2022-2023 pH Pilot Study

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This study was performed for the sole purpose of determining the best PH probes for Denver Water based on its treatment practices and source water. Nothing in this study is meant to indicate that the same or similar results can or will be obtained in other circumstances or environments. Results likely will vary depending on the treatment practices and source water of each water treatment site. References to particular products do not constitute testimonials or endorsements of such products, nor are they a guaranty, warranty or prediction of suitability of that product for a particular purpose.

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Executive Summary

Finished water pH requirements at Denver Water were increased in March of 2020 to maintain a pH range of 8.5-9.1 SU in the distribution system. Internal goals at the treatment facilities are 8.6-9.1 SU. pH probes from multiple vendors are currently installed across the system, revealing varying performance and maintenance requirements. This prompted a pilot study evaluating 11 inline pH probes at the Marston and Moffat Water Treatment Plants to identify the most suitable probes. pH probes were assessed on precision (i.e., relative standard deviation), accuracy, data points within the defined pH range, maintenance, and probe availability. While results between sites varied, the consensus top four probes following testing were the Electrochemical Device S80 (ECD), Mettler Toledo pHure ISM, Yokogawa FU24, and Rosemount 3900. The ECD probe consistently performed the best of all probes tested and has inventory available for procurement, making it a promising option for Marston and the South System. While it also scored the highest at Moffat (North System), further testing during load season and a better understanding of the water matrix (i.e., pH A3, alkalinity, mixing) is needed to confidently recommend a pH probe.

Introduction

Denver Water serves potable water to over 1.5 million customers in the city of Denver and surrounding suburbs. Nearly all the supply is surface water, originating as mountain snowmelt, across approximately 4,000 square miles of watershed. This collection system is split into the *North* and *South* Systems. The South System provides about 80% of Denver Water's supply and the North System provides 20%. There are two potable treatment facilities in the South System, Foothills Water Treatment Plant and Marston Water Treatment Plant. The North System currently operates one potable facility, Moffat Water Treatment, and has another, the Northwater Treatment Plant, under construction. Due to differences in the North and South areas of the collection system, the source water quality between the systems varies.

Despite differences in source water quality, the treatment facilities in the North and South systems have the same finished water quality targets. Historically, the pH target of the finished water was 7.8 SU, with a range of 7.5-8.5 SU. As of March 2020, Denver Water increased its finished water pH to maintain a required range between 8.5-9.1 SU in the distribution, with a target of 8.8X. The target pH of 8.8X denotes treatment teams targeted finished pH levels to the hundredths place of precision. The treatment plants pH regulatory requirement is even tighter at 8.6-9.0. The increased pH target is part of Denver Water's Lead Reduction Program (LRP), approved by the Environmental Protection Agency (EPA) and Colorado Department of Public Health and Environment (CDPHE) in December 2019. The higher pH passivates lead service lines and creates a protective coating on the inside of the pipe that reduces the lead that leaches from customer-owned water service lines, faucets, or solder into the drinking water. Denver Water is dedicated to maintaining this tight pH range with rare excursion in the finished water at treatment facilities and throughout the distribution system. Reliable, accurate, and precise measurement of pH in the North and South System facilities is paramount and highlights the need to assess our instrumentation.

As a result of the tight pH control since March 2020, Denver Water's 90th percentile lead levels have dropped 72%, as seen in the Figure below.

