THE NEED FOR FAST REAL-TIME BOD, COD & TOC MONITORING

for enhanced process control

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INTRODUCTION

High quality Biochemical Oxygen Demand (BOD), Chemical Oxygen Demand (COD) and Total Organic Carbon (TOC) data is the lifeblood of effective water management and treatment across many industries. This is due to them being the primary parameters for evaluating the organic strength of water and wastewater.

Without rapid and reliable identification of changes in organic content and composition, industries and municipalities alike face potentially harmful outcomes in terms of water quality, operational health and increased costs as well as public impact.

Some applicable examples for municipalities and/or industries include:

- **Overdosing of treatment chemicals** to be on the safe side when no reliable and relevant data is available, e.g., excessive coagulant dosing
- **Treatment efficiency** being compromised when sudden high loads of organics (slugs) are received at the treatment plant, e.g., biological treatment being overwhelmed
- **Product loss through spills and leaks** that can take hours to detect and remedy without proper monitoring

Traditional lab-based BOD, COD and TOC methods are now being replaced by faster UV-Vis spectrophotometry-based analysis, such as ABB's UviTec family that delivers accurate results in as little time as 5 seconds, compared to 5 days for a standard lab-based test like BOD.

Waiting for results impacts the value of water quality data, which diminishes with each passing minute, posing risks to treatment operations, public health and the environment. An operator's ability to control treatment processes and manage water is compromised when analysis is delayed (see Figure A).

Optimization of treatment, chemical dosing and energy consumption as well as cost savings in several areas all hinge on having real-time and accurate water quality data.

