ZAPS TECHNOLOGIES
www.zapstechnologies.com

ONLINE OPTICAL MONITORING

HYBRID MULTISPECTRAL ANALYSIS OF BOD & cBOD

Presented & Written by:

Nathan Klinkhammer Info@zapstechnologies.com (866) 390-9387

Chris Russo, Ph.D.

Contents

ZAPS Technologies, Inc.

ZAPS Technologies, Inc. creates real-time, water quality monitoring equipment to aid professionals involved in water treatment, water analysis, and environmental analysis. We apply solid-state optical techniques requiring no chemicals, reagents, operators or routine maintenance. This results in equipment that runs unattended 24/7 while producing thousands of tests per day on flowing water; from raw wastewater to finished drinking water (rivers, lakes and marine environments).

Online Monitoring – The Promise

Treatment plants, much like rivers, are influenced by natural and societal patterns that, when monitored continuously, lead to identifiably regular and predictable daily, weekly and seasonal cycles. These cycles generate the pulse of our water systems, and through real time online methods we now have an even greater ability to monitor these, the vital statistics of our water processes. Process efficiencies, overall treatment quality and the regulatory approach can be enhanced by knowing these patterns and recognizing when unpredicted deviations occur. Online monitoring allows operators to focus on the question of what drives these patterns (and anomalies) in their processes.

Because online, continuous measurements run automatically, water quality managers need not devote resources to manual sample collection and processing. Rather, these resources can be focused more directly on protecting human health and the integrity of watersheds and aquatic ecosystems by facilitating greater process control while enabling more timely and effective enforcement of environmental laws and by ensuring compliance with wastewater treatment regulations.

Keys:

- **Direct measurements, no sample alteration** (adulteration and/or preservation): No surrogates (bacteria, chemical processes, etc), no filtration, no handling.
- **Observe compounds in their natural matrix** (in time and location)**:** Measure immediately, and at the point of interest.
- **High definition data available online:** Millions of readings build statistical strength to better characterize complex matrices. Enable control systems efficiency and oversight with real time data.

The three keys listed above lead to an **increased commitment to water efficiency** achieved by deploying water professionals to high value activities such as process oversight; prevent, detect and respond.

A continuous, accessible process enables more timely and effective enforcement of environmental laws to ensure compliance with regulations on drinking water purity and wastewater effluent discharge.

An optical approach: 'HMA' and the LiquID

Hybrid Multispectral Analysis (HMA) is an optical approach to online monitoring which uses a combination of in situ fluorescence, absorption and scattering measurements in a single flow-cell to characterize chemical bonding and molecular structure continuously over time.

Hybrid Multispectral Analysis (HMA) is the hybridization of three optical approaches

- Light Absorption
- Light Scattering
- Light-induced Fluorescence

These three types of optical measurements are applied at multiple wavelengths from the deep UV through the Visual portions of the light spectrum. Finally, data from these three types of optical measurements are automatically analyzed and interpreted.

Wastewater is a highly complex matrix consisting mainly of organic material made up of carbon, hydrogen, oxygen and nitrogen atoms bonded together in the forms of proteins, carbohydrates and oils/fats. The HMA approach measures the presence of these bonds by analyzing the interaction of light at different energies (wavelengths) with the wastewater matrix. Different types of bonds are excited by different energies and will either absorb the energy or absorb and release this energy in the form of fluorescence. The relative response of the matrix at different energies is analyzed and used to determine the relative 'strength' of the overall matrix. In this sense the HMA approach views a complex wastewater matrix in a similar way microbes do by focusing on the bonding and energy potential of the collective matrix and not solely on specific compounds present at any given time.

The most complete characterization of the matrix is achieved when the third optical approach, scattering, is factored into the analysis. Scattering at different energies is used to characterize the particle load and relative particle size distribution in the wastewater matrix.

The HMA approach benefits from the speed and reliability of decades old spectrophotometric technology combined with rapid modern computational and communication technology to measure, analyze and report matrix characterizations. Thousands of readings are taken in each cycle to produce a reported parameter value approximately every two minutes.

The ZAPS Technologies' LiquID is an industrialized and fully automated machine developed around the HMA approach. The machine itself brings additional technology into the process such as digital valves that allow for automated cleanings and internal calibrations to be performed without human intervention and at an appropriate frequency for the rate at which data is being generated (i.e. higher sampling frequency – higher calibration frequency).

3 of the Benefits:

- **Continuous Data Record:** Readings every 2 minutes with embedded, automated calibration validation.
- **Efficiency:** Allow permit-holders to focus on their business while increasing awareness of the regulatory impact of their processes.
- **Direct measurement:** Characterize complex water matrices at the molecular level.

Real-time BOD : The next evolution

At the heart of BOD, its most basic definition of the concept is as a measure of wastewater strength. As the story goes, the traditional 5 day incubation period relates to the transit time from source to mouth of the longest river in England, the Thames.

Note: *Throughout this paper the term BOD (or cBOD) refers to the traditional 5-day measurement (e.g. BOD-5).*

History

Biochemical oxygen demand (BOD) was first proposed in England in the mid-19th century as a way to quantify the effect of human and industrial waste discharged into rivers. Initially existing as a conceptual idea, over time different methods were developed in an effort to quantify BOD. Modern BOD methods have since been further refined to include microbial seeds in an effort to normalize this quantification. The current method, however previously useful, by definition is incapable of producing results in a timely manner and is not compatible with a technologically advancing world. Inevitable scenarios such as population growth and evolving environmental concerns continue to put increased strain on waste water plant operations and regulatory monitoring, necessitating improvements to continuous process control and discharge monitoring.

A few of the important events in the evolution of BOD from concept to modern day regulatory procedure include:

- 1849 – Wastewater oxidation studies (Birth of BOD theory)
- 1911 – Link established between oxygen depletion and microbial activity
- 1955 – First modern BOD test in Standard Methods
- 1962 – Introduction of galvanic electrodes for DO measurement improvement to the titration approach
- 1972 – Clean Water Act becomes law
- 1989, 1992, 1998 – Standard methods released with no additional changes to the BOD method.
- 2012 –Optical sensors are approved for measurement of dissolved oxygen within the BOD method.

Although this is a very short and undetailed look at the history of BOD a few important facts can still be drawn from it;

- **Legacy:** BOD has a long legacy within wastewater regulations and as such has played an important role in improving the quality of our nation's water as mandated by the Clean Water Act.
- **Technology:** Since its inception as a concept BOD has advanced along with technology.
- **Continuity:** The concept of BOD remains the best measure of wastewater strength and - along with its historical data record - should be preserved by any new approach.

A Path Forward

Hybrid Multispectral Analysis (HMA) provides a rapid and precise technique for characterizing the driving force behind oxygen demand in a real-time basis. In the HMA approach, high intensity light is used to identify molecular bonds and particles in the sample stream characterizing the potential demand of the oxidants and oxidizers present. HMA does not produce an equivalent measure of BOD, but rather a more precise and accurate one than the standard test. The HMA method's use of light allows for a very rapid and precise characterization of the sample stream without the need of surrogate microbial seeds or other sample disruptions. The end result is a more continuous, direct and efficient form of monitoring.

Because the HMA method has been conceived and developed in connection with the current methodology it is demonstrated to scale similarly. As shown in the following graph, comparison data generated using the HMA method correlate well with measurements made using the traditional laboratory approach. Figure 1 compares a total of 100 grab samples taken from 11 different LiquID stations and tested by 7 different certified labs. The grab samples were performed at 6 wastewater raw influent and 5 wastewater final effluent locations. This is an important point because it connects the new method to the historical data record and to current regulatory permits. The ability to link the new method to those measurements collected in the past is a key step required for defining acceptable limits within which the new method can be evaluated.

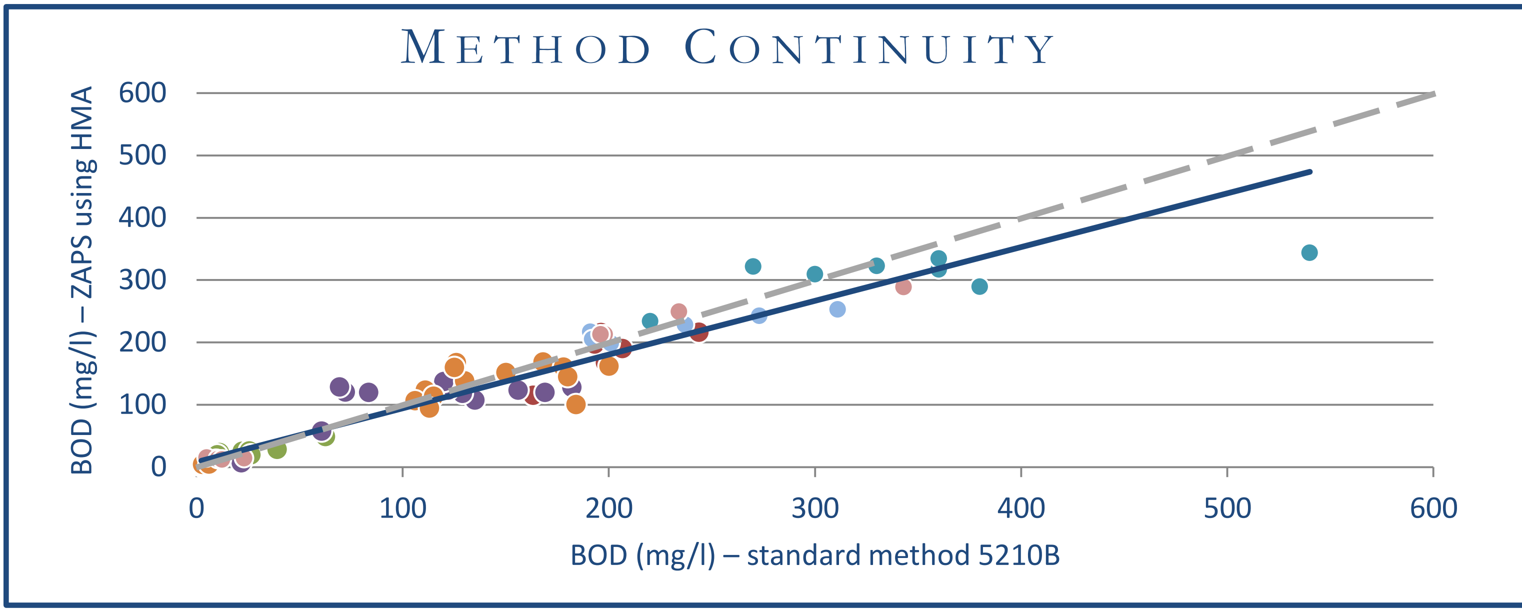


Figure 1: LiquID Data vs. Standard Method 5210B

LiquID Data vs. Standard Method 5210B	
Installation Locations	7
Number of LiquID Stations	11
Grab Samples (N)	100
Correlation (R^2)	0.94

In addition to the point-in-time correlation of HMA-based BOD/cBOD to the traditional method, the higher frequency of data supplied by HMA-based BOD/cBOD allows that data to be averaged to the frequency referred to by existing permit structures. Commonly, current BOD/cBOD sampling is performed on a daily composite basis consisting of many samples taken over the course of a day and analyzed in a batch.

