analytical quality control required for a valid measurement are infinitely more complicated. The analysis is an indirect measure of organic material in that it measures the oxygen required for biological stabilization of that material; as such it is essentially a bioassay procedure. Although the results indicate the amount of organic material in the water, they are also a function of the condition and type of microorganisms in the sample, which are in turn a function of the history of the sample itself.

The effect of nitrification

Development of the BOD test began around 1870 with the application of the theory of oxidation to the measurement of organic material. The test was formally introduced in the 3rd edition of "Standard Methods" in 1917. The next major development was the recommendation of 5 days as the standard incubation period in the 7th edition in 1933.

many researchers had demonstrated the two-stage nature of BOD exertion—oxidation of only carbonaceous material for the first 10 or 12 days of incubation, and oxygen uptake for nitrification (NOD) by nitrifying bacteria after that time. An example of the classic curve is shown in Figure 1.

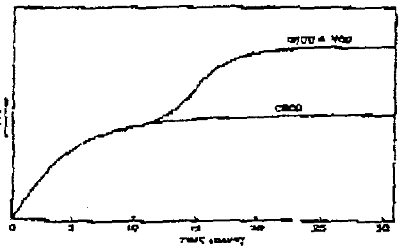

Figure 1—The BOD curve showing the effect of nitrification.

In 1955, the 10th edition of "Standard Methods" noted that some samples, particularly secondary effluents or natural waters, contained established populations of nitrifiers, and thus nitrification could easily begin before the end of the 5-day incubation period. Procedures were suggested for nitrification supression. Nitrification has consistently been referred to in the literature as an interference in the BOD test, rather than as a characteristic of interest in the wastewater. Indeed, a strong argument has been made that the test was never intended to measure the oxygen demand of nitrogenous substances, and that the BOD referred to in the regulations governing secondary treatment should always have been only carbonaceous. The 15th edition of "Standard Methods" explicitly states that "The inclusion of ammonia in the dilution water demonstrates that there is no intent to include the oxygen demand of reduced nitrogen forms in the BOD test."

Normal operation of activated sludge processes does not provide sufficient detention time to develop substantial populations of nitrifiers. These organisms grow slowly and require more time to establish themselves in the biological process than do organisms that metabolize carbonaceous material. For this reason raw wastewater may contain very few nitrifiers, but as the wastewater passes through the various processes the detention time may be sufficient for them to develop into an actively nitrifying population. By the time the treated wastewater leaves the plant, nitrification may be in full swing. This can be a problem in plants that are treating less than their design flow so that the actual detention time in the aeration basins is longer than intended.

Misleading results

The impact of nitrification on the BOD test is that the results of the analysis may not accurately represent treatment efficiency. While the process may indeed be stabilizing carbonaceous material so that CBOD is quite low, and further improving effluent quality by removing nitrogenous pollutants (ammonia), the BOD test could easily indicate little or no improvement in water quality. In an extreme case, the effluent BOD could actually be higher than that in the influent because of the influence of nitrification.

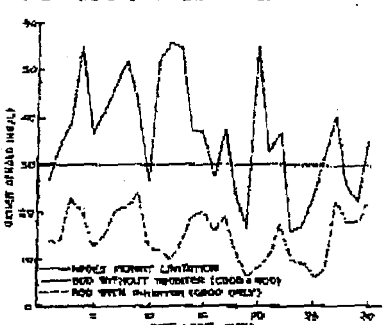

Figure 2—Effluent oxygen demand data from the Dubuque Wastewater Treatment Plant.

A plant may very well be removing even more pollution from the water than it was designed to remove, but seem to perform poorly according to the BOD data. Figure 2 illustrates this situation. Such problems have led many treatment plant administrators to request construction grants funds for filtration facilities over and above their secondary processes for additional BOD removal. When EPA examined the plant data, the oxygen demand that had been measured often included that from nitrification so that the plant was actually meeting and exceeding its removal requirements, and removing ammonia as well. Recognition of this problem saved many millions of dollars in unnecessary construction.

But what about the bottom line on the issue of organic removal—oxygen demand on the receiving water? If the wastewater contains an oxygen demand from nitrogenous substances instead of carbonaceous substances, is that less harmful to the stream? (Translation: "oxygen demand by any other name . . .") The key to this question is that for the nitrogenous oxygen demand to be exerted in the stream, nitrifying populations must be present and active there. While these organisms may thrive in treatment processes or the BOD bottle where conditions favor their growth and where they are much more concentrated, they may not be able to manifest their effect in the receiving water.