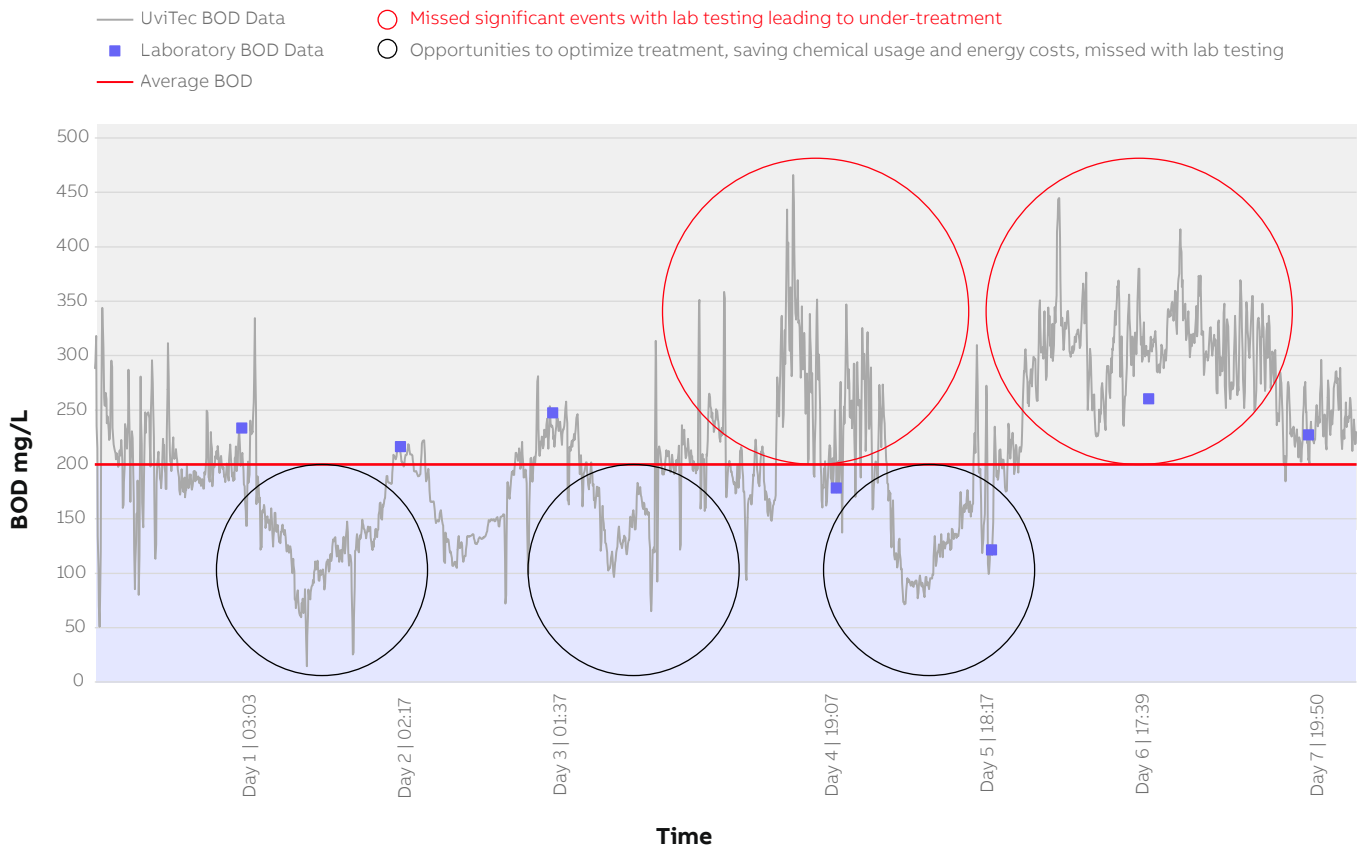

FIG. A. Averaged out BOD values from grab or composite samples do not typically represent the many fluctuations in water quality that take place throughout the course of a week. BOD values significantly above and below the average do occur and present significant process optimization opportunities.

NO TIME TO WASTE

It is very difficult and expensive to measure organic compounds individually. Because of this, the industry standard is to use aggregate parameters such as BOD, COD and TOC that give an indication of the organic strength of the water.

Although these parameters are used universally in water and wastewater analyses, all three have certain limitations (see Table 1).

Water composition can change in an instant. For example, municipal wastewater treatment plants that receive residential wastewater as a baseline would be greatly affected when they are hit with unexpected slugs of industrial wastewater discharge.

In the industrial sector, spill and/or leak events in production can cause issues for both the manufacturing and wastewater operations. In addition, unexpected fluctuations and contamination risks also pose a threat.

Often, there is only a small window to see this happening. Therefore, if measurements are only taken periodically, there is a significant risk that high-impact events could be missed and possibly lead to expensive and/or catastrophic results.

Taking the dairy industry as an example, consider a product spill event that lasts only a few brief minutes, but causes extremely large shifts in the organic strength of the wastewater. When missed, events like this can easily overwhelm the wastewater treatment system and lead to surcharges being imposed.

Real-time analysis delivers reliable and actionable data immediately, improving process control, boosting confidence in results and ensuring that nuanced data can be leveraged to increase efficiency.

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TABLE 1. Typical uses and limitations for BOD, COD and TOC.

	BOD (Biochemical Oxygen Demand)	**COD** (Chemical Oxygen Demand)	**TOC** (Total Organic Carbon)
Uses	• Determine oxygen required to stabilize organic matter • Size waste treatment facilities • Measure treatment efficiency • Ensure compliance with discharge permits	• Measure organic matter in wastewater and natural waters • Correlate with BOD for many water types	• Measure organic matter in water
Limitations	• 5-day lab-based test period unsuitable for process control • Imprecise and unpredictable • Difficult to conduct, requiring years of mastery • No universally accepted accuracy standard	• Considerable time delay reduces process control value • Hazardous reagents require proper disposal, increasing costs	• Limited accuracy for online analyzers due to sampling and calibration issues • Expensive with high operating costs due to consumables and maintenance

CHALLENGES WITH LABORATORY METHODS

In addition to limitations that arise from long turnaround times, the traditional lab-based BOD and COD tests also suffer from relatively high error margins.

As shown in Table 2, uncertainty is as high as ±15% for BOD and ±8% for COD when conducted with standardized solutions.