The following graph (fig. 2) and summary table describe three years of cBOD data from the influent of a wastewater treatment plant. This LiquID Station was field commissioned in August of the previous year (2012) and was not adjusted during the period shown other than to perform routine cleaning and general maintenance. The data shown as orange triangles is the daily flow-weighted composite regulatory reported data from the municipal Class A laboratory and is compared with the daily average of the real time data from the LiquID station. The highlighted overlaid regions show the winter low-points of each of the three years.

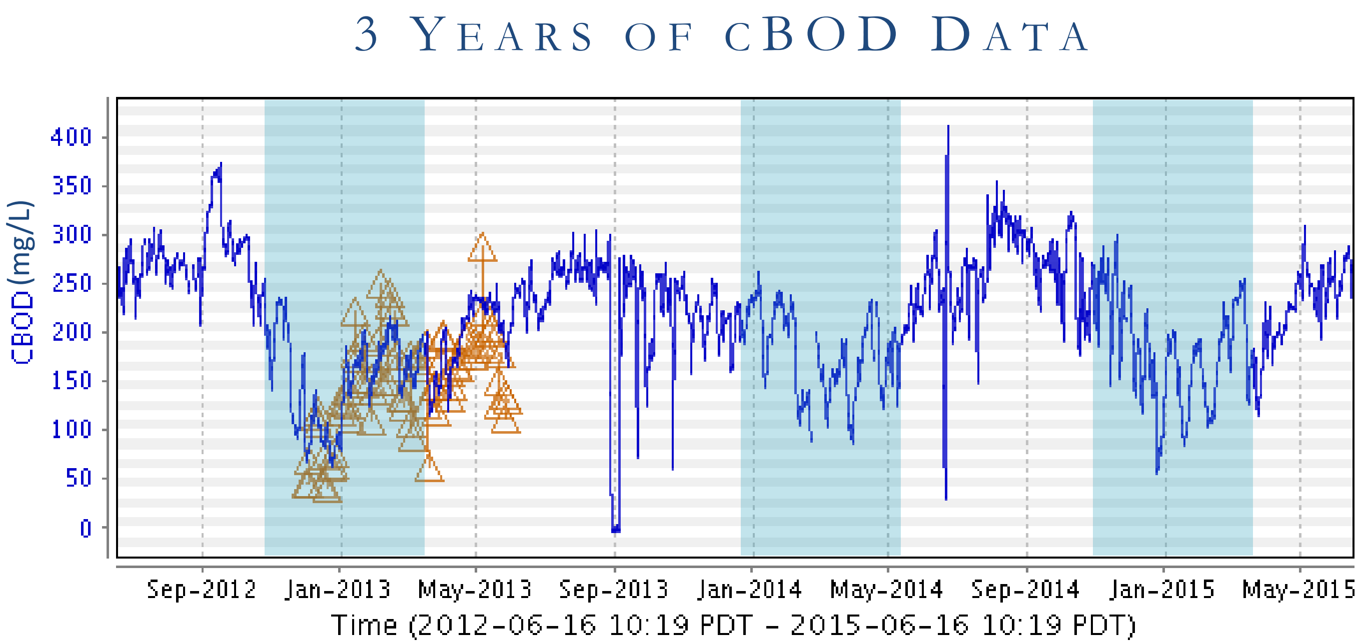


Figure 2: 3 years of cBOD wastewater influent data.

	Traditional Lab	HMA (LiquID)
Readings (#)	3 per week	4,300 per week (677,244 total)
Data Type	Daily Composite	Daily Average
Data availability	5-day delay	Every 2 min.

***Note**: The LiquID data strictly represents data generated by the LiquID (a regular daily average) as opposed to the flow-weighted composite value produced by the municipal lab. In practice, flow (or other) data can be combined with real time data as dictated by the relevant permit.*

Online Optical Monitoring

The graph below represents 6 **months of daily composite regulatory cBOD measurements** performed at a municipal (NELAC certified laboratory producing legally defensible Class A data) taken from the raw influent of a wastewater treatment plant **compared to daily averages using the HMA method (LiquID)**. Although over 106,000 reported parameter readings were generated by the LiquID over this 6 month period, each 2-minute reported value actually consists of over a thousand combined measurements of scattering, absorption and fluorescence lending additional statistical strength to each reported value.

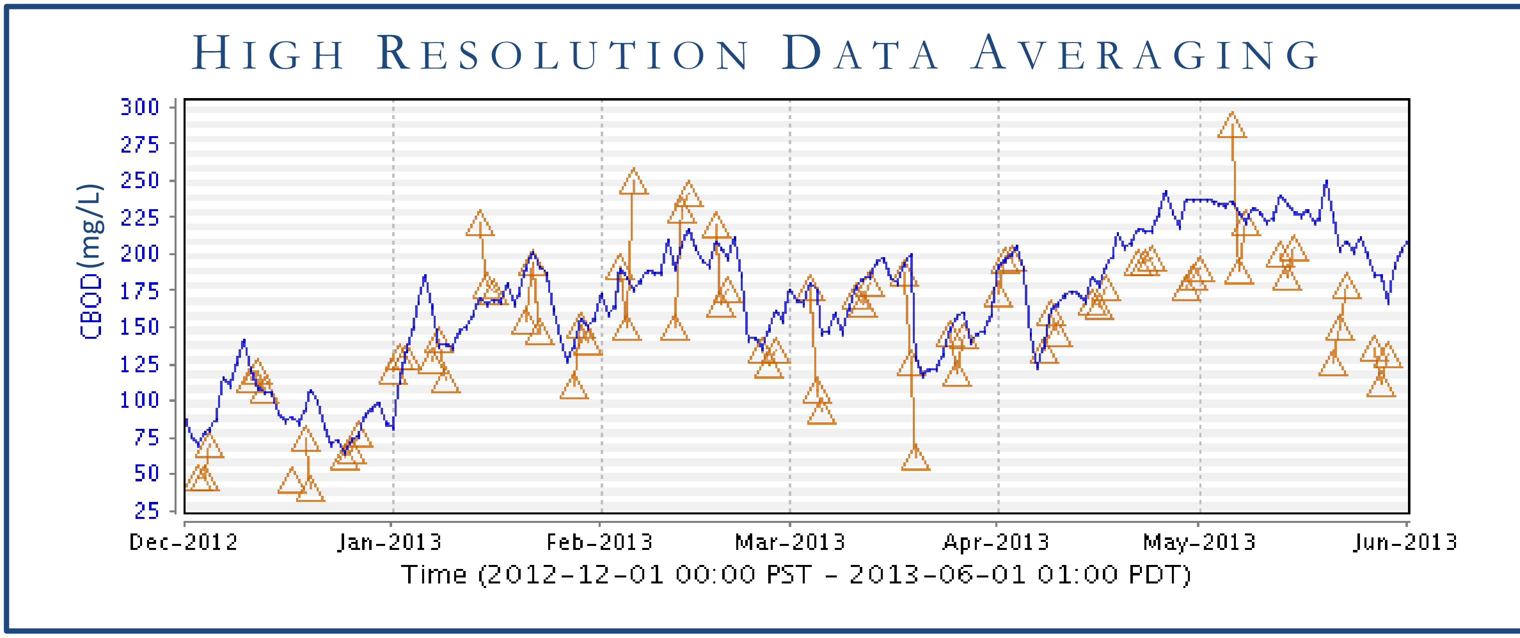


Figure 3: HMA cBOD Daily Average vs Regulatory Composite readings (wastewater influent).

	Traditional Lab	HMA (LiquID)
Readings (#)	78 (3/week)	106,790 (4,000/week)
Data Type	Daily Composite	Daily Average
Data availability	5-day delay	Every 2 min.
Correlation		$R^2 = 0.69$

***Note**: The LiquID data strictly represents data generated by the LiquID (a regular daily average) as opposed to the flow-weighted composite value produced by the municipal lab. In practice, flow (or other) data can be combined with real time data as dictated by the relevant permit.*

Wastewater Diurnal Cycles

The HMA approach provides a much higher resolution view into what these values actually represent, a view that cannot be achieved using the current standard method. The following graph (figure 4) provides a striking contrast between one week described by the three regulatory daily composite readings (available 5 days after the samples are taken – orange triangles) and real-time data available every few minutes via the LiquID station using HMA (in blue). Data gathered continuously over a 24-hour period record the typical diurnal nature of a wastewater treatment plant for process control and analysis, while preserving the overall average represented by composite sampling.

