

*Protecting Our Water Environment*



*Metropolitan Water Reclamation District of Greater Chicago*

***MONITORING AND RESEARCH  
DEPARTMENT***

*REPORT NO. 17-22*

*STICKNEY PHOSPHORUS TASK FORCE*

*TECHNICAL MEMORANDUM NO. 12*

*READILY BIODEGRADABLE CHEMICAL OXYGEN DEMAND DATA  
ANALYSES FOR STICKNEY PRIMARY EFFLUENT AND ITS EFFECT  
ON ENHANCED BIOLOGICAL PHOSPHORUS REMOVAL*

*May 2017*

**Metropolitan Water Reclamation District of Greater Chicago**

**100 East Erie Street Chicago, Illinois 60611-2803 312-751-5600**

**STICKNEY PHOSPHORUS TASK FORCE**

**TECHNICAL MEMORANDUM NO. 12**

**TITLE**

**By**

**Joseph Kozak  
Supervising Environmental Research Scientist**

**Cindy Qin  
Environmental Research Scientist**

**Yvonne Lefler  
Principal Civil Engineer**

**Joseph Cummings  
Managing Engineer**

**Brett Garelli  
Deputy Director of Maintenance and Operations**

**Glen Rohloff  
Managing Civil Engineer**

## **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 Data Analyses for Stickney Primary Effluent and Its Effect on Enhanced Biological Phosphorus Removal

Technical Memorandum 12

---

**Date:** April 11, 2017

**To:** Phosphorus Task Force & Advisory Committee

**From:** Phosphorus Study/Planning Team

**Subject:** Readily Biodegradable Chemical Oxygen Demand Data Analyses for Stickney Primary Effluent and Its Effect on Enhanced Biological Phosphorus Removal

The availability of readily biodegradable organic carbon in the anaerobic zone of an enhanced biological phosphorus (P) removal (EBPR) process is critical for its success. There are a number of ways to determine the probability that a plant will reliably remove P based on the process's carbon demand, e.g. the process influent chemical oxygen demand (COD) to total P (TP) ratio, biochemical oxygen demand (BOD) to TP ratio, or volatile fatty acids (VFA) to TP ratio. Evaluating COD:TP and BOD:TP ratios can only provide a rough estimation of EBPR capabilities since only the readily biodegradable portions of COD and BOD can be utilized by the EBPR biomass, phosphate-accumulating organism (PAOs). Many studies have focused on VFA content as this is the substrate 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 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: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 to herein as the flocculation method outlined below (2).

A wastewater sample is flocculated by adding two mL of 100 g/L zinc sulfate solution to 200 mL of the sample, and then mixed vigorously with a magnetic stirrer for approximately one minute. The pH of the mixed sample is adjusted to approximately 10.5 with a 6 M sodium hydroxide solution, and the sample is settled for five minutes. The clear supernatant is withdrawn and filtered using a 0.45  $\mu\text{m}$  membrane. The COD of the supernatant filtrate is analyzed and termed ffCOD. The difference in ffCOD results for the EBPR process influent and effluent samples is considered to be rbCOD; the effluent ffCOD accounts for the recalcitrant soluble carbon.

Incoming wastewater flow enters the Stickney WRP at two locations, the West Side and Southwest Side. The West Side receives wastewater from the Salt Creek interceptor, the West Side interceptor, and recycle flows from the grit dewatering and scum concentration tanks. The primary treatment in the West Side is currently through 72 Imhoff tanks which will be demolished and changed to circular primary settling tanks in 2019. The Southwest Side receives wastewater from the Southwest interceptor, Argo interceptor, Tunnel and Reservoir Plan pumpback, recycle from desilting basins, sludge concentration tank overflows, lagoon decant, and centrate. The primary treatment in the Southwest is currently through 20 rectangular preliminary settling tanks. The Southwest and West Sides are also linked through a connecting sewer. Upon preliminary treatment, the West Side preliminary effluent and Southwest Side preliminary effluent are mixed together prior to entering the four aeration batteries as combined primary effluent (PE).

