a new method for upset prediction: ATP-based biomonitoring and statistical process analysis at two refinery wastewater plants

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abstract

Biological wastewater treatment processes are notoriously unstable when used in a variety of industries, but none more so than the chemical and refining industries. This is primarily due to frequent release of toxic substances into wastewater by manufacturing operations. Operators of these downstream wastewater treatment facilities would benefit from reliable and fast information on the quantity and quality of biomass contained in their process. In this study, a new Adenosine Triphosphate (ATP) monitoring tool was used to survey two separate oil refinery wastewater treatment processes over a period of weeks. The results demonstrate that the chosen ATP-based monitoring tool offered significant advantages over traditional monitoring techniques such as suspended solids and oxygen uptake. ATP-based measurements of active biomass correlated strongly with bio-reactor performance and subsequent effluent quality. Novel means of measuring biomass stress also allowed identification of likely sources of toxicity when faced with multiple upstream possibilities. The results of these studies suggest that ATP-based monitoring is a very useful tool to facilitate an earlier warning of toxicity than currently available and to more quickly arrive at sound conclusions when performing troubleshooting activities.

keywords

ATP, adenosine triphosphate, activated sludge, wastewater, biomass, cellular ATP, biomass stress index, biological monitoring, toxicity, upset, early warning, correlation.

introduction

Biological wastewater treatment systems in industrial facilities often suffer from instability due to shocks of toxic or inhibitory contaminants being released into the wastewater. Operating personnel often are caught unaware, with the result that effluent water quality suffers. Both routine monitoring and troubleshooting is often difficult and time consuming, if not impossible, given that existing monitoring techniques have several limitations including one or more of: inability to directly measure active biomass; lack of sensitivity to process changes; inability to detect multiple contaminants; poor accuracy and/or poor repeatability; and difficulty of use.

Traditional parameters and their limitations are as follows:

- Mixed Liquor Suspended Solids (MLSS) and Mixed Liquor Volatile Suspended Solids (MLVSS): gross parameters that do not directly measure active biomass; common interferences in the refining industry are oil, grease, and dead biomass. Active biomass may be a very small fraction of these solids, which therefore do not provide quick and sensitive reaction to toxicity. MLSS and MLVSS measurements are also notoriously error prone and can fluctuate widely from day to day, even when the plant is apparently stable and performing well.
- Oxygen Uptake Rate (OUR): Various modifications to these respire metric methods have been in use for many years and can be useful in some circumstances. However, sampling and analytical inaccuracies and kinetic limitations can result in errors that make this technique hard for operators to use reliably. Furthermore, OUR measurements only estimate activity based on aerobic respiration and so does not include anaerobic biomass.
- Protozoan examination: Microscopic examination of protozoan diversity is a very useful tool, but is subjective, limited to relatively severe biomass toxicity effects and not always easily adopted and mastered by industrial plant operators. Subtler chronic effects can be missed.
- Water Quality Analyses: These are typically done using grab samples only a few times a week, or at most once per day. Brief but potent toxic shocks can be missed and only those events linked to specific parameters which are monitored are caught. Some plants attempt to overcome this limitation by measuring many parameters more frequently. This is a large expense in both manpower and equipment. In addition, toxicity due to synergistic effects of several parameters working together at low levels are not caught by this traditional monitoring technique. This is also true for chronic stress effects. When effluent quality parameters are affected, such as BOD or TSS, the event is usually well under way and the influent perturbation may have passed and recovery efforts become significantly more expensive.
- Sludge quality or settle ability measurements: Typically changes occur well after the toxic event has started and are of limited usefulness in troubleshooting and avoiding effluent quality problems.

There is therefore a need for a monitoring methodology that ideally provides a reliable indicator of biomass health, a predictive capability, an aggregate indication of multiple stressors, all while being fast and easy to use.

As early as thirty-five years ago, the value of monitoring ATP (adenosine triphosphate) in biological waste treatment was recognized (Paterson et al., 1970 and Levin et al., 1975). Later, Archibald et al (2001), in a study using a suite of respire metric tests on mixed liquor from paper mill activated sludge processes, concluded that ATP measurements provided a useful monitor of the proportion of viable cells, and a toxicity indicator in an activated sludge process. Despite this work, practical difficulties in analytical technique and inability to extract the most useful ATP fractions from the biomass found in industrial wastewater treatment processes limited the usefulness of this approach.

Recently, Cairns et al (2005) and Whalen et al (2006) have reported the development of a new method for extracting various fractions of ATP from biomass and wastewater, which overcomes previous limitations, and various papers have reported on its use in monitoring for bio-activity in biological wastewater treatment plants (Whalen 2007, Linares et al, 2007, Brault et al, 2008).

This paper reports on efforts to apply this technology to the monitoring of two oil refinery activated sludge wastewater plants and comparison of the correlation of the data so obtained with traditional water quality and performance parameters used at each plant.

methodology

1) ATP Testing Methods

At each refinery ATP tests were conducted on samples from influent streams and from the aeration tanks of the activated sludge systems. The data collected was analyzed together with plant water quality data and examined for trends and correlations with effluent quality parameters.

ATP analyses were conducted on sub-samples removed from the sample containers, usually as soon as the samples had been brought to the plant laboratory. All ATP analyses were performed using reagents manufactured by LuminUltra™ Technologies Ltd. The light produced in the luciferase reaction was measured in a luminometer (the Kikoman Lumitester C-100 and the SUEZ Bioscan2). The measurements obtained in relative light units (RLUs) were converted to actual ATP concentrations (ng/mL) after calibration with a 1 ng/mL ATP standard.

Two separate ATP tests were carried out on each sample: a test for total ATP (tATP™), and one for dissolved ATP (dATP™).

Total ATP is the measurement of all ATP contained inside of a sample, which includes ATP from living cells plus extra-cellular ATP coming from dead or dying biomass.

The dissolved ATP method is different to previous methodologies for measuring extra-cellular ATP in that the dilution reagent targets both free and complexed ATP in the sample. This dATP fraction is termed extra-cellular ATP by this methodology. This fraction represents ATP released from cells that are under stress, or which have died. Further details on this method can be found in Cairns et al., 2005.