The errors introduced during sampling, sample conditioning, storage and transportation to the lab as well as the lab-to-lab differences can exacerbate the error, especially for wastewater samples that show high levels of complexity and heterogeneity.

Table 3. below shows one particular case where disagreement between readings from an ABB UviTec sensor and lab COD results led to further investigation to find out the root cause.

Every sample collected was split into two containers and sent to two different labs for COD analysis. The percentage difference between the two labs' COD results reached 42% for one sample and showed great variability for the whole sample set, with some samples well beyond the standard ±8% margin. The accurate results of the ABB UviTec sensor, compared with the disparities of the lab-based sample tests, highlights the importance of real-time monitoring, where the analysis is done live in the process.

TABLE 2. Uncertainty and response time for BOD, COD and TOC.

Test	**Uncertainty** (APHA, 1998)	**Response Time**
BOD	± 15%	5 days
COD	± 8%	2-3 hours
TOC	± 2%	4-6 minutes

TABLE 3. Even though standard uncertainty is only ±8% for the COD test, sampling, sample conditioning, sample storage and sample transportation errors can add up to create larger errors.

This table shows COD results for the same sample as analyzed by two different labs.

As seen in the table, the error can be much larger than 8% at times.

Sample	**LAB 1 COD mg/L**	**LAB 2 COD mg/L**	**% ERROR**
1	2890	3060	5.9
2	4390	4950	12.8
3	1880	2350	25.0
4	1834	2240	22.1
5	2420	2200	-9.1
6	1970	2800	42.1
7	745	693	-7.0
8	3670	3520	-4.1
9	3500	3430	-2.0
10	3780	3690	-2.4
11	3220	2980	-7.5

SPECTROPHOTOMETRY IN WATER ANALYSIS

Use of spectrophotometry for water analysis, and particularly for organics (BOD, COD and TOC) monitoring, holds significant real-time detection opportunities within the water treatment and manufacturing process environments.

This principle is also known as the ultraviolet and visible (UV-Vis) absorbance measurement and involves measuring light absorption at wavelengths that fall in the UV, visible and sometimes near infrared (NIR) regions of the light spectrum.

The relationship between absorbance at a given wavelength and the concentration of a compound dissolved in water is explained by the Beer-Lambert Law, which is:

Absorbance (A) = $a(\lambda) \times b \times c$

The Beer-Lambert Law states that:

- Every compound has a specific absorptivity at each wavelength (denoted by "a")
- The amount of light that gets absorbed by the compound ("A") is directly proportional to the concentration of that compound ("c") and the path length traveled by the light ("b" as shown in Figure B)

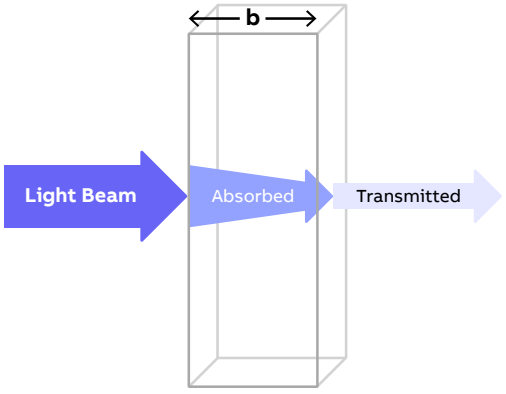

FIG. B. Absorbed and transmitted light over a water column of thickness b.

In practice, this means that if absorbance is measured using a fixed path length (so that the thickness of the sample column remains unchanged), the following rule applies:

> The higher the concentration, the higher the absorbance.

Changing the path length, on the other hand, provides versatility in terms of measurement range. Offered in path length ranges spanning from 0.5 mm to 250 mm, products in the ABB UviTec portfolio can be used both for ultrapure water applications and high strength industrial wastewater applications (Figure C).

All combined, this allows for fitting the device's range and sensitivity as much as possible to the customer's and the application's needs.