Nitrification in action

The significance of the nitrification problem is clearly illustrated by the experience of the Colorado Springs Utilities Department Wastewater Division. In the fall of 1979, plant management suspected the interference of nitrification in their BOD tests. They began to analyze their samples in duplicate, one by the standard BOD method, and one sample with the addition of a chemical to inhibit nitrification. These results verified the suspicion, and they requested permission from the Colorado Department of Health Water Quality Control Division to report the results of the inhibited BOD test because their standard BOD data was erroneous. Because EPA had not approved the inhibited BOD method for use in compliance testing, the state denied the request and Colorado Springs went to the EPA

Region VIII administrator to request modification of their permit.

However, EPA headquarters maintained that the "30/30" (30 mg/L BOD, and 30 mg/L suspended solids) effluent limitation had been intended to include the incidental contribution of NOD, and so a redefinition of the parameter and a review of the numerical limitation would be necessary. This launched Colorado Springs on a 4-year struggle with state and federal regulatory agencies that included a campaign of letters to their state legislators and three different EPA Administrators. They also sponsored an in-depth study by Owen Callaway and James C. Young, the BOD Task Force chairman for the "Standard Methods" Joint Editorial Board. Although the technical groups in the various agencies seemed to understand the issue and support Colorado Springs' request, the dispute became essentially a legal battle.

In late 1980 Colorado Springs solicited the help of the Association of Metropolitan Sewerage Agencies (AMSA). AMSA surveyed its members on the question of compliance with EPA secondary treatment regulations in plants with nitrified effluents. Of 71 plants surveyed, 41 experienced incidental nitrification in their secondary systems. In 41% of those plants, the effluent BOD was artificially high as a result of nitrification; NOD represented between 9 and 86% of the total BOD.

Of the plants with incidental nitrification, 34% responded that they had experienced compliance problems. The survey concluded that plants with compliance problems "generally implemented facility or operating technique modifications at additional cost in an attempt to control the partial nitrification or attenuate its effects." In many cases it was not initially clear that nitrification was the problem, and remedies such as the addition of gravity filtration mentioned previously were considered. Some higher-than-expected BOD results were interpreted simply as inadequate biological treatment, and measures such as increased aeration were tried. This served to encourage nitrification and aggravate the problem. When nitrification was identified, some plants decreased their mixed-liquor DO and wound up with a sludge bulking problem to add to their woes. Although a decrease in mean cell residence time (MCRT) would help discourage nitrification, it often produced a sludge disposal problem.

In Minneapolis-St. Paul, the Metropolitan Waste Control Commission (MWCC) began struggling with the nitrification interference problem in 1975. Under summertime conditions, their BOD was anywhere from half-again to three times as high as normal. Once they established that their problem was not inadequate but actually excess treatment efficiency, they began unsuccessful efforts to have their permit rewritten for CBOD. After trying such methods as reduced aeration and additional sludge wasting, they finally hit on a reliable way to eliminate the nitrifiers in their effluent—overchlorination. There was no question that this practice was not environmentally sound, but it did bring their effluent BOD within the limits of their permit. In 1981, a dispute with the Minnesota Pollution Control Agency over the practice of year-round chlorination produced a stand-off of sorts. The MWCC discontinued overchlorination and now reports data for both CBOD and total BOD to the state to demonstrate their good faith efforts to comply with their permit, but theoretically the state could initiate enforcement action at any time.

Enforcement prerogative

A much more heated battle with the regulatory powers occurred in Dubuque, Iowa. The city's problem with nitrification stemmed from efforts to control a problem of excessive solids in the biological process. Increasing the sludge age to facilitate solids handling resulted in nitrification, not in the plant but in the BOD bottle. Their problem was brought to the attention of the Iowa Department of Environmental Quality in late 1978. In a situation similar to that in Colorado Springs, they found that the regional engineers were receptive but the problem was held up administratively. Eventually the city was threatened with retroactive fines of $10 000/day which would have amounted to millions of dollars. An out-of-court settlement required the city to take several measures directed at correcting their solids handling problems and pay a fine of $15 000. The consent agreement provided for the use of the inhibited BOD test for a specific period. Now the city reports both CBOD and BOD to the state, and is planning to take advantage of the opportunity to have their permit modified permanently.

