Metropolitan Water Reclamation District of Greater Chicago

MONITORING AND RESEARCH DEPARTMENT

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CALUMET PHOSPHORUS TASK FORCE

TECHNICAL MEMORANDUM NO. 5

READILY BIODEGRADABLE CHEMICAL OXYGEN DEMAND IN CALUMET PRIMARY EFFLUENT DATA

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Metropolitan Water Reclamation District of Greater Chicago

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FOREWORD

The Metropolitan Water Reclamation District of Greater Chicago (MWRD) recognizes the value of phosphorus as a non-renewable resource. In an effort to optimize the sustainable removal of phosphorus from its wastewater influents and the subsequent recover of phosphorus in various forms suitable for use as an agronomic fertilizer, the MWRD initiated a Phosphorus Removal and Recovery Task Force in 2012. The Task Force initiated a study phase at several of the MWRD's Water Reclamation Plants to evaluate the feasibility of implementing enhanced biological phosphorus removal and to develop operational guidelines for optimizing its effectiveness. The Task Force has created WRP specific study workgroups that are focused on each of the WRP's that have been identified to participate in this initiative. As the workgroups complete various phases of their studies and evaluations they are documenting their findings and recommendations in technical memoranda. These memoranda are written by the WRP specific workgroups and vetted by the Task Force before being published. Their purpose is to capture the state of knowledge and study findings and to make recommendations for implementation of enhanced biological phosphorus recovery as they are understood at the time the memoranda are published.

DISCLAIMER

The contents of this technical memoranda constitute the state of knowledge and recommendations developed by the MWRD's Phosphorus Task Force at the time of publication, and are subject to change as additional studies are completed and experience is attained, and as the full context of the MWRD's operating environment is considered.

Readily Biodegradable Chemical Oxygen Demand in Calumet Primary Effluent Data

Technical Memorandum 5

Date: June 23, 2015

To: Phosphorus Task Force & Advisory Committee

From: Phosphorus Study/Planning Team

Subject: Readily Biodegradable Chemical Oxygen Demand in Calumet Primary Effluent Data

The availability of readily biodegradable organic carbon (C) in the anaerobic zone of an enhanced biological phosphorus (P) removal (EBPR) is critical for its success. There are a number of ways to determine the probability of a plant to reliably remove P based on the process's C demand, e.g. the process influent chemical oxygen demand (COD) to total phosphorus (TP) ratio; five day biochemical oxygen demand (BOD_5) to TP ratio, or volatile fatty acid (VFA) to TP ratio. Evaluating COD:TP and BOD_5:TP ratios can only provide a rough estimation of EBPR capabilities since only the readily biodegradable portions of COD and BOD_5 can be utilized by the EBPR microorganisms, phosphate accumulating organism (PAOs). Many studies have focused on VFA content as this substrate is directly used by the PAOs, but the VFA method is not standardized, and there is a lot of uncertainty regarding sample preparation and preservation prior to analysis. Recently, readily biodegradable chemical oxygen demand (rbCOD) has been identified as being of fundamental importance in designing and assessing a biological P removal system. rbCOD includes the actual VFA in the influent as well as other readily biodegradable carbons which can be potentially fermented/converted to VFAs. An rbCOD to total phosphorus (TP) ratio of 11–16 is considered a requirement for desired EBPR performance (1).

Various methods, categorized as physical or bioassay, have been proposed to measure rbCOD. An efficient physical testing method was published and referred herein as the flocculation method outlined as below (2).

For this method, a wastewater sample is flocculated by adding 2 mL of 100 g/L zinc sulfate solution to 200 mL of sample and then mixing vigorously with a magnetic stirrer for approximately 1 minute. The pH of the mixed sample is adjusted to approximately 10.5 with 6 M sodium hydroxide solution, and the sample is settled for 5 minutes. The clear supernatant is withdrawn and filtered using a 0.45 μm membrane. The COD of the filtrate is analyzed and

termed ffCOD. The difference in ffCOD results for the EBPR process influent and effluent samples is considered to be rbCOD; this difference excludes the recalcitrant soluble C.