The objectives of this rbCOD study are discussed in three aspects:

1. Evaluate Southwest preliminary effluent characteristics under current conditions both overall and seasonally.
2. Evaluate combined Southwest Side and West Side PE for summer and winter conditions.
3. Find relationship between rbCOD and soluble COD (solCOD) in order to make an estimate of readily degradable carbon in the future for both Southwest Side preliminary effluent and combined PE.

### **Southwest Preliminary Effluent Under Current Conditions**

Since the remaining West Side Imhoff tanks will be demolished in a few years and replaced with primary settling tanks, samples from the West Side are not representative of the future. Therefore, only Stickney Southwest Preliminary Effluent (STPREF) was tested under current conditions for rbCOD for a one-year period from August 2013 to August 2014. Battery D was the first converted EBPR battery, and the whole plant conversion was not completed until late October 2013; as such, Battery D effluent (STFN\_D) was used as the effluent sample using the flocculation method during the entire study as described below. STPREF sample (24-hour composite) and STFN\_D (24-hour composite) were tested for ffCOD in order to calculate rbCOD.

Sixty five (65) STPREF and 65 STFND\_D samples were collected for rbCOD analysis during the one-year study period (August 2013 to August 2014). The solCOD and TP were analyzed for these STPREF and STFND\_D samples as well. Statistical data of STPREF are shown in [Table 1](#). The rbCOD of STPREF varied in a wide range, from two mg/L to 457 mg/L. The %rbCOD in solCOD also ranged widely, from four percent to 97 percent. The average rbCOD of STPREF and %rbCOD in solCOD were 70 mg/L and 53 percent, respectively. There was a good fit using the linear regression model  $rbCOD = 0.53 * solCOD$ , which accounted for 89 percent of the variation in the data (3, 4). [Table 1](#) also indicates that Stickney Southwest preliminary effluent rbCOD:TP had an average of 10.9, which is close to the minimum recommended value of 11 suggested above.

[Figure 1](#) shows the rbCOD concentrations of STPREF and the %rbCOD in solCOD of STPREF over the entire year of the study. It can be seen that both parameters are scattered over a wide range during the one-year study period. However, both rbCOD concentrations and the ratios of rbCOD in solCOD were quite low when the sewage temperature transitioned from cold to warm, i.e. early May 2014 (15°C) to late July 2014 (22°C). [Figure 2](#) indicates higher concentrations of both solCOD and rbCOD during cold weather at around 10°C sewage temperature (February to April 2014) and lower values during warm months at around 19°C (August to October 2013 and May to August 2014).

The seasonal correlation between rbCOD, solCOD, and influent TP was investigated by separating data into two seasons: November to March as the winter season and April to October as the summer season based on the wastewater temperatures coming into the plant. The results are summarized in [Table 2](#). The linear regression analysis shows good fits of  $rbCOD = 0.66 * solCOD$  in winter and  $rbCOD = 0.41 * solCOD$  in summer in Stickney WRP Southwest preliminary effluent (3, 4). The rbCOD to TP ratios in the Southwest preliminary effluent were an average of 15 in the winter season and five in the summer season during the study period, respectively. The lower rbCOD during warm sewage temperatures and higher rbCOD during cold sewage temperatures may be due to the fact that fermentation in sewer pipes is more active during warmer conditions, thereby generating VFAs which may be used up immediately and leaves less readily available carbon to be further fermented to VFA in the plant. A correlation between wastewater temperatures and STPREF rbCOD concentrations is shown in [Figure 3](#); a slight visual trend can be observed that at lower temperatures, higher rbCOD concentrations are observed.

The rbCOD:TP results shown in [Table 1](#) suggest that the average Stickney Southwest preliminary effluent rbCOD:TP ratio is just under the minimum recommended value of 11. However, the STPREF rbCOD to TP ratios were spread over a wide range, and about 58 percent of the time it was less than 11, as shown in [Figure 4](#), suggesting no consistent carbon source was provided to the PAOs. The inconsistency of a food source to the microbial population adds complexity to understanding the system's performance.