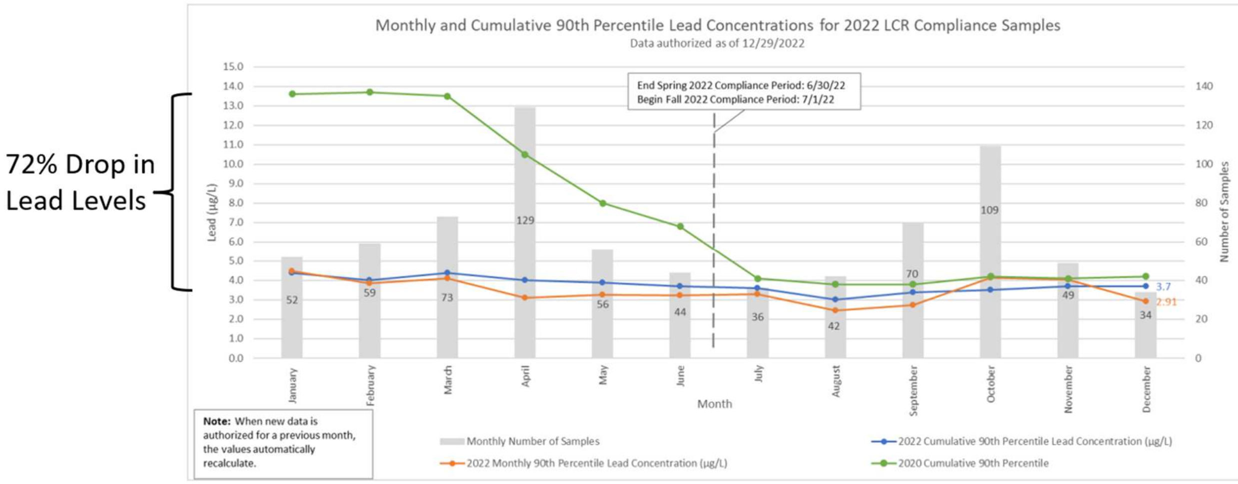


Figure 1. 90th Percentile lead levels in 2020, 2021, and 2022.

The current inventory of inline pH probes installed in the treatment plants and distribution system is from multiple vendors. There are several performance and maintenance issues among the probes that cause variable performance in pH measurement. The probes have unspecified drift, precision/accuracy, and maintenance frequency, affecting data integrity and defensibility. Vendors also have different criteria to determine if a pH probe is operating within specification. The lack of standardization across probes adds complexity to training staff and maintaining, troubleshooting, and replacing instruments. Due to site specific variables (e.g., water quality, installation location, personnel) and stringent pH requirements at Denver Water, a comprehensive study evaluating available probes is needed.

This study evaluates inline pH probes and related accessories such as controllers, communication equipment, and maintenance supplies from different manufacturers to identify the most suitable instruments for use by Denver Water's process control teams (e.g., O&M Division, Water Quality and Treatment, and Water Distribution). The goals are to:

- Identify pH probes that have the least amount of inherent measurement "drift";
- Identify pH probes that are capable of precise and accurate measurements at the required pH;
- Identify pH probes that require the least amount of planned and unplanned maintenance.

Materials & Methods

Probe Selection

A pilot study was conducted to evaluate multiple inline pH probes and related accessories across Denver Water treatment facilities in the North and South Systems. Vendors were contacted to request participation in the study and commitment by donating equipment. The intent was to have multiple vendor options, limiting single source scenarios (e.g., supply-chain disruptions), and evaluate other promising technologies on the market. The 11 probes selected for this study are summarized in Table 1. The "maintain/ replace" category refers to whether the probe is maintainable, through salt bridge or electrolyte replacements, or if it must be replaced. Only the specifications or maintenance information provided in the probe manual is summarized.

Table 1. Summary of pH probe specifications and features, as described in each associated probe manual.