Battery A of the Calumet WRP was converted to EBPR using the anoxic/anaerobic/aerobic (AAnO) set-up in February 2013 using the existing infrastructure. Poor P removal has been observed since conversion. This is largely considered to be due to insufficient influent biodegradable C to the EBPR process. This study is to evaluate the rbCOD availability in the Calumet WRP primary effluent (CAPREF).

CAPREF and Battery A final effluent (CAFN_A) were tested for rbCOD using the flocculation method. Seventy (70) CAPREF and 70 CAFN_A samples were collected during a year period, August 2013 thru July 2014. The soluble COD (solCOD) and TP were analyzed as well in each sample. Table 1 summarizes the statistical data of CAPREF C and P concentrations. The rbCOD of CAPREF varied in a wide range from 1 mg/L to 107 mg/L. The percent of rbCOD in solCOD also ranged widely from 3 percent to 97 percent. The average rbCOD of CAPREF and percent rbCOD in solCOD were 40 mg/L and 52 percent, respectively. A relationship of rbCOD = 0.52*solCOD was found with an R^2 value of 0.87, which means that 87 percent of the variation of data can be explained through a linear regression method analysis (3,4). The 95% confidence interval of slope β was also evaluated and found to be (0.475, 0.567), meaning it is 95% confident that the actual slope β lies between 0.475 and 0.567 against the sample b value of 0.52 with 76 degrees of freedom. Table 1 also indicates that Calumet primary effluent rbCOD:TP had an average of 7.5 which is much lower than the minimum recommended value of 11 suggested above.

Since Battery A in the Calumet WRP did not show any sign of EBPR performance during the sampling period, the rbCOD/TP ratios versus Battery A effluent TP concentrations will not be discussed here. Figure 1 shows the rbCOD concentrations of CAPREF and the percent rbCOD in solCOD of CAPREF. It can be seen that both parameters are scattered over a wide range. However, both rbCOD concentrations and the ratios of rbCOD in solCOD were declining from high to low as shown in the moving average line when the wastewater temperature transitioned from cold to warm, i.e. early May (15°C) to late July (22°C). Figure 2 indicates higher concentrations both in solCOD and rbCOD at an average wastewater temperature of 9.2°C during cold weather months, January to March, and lower concentrations at an average wastewater temperature of 19.5°C during warm weather months, June and July. The seasonal correlation between rbCOD, solCOD and influent TP was investigated by separating data into two seasons: November to March as winter season and April to October as summer season. The results are summarized in Table 2. It shows that both %rbCOD in solCOD and rbCOD/TP were slightly higher in the winter season (average of 55% rbCOD in solCOD and rbCOD/TP=8.9) than in the summer season (average 50% rbCOD in solCOD and rbCOD/TP=6.3) in Calumet WRP primary effluent. Although the average %rbCOD in solCOD is slightly different in summer and winter, the linear regression method analysis shows that the difference is not statistically significant with 95% confidence (3,4). The lower rbCOD during warm wastewater temperatures and higher rbCOD during cold wastewater temperatures may be due to the trend of solCOD being lower in warm months and also the fact that microbial activity in the sewer pipes are more active during warmer conditions thereby resulting in soluble carbon being used up immediately and leaving less readily available C entering the wastewater treatment plant.

In summary, the study results suggest that the average Calumet WRP primary effluent rbCOD:TP ratio is much lower than the minimum requirement for EBPR process of 11. The distribution curve in Figure 3 shows that during the study period the Calumet primary effluent was in a C deficit over 80 percent of the time to meet the minimum recommended rbCOD:TP ratio of 11 for EBPR. It should also be noted that the available C can also be used by both anoxic and aerobic heterotrophs, thus competing with the PAOs for the rbCOD. Seasonal solCOD and rbCOD differences were found, but the two parameters were also scattered over a wide range in all seasons. On average, rbCOD concentration in Calumet primary effluent is about 52 percent of its solCOD concentration.