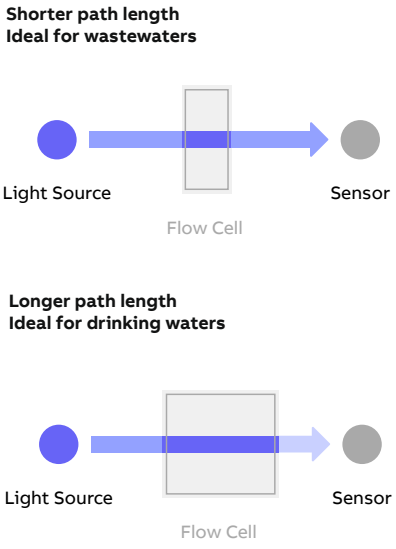

FIG. C. Path lengths ranging from 0.5 mm to 250 mm allow for use of this technology in a wide array of applications.

SPECTROPHOTOMETRY IN WATER ANALYSIS (CONT'D)

This simple principle of correlating the absorbance information to concentration can be applied to measure and monitor many parameters of high importance for water and wastewater treatment and management.

Organics show particularly strong potential for providing high value to water and wastewater operators, engineers and other stakeholders involved in the management of water. The primary reason for this is that traditional laboratory methods used for measuring organics (BOD and COD) are time and labor intensive, and have long turnaround times, which as noted earlier makes them of little or no value for process control and decision-making purposes.

As shown in Figure D, most organics absorb light strongly in the UV region of the spectrum (particularly 200 to 300 nm) while suspended solids (turbidity) typically absorb light across the entire UV-Vis spectrum. Some inorganic compounds like Nitrite (NO_2) and Nitrate (NO_3) absorb light in the deep UV regions of the spectrum (wavelengths shorter than 250 nm).

By measuring absorbance at different wavelengths across the UV and visible light spectra, it is possible to account for interferences while accurately measuring the concentration of organics and other parameters of interest. Accounting for interferences is a function of measuring absorbance at multiple wavelengths.

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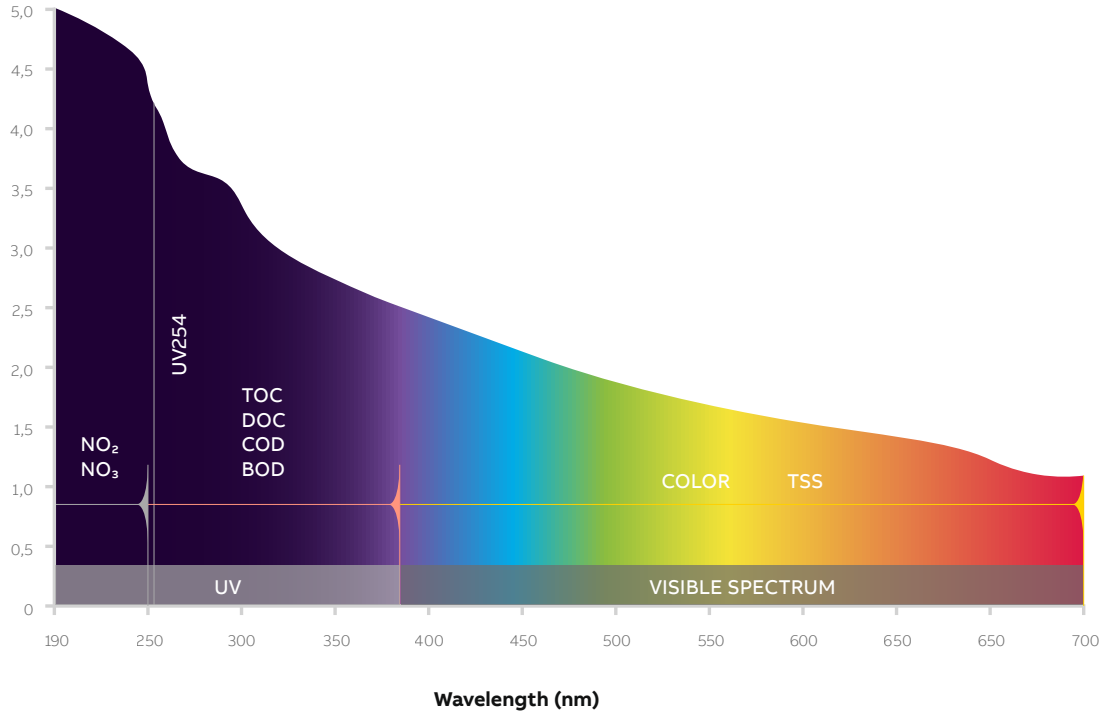
FIG. D. Regions of interest in the UV and visible light spectra for water quality parameters.