Nitrification and process modifications to control it can often result in other problems, not just with operation but with compliance as well. Partial nitrification in a plant produces excess nitrite concentrations which play havoc with the reactions of chlorine disinfection. A plant with this problem may violate not only its BOD standard, but its limit for fecal coliform as well. In these three cases the discharger has finally resorted to simply reporting data for both types of BOD and relying on the judgment of the permitting authority with regard to enforcement action.

BOD redefined

EPA is now well on its way toward promulgating a regulation to provide publicly owned treatment works (POTWs) the option of reporting either type of BOD. The controversy is not over whether EPA should have addressed the issue, but the way in which it was done. The debate goes back through the history of the secondary treatment regulations required in the Clean Water Act, and into the history of the BOD method itself. The two principal issues are: whether

EPA needed to or even should have redefined BOD to include NOD and introduced a new parameter, CBOD; and whether the effluent standard for CBOD should be different than the 30 mg/L originally set for BOD.

Central to both questions is the issue of whether BOD was intended to include NOD at all. If not, BOD can be considered to have been CBOD all along. (Translation: why change the number?) If it was CBOD all along, then why didn't EPA just approve the inhibited method for BOD analysis proposed in December 1979 (44 FR 69464) to amend the pollutant sampling and analysis procedure regulation (40 CFR Part 136)?

A review of the regulatory history of BOD was made by Hall and Foxen and published in the December 1983 *Journal*. Their conclusion was that EPA did not intend the BOD test results to reflect the contribution of NOD. An exceedingly detailed review of the literature by Vinton Bacon and Jerry Huang for the City of Dubuque, Iowa, concluded that in the development of the BOD procedure, there was no intention to include the oxygen demand of nitrogenous substances.

EPA's own review of the regulatory history concludes that because they recognized the potential contribution of NOD to the BOD test results at the time that they promulgated the "30/30" regulation, they intended to include it. The regulations were developed based on the results of a survey of wastewater treatment plant effluents across the country. The data base that these results represented was indeed produced by the standard uninhibited BOD procedure, which may well have included an unquantifiable amount of NOD. According to EPA, the plants surveyed were "well designed and operated." There are those who ask, given that nitrification in a secondary process is a product of underloaded or improperly operated facilities, whether there would have been significant nitrification in the plants EPA surveyed in the early 1970s.

Which came first?

Another question about EPA's intent is that of how the original number, 30 mg/L, was chosen. Some maintain that EPA took an average concentration of 200 mg/L BOD in raw wastewater (which would not have significant nitrifying populations), required that POTWs remove 85% of that, and arrived at 30 mg/L. If the influent concentration did not represent any NOD, then by definition neither did the effluent limit. EPA did include two requirements in the regulation—a 30 mg/L effluent limit, and a requirement for 85% removal of influent BOD. The significant question is: which came first? The statutory basis for the regulation required the Administrator to publish "information, in terms of amounts of constituents and chemical, physical, and biological characteristics of pollutants, on the *degree of effluent reduction attainable* through the application of secondary treatment" [emphasis added]. That this language specifically directs attention to removal efficiency has led some to believe that the requirement for 85% removal came first. Another interesting point is that the figure of 85% removal was also mentioned in the public works grants regulations that preceded the Clean Water Act (18 CFR 601.25).

However, a close look at the documentation for EPA's decision indicates that they first selected 30 mg/L as the effluent quality attainable by secondary treatment, and included the specified 85% removal requirement to prevent dischargers with infiltration/inflow problems from meeting their permit limits by dilution. It is difficult to make an uncontestable case for either conclusion; the written record as well as the recollections of people involved in the decision are very ambiguous.

Other measurements

The secondary treatment information regulation as promulgated on August 17, 1973 (38 FR 22298) included a provision that COD or TOC analyses, which both measure only the oxygen demand exerted by organic material (no appreciable interference from reduced nitrogen forms), could be substituted for BOD if a significant correlation could be established between either of those parameters and BOD for a given wastewater. This seems to indicate that EPA intended to limit the analysis to carbonaceous oxygen demand, without NOD.