References

1. Barnard, J., Shaw, A., and Lindeke, D. Using alternative parameters to predict success for P removal in WWTPs. Nutrient 2013 Proceedings. 1970–1984, 2013
2. Mamais, D., Jenkins, D., and Pitt, P. A rapid physical-chemical method for the determination of readily biodegradable soluble COD in municipal wastewater. Water Research. 27, 195–197, 1993
3. Rao, C. R. Linear Statistical Inference and Its Application, John Wiley and Sons, New York, 1965, Page 263-288.
4. Draper, N. R. and Smith H. Applied Regression Analysis, John Wiley and Sons, New York, 1966, Page 1-85.

TABLE 1: CALUMET PRIMARY EFFLUENT CHARACTERISTICS
8/2013–7/2014

	rbCOD (mg/L)	rbCOD/solCOD (%)	CAPREF TP (mg/L)	rbCOD/TP
Count	70	70	69	69
10 percentile	12	24	3.10	2.8
25 percentile	20	31	4.07	3.7
50 percentile	38	49	5.47	6.9
75 percentile	56	75	7.78	8.6
90 percentile	74	87	9.30	15.4
Minimum	1	3	2	0.1
Maximum	107	97	12	23.8
Average	40	52	6	7.5

FIGURE 1: CALUMET PRIMARY EFFLUENT READILY BIODEGRADABLE CHEMICAL OXYGEN DEMAND CONCENTRATIONS AND PERCENT READILY BIODEGRADABLE CHEMICAL OXYGEN DEMAND IN SOLUBLE CHEMICAL OXYGEN DEMAND

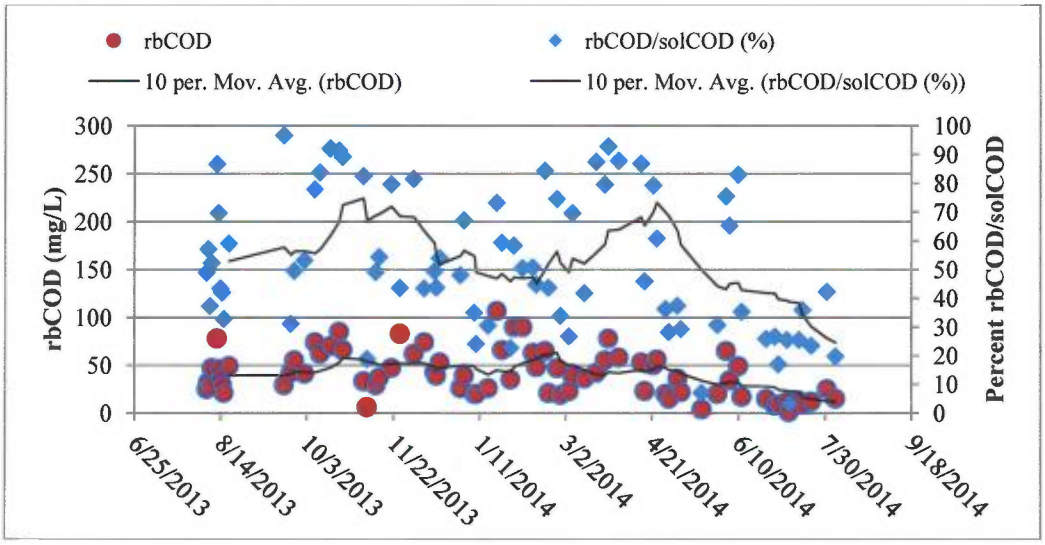

FIGURE 2: CALUMET PRIMARY EFFLUENT SOLUBLE CHEMICAL OXYGEN DEMAND AND READILY BIODEGRADABLE CHEMICAL OXYGEN DEMAND CONCENTRATIONS