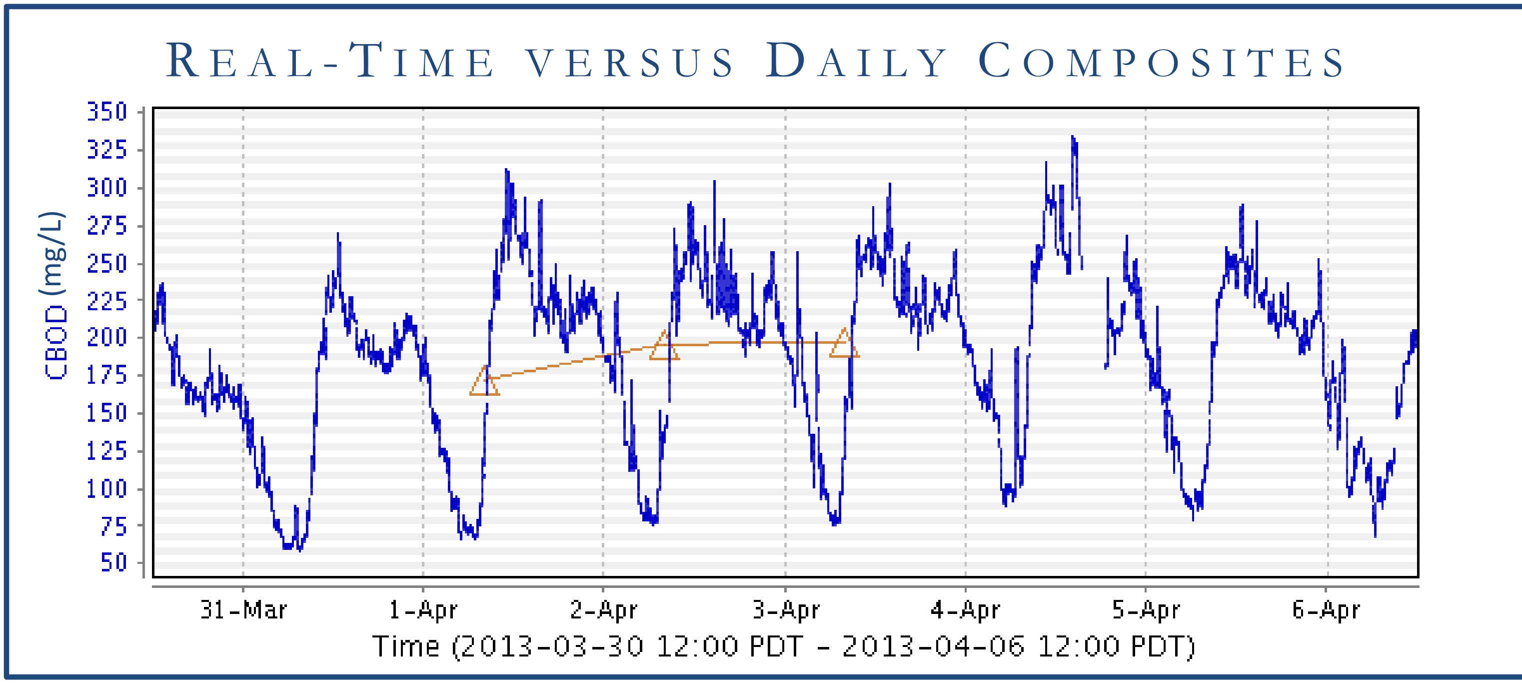


Figure 4: One week of regulatory data (orange) contrasted with one week of real time HMA data (blue).

	Traditional Lab	HMA (LiquID)
Readings (#)	3	4,687
Data Type	Daily Composite	Real-time
Data availability	5-day delay	Every 2 min.
Average Value	189	198

Taking a deeper look into a plant with multiple continuous data records being generated by multiple instruments performing HMA documents a fascinating view of a modern wastewater treatment plant at work. Looking at a week of around-the-clock monitoring reveals that, although plants operate at and maintain a very high level of efficiency, even small changes observed at the influent of a plant can be traced throughout the treatment process. As shown in the graph below, real time monitoring exposes a wealth of process information that is masked by the traditional composite measurements.

The following graph (figure 5) shows three days of minute-by-minute cBOD data from the Raw Influent (blue), Primary Effluent (orange) and Final Effluent (red) of a wastewater treatment plant recorded by **three separate LiquID stations** (1,900 individual measurements per station). The raw influent exhibits a predictable diurnal (24 hour) cycle which is compressed and lowered through the treatment process, resulting in the stable Final Effluent values shown in red. This cycle, once known, can be managed by plant personnel to assure regulatory compliance while maximizing efficiency.

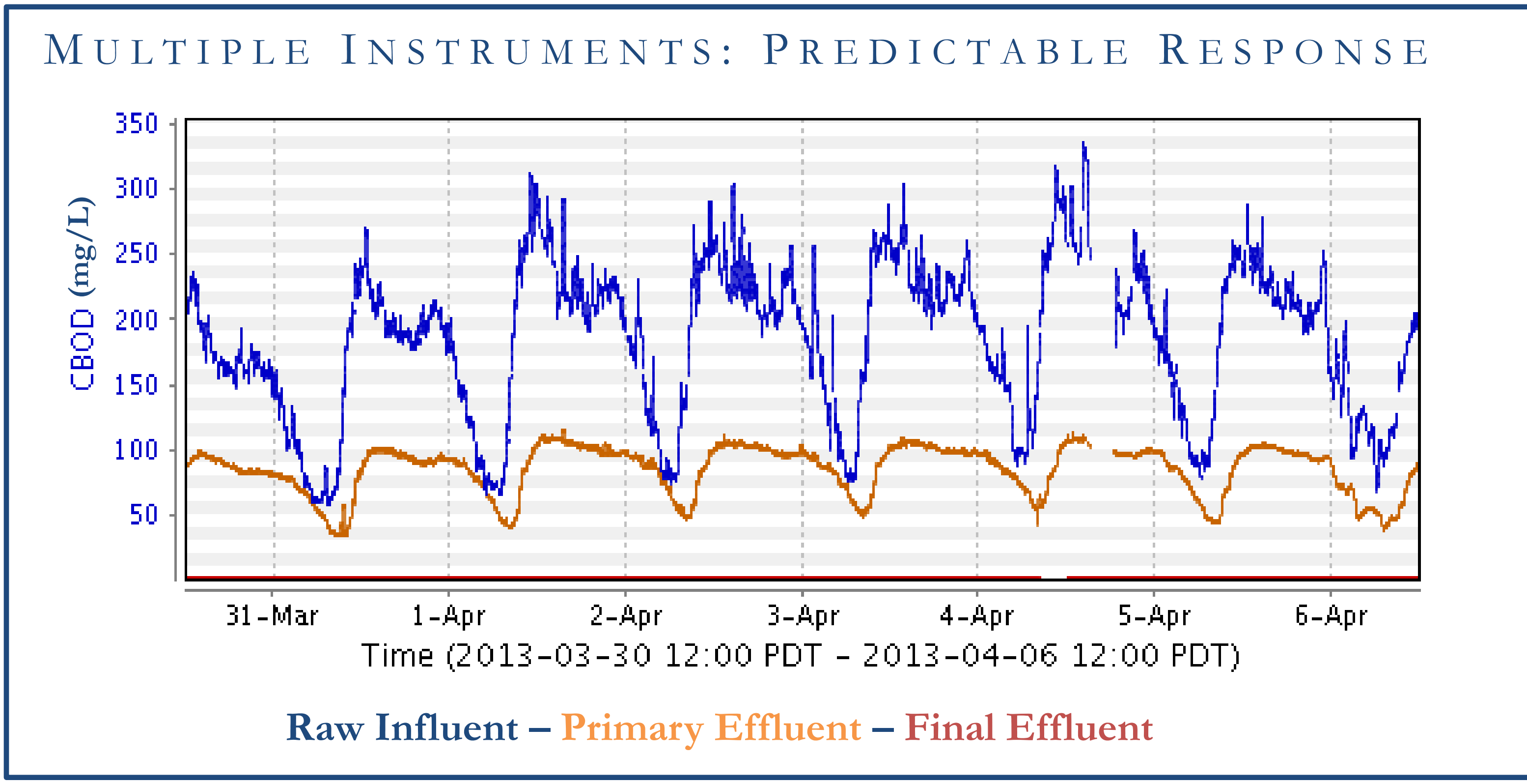


Figure 5: One week of cBOD data from three LiquID stations at different points within a wastewater treatment plant.

Figure 5 also demonstrates the predictable response of independent LiquID stations. Peaks in the Raw Influent, though diminished, are consistently visible in the Primary Effluent (see highlighted example). The offset between these peaks is one hour and fifteen minutes – the transit time of the plant between these two stages. The correlation (r^2) of the data from these two instruments, when offset by this process transit time, is 0.87 (0.61 when unadjusted for transit time).

This plant-wide view gives operators the ability to trace the impact influent spikes have on the system and also allows highly accurate efficiency calculations to be made over various durations. Furthermore, as is discussed in the case studies below, evaluation of these trends can help operators identify and manage;

1) regular loading events,
2) seasonal variability and
3) overall plant efficiency.

Taking a step closer and examining these overall trends it is possible to trace both short duration influent spikes as well as the dominating diurnal cycle from influent, through primary, to the point at which it is leaving the plant. The graph below (fig. 6) shows how the diurnal cycle can be detected in final effluent with a diurnal concentration variability of less than 1 mg/L. The transit time for a packet of wastewater from the raw influent to final effluent in this system is approximately seven hours.