Probe	Manufacturer (abbrev.)	Maintain/ Replace	Technology	Operating Specs.	Recommended Maintenance	Maint. Cost [1]
100GP-D ¾" pH/ORP electrode (EZlink Digital)	ABB	Replace	Digital, smart probe	pH 0 to 14 Temp –5 to 60 C Pressure 0 to 90 psi	Cleaning	$850
Q25P	ATI	Maintain	Replaceable salt bridge	0 to 14.00 pH Sensitivity 0.01 pH Temp -5 to +95 °C Pressure 0 to 100 psi	Cleaning, salt bridge	340
pH2 Sensor	Chemtrac	Replace	-	pH 0 to 14	Maintenance-free	204
S80 Electrode pH gen purpose Radel two tine w/viton o-ring	Electro-chemical devices (ECD)	Maintain	Gel filled, replaceable electrode cartridge	pH 0 to 14 Temp 0 to 90 C Pressure 0 to 100 psi	Cleaning, replace electrode cartridge	136
Memosens CPS31E	Endress+ Hauser (EH)	Replace	Smart probe, digital, inductive connection	pH 1 to 13 Temp –15 to 80 C Pressure 11.6 to 58 psi	Cleaning	204
DPD1P1	Hach	Maintain	Smart probe, replaceable salt bridge	pH -2 to 14 Temp -5 to 70 C Pressure 0 to 100 psi	Cleaning, electrolyte, salt bridge replacement	340
SE555 Memosens pH	M4 Knick (Knick)	Replace	Smart probe, digital, inductive connection	pH 1 to 14 Temp 0 to 140 C Pressure 0 to 180 psi	Cleaning	272
pH Sensor Pure Water pHure ISM / 120 mm	Mettler Toledo (Mtoldeo)	Replace	Smart probe, gel, advanced diag	pH 1 to 11 Temp 0 to 80C Pressure 0 to 101 psi	Cleaning	136
3900	Rosemount	Replace	Smart probe	pH 0 to 14 Temp -10 to 100C 100 psi	Routine cleaning	136
pH::lyser	S::Can	Maintain	Unique, combined, non-porous reference electrode (no salt bridge)	pH 2 to 12 Temp 0 to 70C Pressure 0 to 145 psi	Maintenance-free	374
FU24 Universal pH/ORP sensor	Yokogawa	Replace	Smart probe	pH 0 to 14 Temp -10 to 105 C Pressure 0 to 145 psi	Routine cleaning	204
DPD1P1	Hach (Plant[2])	Maintain	Smart probe, replaceable salt bridge	pH -2 to 14 Temp -5 to 70 C Pressure 0 to 100 psi	Cleaning, electrolyte, salt bridge replacement	-
IntelliCal PHC281	Hach (Bench[3])	Maintain	-	-	-	-

[1] Description of how maintenance costs were calculated during the pilot is described in the Methods section. [2] Plant pH probe is used for online monitoring in the treatment plants. [3] Serves as the baseline probe throughout this study for comparison to the 11 test probes.

The Hach benchtop probe (IntelliCal PHC281) served as the baseline comparison probe in this study for grab samples as it is used regularly by treatment operations and lab personnel at Denver Water and has demonstrated quick response time, accurate and reliable measurements.

Pilot Description

The pH pilot skid consists of a PVC panel with pH probes and controllers mounted in-line, downstream of the finished water sample supply. Flow meters for each instrument are mounted below the PVC panel for control of flow to each individual pH probe. A photo of the pH pilot skid is presented in Figure 2.

Figure 2. Photo of the pH skid used throughout the duration of the study.

Site Water Quality

The pH pilot was deployed in the South System at Marston Water Treatment Facility from 3/30/22 to 11/2/22. Following Marston deployment, the skid was relocated to the North System at Moffat Water Treatment Facility for continued testing from 11/9/22 to 2/28/23. The study included testing at both sites to evaluate the impacts of water quality on pH probe performance. Water quality varies significantly between the North and South Systems; bulk water quality parameters are summarized in Table 2.

Table 2. Summary of average finished water quality parameters at Marston and Moffat Treatment Plants during the study. Parameters are reported as: average (standard deviation).