### **Combined Primary Effluent in Summer and Winter Conditions**

Since the West Side preliminary treatment will not be altered until 2019, a subsequent short-term rbCOD test of Southwest Side and West Side PE composite samples (50/50) was

conducted from December 14, 2014, to January 12, 2015, to represent winter conditions and September 29, 2015, to October 22, 2015, to represent summer conditions; results are summarized in Table 3.

During the winter period (December 14, 2014, to January 12, 2015), the rbCOD of Southwest and West Side PE (50/50) varied from 31 mg/L to 137 mg/L. The %rbCOD in solCOD of Southwest and West Side combined PE ranged from 50 percent to 96 percent. The average rbCOD and %rbCOD in solCOD of Southwest and West Side combined PE were 80 mg/L and 80 percent, respectively. There was a good fit using the linear regression model  $rbCOD = 0.67 * solCOD$ , which accounted for 98 percent of the variation in the data (3, 4). The average sewage temperature during this test period was 11.6°C.

During the summer period (September 29, 2015, to October 22, 2015), the rbCOD of Southwest and West Side PE varied from 49 mg/L to 204 mg/L. The %rbCOD in solCOD of combined PE ranged from 43 percent to 78 percent. The average rbCOD and %rbCOD in solCOD of Southwest and West Side combined PE were 95 mg/L and 61 percent, respectively. There was a good fit using the linear regression model  $rbCOD = 0.61 * solCOD$ , which accounted for 98 percent of the variation in the data (3, 4). The average sewage temperature during this test period was 20.4°C.

A good fit relationship was found between rbCOD and solCOD in both winter and summer seasons; however, the influent rbCOD effect on EBPR performance is not discussed in this data report due to the complexity of the EBPR process. EBPR is affected by multiple factors. Some of these factors also have a direct impact on influent carbon, e.g. return activated sludge (RAS) characteristics (return rate, nitrate and dissolved oxygen concentrations in RAS), while others have less impact, i.e. temperature, mixed liquor suspended solid concentrations, and solids retention time.

The Southwest Side receives all the recycle streams in the plant. The STPREF characteristics will change when the P recovery process, Ostara<sup>®</sup>, comes on line in 2016. The Southwest Side preliminary effluent and combined PE rbCOD will be reevaluated after Ostara<sup>®</sup> is operational.

### **Comparison Between the Southwest Preliminary Effluent and Combined Primary Effluent**

To compare the carbon characteristics between the Southwest preliminary effluent and the combined PE, analysis of variance (ANOVA) tests were performed. Results indicate that solCOD, rbCOD, and %rbCOD in solCOD were all statistically identical in the winter season between these two influents. However, there is significant difference of solCOD, rbCOD and %rbCOD in solCOD in the summer season between these two influents; the Southwest preliminary effluent was statistically higher than the combined PE in solCOD, rbCOD and the %rbCOD in solCOD through the ANOVA tests. The carbon character difference during the summer may be due to the two different types of influent. It is also possibly because the two sets of samples were collected during different years (2014 for Southwest preliminary effluent vs

2015 for combined PE) or because the length of data collection (six months for Southwest preliminary effluent vs one month for combined PE) was different.

## Summary

Seasonal rbCOD in solCOD ratios were analyzed in both Stickney Southwest Side preliminary effluent and combined PE. The average STPREF %rbCOD in solCOD in winter and summer seasons were 66 percent and 41 percent, respectively, during the year study period. The average combined PE %rbCOD in solCOD in winter and summer were 80 percent and 61 percent, respectively, during the short-term study (one month to represent each season). Finally, solCOD can be used as a seasonal indirect measurement of rbCOD due to a strong correlation between the parameters for both Stickney Southwest Side preliminary effluent and combined PE.