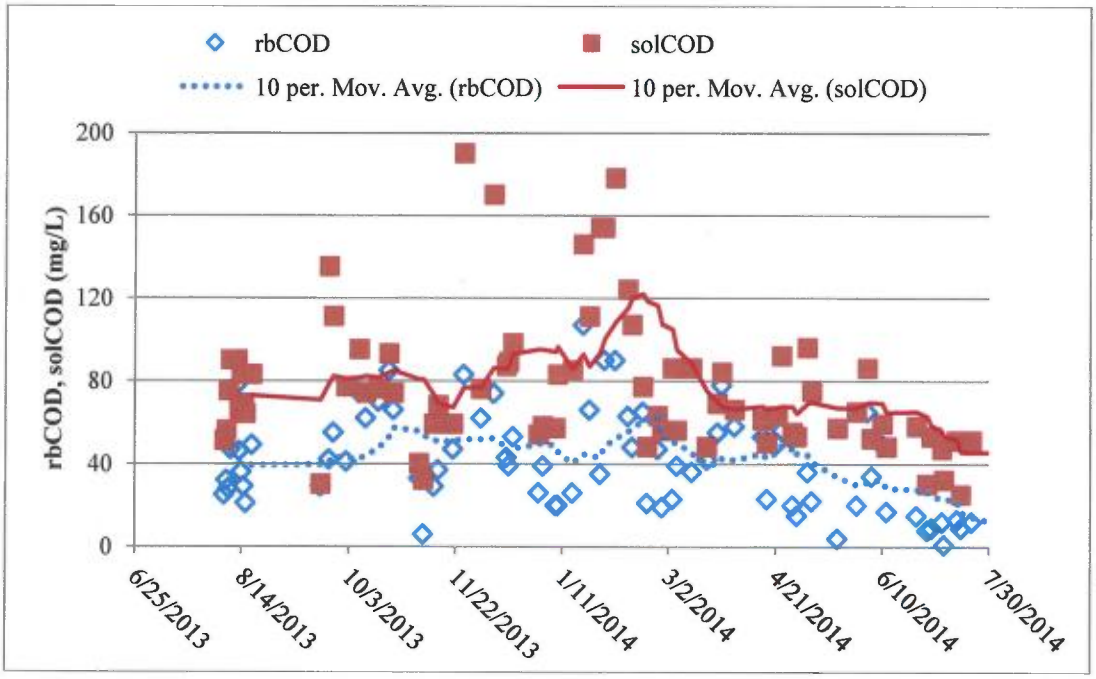

TABLE 2: CALUMET PRIMARY EFFLUENT SEASONAL CHARACTERISTICS

	rbCOD	rbCOD/solCOD (%)	CAPREF TP	rbCOD/TP
Winter (November 2013 - March 2014)				
Count	33	33	33	33
10 percentile	20	28	3.46	3.2
25 percentile	29	44	4.62	5.3
50 percentile	42	51	5.44	7.7
75 percentile	63	73	8.18	10.5
90 percentile	82	82	9.25	17.6
Minimum	6	19	1.79	1.6
Maximum	107	93	12.16	23.5
Average	47	55	6.09	8.9
Summer (August 2013-October 2013; April 2014 - August 2014)				
Count	37	37	36	36
10 percentile	9	22	3.00	2.1
25 percentile	15	28	3.74	3.4
50 percentile	27	40	5.93	4.9
75 percentile	54	78	7.36	8.4
90 percentile	66	89	9.34	10.4
Minimum	1	3	2.23	0.1
Maximum	85	97	11.78	23.8
Average	34	50	5.88	6.3

FIGURE 3: CALUMET PRIMARY EFFLUENT READILY BIODEGRADABLE CHEMICAL OXYGEN DEMAND:TOTAL PHOSPHORUS DISTRIBUTION CURVE