The proposed amendment to the regulation includes a discussion of the ultimate oxygen demand (UOD) of wastewater as it relates to BOD. The equation given by EPA is:

$$UOD = (1.5\ CBOD) + (4.6\ NH_3{-}N).$$

The terms representing organic oxygen demand and reduced nitrogen are clearly separate. Although the concept of UOD is not specifically addressed in the 1973 regulation, in 1975, the EPA "Process Design Manual for Nitrogen Control" contained a calculation for total oxygen demand that included the separate terms BOD and NOD. A similar equation appears in the 1975 EPA document "Alternative Waste Management Techniques for Best Practicable Waste Treatment." The implication of the separate terms is that EPA did not consider BOD to include the oxygen demand from reduced nitrogen forms.

No backsliding

Regardless of what EPA intended BOD to mean, the decision was made that in order to address the effect of nitrification, the parameter would have to be redefined. Although it may have been infinitely simpler to approve the inhibited BOD method as proposed in 1979, that action would have undoubtedly drawn criticism from those who would have regarded it as a relaxation of the standard.

EPA makes a point that changes in regulations should not have the effect of negating prior progress toward cleaner water. The lengthy language included in the proposed redefinition of secondary treatment (40 CFR Part 133) to prevent "backsliding" is evidence of that. Likewise, EPA reconsidered the numerical standard of 30 mg/L BOD when it provided the option of reporting CBOD. If indeed the original standard was intended to account for the contribution of NOD, then because the CBOD procedure eliminates that contribution so that the results would be somewhat lower than those of the uninhibited test, it follows that the standard for that parameter should be lower as well.

EPA reviewed the data on which the original standard was based, as well as more recent data. The average difference between CBOD and BOD in those samples was 3 to 5 mg/L under conditions that minimized the possibility of nitrification. Although the regulation does not explicitly state whether CBOD was consistently lower than BOD, EPA considered it prudent to establish the CBOD effluent requirement at 25 mg/L. The limited accuracy of the BOD test does not justify an incremental change in the standard of less than 5 mg/L. The rationale for lowering the standard seems based more on the need to eliminate the possibility of backsliding than on scientific justification. This is one of two principal points brought out by critics of the regulation.

Administrative chaos

The other, and perhaps the most significant, criticism is that the regulation could easily produce administrative chaos among the permitting authorities. It effectively establishes a separate parameter to be regulated because it is not likely that all POTWs will request a revision of their permits. The regulation is not required across-the-board, and is not likely to be applied uniformly. Even the various EPA regional administrations do not agree on the issues, as illustrated by the different responses to the problem in Iowa where EPA Region VII granted Dubuque permission to use the inhibited test, and in Minnesota where EPA Region V refused to accept a permit written without BOD. Perhaps the official sanction of EPA headquarters for the substitution of CBOD will reduce the degree of disagreement.

As is common in any regulatory decision, the proposed revision to the secondary treatment regulation represents a compromise. In the decade since EPA exercised its best judgment in the form of the 30/30 effluent limitations, wastewater treatment practice has improved substantially and brought the problem of nitrification in the BOD test to light. EPA looked back and has acted again on its best judgment. Interested parties are almost unanimous that some regulatory action was necessary, although many do not find EPA's proposal perfect. But after years of struggling to comply with an often unmeetable standard, and negotiating with varying success with the permitting authorities for relief, the proposed regulation is a welcome compromise.

Karen B. Carter

Attachment C

5210 BIOCHEMICAL OXYGEN DEMAND (BOD)*

5210 A. Introduction

1. General Discussion

The biochemical oxygen demand (BOD) determination is an empirical test in which standardized laboratory procedures are used to determine the relative oxygen requirements of wastewaters, effluents, and polluted waters. The test has its widest application in measuring waste loadings to treatment plants and in evaluating the BOD-removal efficiency of such treatment systems. The test measures the molecular oxygen utilized during a specified incubation period for the biochemical degradation of organic material (carbonaceous demand) and the oxygen used to oxidize inorganic material such as sulfides and ferrous iron. It also may measure the amount of oxygen used to oxidize reduced forms of nitrogen (nitrogenous demand) unless their oxidation is prevented by an inhibitor. The seeding and dilution procedures provide an estimate of the BOD at pH 6.5 to 7.5.