Site	Duration	TOC (mg/L)	Conductivity (µS/cm)	Alkalinity (mg/L)	Turbidity (NTU)	Temp (°C)
Marston	03/2022 – 11/2022	1.83 (0.24)	341 (21)	70.7 (8.3)	0.03 (0.01)	13.3 (5.1)
Moffat	11/2022 – 02/2023	1.43 (0.08)	150 (11)	46.3 (0.6)	0.03 (0.00)	8.2 (3.2)

Grab Samples

Grab samples served as the baseline comparison and were collected every four hours beginning at 0300 and ending at 2300 for every day of this study. Grab samples were collected from specified taps in beakers that were triple rinsed with deionized water (DI) and dried with a lint free napkin. The grab sample pH value and the plant online pH probe value was then recorded on the data sheets located near the study panel. The bench probe, located next to the panel, was calibrated once per 12-hr shift using the specified buffer packets that were cooled with sample water from the tap. Sample data was entered into the laboratory information management system (LIMS) for later acquisition. Treatment operators at Marston and Moffat Water Treatment Plants were provided the same guidelines and instructions on collecting grab samples. Members of the core study team did frequent spot checks to ensure the outlined standards were followed. SOPs provided to plant staff are located in the Appendix.

Probe Maintenance

Planned Maintenance

A hybrid planned maintenance schedule was followed, ensuring that manufacturer guidance and Denver Water standards were met. Some probes had different required maintenance needs than others. For example, Hach, ATI, and ECD contain a refillable/replaceable salt bridge that other probes do not. Manufacturer recommendations were followed with the exception of quarterly calibrations per Denver Water standards; this exceeds manufacturer recommendations.

Calibrations varied by analyzer programming, with some analyzers requiring pH 4 and 10 buffers and others requiring pH 4 pH and 7. The same calibration process was used regardless of buffer pH. Individual Hach buffer packets were used for a single calibration and then were disposed of. Buffer packets were cooled to the sample temperature by storing them in a stream of process water that was split off the sample tap feeding the analyzers. This ensured that the buffers were the same temperature as the sample water, reducing impacts of temperature variation on pH measurement.

Unplanned Maintenance

If a probe read out of specification, displaying an error or failure, manufacturer guidance was followed to troubleshoot it. If troubleshooting was unsuccessful, the vendor/ manufacturer was called for corrective action. Response time to identify issues and conduct trouble shooting was performed within 48 hours. A fix only exceeded 48 hours if there was a delay for parts and materials.

Data Collection

Data was logged by SCADA at various frequencies. The online plant pH probe (validation) logged data every 5 minutes and the 11 pilot probes logged data every 15 minutes. For consistency, only pH data on 15-minute intervals was collected from SCADA for analysis. Temperature data was also monitored and recorded to ensure no drift occurred but is not presented in this report.

Grab samples were invalidated by comparing the online analyzer and grab sample measurements. If the difference between the two readings was greater than 0.20 SU or less than -0.20 SU, the grab sample was considered invalid and removed from the data set. Since grab samples were collected every four hours, SCADA data were invalidated ±2 hours on either side of the grab sample. The data were also reviewed for operator error. All reported SCADA data are raw, with the exception that pH values were rounded to two decimals. The data was intentionally not manipulated beyond the broad invalidations described above.

The graphs presented in the following sections also have grab samples that were averaged using a 250-point moving average to show overall trends.

Data Analysis

Corresponding to the goals of this study, probes were evaluated on multiple parameters, including the precision (relative standard deviation, RSD), percent of data points within the required pH range, accuracy, maintenance cost, and probe availability. The overall performance of each probe was scored using three criteria: precision (RSD), percent of data within limits, and accuracy. Each factor was calculated as follows:

Maintenance Cost

- The total maintenance cost of each probe throughout the duration of the study was calculated by multiplying time spent on maintenance, troubleshooting, and calibrations by $68.00 per hour. It should be noted that this is the total cost during pilot testing and results reported are not separate for Marston and Moffat Treatment Plants. The study required approximately 1500 hours of human labor to complete.