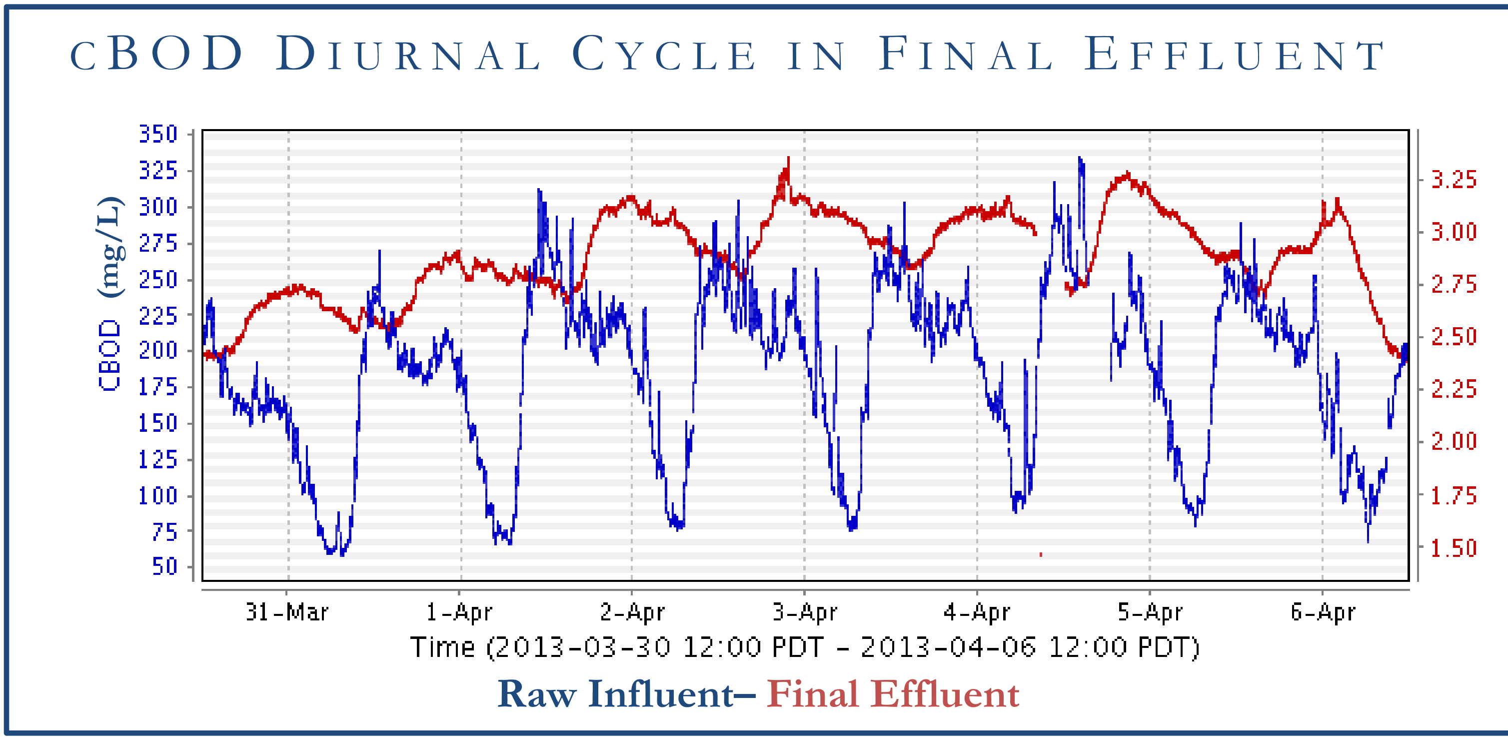


Figure 6: cBOD diurnal cycles over one week compared between Raw Influent and Final Effluent of a WWTP.

This cyclic analysis – related to the influent flows of this specific plant – has been extended in the following graph (fig. 7) to visualize the similarities in diurnal cycles at three separate wastewater treatments plants denoted here by their distinct sizes and treatment methodologies:

a) WWTP Small: 0.25 MGD dry weather average, UV-oxidation plant.
b) WWTP Medium: 5 MGD dry weather average, hybrid trickling filter solids contact plant.
c) WWTP Large: 17.5 MGD average flow, activated sludge.

As shown in the following graph (fig. 7), the diurnal characteristics of cBOD in the raw influent show extreme similarities although the size of the plants in this example are inversely related to the variability of their influent (i.e. at smaller plants, individual contributors to the influent have more of an impact on the whole.) However, the final effluent (as measured by three separate LiquID stations) reflects the unique efficiencies and treatment designs of each plant. In particular, the small UV treatment plant exhibits less diurnal characteristics in their final effluent. This type of data can be used to model the effect of sudden or persistent fluctuations in influent on the plant's treatment capabilities (i.e. stress testing).

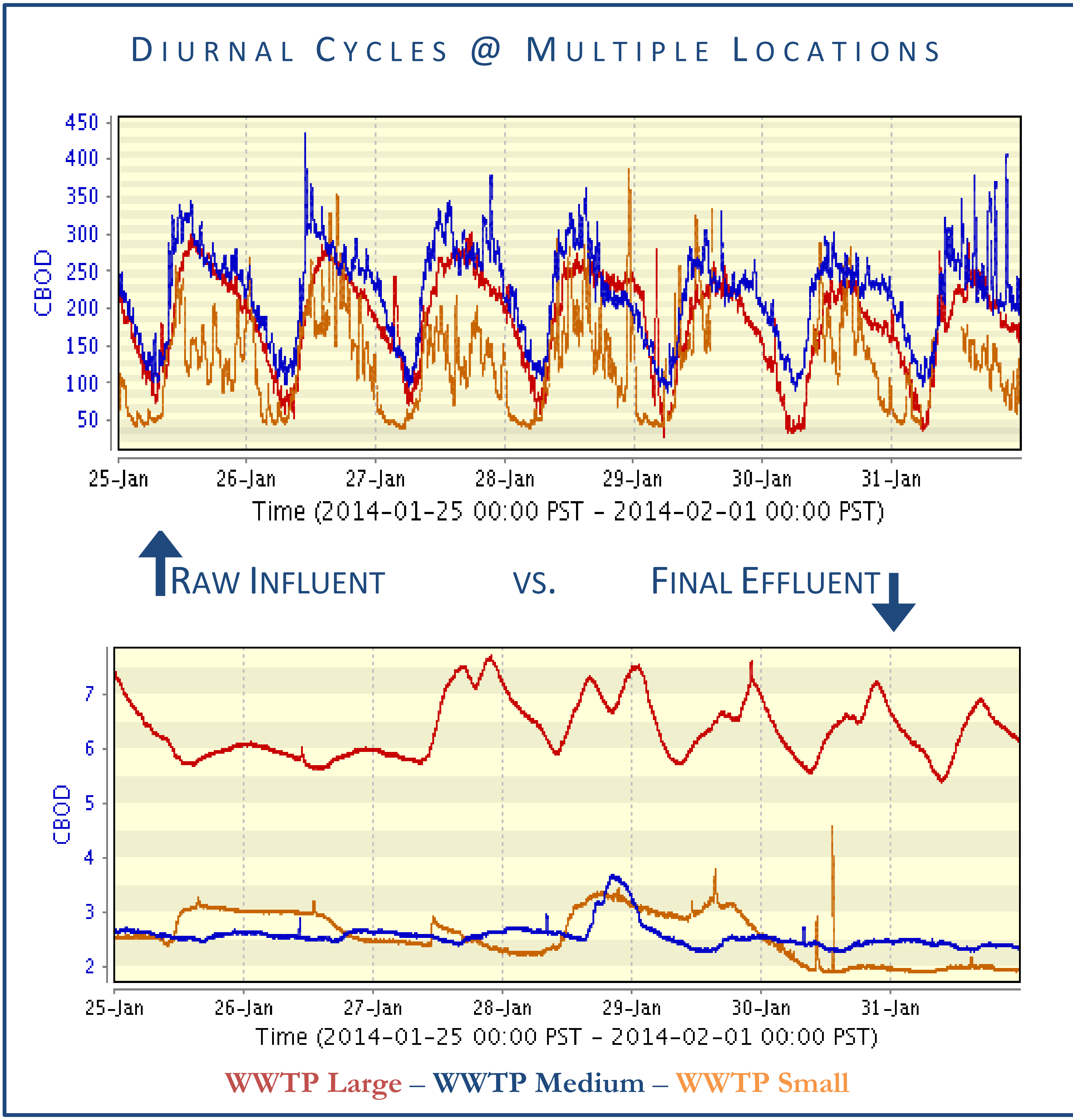


Figure 7: Influent and Effluent cBOD data over one week at three differently-sized WWTPs.

Note: *This approach can easily be extended to calculate BOD load or efficiency by combining this data with plant flow, but for the purpose of this report we have limited the analysis to data generated by the LiquID using HMA techniques.*

To extend the concept of BOD diurnal cycles, we have taken data from an extended period (one year) and used it to examine the average cBOD concentrations over that period.

During this one year period, a single LiquID placed at the raw influent location of a wastewater treatment plant collected 213,642 cBOD data points. The average values were then plotted for a 24-hour period (midnight to midnight) to show the average values at each point in a typical day. The diurnal cycle is visible even through the middle 80% of the data, and only disappears in the minimum and maximum values – demonstrable events of concern well outside the regular operating conditions of the plant. (fig. 8)

Control limits can be set based on the historical data collected and the average expected value for any point in a specific day. For example, a value of 300 mg/L would be of concern at 6 am, but would be well inside of normal expectations if the same value occurred six hours later at noon. This insight enables operators to immediately react and adjust treatment processes based on current events.