Measurements of oxygen consumed in a 5-d test period (5-d BOD or BOD_5, 5210B), oxygen consumed after 60 to 90 d of incubation (ultimate BOD or UBOD, 5210C), and continuous oxygen uptake (respirometric method, 5210D) are described here. Many other variations of oxygen demand measurements exist, including using shorter and longer incubation periods and tests to determine rates of oxygen uptake. Alternative seeding, dilution, and incubation conditions can be chosen to mimic receiving-water conditions, thereby providing an estimate of the environmental effects of wastewaters and effluents.

The UBOD measures the oxygen required for the total degradation of organic material (ultimate carbonaceous demand) and/or the oxygen to oxidize reduced nitrogen compounds (ultimate nitrogenous demand). UBOD values and appropriate kinetic descriptions are needed in water quality modeling studies such as UBOD: BOD_5 ratios for relating stream assimilative capacity to regulatory requirements; definition of river, estuary, or lake deoxygenation kinetics; and instream ultimate carbonaceous BOD (UCBOD) values for model calibration.

2. Carbonaceous Versus Nitrogenous BOD

A number of factors, for example, soluble versus particulate organics, settleable and floatable solids, oxidation of reduced iron and sulfur compounds, or lack of mixing may affect the accuracy and precision of BOD measurements. Presently, there is no way to include adjustments or corrections to account for the effect of these factors.

Oxidation of reduced forms of nitrogen, such as ammonia and organic nitrogen, can be mediated by microorganisms and exert nitrogenous demand. Nitrogenous demand historically has been considered an interference in the determination of BOD, as clearly evidenced by the inclusion of ammonia in the dilution water. The interference from nitrogenous demand can now be prevented by an inhibitory chemical.[1] If an inhibiting chemical is not used, the oxygen demand measured is the sum of carbonaceous and nitrogenous demands.

Measurements that include nitrogenous demand generally are not useful for assessing the oxygen demand associated with organic material. Nitrogenous demand can be estimated directly from ammonia nitrogen (Section 4500-NH_3); and carbonaceous demand can be estimated by subtracting the theoretical equivalent of the reduced nitrogen oxidation from uninhibited test results. However, this method is cumbersome and is subject to considerable error. Chemical inhibition of nitrogenous demand provides a more direct and more reliable measure of carbonaceous demand.

The extent of oxidation of nitrogenous compounds during the 5-d incubation period depends on the concentration and type of microorganisms capable of carrying out this oxidation. Such organisms usually are not present in raw or settled primary sewage in sufficient numbers to oxidize sufficient quantities of reduced nitrogen forms in the 5-d BOD test. Many biological treatment plant effluents contain sufficient numbers of nitrifying organisms to cause nitrification in BOD tests. Because oxidation of nitrogenous compounds can occur in such samples, inhibition of nitrification as directed in 5210B.4e6) is recommended for samples of secondary effluent, for samples seeded with secondary effluent, and for samples of polluted waters.

Report results as carbonaceous biochemical oxygen demand ($CBOD_5$) when inhibiting the nitrogenous oxygen demand. When nitrification is not inhibited, report results as BOD_5.

3. Dilution Requirements

The BOD concentration in most wastewaters exceeds the concentration of dissolved oxygen (DO) available in an air-saturated sample. Therefore, it is necessary to dilute the sample before incubation to bring the oxygen demand and supply into appropriate balance. Because bacterial growth requires nutrients such as nitrogen, phosphorus, and trace metals, these are added to the dilution water, which is buffered to ensure that the pH of the incubated sample remains in a range suitable for bacterial growth. Complete stabilization of a sample may require a period of incubation too long for practical purposes; therefore, 5 d has been accepted as the standard incubation period.

If the dilution water is of poor quality, the BOD of the dilution water will appear as sample BOD. This effect will be amplified by the dilution factor. A positive bias will result. The methods included below (5210B and 5210C) contain both a dilution-water check and a dilution-water blank. Seeded dilution waters are checked further for acceptable quality by measuring their consumption of oxygen from a known organic mixture, usually glucose and glutamic acid.

The source of dilution water is not restricted and may be distilled, tap, or receiving-stream water free of biodegradable organics and bioinhibitory substances such as chlorine or heavy metals. Distilled water may contain ammonia or volatile organics; deionized waters often are contaminated with soluble organics leached from the resin bed. Use of copper-lined stills or copper fittings

* Approved by Standard Methods Committee, 1997.

attached to distilled water lines may produce water containing excessive amounts of copper (see Section 3500-Cu).