The results of these analyses yield three control parameters as calculated below:

cATP (ng/mL) = tATP – dATP(Cellular ATP)

ABR (%) = (cATP x 0.5)/MLSS (Active Biomass Ratio)

BSI (%) = $^{dATP}/_{tATP}$ (Biomass Stress Index)

The difference between the tATP and dATP results is termed cellular ATP (cATP™), and is believed to be a better measure of active biomass concentration or energy level. A derived parameter, the active biomass ratio (ABR™) was also evaluated (where cATP is first converted to active biomass equivalent, Whalen et al, 2006). The Biomass Stress Index (BSI™) is calculated as the ratio of extra-cellular ATP to total ATP; put another way, it is the ratio of dead cell ATP to total sample ATP.

The first two parameters can be used for routine reactor biomass activity monitoring, as a replacement for the MLSS or MLVSS parameters for the purpose of active biomass measurement. In addition, the BSI parameter can be used in both biomass inhibition and wastewater toxicity evaluation studies. Time required for all testing was ~30 minutes per day at each site. Additional samples do not add significant extra time due to efficiencies in method design. e.g. setting up multiple tubes allows multiple samples sharing wait times between steps.

One toxicity evaluation method used in Refinery 1 comprised dosing samples of return activated sludge (RAS) with the suspect wastewater, in the same ratio as exists in the reactor, and then measuring the BSI. Those samples that resulted in a significantly higher stress index than that of the normal combined wastewater stream were deemed to contain more toxic or inhibitory material, at that time, and thus prime suspects in the source identification. Conversely, those streams that showed reduced BSI were considered more degradable than the combined waste. Excluding sampling, this methodology took about 1 hour. Toxicity measurement via BSI of the indigenous microorganisms in the target streams was evaluated during the second refinery study.

2) Standard Testing

In each refinery process control monitoring comprised routine collection of grab samples for standard water quality testing by the refinery operators and laboratory personnel. Parameters analyzed in each location were as follows:

Refinery 1:

- Influent (at various locations): pH, conductivity, ammonia, fluoride, oil & grease (hexane gravimetric), phenol, COD. Parameters measured on the combined bio-reactor inlet were pH, conductivity and COD.
- Bio-Reactors: Temperature, pH, dissolved oxygen, MLSS, MLVSS, SSV30/SVI, # stalked ciliates, OUR, phosphate (filtered), ammonia (filtered). The ATP parameters were measured in one reactor only.
- Effluent: Combined effluent Ammonia, alkalinity, TSS, COD, conductivity, phenol, fluoride, pH, temperature, and others as required by permit.

Frequency of measurement varied by parameter, but most were in the range of 5 – 7 times/week. OUR and ciliates were more sporadic.

Refinery 2:

- Influent: Ammonia, conductivity, pH, alkalinity, sulfide, phenols, temperature, turbidity, COD, and fluoride (ex-API). ATP parameters were measured in the wastewater prior to the reactors.
- Bio-Reactors: pH, Dissolved Oxygen (DO), temperature, SSV60/SVI, MLSS, MLVSS and ATP parameters.
- Effluent: Ammonia, COD, TSS, alkalinity, phosphate, nitrite, phenols, pH, conductivity, fluoride, sulfide, amount of foam.

Frequency of monitoring was mostly 1 to 2 times per day, 7 days per week. The ATP parameters were collected 1/day, 5 days/week.

3) Data Analysis

All data was trended and statistically analyzed. Software used was a modified excel workbook, allowing data smoothing, and data time shifting. i.e. correlation coefficients were determined for various combinations of parameters. Usually influent parameters were used as the independent variable and one of the reactor or effluent parameters as the dependent variables.

Visual trend graph correlations and correlation coefficient significance both in the raw data and with smoothing (1-3 day running averages) were studied. In addition, correlations were calculated by time shifting the independent variable backward from one to several days. With a hydraulic retention time of 1.4 days and a sludge age (solids retention time) of >20 days, some water quality perturbations could take several days to have an impact. If a significant correlation was observed with influent parameters in advance of the effect, then that would suggest those parameters had predictive capabilities.

Correlation coefficients (R-values) of >0.5 were taken as significant, with those >0.7 being most meaningful. Typically, troubleshooting by this method using simple two-variable correlations between traditional parameters, does not produce correlation coefficients much better than 0.4- 0.5.

results and discussion

1. Process Configurations

The wastewater treatment operation was similar in both refineries, with several source wastewater streams (desalter, strippers, etc.) flowing through various collection tanks and combining before a gravity separation device, known as an API separator for free oil, and heavy solids removal. Following the API(s), the majority of residual oil (usually emulsified) and solids were removed in Air flotation separators. This preliminary treatment is termed primary treatment. Following this stage, the secondary or biological treatment stage begins.

Characteristics of the two systems were as follows:

Refinery 1 (Gulf Coast, USA):

Oily process wastewaters pass through the API and Dissolved Air Flotation (DAF) units, with less contaminated wastewaters, including rain runoff combining just before the bio-reactors. The ratio changes considerably, from 25% to 60% non-oily wastewater making up the bio-reactor inlet.

Two bio-reactors operate in parallel, and effluent 'mixed liquor' is combined in a tank following the reactors, before splitting again to two clarifiers. Separate recycle streams return to the two reactors, but mixing sludge means that bio-activity in each reactor is influenced ultimately by the conditions in the other reactor/clarifier and by separate wastage streams. In this refinery only one reactor was sampled for the ATP testing, while only combined effluent quality was available. This was a weakness in the study.

Additives to the bio-reactors comprised: periodic hydrogen peroxide addition to the wastewater influent to the reactors (when COD was above a pre-set level); Calcium chloride when fluoride was considered high; powdered activated carbon (when oil was high); a suspended zeolite-type media for enhanced nitrification; commercial bacteria during and following upsets; cationic flocculent polymer fed to both clarifiers routinely. During the survey, the only additives used were periodic additions of the hydrogen peroxide and commercial bacteria, and continuous dosage of the polymer. The testing took place from July 18 to August 14, 2007.

Wastewater flow averaged 1788 gpm total, through two 750,000-gallon diffused air bio-reactors. Average inlet COD during survey was 559 mg/l, with an effluent of 123 mg/l (78% removal). The F/M ratio for the whole system during this period was estimated at 0.25 (COD-basis), or 0.11 (BOD-basis). MLSS averaged 5612 mg/l, with 67% MLVSS, and 43% BOD/COD ratio.