SOLUTIONS FOR IMPROVED PERFORMANCE

Fouling happens naturally and affects all real-time sensors. Even in drinking water applications mineral deposition can lead to significant fouling. Fouling must be addressed because even the best sensors will give unreliable readings if neglected.

The real-time products in ABB's UviTec portfolio are offered in two different form factors (bypass and probe) that allow for a versatile approach to cleaning accessories. For example, automatic chemical cleaning, which is very effective against mineral deposition, is used in bypass systems, while pressurized air or water is used for cleaning via physical agitation in probes. This ensures that maintenance requirements are kept at a minimum while reliability is maximized.

Additionally, when real-time monitoring is not needed, portable meters that allow for rapid measurement can be used. Figure E, depicts examples of these three form factors. Site specific calibration services further enhance accuracy when needed. This can be especially important in industrial applications where no two sites have the same water characteristics.

As opposed to relying solely on factory calibrations, ABB's UviTec products can be coupled with data services such as the Liquid Ai® platform. This allows for custom calibration of the instrument to site-specific samples collected after the installation of the unit, ensuring the complete calibration of the device for reliably consistent, long-term use.

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Having more data does not necessarily provide a clearer picture of the ongoing fluctuations in water quality. Just like a camera that has high resolution but is out of focus will not provide a clear image, a spectrophotometer that is not calibrated to site-specific conditions may not provide the most accurate BOD and COD data.

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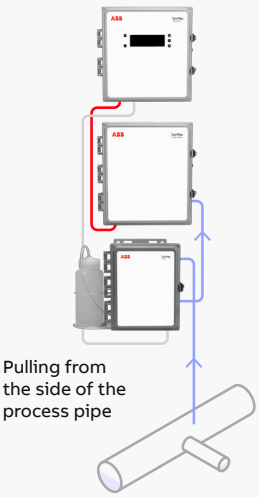
FIG. E. The UviTec technology comes in three different form factors.

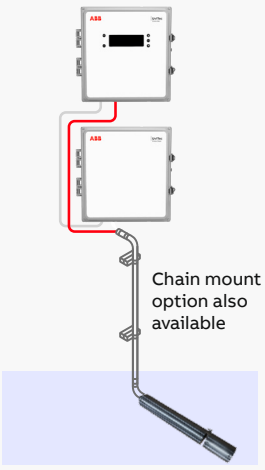
Left to right: rapid measurement portable field meters, real-time bypass configuration, real-time probe configuration.

Portable field meter for rapid measurement

Bypass sensor for real-time measurement



Probe sensor for real-time measurement



UVITEC REAL-LIFE APPLICATIONS, CHALLENGES AND OPPORTUNITIES

In real-world applications, samples contain thousands, even millions of compounds in a wastewater matrix, complicating the correlation between absorbance and concentration.

Imagine the differences between a dairy plant, where COD would be made of milk components, versus a pulp and paper plant, where it would be made of plant matter such as lignin and cellulose.

Even if the COD measurements are the same (e.g., 300 mg/L), it would be a completely distinct set of organics that make up that number and therefore the samples would absorb light differently – and be detected differently by UV-Vis sensors (Figure F).

This is why custom site-specific calibrations can make a significant difference when high accuracy is needed. Custom calibrations can also be employed to provide more insights into the composition of the organics. As explained earlier, tests like BOD and COD are blind to the composition of organics and only indicate the total concentration, while UV-Vis absorption can differentiate between the different groups of organics present and provide multidimensional information.