4. Reference

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5. Bibliography

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5210 B. 5-Day BOD Test

1. General Discussion

a. Principle: The method consists of filling with sample, to overflowing, an airtight bottle of the specified size and incubating it at the specified temperature for 5 d. Dissolved oxygen is measured initially and after incubation, and the BOD is computed from the difference between initial and final DO. Because the initial DO is determined shortly after the dilution is made, all oxygen uptake occurring after this measurement is included in the BOD measurement.

b. Sampling and storage: Samples for BOD analysis may degrade significantly during storage between collection and analysis, resulting in low BOD values. Minimize reduction of BOD by analyzing sample promptly or by cooling it to near-freezing temperature during storage. However, even at low temperature, keep holding time to a minimum. Warm chilled samples to 20 ± 3°C before analysis.

1) Grab samples—If analysis is begun within 2 h of collection, cold storage is unnecessary. If analysis is not started within 2 h of sample collection, keep sample at or below 4°C from the time of collection. Begin analysis within 6 h of collection; when this is not possible because the sampling site is distant from the laboratory, store at or below 4°C and report length and temperature of storage with the results. In no case start analysis more than 24 h after grab sample collection. When samples are to be used for regulatory purposes make every effort to deliver samples for analysis within 6 h of collection.

2) Composite samples—Keep samples at or below 4°C during compositing. Limit compositing period to 24 h. Use the same criteria as for storage of grab samples, starting the measurement of holding time from end of compositing period. State storage time and conditions as part of the results.

2. Apparatus

a. Incubation bottles: Use glass bottles having 60 mL or greater capacity (300-mL bottles having a ground-glass stopper and a flared mouth are preferred). Clean bottles with a detergent, rinse thoroughly, and drain before use. As a precaution against drawing air into the dilution bottle during incubation, use a water seal. Obtain satisfactory water seals by inverting bottles in a water bath or by adding water to the flared mouth of special BOD bottles. Place a paper or plastic cup or foil cap over flared mouth of bottle to reduce evaporation of the water seal during incubation.

b. Air incubator or water bath, thermostatically controlled at 20 ± 1°C. Exclude all light to prevent possibility of photosynthetic production of DO.

3. Reagents

Prepare reagents in advance but discard if there is any sign of precipitation or biological growth in the stock bottles. Commercial equivalents of these reagents are acceptable and different stock concentrations may be used if doses are adjusted proportionally.

a. Phosphate buffer solution: Dissolve 8.5 g KH_2PO_4, 21.75 g K_2HPO_4, 33.4 g $Na_2HPO_4 \cdot 7H_2O$, and 1.7 g NH_4Cl in about 500 mL distilled water and dilute to 1 L. The pH should be 7.2 without further adjustment. Alternatively, dissolve 42.5 g KH_2PO_4 or 54.3 g K_2HPO_4 in about 700 mL distilled water. Adjust pH to 7.2 with 30% NaOH and dilute to 1 L.

b. Magnesium sulfate solution: Dissolve 22.5 g $MgSO_4 \cdot 7H_2O$ in distilled water and dilute to 1 L.

c. Calcium chloride solution: Dissolve 27.5 g $CaCl_2$ in distilled water and dilute to 1 L.

d. Ferric chloride solution: Dissolve 0.25 g $FeCl_3 \cdot 6H_2O$ in distilled water and dilute to 1 L.

e. Acid and alkali solutions, 1*N*, for neutralization of caustic or acidic waste samples.

1) Acid—Slowly and while stirring, add 28 mL conc sulfuric acid to distilled water. Dilute to 1 L.

2) Alkali—Dissolve 40 g sodium hydroxide in distilled water. Dilute to 1 L.

f. Sodium sulfite solution: Dissolve 1.575 g Na_2SO_3 in 1000 mL distilled water. This solution is not stable; prepare daily.

g. Nitrification inhibitor, 2-chloro-6-(trichloromethyl) pyridine.*

h. Glucose-glutamic acid solution: Dry reagent-grade glucose and reagent-grade glutamic acid at 103°C for 1 h. Add 150 mg glucose and 150 mg glutamic acid to distilled water and dilute to 1 L. Prepare fresh immediately before use.

* Nitrification Inhibitor, Formula 2533, Hach Co., Loveland, CO, or equivalent.