Just prior to the start of the survey (July 12- 15) an upset occurred where much higher COD waste entered the bio-reactors, resulting in loss of biomass (through flotation and carryover). MLSS and biomass levels fell significantly from 6000- 8000 mg/l, down to <2000 mg/l by the 18th. MLSS began to recover from about 21st/22nd and steadily climbed during the survey as the plant recovered, so the F/M was actually higher at the start and ended up lower at the end. Sludge age is difficult to measure at this plant, due to problems with waste biomass (i.e. WAS) flow measurement, but it is believed to have been around 30 – 50 days during this survey (at the lower end at the start, due to the loss of biomass). Sludge age often climbs above this range in normal operation.

Refinery 2 (Mid-West, USA):

All the wastewater going through the WWTP (~500 gpm) passes through the primary treatment area (API and Induced Air Flotation units), followed by the secondary biological system. The bio-system comprises two completely separate, parallel activated sludge systems. Each system includes a diffused air reactor of 500,000 gallons. Typical BOD F/M ratios are in the 0.10- 0.20 range, with sludge ages in the 20 – 40-day range. Bio-inlet COD is normally in the 650- 950 mg/l range, averaging 882 mg/l during the survey (BOD assumed to be 60% of COD). COD removal averaged 82%. One reactor averaged an MLSS of 3039 mg/l, 78% VSS, with estimated F/M of 0.14, while the other averaged an MLSS of 2350 mg/l, 71% VSS and F/M of 0.20. Both reactors were tested for the ATP parameters. Individual system effluent quality was available.

This refinery WWTP also suffered an upset just prior to the start of the special monitoring. This resulted in loss of nitrification at the start. It was regained during the monitoring period.

During the survey, the only additives to the bio-reactors were commercial bacteria added for enhancing COD and ammonia removal. The testing took place from May 19 to June 29, 2008.

Table 1 compares the main operating criteria for the two treatment systems.

Table 1: Comparison of Key Operating Criteria for Study Treatment Systems

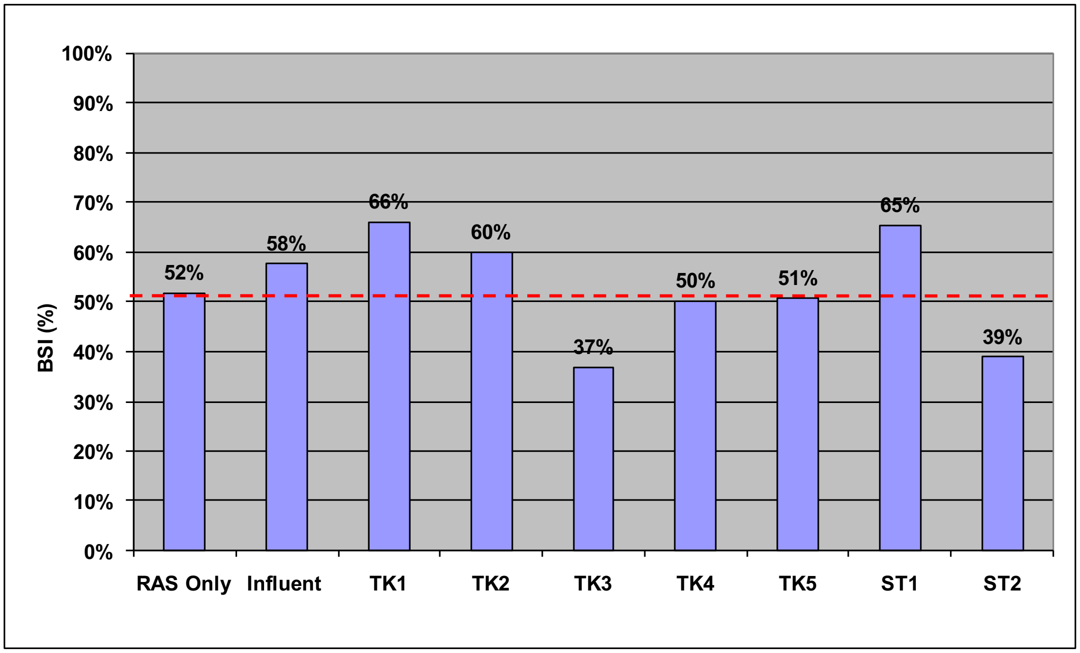
Parameter Range	Refinery 1	Refinery 2
Study Period	July16 to August 14 2007	May 19 to June 29 2008
Wastewater Flow (gpm)	1788	500
Reactor Volume (gal)	750,000	500,000
Inlet COD (mg/L)	559	882
Effluent COD (mg/L)	123	159
COD Removal (%)	78%	82%
F/M Ratio	0.25	0.10 to 0.20
MLSS (mg/L)	5612	2300 to 3100
MLVSS/MLSS (%)	67%	70 to 80%
Sludge Age (d)	30-50 (estimated)	20-40
Additives	Bacteria, Polymer, Peroxide	Bacteria

2. Results from Refinery 1

(i) Influent Water Quality

Following the upset situation, which occurred just before this survey started, attempts were made to identify the most likely sources of the material responsible. This refinery has several wastewater storage tanks and component sumps and wastewaters "upstream" of the main WWTP. Sampling was carried out at the main tanks, a lift station, and a scrubber purge stream, and ATP testing conducted on blends of collected wastewater with RAS samples. Incubations were set up by diluting RAS in the collected wastewater to the approximate concentration of the MLSS (i.e. similar to OUR methodology) and measuring ATP after 15 minutes. Figure 1 shows the results from an audit done on 7/19/07. Two tanks (TK1 and TK2) and one small stream (ST 1) showed significantly higher BSI than the combined wastewater, which itself had an elevated BSI, compared to the recycled biomass (RAS only; red line across Figure 1). These two tanks were associated with the desalted wash water and had previously been one of the prime suspects. The ST1 stream was the scrubber blowdown water and had also been suspected of toxicity, but without a conclusive determination until now.