Precision

Precision was evaluated by calculating the relative standard deviation (RSD) from the benchtop probe average. This shows the spread of the data and how precise they are compared to the average. A lower RSD indicates the data within the set are not very dispersed, and thus more precise. The calculation used in this study is:

=STDEV.P(Population)/Average(Population)*100

Percent Within Limits

Percent within limits calculates the percentage of points that were within the specified pH limits. Denver Water's required pH range in the distribution system is 8.5-9.1, so these limits were used. The calculation listed below counts the total sum of data points within 8.5 and 9.1:

=SUMPRODUCT((Population>=8.5)*(Population<=9.1))

This number was then converted to a percentage with the following calculation:

=Total points within limits/Total points*100

Accuracy

This formula calculates the total number of points the vendor's probe was within ±0.1 SU relative to the benchtop probe. This criterion indicates how close the data within a set are to their true value, in this case the benchtop probe. The calculation used in this study follows:

=SUMPRODUCT((Vendors Population>(Benchtop Population+0.1))+(Vendors Population <(Benchtop Population -0.1)))

Example with actual values plugged in:

SUMPRODUCT((8.76>8.87)+(8.76<8.67))

SUMPRODUCT((False)+(False))

SUMPRODUCT(0)

From here, the total number of times the vendor's probe was within ±0.1 SU of the benchtop probe was calculated:

=COUNTIF(Vendors Population),"0")

Lastly, this value was converted to a percentage, giving the percent of data points the probe was within 0.1 SU of the benchtop probe:

=Total Points within 0.1 pH/Total Points*100

Overall Scores

The overall score of each probe was calculated by multiplying the criteria described above by its weight and summing the three criteria. The RSD was normalized to the maximum RSD at the test site (i.e., lowest performing probe) to have the same scale (0-100%) as the percent within limits and accuracy criteria. The percent of data within limits and the accuracy were both weighted by a multiplier of three as they are high priority relative to the tight pH range and performance that is desired of a probe in the North and South Systems. If data falls outside of the limits, it triggers maintenance at Denver Water. Accuracy is calculated relative to the benchtop probe, which is routinely calibrated, serving as a strong indicator for performance. In comparison, precision (RSD) is weighted by a multiplier of two as it is possible to maintain a small spread along a single data point (e.g., having an RSD < 1% with < 70% accuracy). This can be misleading when determining the performance of an instrument. In this study, scores are reported separately for Moffat and Marston to better evaluate data with different water quality matrices, and are also reported combined.

Results

Marston Water Treatment Plant

The first phase of the study was conducted in the South System at the Marston Water Treatment Plant. Data from the 11 probes was continuously logged on SCADA, similar to the online plant pH probe. Grab sample data from the benchtop probe was recorded every four hours. The pH probes were rated on the following criteria:

- Precision, RSD from the benchtop probe;
- Percent of data within the pH 8.5-9.1 limit;
- Accuracy, data within ± 0.1 SU of the benchtop pH probe.

Probe availability and maintenance cost are not factors in the calculated score but were considered in the overall evaluation of the probe and discussion of future procurement.

Maintenance as a function of performance and time (i.e., cost) are reflected in the raw pH data for each probe and the maintenance cost. Data was intentionally left raw and was only invalidated when grab samples were outside acceptable limits. Therefore, if a probe required additional maintenance, it is reflected in the data via downtime or an abrupt shift in measured pH following a calibration or installation of a replacement part or probe. As expected, the top probes in the study at both treatment sites required minimal maintenance, resulting in more consistent pH trends and lower maintenance costs.

Table 3 summarizes the evaluation criteria for all probes tested at the Marston Water Treatment Plant, including the RSD, percent of data within the pH 8.5-9.1 limit, and accuracy (± 0.1 SU of the benchtop probe). As discussed in the Materials and Methods section, the data reported in this table is calculated from the raw pH measurements of all probes. Conditional formatting was applied to the table, where green is best and red is poor. Based on the three criteria, the ECD pH probe was noticeably the best, followed by Mtoledo, Rosemount, and Yokogawa. Results showing pH as a function of time for the top four performing probes at Marston are presented in Figures 3-6. Data from the remaining seven pH probes is located in the Appendix.

Table 3. Summary of evaluation criteria for pH probes at Marston Water Treatment Plant. Green denotes a high, favorable, score while red is a low score.