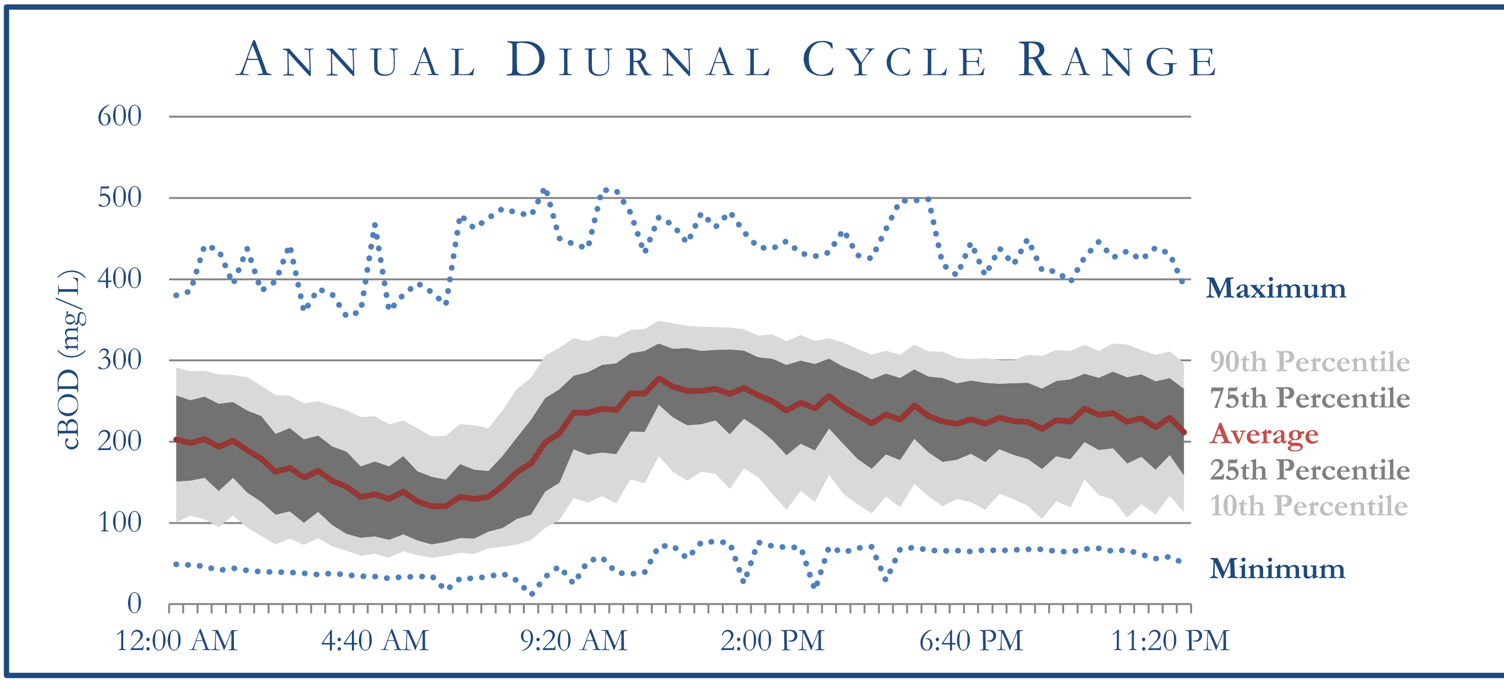


Figure 8: Average cBOD diurnal cycle at a WWTP constructed from one year of real-time HMA data.

Just as a day can be analyzed to expose a predictable underlying pattern (depending on the location) the same differentiation can also be observed during other periods such as, over a yearly cycle, seasons. Separating this year-round record into winter and summer periods (see figure 9) demonstrates the effect dilution has at this combined sewer community's plant during the wetter winter months. Detailed continuous data records allow seasonal data to be easily generated and can aid in deciding the appropriateness of seasonal versus year-round permit requirements. Such data reviews and reports also become less costly and less burdensome to generate and as such lend themselves to more frequent review should such appropriateness come into question or prove beneficial. The ability to generate these types of reports is an example of one way these data records can add efficiency and depth to the regulatory permit review process.

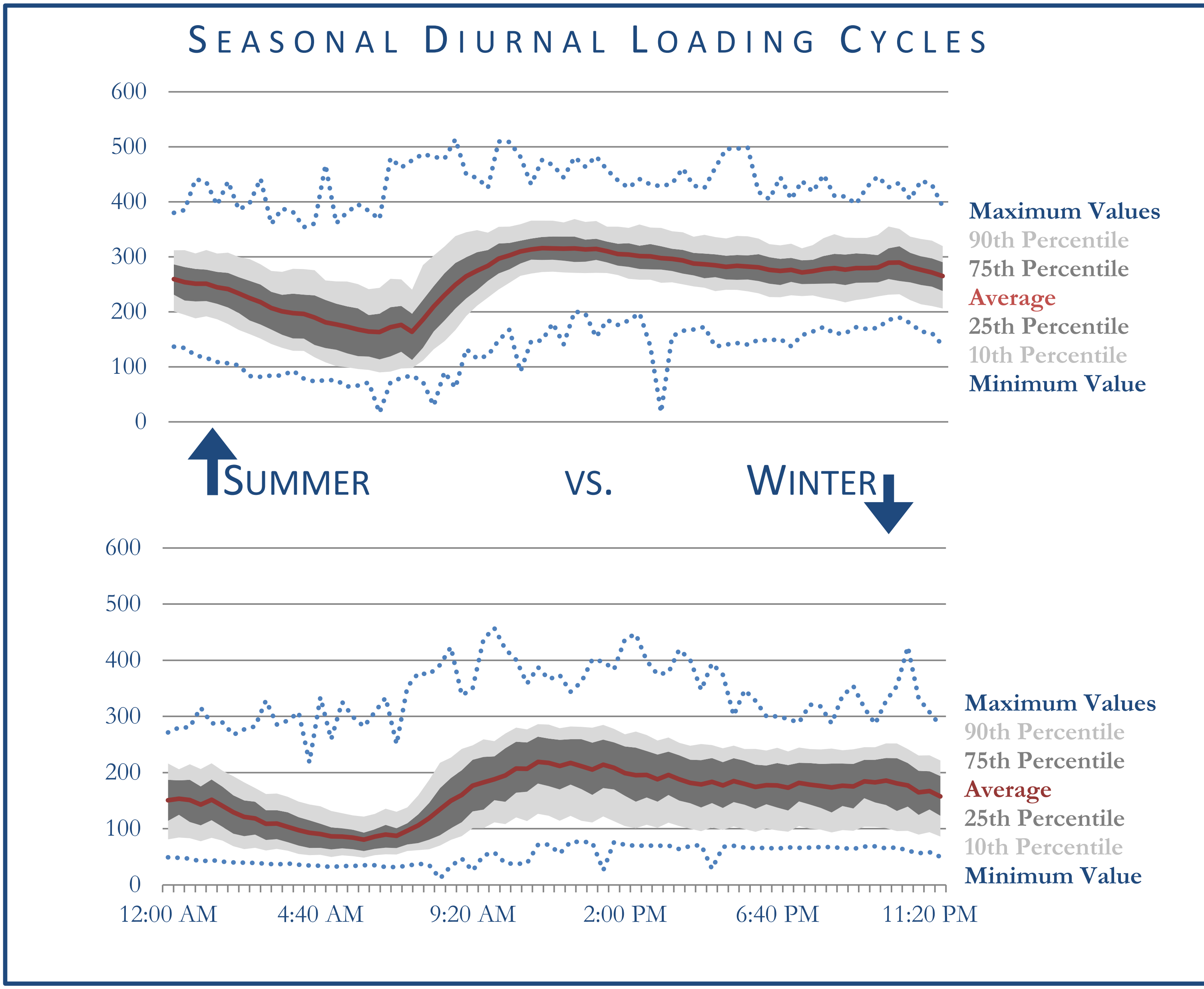


Figure 9: Average cBOD diurnal cycle at a WWTP during summer and winter permit seasons constructed from one year of real-time HMA data.

Challenges and Opportunities:

With any advancement comes the challenge of maximizing its usefulness while understanding the advancement's limitations and how to best fit it into the system it aims to improve. Some additional challenges for online monitoring devices include;

1. Bio-fouling- maintaining data integrity in a real matrix,
2. Interferences- identifying and managing interferences and
3. Data Management- making the large amounts of data generated accessible and easily organized.

Generally speaking defining answers for challenges 1 and 2 will be addressed in terms of defining appropriate QA/QC procedures whereas 3 needs to be addressed in terms of defining data ownership, appropriate chain of custody, and ensuring data security/integrity.

Bio-fouling

Waste streams are messy places with lots of thriving microbial activity and therefore careful attention must be paid to repeatedly track and adjust for unavoidable occurrences such as bio-fouling in order to reliably produce accurate data. The tracking of bio-fouling also allows for automated alarms or reminders to be sent if for some reason fouling has increased and cleaning is necessary prior to regularly scheduled maintenance. The approach of using automated jet-rinse cleanings and air calibrations is typically capable of tracking and accurately correcting for bio-fouling over one to four weeks without any human intervention. Typical calibration cycles run for approximately six minutes every hour or two depending on the environment. Manual cleaning when necessary typically produces an approximately 20 minute interruption in data collection. A single set of optical surfaces minimizes vulnerability to bio-fouling.

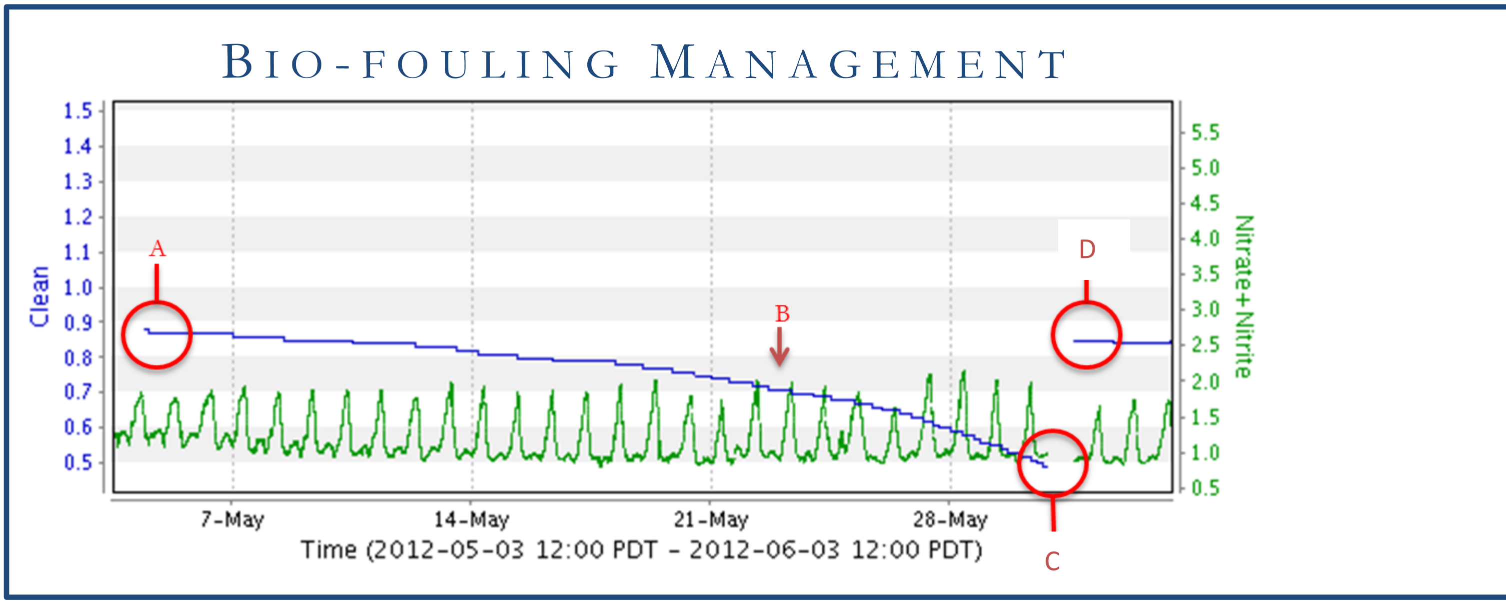


Figure 10: The impact and management of short term degradation (biofouling) management on a LiquID station.