Figure 1: Biomass Stress (BSI) Response in Various Source Waters at Refinery 1



The combined wastewater is routinely sampled and analyzed at several locations for numerous water quality parameters, and Table 2 shows data for two of these locations: the combined wastewater to bio-reactors, as well as the DAF outlet. The survey was from July 18th to August 14th,2007. Note that the DAF outlet is diluted with less contaminated, non-oily wastewaters (e.g. stormwater) to form the Bio-Inlet. During this survey, the combined flow averaged 60% non-oily wastes and so some DAF process contaminants were diluted substantially e.g. oil, phenol, sulfide, and other non-monitored contaminants

At this plant, combined influent ATP results were not used because of the periodic presence of excess hydrogen peroxide at the Bio-Inlet which would have interfered with the test (i.e. biomass would have been negatively impacted by peroxide). No other sample point was available for testing the combined influent.

Table 2: Bio-Reactor Influent Water Quality

Parameter	Bio-Inlet		DAF Effluent	
	Average	Maximum	Average	Maximum
pH	8.7	9.4		
Conductivity (umhos)	5141	6105	5962	10,060
COD (mg/l)	559	879	945	2007
Oil & Grease (mg/l)			9.7	18
NH3 (mg/l)			43	67
Fluoride (mg/l)			5.9	10.2
Phenols (mg/l)			21	33
Sulfide (mg/l)			12.4	30

(ii) Reactor Parameters

Tables 3a and 3b shows survey data for the reactor parameters, including the three ATP biomass parameters. For the ATP parameters, a comparison with" Previous Guidelines" obtained from municipal, food and paper industry studies is shown. Data was collected from one of the two linked reactors (labeled Rx-A).

An upset took place on about July 12th, with normal MLSS not regained until about July 23rd.

Table 3a: Reactor A ATP Data Averages for Refinery 1

Parameters	Survey Data- Rx A		Previous Guidelines		
	Average	Range	Good	Marginal	Poor
CATP (ng/mL)	712	319 - 1216	Site specific		
BSI (%)	40	24 - 65	<30	30- 50%	>50%
ABR (%)	8.5	2.9 - 17	>25%	10 – 25%	<10%

Table 3b: Other Data Averages for Refinery 1

Parameters	Rx A		Rx B	
	Average	Range	Average	Range
Dissolved Oxygen (mg/l)	4.0	2.5 – 6.8	3.8	2.4 – 7.3
MLSS (mg/l)	5688	1290 - 9530	5301	1740- 8210
MLVSS (mg/l)	3544	526 – 7080		
DOUR (mg/l/hr)	13.5	6.0- 22.8		
SOUR (mg/l/hr/gVSS)	5.0	2.9 – 17.1		
Stalked Ciliates (#/slide)	7.3	0 - 15		
SVI (ml/g)	67	52 - 83		

Note: two parameters for Rx-B are included for comparison.

(iii) Effluent Parameters

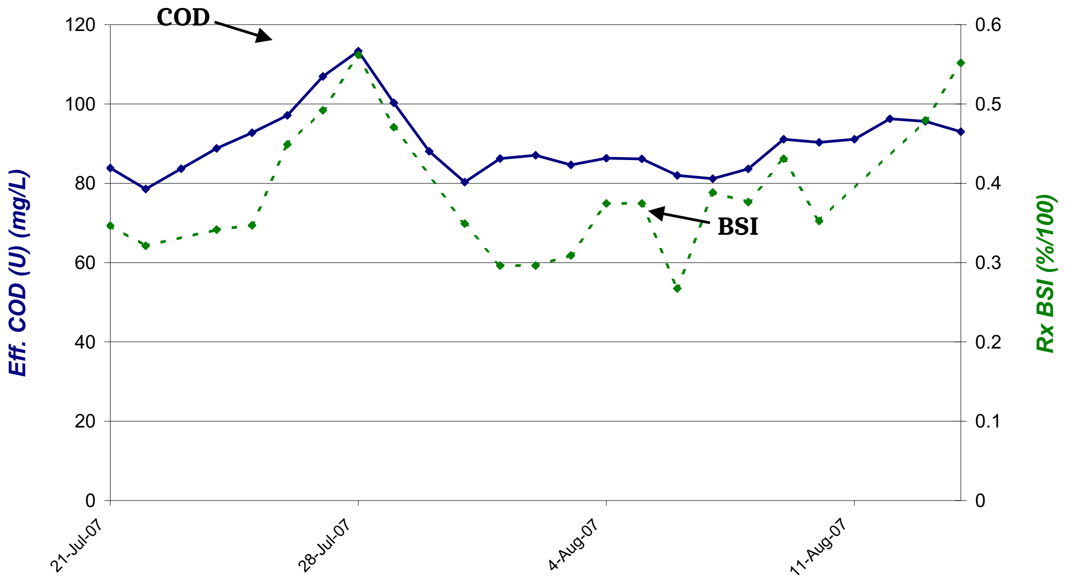
Table 4 shows some of the main effluent parameters that were monitored over the same period (7/18/07- 8/14/07). This data was from the combined effluent from both reactors.

Table 4: Combined Effluent Parameters (systems A+B)

Parameter	Average	Range
TSS (mg/l)	15.9	7.1- 25.5
COD (mg/l - total	105	65 - 502
NH3 (mg/l)	0.3	0 – 2.8
Fluoride (mg/l)	5.0	3.4 – 8.2
Phenol (mg/l)	0	0 - 0
Conductivity (umhos)	5550	4611 - 7090
pH	7.7	6.7 – 8.4

(iv) Trends and Parameter Relationships

Figure 2 shows the trend of Reactor BSI, an indicator of stress or inhibition, compared to effluent COD (Dates: 7/21/- 8/14). This produced a correlation coefficient (R) of +0.79, when the data was smoothed with 2-day averaging. With a one-day forward time shift on the reactor BSI, the correlation fell, but remained at a still respectable +0.68, showing some utility as a predictive parameter. The positive correlation indicates that when BSI ("stress") went up, so did effluent COD. The COD was unfiltered, so affected by both particulate and soluble COD. The BSI may have had an even better correlation with soluble effluent COD (i.e. undegraded food).