## 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: STICKNEY SOUTHWEST PRELIMINARY EFFLUENT CHARACTERISTICS FOR  
AUGUST 2013 TO AUGUST 2014

|                             | solCOD<br>(mg/L) | rbCOD<br>(mg/L) | rbCOD:solCOD<br>(%) | rbCOD:TP |
|-----------------------------|------------------|-----------------|---------------------|----------|
| Count                       | 65               | 65              | 65                  | 49       |
| 10 <sup>th</sup> Percentile | 50               | 7               | 13                  | 0.5      |
| 25 <sup>th</sup> Percentile | 67               | 25              | 30                  | 3.2      |
| 50 <sup>th</sup> Percentile | 97               | 59              | 58                  | 7.3      |
| 75 <sup>th</sup> Percentile | 139              | 88              | 71                  | 13.7     |
| 90 <sup>th</sup> Percentile | 190              | 125             | 82                  | 17.6     |
| Minimum                     | 35               | 2               | 4                   | 0.1      |
| Maximum                     | 532              | 457             | 97                  | 75.0     |
| Average                     | 114              | 70              | 53                  | 10.9     |

TABLE 2: STICKNEY SOUTHWEST PRELIMINARY EFFLUENT SEASONAL CHARACTERISTICS

|   | rbCOD<br>(mg/L) | rbCOD/solCOD<br>(%) | STPREF<br>TP (mg/L) | rbCOD/TP |
|---|-----------------|---------------------|---------------------|----------|
| -----Winter (November 2013 to March 2014)-----                            |                 |                     |                     |          |
| Count   | 22              | 26                  | 19                  | 17       |
| 10 <sup>th</sup> Percentile   | 40              | 26                  | 5                   | 5        |
| 25 <sup>th</sup> Percentile   | 63              | 55                  | 6                   | 7        |
| 50 <sup>th</sup> Percentile   | 80              | 70                  | 6                   | 11       |
| 75 <sup>th</sup> Percentile   | 101             | 82                  | 12                  | 16       |
| 90 <sup>th</sup> Percentile   | 178             | 89                  | 16                  | 38       |
| Minimum   | 32              | 5                   | 5                   | 3        |
| Maximum   | 255             | 100                 | 20                  | 43       |
| Average   | 100             | 66                  | 9                   | 15       |
| -----Summer (August 2013 to October 2013; April 2014 to August 2014)----- |                 |                     |                     |          |
| Count   | 23              | 23                  | 34                  | 23       |
| 10 <sup>th</sup> Percentile   | 5               | 9                   | 5                   | 0        |
| 25 <sup>th</sup> Percentile   | 12              | 25                  | 6                   | 1        |
| 50 <sup>th</sup> Percentile   | 28              | 34                  | 8                   | 3        |
| 75 <sup>th</sup> Percentile   | 49              | 57                  | 18                  | 9        |
| 90 <sup>th</sup> Percentile   | 87              | 70                  | 30                  | 14       |
| Minimum   | 2               | 4                   | 3                   | 0        |
| Maximum   | 115             | 96                  | 36                  | 15       |
| Average   | 48              | 41                  | 12                  | 5        |

TABLE 3: STICKNEY SOUTHWEST PRELIMINARY EFFLUENT AND COMBINED PRIMARY EFFLUENT CHARACTERISTICS FOR TWO STUDY PERIODS

|   | solCOD<br>(mg/L) | rbCOD<br>(mg/L) | rbCOD/solCOD<br>(%) | rbCOD/TP |
|---|------------------|-----------------|---------------------|----------|
| Southwest Preliminary Effluent: West Side Primary Effluent = 50:50 Composite<br>(Winter: December 14, 2014, to January 12, 2015)  |                  |                 |                     |          |
| Count   | 12               | 12              | 12                  | 9        |
| Minimum   | 47               | 31              | 50                  | 4.6      |
| Maximum   | 157              | 137             | 96                  | 22.7     |
| Average   | 98               | 80              | 80                  | 14.1     |
| Southwest Preliminary Effluent: West Side Primary Effluent = 50:50 Composite<br>(Summer: September 29, 2015, to October 22, 2015) |                  |                 |                     |          |
| Count   | 21               | 21              | 21                  | 16       |
| Minimum   | 95               | 49              | 43                  | 10.3     |
| Maximum   | 273              | 204             | 78                  | 34.3     |
| Average   | 154              | 95              | 61                  | 16.8     |