Score	pH Probe	RSD %	Average	Data Points	% within Limits	Accuracy	Maint. Cost
786	ECD	0.65	8.80	20322	99.95	97.21	$136
757	Mtoledo	0.94	8.81	20322	99.97	88.21	$136
748	Rosemount	0.86	8.80	20322	99.95	84.93	$136
744	Yokogawa	1.51	8.77	20322	99.92	85.16	$204
702	Hach	0.86	8.72	20322	99.92	69.59	$340
653	Knick	1.08	8.71	20284	99.92	53.97	$272
648	Chemtrac	1.34	8.70	20322	99.85	53.03	$204
585	S:Can	3.44	8.77	20322	89.41	47.74	$374
553	ABB	20.80	9.18	20322	92.52	78.69	$850
461	EH	25.95	9.60	20322	89.24	64.32	$204
442	ATI	1.29	8.57	20322	73.69	10.42	$340
	Plant pH Probe	24.20	8.79	20827	99.92	-	-

In Figure 3, the ECD probe maintained a narrow bandwidth with limited deviation from the Marston benchtop probe and the plant pH probe. Compared to the baseline Marston benchtop probe, the ECD probe had an RSD of only 0.65% and was within the target pH limit 99.95% of the time. It was also 97.21% accurate (Table 3; ± 0.1 SU of the benchtop probe). The ECD probe did not require any additional maintenance beyond the quarterly calibrations that were performed on every probe. The data spikes observed in the ECD and plant pH probe in Figure 3 are associated with quarterly calibrations and power outages at the treatment plant. Maintenance logs, including dates, are provided in the Appendix.

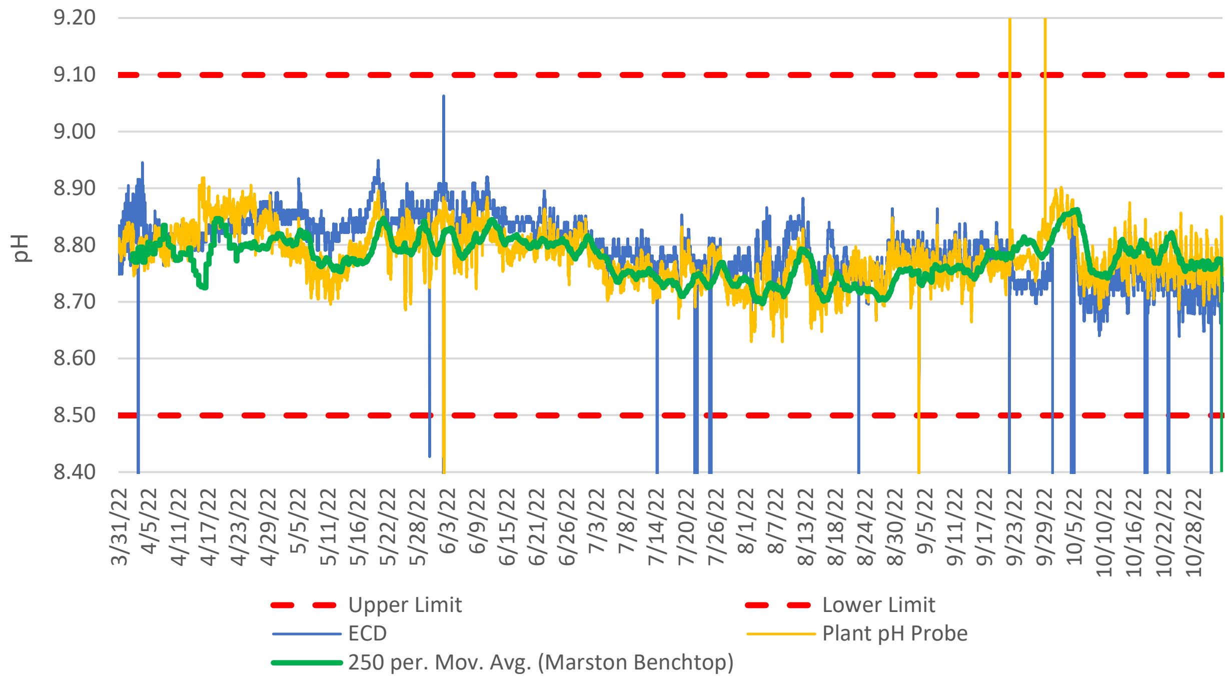


Figure 3. Marston ECD data as a function of time.