Note: R= +0.79 from 7/21; No data-shifting; 2-day averaging

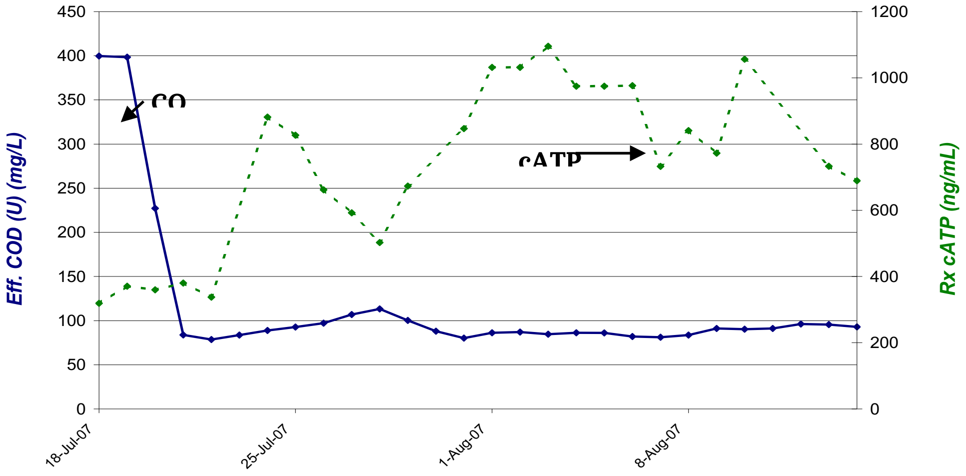
Figure 2: Refinery 1- Reactor BSI vs Effluent COD

Correlation of effluent COD with reactor BSI during the first few days of monitoring was low and this is believed to be due to the system still recovering from biomass washout. The high effluent COD during 7/18 – 7/21 was more due to insufficient biomass present, at that point, than due to toxicity present. See discussion on cATP below.

The correlation between reactor BSI and combined effluent TSS was also checked and was moderately strong with a 1 to 2-day lead time and 2-day data averaging (R= ~ +0.6).

The cATP bio-activity parameter, provided reasonable correlations with MLVSS and effluent COD from the start of the survey (7/18). Generally, the cATP fell and then began to rise with MLVSS, with an overall correlation of +0.62. However, variations in cATP were large as the biomass struggled to recover from the upset and did not show the continued increase that MLSS and MLVSS showed. This suggests that cATP measurements are able to show recovery of active biomass much more quickly and therefore expedite troubleshooting, whereas MLSS and MLVSS require much longer to recovery as operating parameters.

The cATP provided a correlation with effluent COD of approximately -0.6 with 2 – 3-day data averaging. (cATP up, effluent COD down). See Figure 3. One can see that the low levels of cATP, present after the biomass washout, were associated with high effluent COD, and as the cATP rose (along with the MLVSS), the COD fell. This relationship was mostly one of the necessity for a critical minimum level of cATP (and VSS) to achieve the target effluent COD. Once that was passed, additional biomass increase did not significantly lower COD removal. The bioactivity parameter (cATP) showed a better correlation with COD as it became more range-bound, unlike the MLVSS which continued to increase.



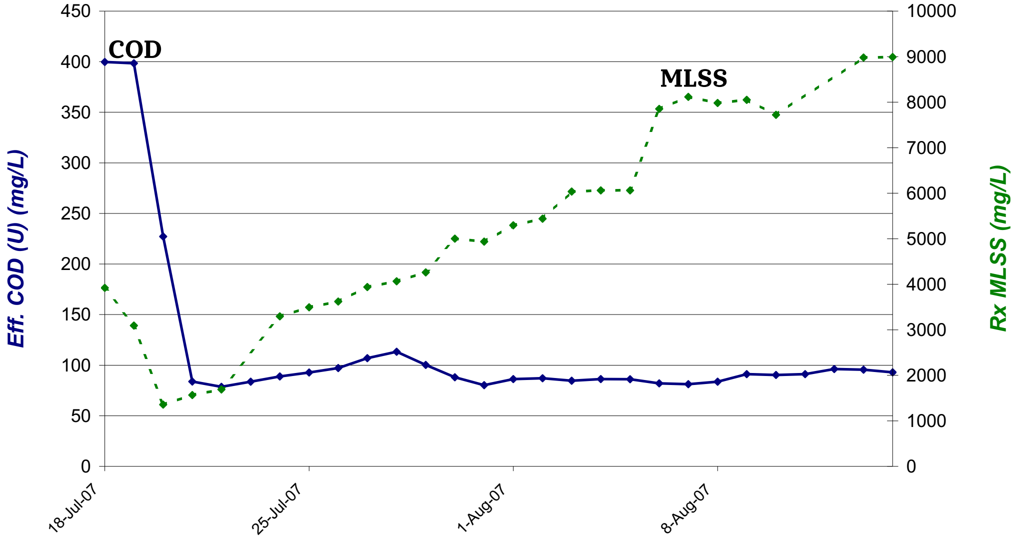
Note: R = -0.6; 2-day averaging

Figure 3: Refinery 1- Reactor cATP vs Effluent COD

The cATP parameter did not have a good correlation with effluent TSS, which was high right after the upset, then quickly fell to normal levels and remained relatively constant thereafter. There was not enough data to make a good conclusion about this pair of parameters.

The ABR parameter did not have a good correlation with effluent COD or TSS. The biomass washout and strong regrowth in MLSS seems to have overwhelmed this parameter.

MLSS and MLVSS did not have a strong overall correlation with effluent COD or TSS, possibly for the reason outlined above. See Figure 4 covering the same period, with 2-day averaging (R= -0.33). MLVSS was similar.



Note: R = -0.33; 2-day averaging

Figure 4: Refinery 1: Reactor MLSS vs Effluent COD (R= -0.33)

Other traditional wastewater parameters were studied for their impact on reactor BSI and cATP and on effluent quality. Table 4 shows the most significant correlations. No significant correlations were seen between any of the other parameters mentioned in Table 2 and 3 and effluent quality.