FIGURE 1: STICKNEY SOUTHWEST PRELIMINARY EFFLUENT READILY BIODEGRADABLE CHEMICAL OXYGEN DEMAND CONCENTRATIONS AND PERCENT READILY BIODEGRADABLE CHEMICAL OXYGEN DEMAND IN SOLUBLE CHEMICAL OXYGEN DEMAND

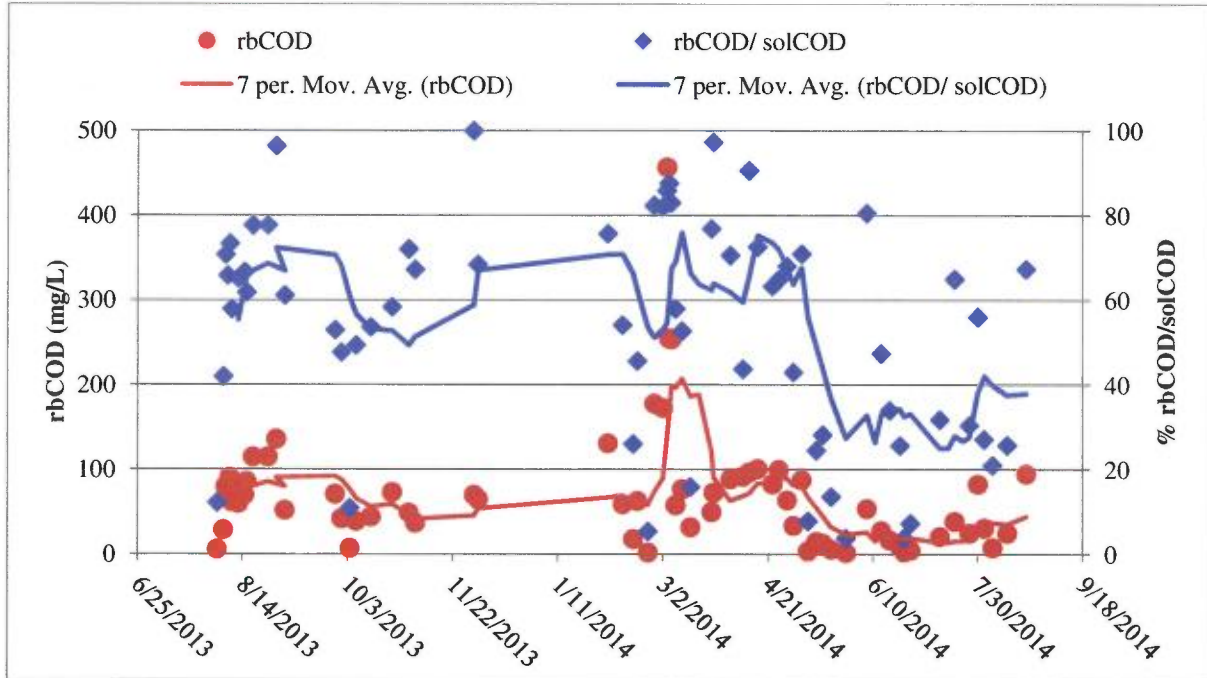


FIGURE 2: STICKNEY SOUTHWEST PRELIMINARY EFFLUENT SOLUBLE CHEMICAL OXYGEN DEMAND AND READILY BIODEGRADABLE CHEMICAL OXYGEN DEMAND CONCENTRATIONS