Figure 10 (above), an annotated screenshot from the Web User Interface of a LiquID station shows how the system responds to and manages bio-fouling in a field deployment. Unseen in the graph are over a thousand automated cleanings and calibrations within this one month period. The following points of interest are also indicated on the graph:

A. Instrument 'Clean' parameter.
B. Degradation over time as biofouling occurs. No impact/drift to parameter readings.
C. User-defined Clean alert level. Consistent parameter readings before and after cleaning.
D. Recovery after manual clean & automatic self-calibration.

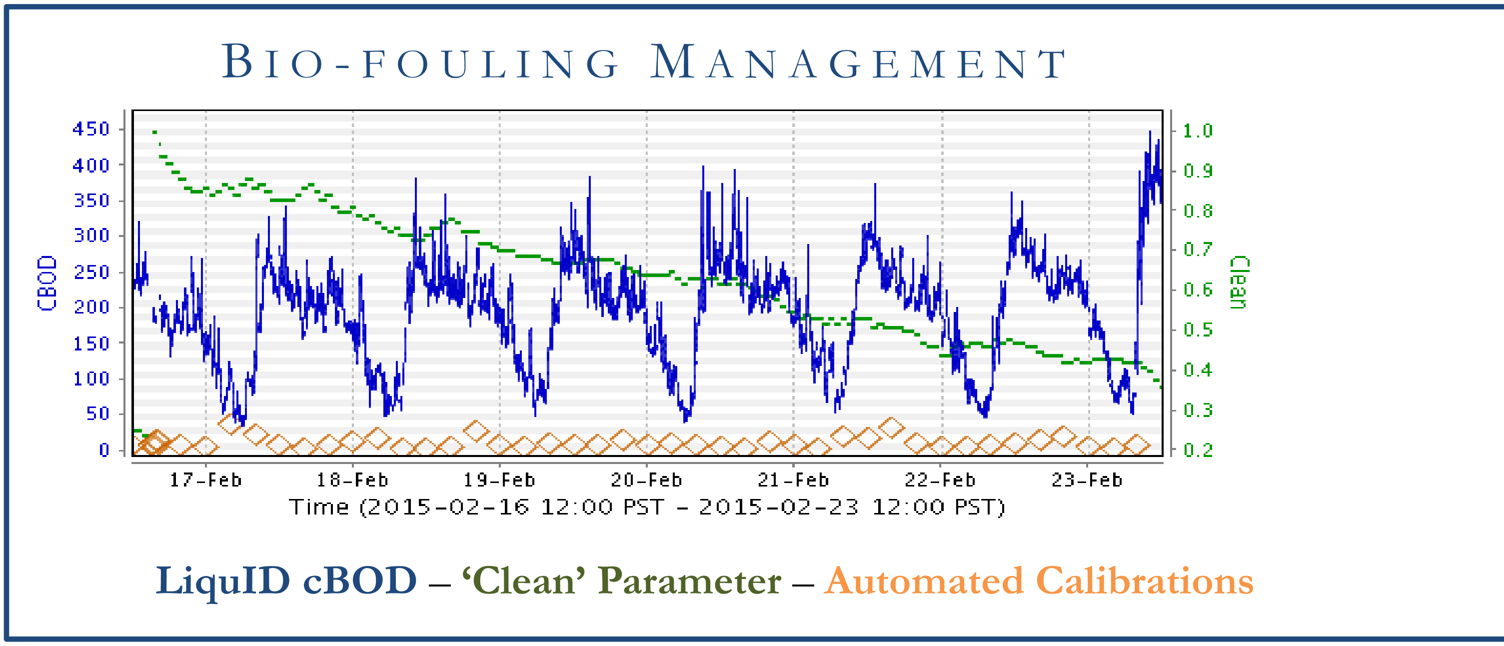


Figure 11: Visualization of the automated calibration and cleaning processes utilized by the LiquID station.

	Total	Per Day
Days	7	
Automated Cleaning Cycles	219	31
Automated Calibration Checks (plotted)	47	7
cBOD Parameter Readings (plotted)	4,529	647
Manual Optics Cleans	1	

The graph above (fig. 11) shows a single week of cBOD data (blue) alongside the LiquID Clean parameter (green) and the Automated Secondary Calibrations (orange) performed by the instrument. This clearly demonstrates the rate at which these automated cleans and calibrations are performed, and that the loss of available light due to fouling is being correctly managed – confirmed in this case by the absence of drift in both the normal sample output and the secondary calibrations. In addition to the hourly automated calibrations that inform the 'Clean' parameter there is also a secondary calibration, performed at a frequency determined by the specific application (in this case approximately 7 times a day).

Interferences

Interferences can also vary from plant to plant and this is especially the case when comparing between plants operating with different treatment approaches such as plants operating using chlorination versus UV-disinfection. As a precautionary measure as well as to ensure proper scaling and interference adjustments each device goes through a commissioning process during initial installation during which HMA results are compared to those gathered using traditional methods. This commissioning process typically requires a handful of samples, very rarely leads to adjustments of the spectral interpretation and the duration is largely governed by the amount of time required to produce laboratory results. The commissioning period also provides the time needed to evaluate the fouling rate and appropriate cleaning/calibration schedule at any given location.

One additional challenge of the commissioning process is ensuring that samples collected for comparison accurately represent the sample being analyzed by HMA. For instance, an influent waste stream can be highly variable on short timescales due to solids and other heterogeneous components. As a result of this heterogeneity a one liter sample collected over 20 or 30 seconds may not be fully representative of the sample stream being analyzed during a two and a half minute HMA data gathering cycle and in these instances composite sampling may be a better choice.

Data Management

One advantage of the HMA approach is the rapidness at which it generates data. However, large amounts of data are most useful when they can be managed, observed and packaged in an organized manner. Overcoming this challenge is another part of what separates the HMA approach from the traditional method by allowing important wastewater metrics like BOD to be integrated into a continuous record of plant performance. For example, the HMA approach to BOD provides necessary information on waste concentration which can then be easily merged with other continuously monitored data such as flow for continuous load and removal calculations. Automated reports can be created with appropriate influent-effluent offsets to produce accurate and detailed efficiency reports. There is a technological track record for meeting this type of challenge using SCADA and other warehousing systems already in place for other operational parameters. However, whether the data is managed through the instrument itself or via a third party management system, this type of ability is critical to separate the noise of the system from the signal of a true event. Additional meta-data is also regularly collected by the instrument and available for use in generating reports that document such important records as instrument uptime, number of automated cleans/calibrations, and occurrence/frequency of manual cleans.

Shown below (fig 12) is the previously-examined three-year cBOD record. This supplemental view also includes an additional two months of reported regulatory composite samples from a recent period. During the intervening two years between the regulatory comparisons, no adjustments were made to the instrument other than routine cleanings and preventative maintenance. This view demonstrates how the combination of initial factory calibration and regular automated field calibrations successfully maintain an accurate output over the long-term.