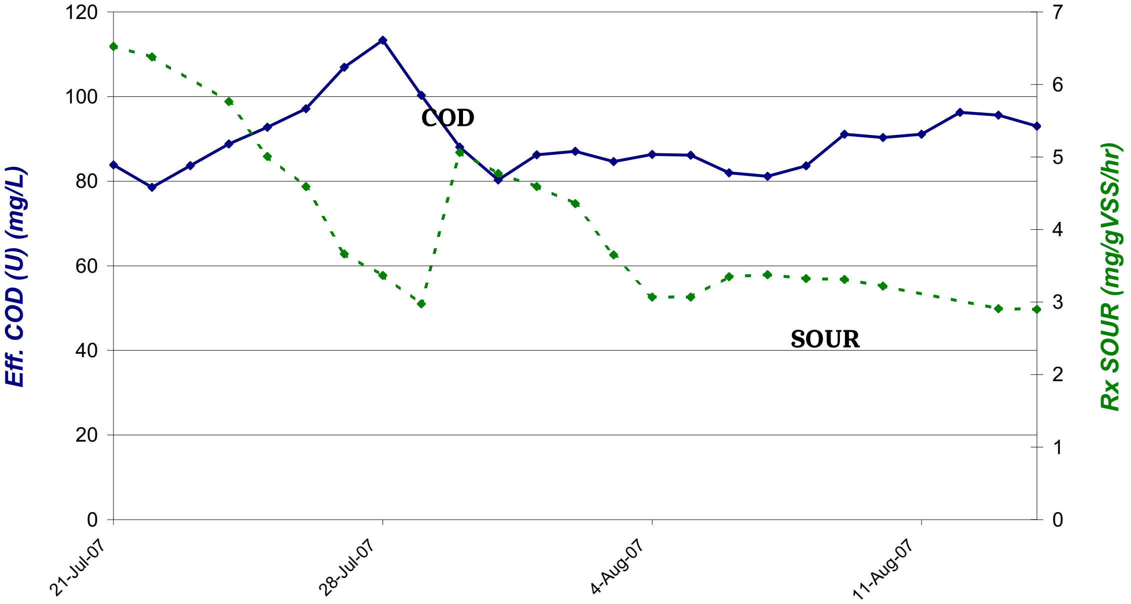
Table 5: Refinery 1- Other Significant Correlations (R)

Independent Variable	Dependent Variable				Notes
	Rx BSI	Rx cATP	Effluent COD	Effluent TSS	
DAF Fluoride	+0.80	-0.71		+0.81 (from 7/12)	1 day lead
DAF Sulfide	+0.73				2 day lead
Bio-inlet Conductivity		-0.76 (3)	+0.78 (4)	+0.75 (2)	(days lead)

Note: data from 7/21 to 8/14 unless otherwise noted

Reactor oxygen uptake rates (DOUR/SOUR) were not good predictors of effluent COD during this survey. In fact, data suggested that SOUR lagged effluent COD. There was poor correlation after the upset (Figure 5) and while correlation was reasonable right after the upset, it actually was better if the SOUR was time-shifted back a day. SOUR levels were higher right after the upset, with DOUR lower and vice versa after recovery. That information together with the BSI data (low right after upset, higher afterwards, like SOUR), suggested that the loss of biomass was either due to a short-lived toxicity episode (ca 7/12), and/or more of a physical washout effect. This would explain the low correlation with BSI in the immediate aftermath, but a much better correlation afterwards.

The high wastewater conductivity in this refinery seems to makes the biomass more vulnerable to washout, especially in the presence of contaminants with dispersant effects. Table 5 shows the conductivity correlations, confirming the importance of this parameter.



Note: 2-day averaging

Figure 5: Refinery 1: Reactor SOUR vs Effluent COD (R= -0.33)

3. Results from Refinery 2

An upset took place on about May 12th, which resulted in loss of nitrification. Nitrification was partially regained on or about June 11th and fully on June 20th.

(i) Influent Water Quality

Table 6 shows combined wastewater quality to bio-reactors, during the period of the survey: May 19th to June 27th 2008. Note that the Fluoride was taken upstream of the flotation unit (IAF) and so could have been lower entering the reactors.

Table 6: Refinery 2- Bio-Reactor Influent Water Quality

Parameter	Average	Range
BSI (%)	87	37 - 100
pH	7.1	6.4 – 8.2
Conductivity (umhos)	2150	1328 - 3775
COD (mg/l)	883	628 - 1607
Turbidity (ntu)	19.0	5 - 76
NH_3 (mg/l)	30.0	15 - 49
Phenols (mg/l)	4.6	0 - 12
Sulfide (mg/l)	12.5	0 - 242
Fluoride (mg/l) ex-API	4.4	1.3 - 9.6

(ii) Reactor Parameters

Table 7 shows survey average data for two reactors, including the three ATP biomass parameters. Table 3 can be referenced for comparison with the other refinery's data and previously obtained guidelines. Data was collected from May 19th to June 27th 2008.

Table 7: Refinery 2-Reactor Parameters

Parameter	Bio-Reactor N		Bio-Reactor S	
	Average	Range	Average	Range
cATP (ng/mL)	583	281 – 905	653	322 - 1148
BSI (%)	40	22 – 55	34	19 – 57
ABR (%)	10	5 – 20	11	5 - 22
Dissolved Oxygen (mg/l)	4.3	3.4 – 5.1	3.9	2.3 – 5.3
MLSS (mg/l)	3053	1490 - 4280	2308	1660 - 3120
MLVSS (mg/l)	2329	1300 –3680	1793	1098 - 2580
pH	7.4	6.9 – 7.9	7.4	7.1 – 8.1
Temperature (F)	82.4	78 – 86	82.1	78 - 86
SVI	56	24 – 99	67	38 - 134
F/M-7day	0.14	0.10 – 0.18	0.20	0.14 – 0.23

(iii) Effluent Parameters

Table 8 shows some of the main effluent parameters that were monitored. Average data shown. Flows approximately equal through each train.

Table 8: Refinery 2- Clarifier Effluent Quality

	N-Clarifier	S-Clarifier
COD (mg/L)	153	152
TSS (mg/l)	29	32
NH3 (mg/l)	6.8	7.3
pH	7.6	7.5
Total Alkalinity (mg/l)	267	244
Phosphate (mg/l)	5.1	4.6

(iv) Trends

(a) Influent parameters

No influent parameters produced any significant correlations with effluent COD or TSS.