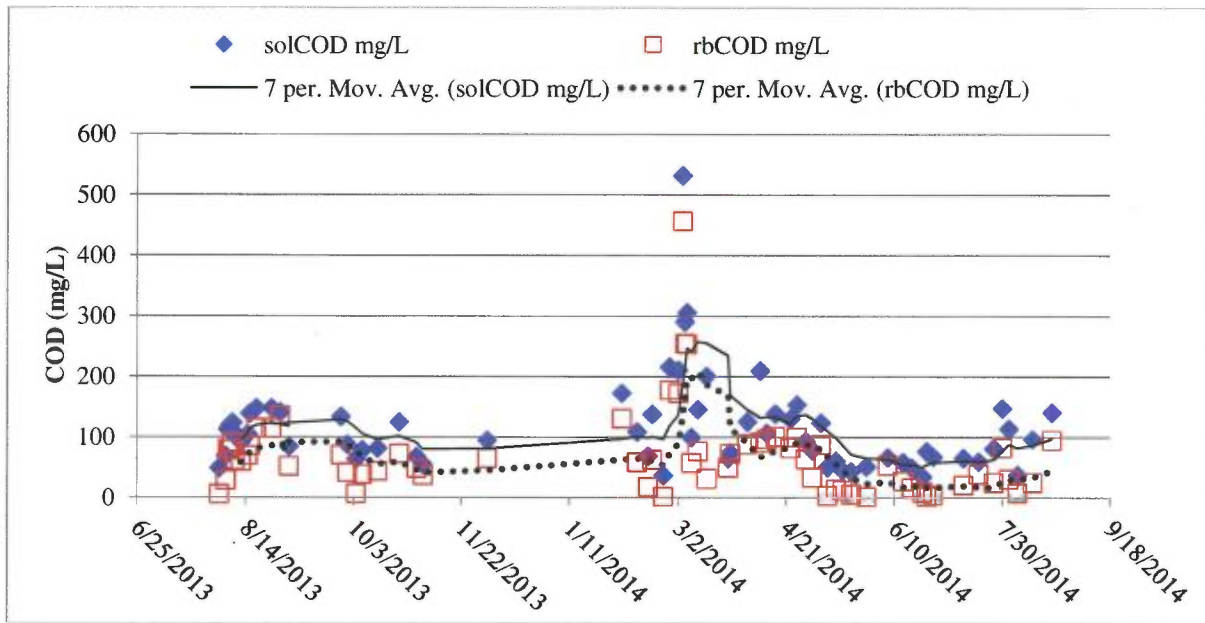


FIGURE 3: CORRELATION BETWEEN STICKNEY SOUTHWEST PRELIMINARY EFFLUENT READILY BIODEGRADABLE CHEMICAL OXYGEN DEMAND AND TEMPERATURES

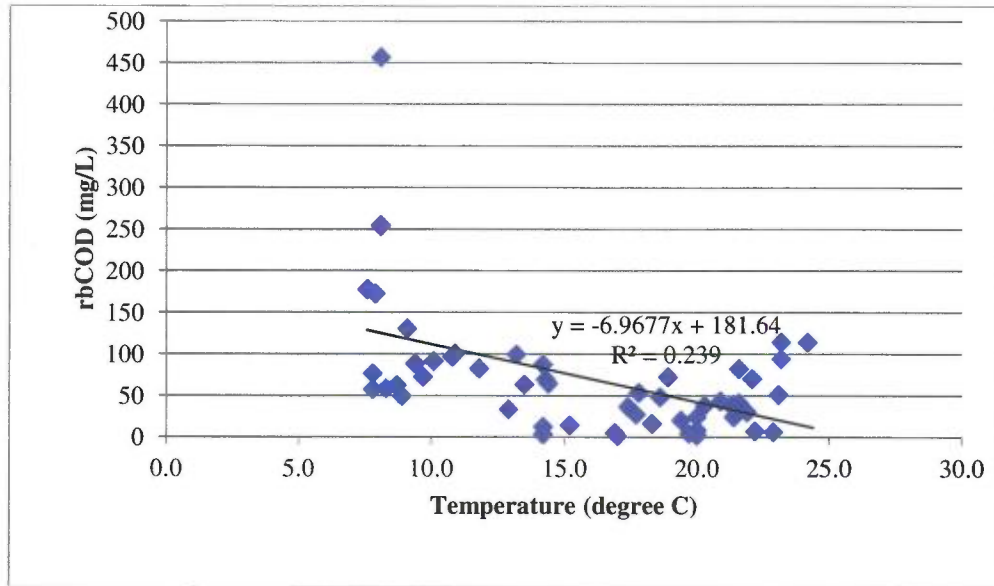


FIGURE 4: STICKNEY SOUTHWEST PRELIMINARY EFFLUENT READILY BIODEGRADABLE CHEMICAL OXYGEN DEMAND:TOTAL PHOSPHORUS DISTRIBUTION CURVE