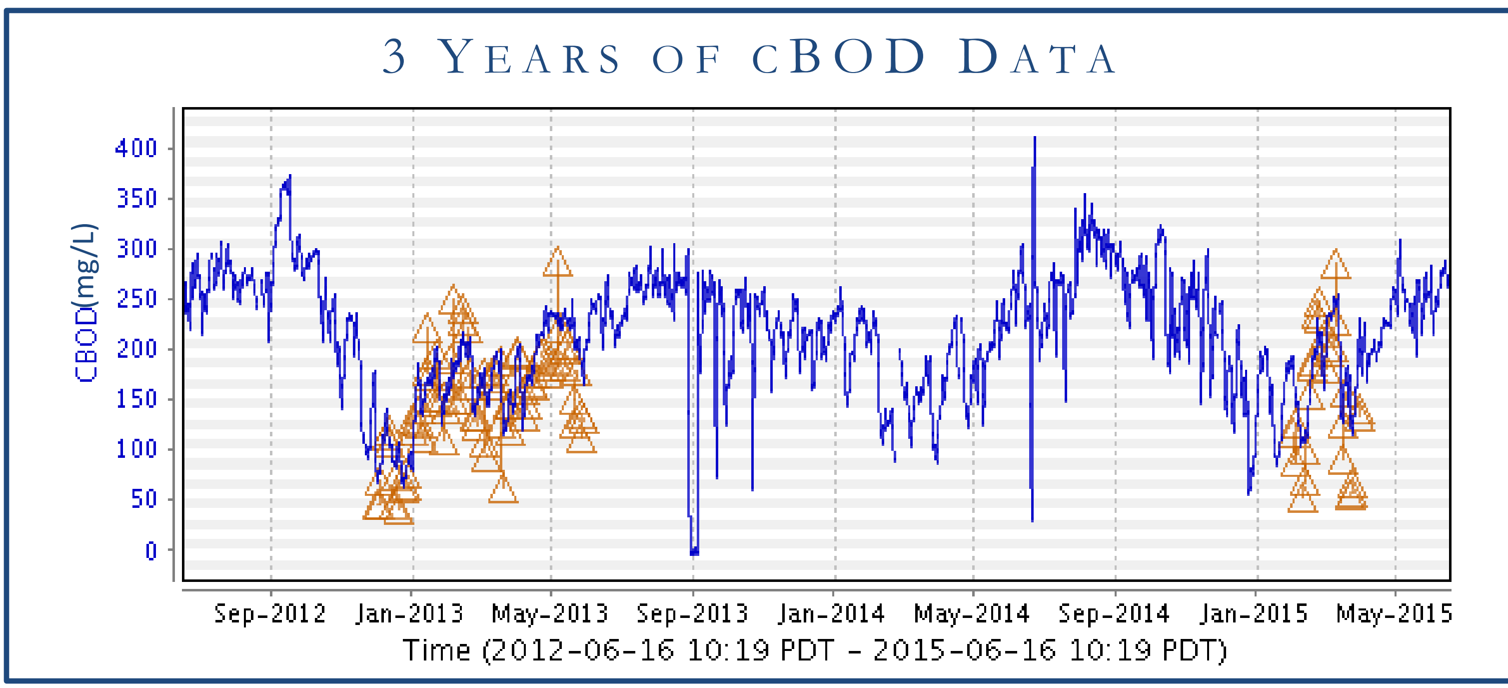


Figure 12: 3 years of cBOD data from a WWTP raw influent location with 8 months of overlaid regulatory data.

	Traditional Lab	HMA (LiquID)
Readings (#)	3 per week	4,300 per week (677,244 total)
Data Type	Daily Composite	Daily Average
Data availability	5-day delay	Every 2 min.
Regulatory Correlation		$R^2 = 0.70$

So what?

The following section contains two scenarios in which LiquID data was used to facilitate control over regulatory and production processes. These examples outline how large amounts of high quality data generated using HMA (through the LiquID) help to illuminate a process and can be used to develop:

- **People-data partnership**: This data exposes how operators and other authorized users can leverage the immediate access to data.
- **Process management**: With access to BOD data in real time, BOD becomes more than a regulatory requirement. It becomes a measure that can be used to add value to the process.

Example 1: The Signal in the Noise

Now that we have described the diurnal cBOD/BOD cycle and how it persists despite variations in treatment plant size and generalized demographics of the communities they serve, we will now take a look at a couple of examples to demonstrate how knowing and analyzing this cycle begins to describe the 'pulse' of the communities from which they are generated.

In the first evaluation (label Ex1 on following graph) we look at data compiled by time of day, for each day of the week, over the course of an entire year. When viewing each day of the week individually we see that a very consistent cycle repeats itself during weekdays (Monday, Tuesday, etc.) However, when the weekend arrives, the community's lifestyle preference to stay in bed a little while longer is revealed by a shift in the diurnal cycle to slightly later in the day. Although this subtle shift is well known and has been documented in relationship to flow, having such resolution available with cBOD further validates the HMA measurement approach. Being able to identify these types of patterns in cBOD/BOD measurements becomes possible with online monitoring and demonstrates the extension of a well-known flow pattern that can now be visualized within the context of a cBOD/BOD measurement. Subtle patterns like these cannot realistically be identified using current methods and therefore are not available for use in refining process control or further defining the 'pulse' of the community being served.

Example 2: People-Data Partnership

In the second example (label Ex2 on figure 13) we return to the same compiled data set. In this example we discuss an operator's ability to use observation and pattern recognition to identify a small, predictable load observed at the plant influent and then trace it back to its source within the community. Focusing again on the daily patterns throughout the week, small cBOD pulses can be identified arriving at the plant's intake every two hours. The magnitude of these shifts represents a small portion (approximately 3%) of the plant's overall influent load at any given time but they become a visually and statistically resolvable signal due to the data's

1) reproducibility,
2) large quantity and
3) high quality.

In this particular instance the operator was able to trace these pulses to the pumping/gravity feed cycle of the sewage delivery infrastructure and eventually to their source at a poultry processing facility. The operator's final analysis determined ultimate cause of the pulses resulted from the pooling and concentration of waste at the pump station and that these pulses could be further managed by altering the pump schedule operating at this station in conjunction with the discharge schedule of the poultry facility. The important point of this example being that with access to real-time continuous data operators can begin to better understand not only processes occurring within the plants they manage but within the entire sewage treatment network.

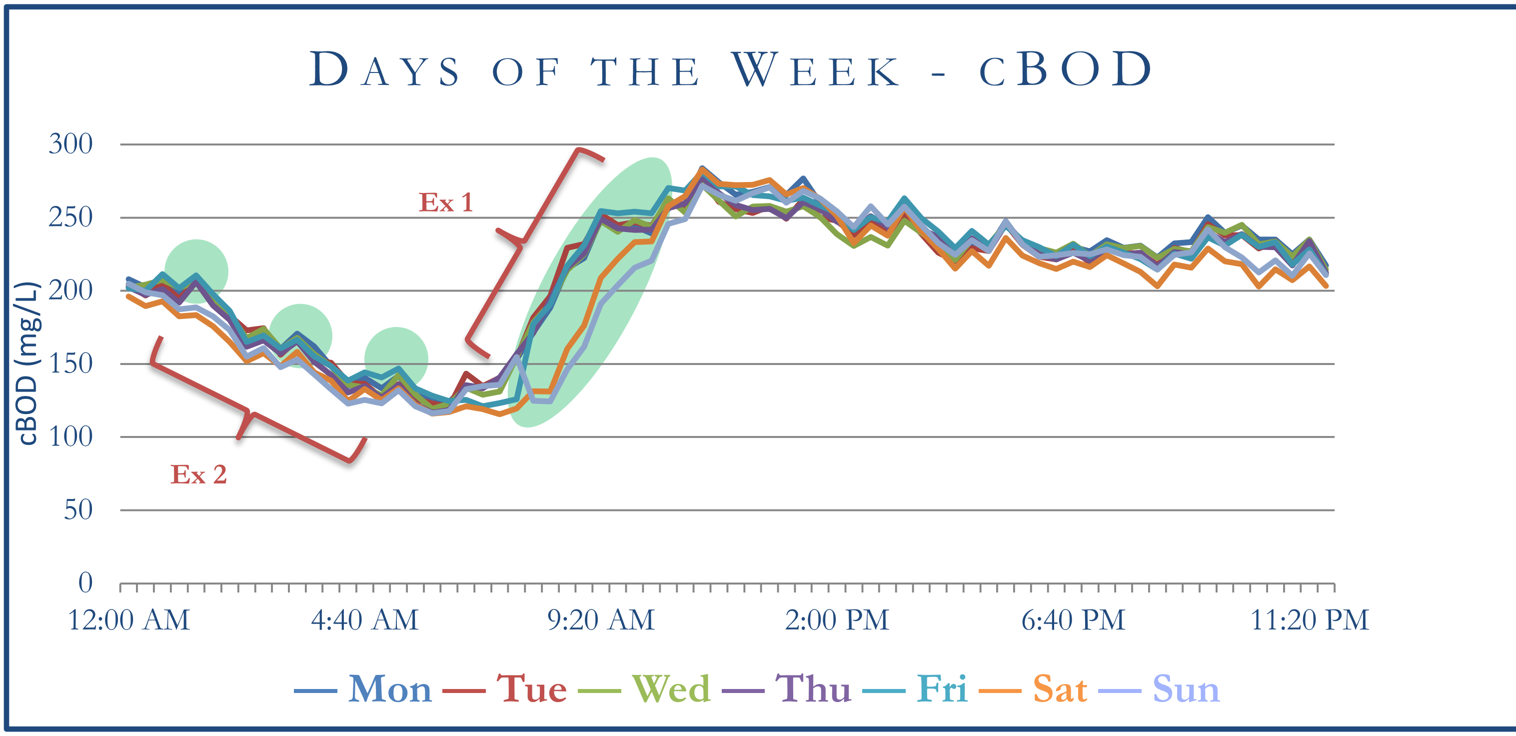


Figure 13: The average cBOD diurnal cycle by the day of the week at a WWTP raw influent location.

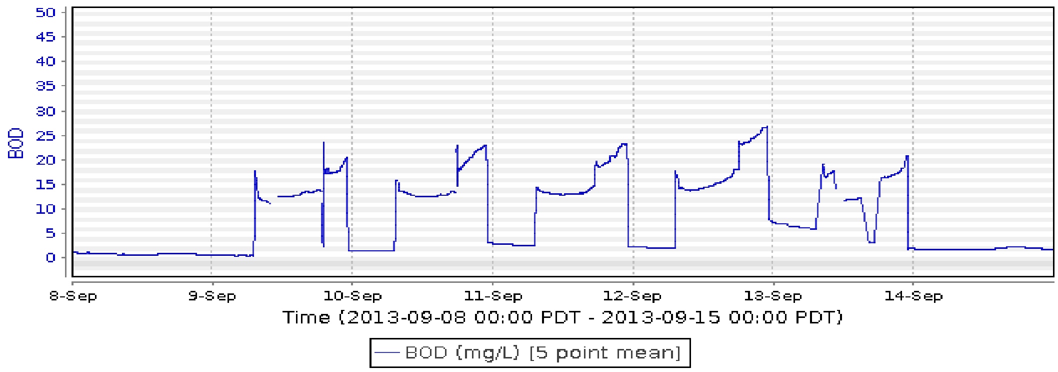
Example 3: Process improvement

Our examples thus far have related to the use of BOD in wastewater treatment plants, but having access to a real time BOD parameter is also important in other areas. The following example examines the implementation and use of a LiquID system at a food processing final effluent location. The company referred to in this example has experienced a period of significant growth over the past three years, and as a result their treatment capacity of their final effluent has struggled to keep up. Under typical loads they were below their permit limits however, during their peak processing season, a series of surges in BOD led them to exceed their permit in three consecutive quarters.