A correlation was seen between influent COD, Phenol, and Conductivity with effluent ammonia. There was a same day negative correlation between COD and phenols and effluent ammonia. This can be explained as an increase in organic-carbon loading resulting in more nitrogen being removed as a nutrient, along with the carbon.

The wastewater conductivity had a negative impact, however, with increasing conductivity associated with rising effluent ammonia. This appears to be related to a toxicity effect and was relatively strong with a 5-day lead time (R = +0.7 to +0.8).

In this second survey, ATP data was measured directly on the biomass indigenous to the influent wastewater. In refinery 1, the wastewater was evaluated by dosing it into RAS samples and measuring the BSI on that mixture (i.e. a seed was provided to evaluate wastewater toxicity). In refinery 2 the "straight" influent wastewater BSI data did not reveal significant correlations with effluent quality. It did reveal a strong correlation with the north reactor BSI, with a 3-day lead, but not with cATP. Hence, stress measured upstream corresponded with later bioreactor stress. Other evidence also suggests the north system was more unstable.

(b) Reactor parameters

(i) cATP showed a strong (negative) correlation to effluent COD, with strength improving with data averaging. Particularly after June 10th when bio augmentation effects kicked in (see discussion later) and bio-activity increased significantly, then both effluent COD and ammonia fell as nitrification started. See Figure 6. North trend chart was similar. Data averaging to account for retention times improved correlation.

When averages of two reactors were plotted versus COD Removal the correlation becomes even more clear (R= +0.6 to >0.8, with 1 to 4+ day averaging). See Figure 7. In addition, a strong correlation was also seen with a 1 to 3-day lead time (providing an early warning to failing COD removal). This logical relationship between bio-activity and effluent COD and COD removal was not strong using the traditional MLSS and MLVSS parameters. In fact, the only good correlations with effluent quality we found with these two parameters were with effluent ammonia in the south system. Higher solids levels generally led to lower ammonia.

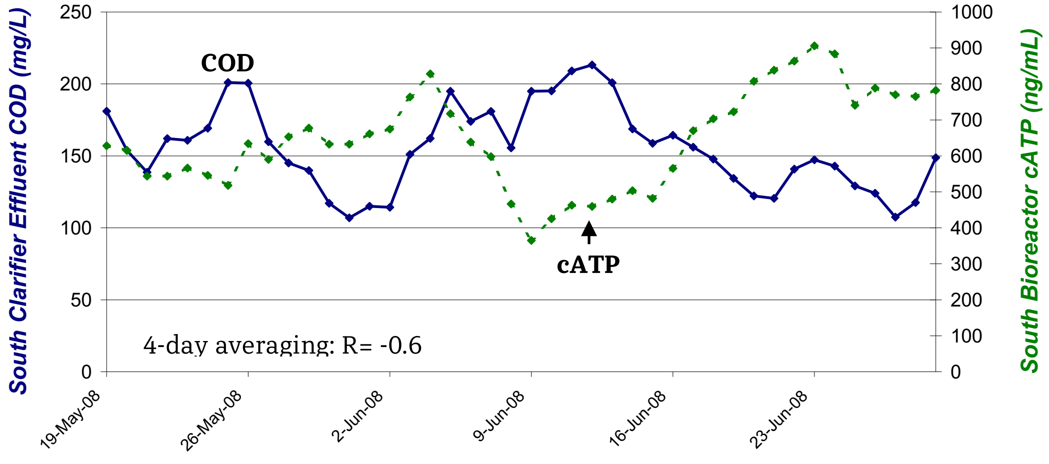


Figure 6: Refinery 2- Reactor cATP vs Effluent COD

The ABR parameter, which relate cATP to the traditional solids level also saw similar relationships as with the cATP, but the correlation factor was slightly lower (reflecting the much poorer correlation with MLSS). This also lends credence to the conclusion that the cATP parameter has superior utility compared to the MLSS and MLVSS parameters for measurement of active biomass.

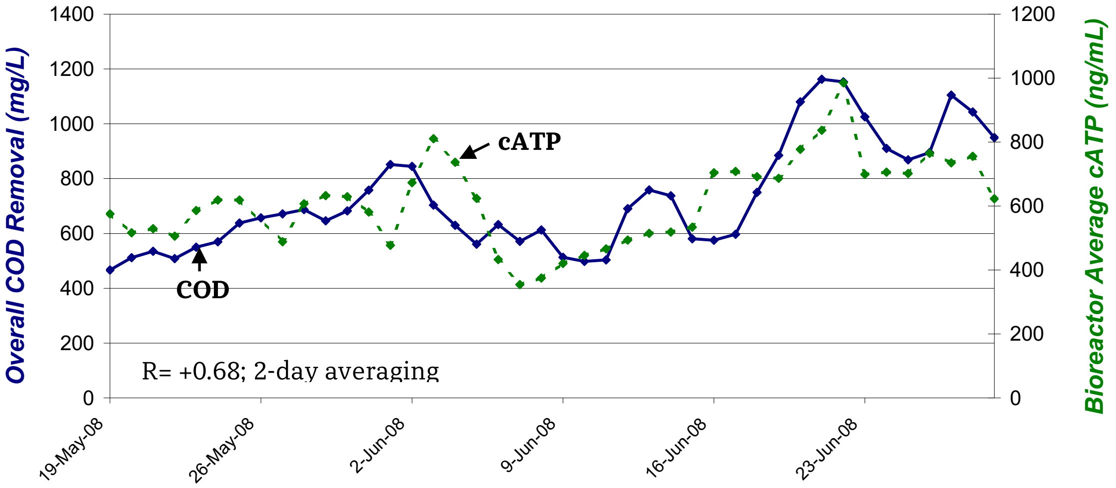


Figure 7: Refinery 2- Average Reactor cATP vs COD Removal

The cATP parameter had low overall correlations with effluent ammonia in the individual systems. However, when the survey was divided into initial no-nitrification, and then post-nitrification periods, the correlation was seen to be very high during nitrification. i.e. as mentioned above the bio-activity rose significantly during this period, and ammonia residual fell. In addition, the overall correlation between average reactor cATP, and overall ammonia removal was one of the highest correlations seen in any of the trials to date. See Figure 8, where a 3-day averaging is shown (R= +0.82). Even raw data, with no data averaging and with a one-day lead, gave an R factor of ~+0.6.