Real-time water quality monitoring has many advantages over laboratory methods of analysis. As more information on the process is obtained, events are revealed that would otherwise go unnoticed with grab sampling (Figure G, on next page).

IMAGE 01. Pulp and paper wastewater

IMAGE 02. Dairy wastewater

IMAGE 01

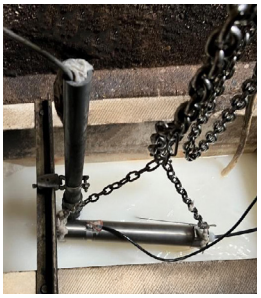
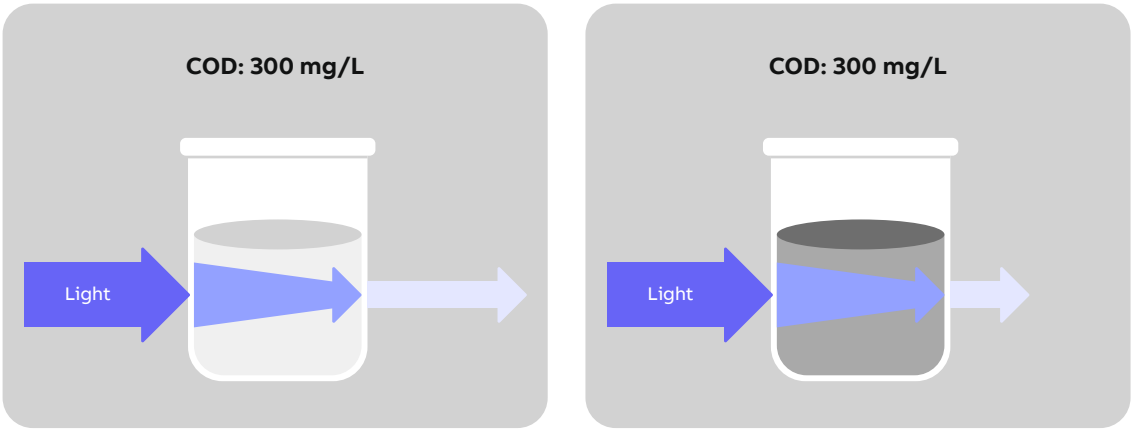


IMAGE 02

FIG. F. The light absorbance of samples with equal BOD and/or COD can be very different from one another depending on the composition of organics present.



UVITEC REAL-LIFE APPLICATIONS, CHALLENGES AND OPPORTUNITIES (CONT'D)

Another major advantage of using real-time UV-Vis spectrophotometers for water and wastewater applications is the simplicity of the method. The measurement process does not require sample preparation, nor does it require reagents or changing the sample composition in any way. For this reason, operation is straightforward, and maintaining the instrument is both easy and low-cost.