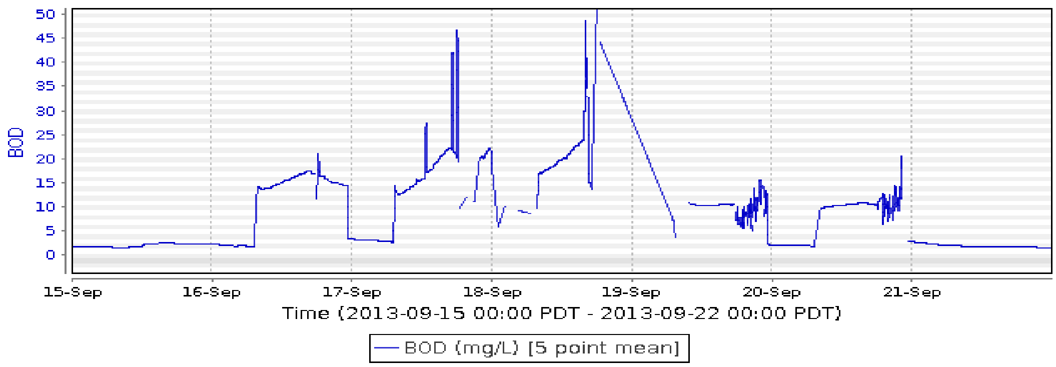
For a company, especially in the midst of a boom, it is difficult (though necessary) to regulate processes and respond to short term surges based on a regulatory measure that will not be completed for five days. Access to real time BOD data that correlates well to the traditional BOD measurement gave this facility the tools to monitor and control their BOD load in the same way that they manage the rest of their process lines; on a continuous basis.

1) The first graph (fig. 14) shows the effluent conditions during a typical week. The clear low points represent off-hours during which the facility monitored tap water while the higher values during each day are reflective of their process filtrate and – later in the day – their effluent holding ponds.
2) The second graph (fig. 14) shows the following week when a process 'improvement' was implemented on their product line. By Wednesday, continuous BOD monitoring showed that the improvement was not effective, and actually had the opposite effect by driving their typical BOD load of 15-20 mg/L up to 55 mg/L in erratic spikes.
3) The real time data enabled the facility to shut down the line, make adjustments and resume processing the next day with a re-improved system. As you can see in the third and final graph (fig. 14), the adjusted process improvement clearly changed the dynamics of their effluent BOD load, reducing the average concentration from 15 mg/L to 11.5 mg/L.

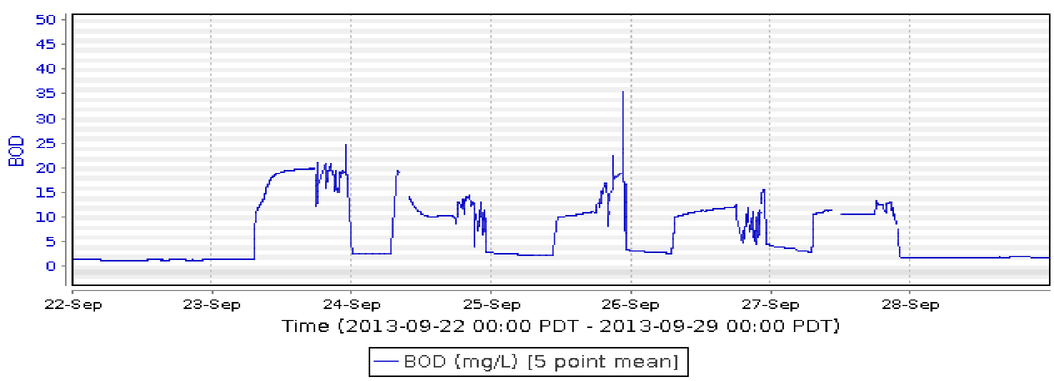
EXAMPLE 3: GRAPHS



Caption 1: Screenshot from LiquID. Pre-process change. Average BOD 14.8 mg/L.



Caption 2: Screenshot from LiquID. Mid-change. Spikes in BOD show process failure. Sporadic data shows periods when the plant was shut down to address the issue. BOD values during this failure period reached as high as 54.6 mg/L.



Caption 3: Screenshot from LiquID. Post process change. Average BOD 11.3 mg/L.

Figure 14: Three graphs of cBOD at an industrial effluent location.

While BOD is already a powerful regulatory measurement and a parameter with strong historical records, the ability to produce a BOD value in real time increases the power of BOD by connecting it directly to the current conditions in a process stream. In this, **BOD becomes more than a regulatory requirement. It becomes a key factor in adding value to and controlling the process.**

Regulatory clarity: Benefits of real time BOD

Benefits of online, continuous monitoring in general and the HMA method in particular are significant and have the potential to beneficially impact the management of our water resources. As with any change, challenges exist with any new method, but the adoption of real time monitoring builds on a long tradition of scientific and technological development elevating the quality of regulatory management. Among the benefits of the HMA method of real time monitoring are the following:

- **Direct, Rapid and Reproducible:** Increases the accuracy and reliability of water quality monitoring because it directly measures the chemical bonding and particulates in the sample stream- instead of inferring their presence by indirect/surrogate, time-consuming, error-prone and labor-intensive means.
- **Continuous Data Record:** By running continuously, automatically, and on-line, it allows water quality managers to focus their efforts more directly on protecting human health and the integrity of watersheds and aquatic ecosystems- instead of on manual sample collection and processing.
- **Enhancement of Regulatory Reporting:** Improved quality and depth of reports generated in less time. Drawing from large digital datasets, available on demand, reports can be automatically generated and sent electronically. It enables more timely and effective enforcement of environmental laws and ensuring compliance with regulations on drinking water purity and wastewater effluent discharge.

In terms of information provided it is interesting to note that it only takes 23 field deployed LiquID stations to generate more BOD/cBOD measurements than are produced by all 16,255 Publically Owned Treatment Works operating within the USA. By enabling regulatory monitoring in real time, we take the pulse of our water systems, simplify reporting and enable our water professionals to accurately control their processes while diagnosing current and future issues.

The references included on this page are intended as a representative sampling of some of the foundational concepts mentioned and built upon in this document. It should not, however, be taken in any means as an exhaustive listing.

References

- Ahmad, S.R., Reynolds, D.M. (1999). Monitoring of water quality using fluorescence technique: Prospect of on-line process control. Water Research 33, 2069-2074.
- Baird, R.B., Smith, R-K., 2002, Third Century of Biochemical Oxygen Demand, Water Environment Federation, Alexandria, VA, U.S.A., pp. 393.
- Brodie, B. (1865) Minutes of Evidence, Royal Sewage Commission of 1857, Rep. Thames River 2, 49.
- Bourgeois W., Burgess J. E., Stuetz R. M., (2001). Review On-line monitoring of wastewater quality: a review. Journal of Chemical Technology and Biotechnology 76: 337-348. Pdf attached
- Brookman, S.K.E. (1997). Estimation of biochemical oxygen demand in slurry and effluents using ultra-violet spectrophotometry. Water Research, 31:372-374.
- Burgess C., (2007). The Basics of Spectrophotometric Measurement. In Thomas O., Burgess C., UV-Visible Spectrophotometry of Water and Wastewater. Techniques and Instrumentation in Analytical Chemistry, Volume 27, Elsevier.
- Dobbs R. A., Wise R. H., Dean R. B. (1972). The use of ultraviolet absorbance for monitoring the total organic carbon content of water and wastewater. Water Research 6: 1173–1180.
- El Khorassani H., Trebuchon P., Bitar H., Thomas O., (1999). A simple UV spectrophotometric procedure for the survey of industrial sewage system. Water Science and Technology 39 (10): 77-82.
- Fogelman S., Zhao H., Blumenstein M., (2006). A rapid analytical method for predicting the oxygen demand of wastewater. Analytical and Bioanalytical Chemistry 386: 1773–1779.
- Froelich, P.N., Klinkhammer, G.P., Bender, M.L., Heath, G.R., Luedtke, N., Cullen, D., Daulphin, P., Hammond, D., Hartman, B., Maynard,V. (1979) Early oxidation of organic matter in pelagic sediments of the Eastern Equatorial Atlantic: Suboxic diagenesis, Geochimica Cosmochimica Acta 43, 1075-1090.
- Klinkhammer, G.P., Bussell, F.J., Haught, R.C., 2012. Zero Angle Photo Spectrophotometer For Monitoring Water Systems, US EPA Patent Program, US Patent: 8,102,518.
- Langergraber G., Fleischmann N., Hofstaedter F., Weingartner A., (2004a). Monitoring of a paper mill wastewater treatment plant using UV/VIS spectroscopy. Water Science and Technology 49 (1): 9–14.
- Langergraber G. , Gupta J.K. , Pressl A. , Hofstaedter F. , Lettl W. , Weingartner A., Fleischmann N., (2004b). On-line monitoring for control of a pilot-scale sequencing batch reactor using a submersible UV/VIS spectrometer. Water Science and Technology 50 (10): 73–80.
- Lourenco N.D., Chaves C.L., Novais J.M., Menezes J.C., Pinheiro H.M., Diniz D., (2006). UV spectra analysis for water quality monitoring in a fuel park wastewater treatment plant. Chemosphere 65: 786–791.
- Maribas A., da Silva M. C. L., Laurent N., Loison B., Battaglia P., Pons M.N., (2008). Monitoring of rain events with a submersible UV/VIS spectrophotometer. Water Science and Technology 57 (10): 1587-1593.
- Matsche N., Stumvohrer K., (1996). UV absorption as control parameter for biological treatment plants. Water Science and Technology 33 (12): 211–218.
- Titze, J., H. Walter, et al. (2008). "Evaluation of a new optical sensor for measuring dissolved oxygen by comparison with standard analytical methods." Monatsschr. Brauwiss.(Mar./Apr.): 66-80.