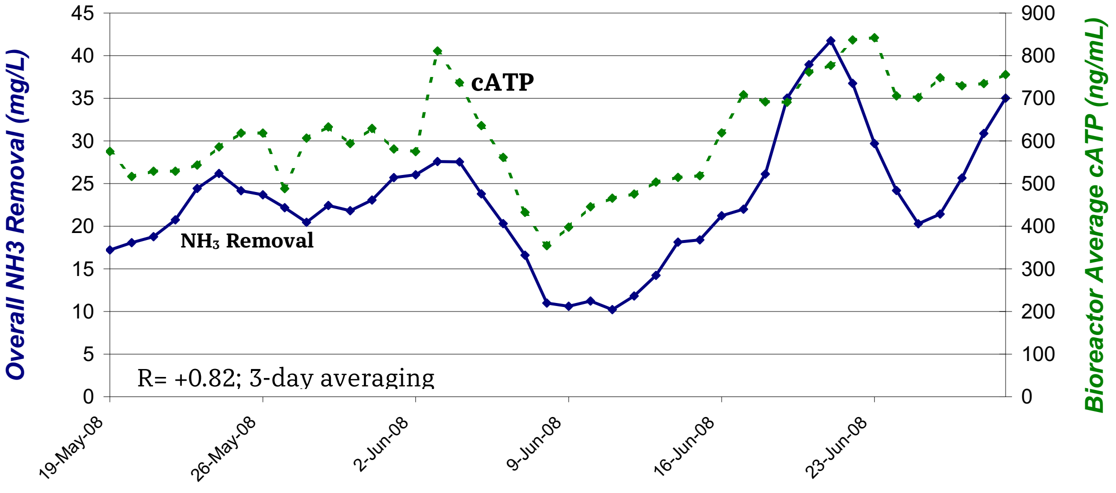


Figure 8: Refinery 2- Average Rx cATP vs Overall Ammonia Removal

Influent COD strongly correlated with reactor cATP (R= +0.7), but not with BSI, indicating that during the survey wastewater COD was biodegradable and not very inhibitory or toxic.

(ii) The BSI or stress parameter had low to moderate overall correlations with effluent COD, but they were much stronger after bio augmentation was ramped up, and nitrification started e.g. from June 12, R= -0.8, for total COD removal (higher BSI → lower removal), with 1-day lead.

BSI had a moderate positive correlation with effluent TSS, with a 2-5-day lead and some data averaging. The correlation was better in the north system. MLSS vs effluent NH3 data suggests that the north system had retained some toxic material within the MLSS and this may have explained the BSI differences between the two systems.

(c) Impact of Bio augmentation

This refinery uses routine bio augmentation at a relatively low level of 2- 6 lb/day of one or more specialty bacterial products for COD removal, and 0- 2 gpd of nitrifying bacteria to each system. Having lost nitrification in mid-May, the plant decided to implement 2- 3-week campaign of heavier dosages of both types of bacteria from about May 22 to June 9th. Dosages of the COD bacteria increased to about 14 lbs./day in the south system and 20 lbs./day in the north system and the nitrifiers to about 4 gpd in both systems.

By June 10- 12th nitrification was regained in both systems, and effluent COD began to decline, despite increasing influent COD.

In the south reactor MLSS/MLVSS rose at about the same time, as did cATP. However, in the north system, MLSS and MLVSS did not rise significantly, while cATP did rise. An increase in bioactivity was expected due to the improved COD and ammonia removal rates. Here again, the cATP parameter proved more reliable than the MLSS or MLVSS parameters.

The rise in cATP was delayed by 1 – 2 weeks after the increased bacteria addition, and took place at the same time as the influent COD was increasing, and so the effect on cATP cannot be definitively linked to either parameter exclusively.

Reactor BSI levels did not seem to correlate with bacteria addition in this survey.

conclusions

A. Refinery 1

The Biomass Stress Index (BSI) ATP parameter proved very useful in identifying influent wastewater toxicity, when used in a RAS/waste water blended incubations. Several component streams were identified as being more "toxic" than other streams.

Reactor BSI showed good correlations with effluent COD and reasonable correlations with effluent TSS, both with at least one day leads (one day before effluent COD change, providing some predicative capability).

Reactor cATP parameter showed little correlation with MLVSS parameter, but reasonably good correlation with effluent COD (with 2-day lead, again providing predictive capability).

MLSS and MLVSS parameters, traditional measures of biomass, showed little correlation with effluent quality parameters.

Reactor oxygen uptake rates, traditionally thought to be a better indicator of biomass activity and inhibition, did not show good correlations with effluent quality.

The only traditional influent water quality parameters that showed significant correlation with any effluent quality parameters were conductivity and fluoride. Influent conductivity also had a significant negative impact on the reactor cATP, and the influent fluoride and sulfide had a significant negative impact on the reactor BSI.

B. Refinery 2

No significant correlations were found between influent wastewater quality parameters and effluent COD and TSS. However, influent COD, Phenol and conductivity had correlations with effluent ammonia.

Reactor cATP had a strong negative correlation with effluent COD (e.g. R= -0.6, with 4-day averaging and higher when both systems averaged.)

There was little to no correlation between reactor MLSS and MLVSS and effluent COD or TSS.

Average reactor cATP had a strong correlation with overall COD and ammonia removal.

Reactor BSI had only low to moderate correlation early in the study period with effluent COD and TSS. However, after nitrification restarted, correlation with effluent COD was very strong.

Bio augmentation using commercial bacteria was used to restart nitrification and the change in bioactivity was noted in both reactors with the cATP parameter, but not reliably with the MLVSS parameter.

C. Overall

In the future, the ATP influent monitoring will be conducted using the wastewater/RAS mixture as was done in refinery 1 and this data will be compared to straight BSI for prediction capabilities.

Reactor cATP measurements proved more useful than MLSS or MLVSS for predicting effluent quality in both refineries, lending credence to claim that cATP is a more reliable indicator of active biomass than either of these traditional parameters.

Reactor BSI measurements were useful for identifying toxicity in refinery 1, but not in refinery 2 when nitrification was lost.

Results to date support the use of this technology as a useful tool for industrial biological system monitoring, with several advantages over traditional techniques.

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