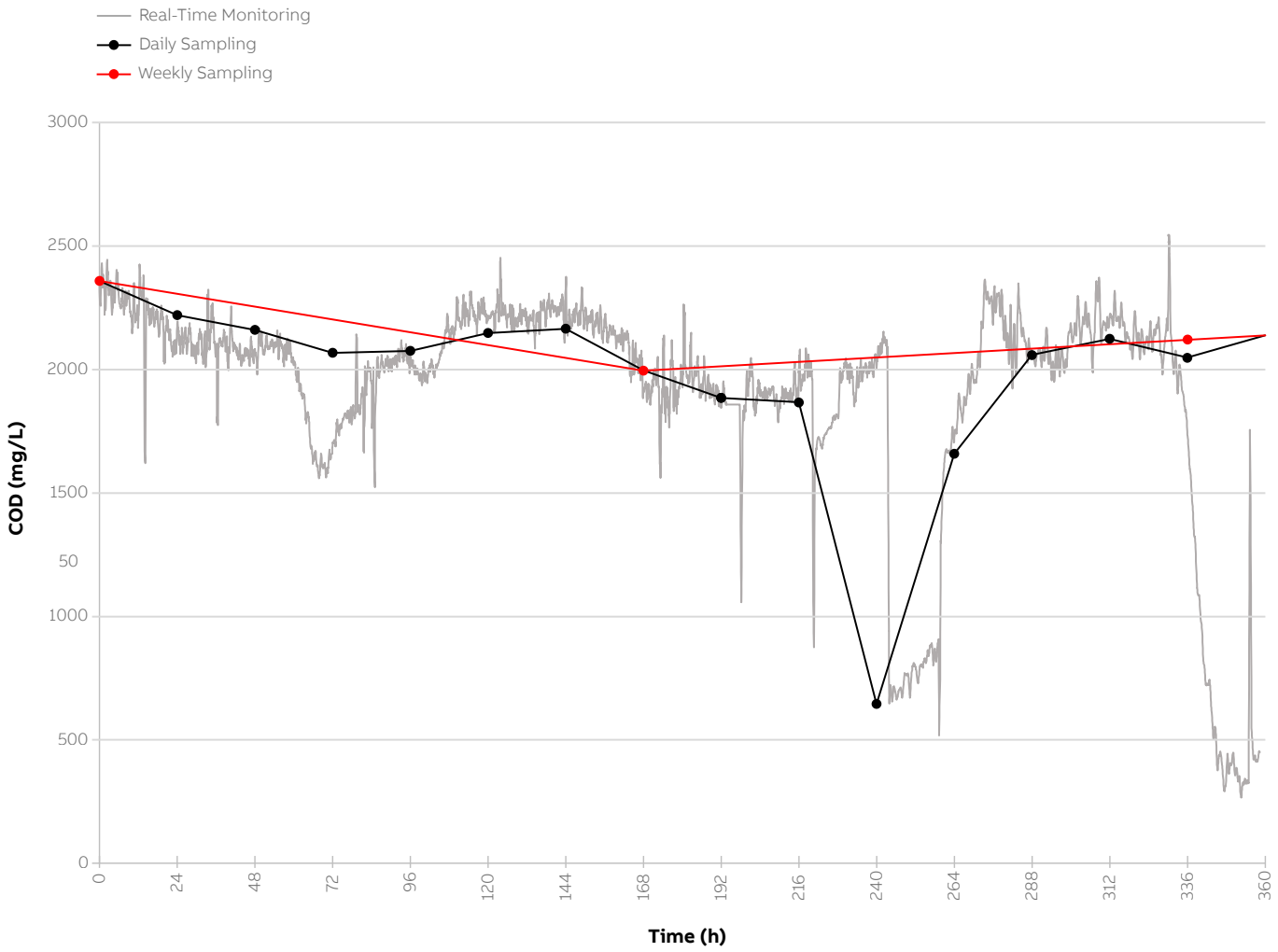


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FIG. G. Data collection frequency is very important for capturing temporal and spatial variations in water quality. As more data is gathered, events affecting the process become visible to the operators.

CONCLUSION

The UV-Vis measurement technique, as utilized in ABB's UviTec product family, provides an excellent opportunity for real-time BOD, COD and TOC monitoring which is essential for better treatment process control and water management.

The benefits of UV-Vis can be summarized in four major points:

1. **Event detection** – Real-time monitoring promptly detects spills, leaks and other water quality events, enabling quicker corrective actions. **You do not know what you do not measure.**

2. **Product loss monitoring** – UV-Vis technology provides information on the composition and quantity of organics, optimizing manufacturing processes.

3. **Process control and optimization** – Real-time data helps optimize water treatment, reducing operational costs and ensuring treatment goals are met.

4. **Compliance assurance** – UV-Vis technology aids in maintaining compliance through optimized treatment processes.

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Dr. Kerim Kollu has over 17 years of academic and industry experience in water and wastewater analysis. He advises customers on the best UV-Vis based solutions for their applications and works on continuous improvement programs for products, applications and data modeling.

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