Figure 4 shows Mtoledo pH measurement at Marston as a function of time. This probe noticeably deviated from the Marston benchtop pH probe more than ECD but improved in late August following calibration. As reported in Table 3, the Mtoledo probe had a calculated RSD of 0.94%, was 99.97% within limits, and 88.21% accurate. No maintenance beyond the planned quarterly calibrations was required.

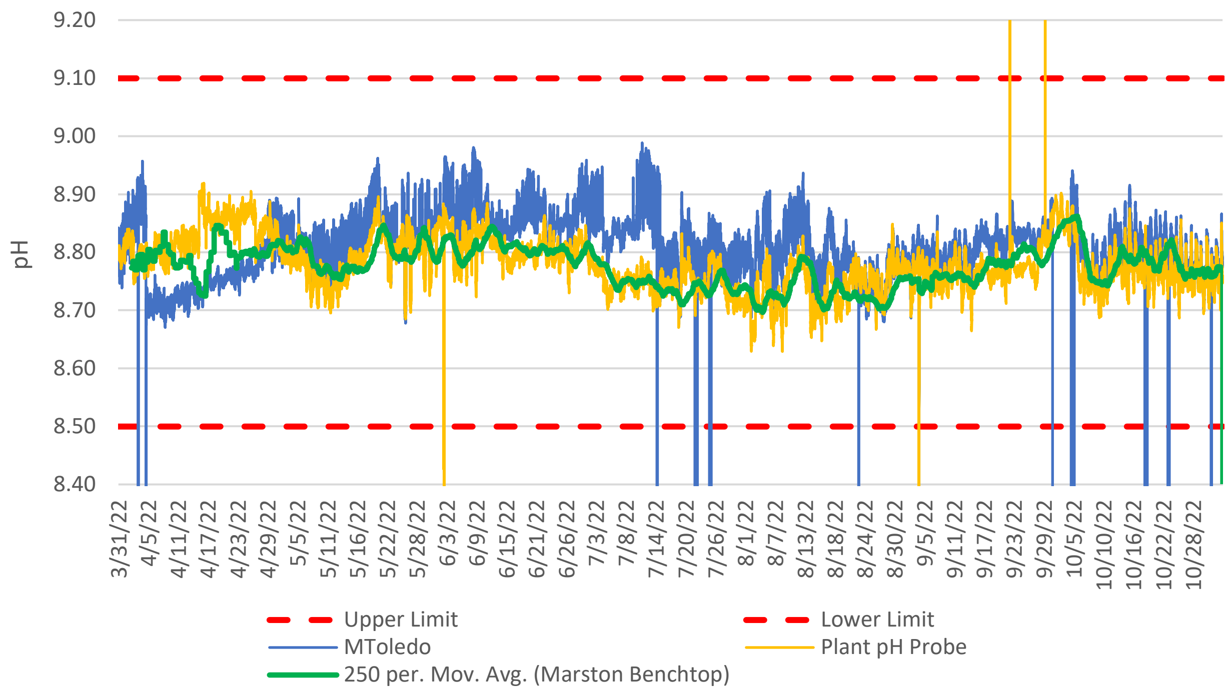


Figure 4. Marston Mtoledo data as a function of time.

The Rosemount pH probe, presented in Figure 5 and Table 3 also performed very well at Marston. The probe tracked with the Marston benchtop probe for the majority of the test period until the last month. The RSD from the benchtop probe was 0.86%, 99.95% of data was within limits, and it was 84.93% accurate. No maintenance beyond the planned quarterly calibrations was performed.

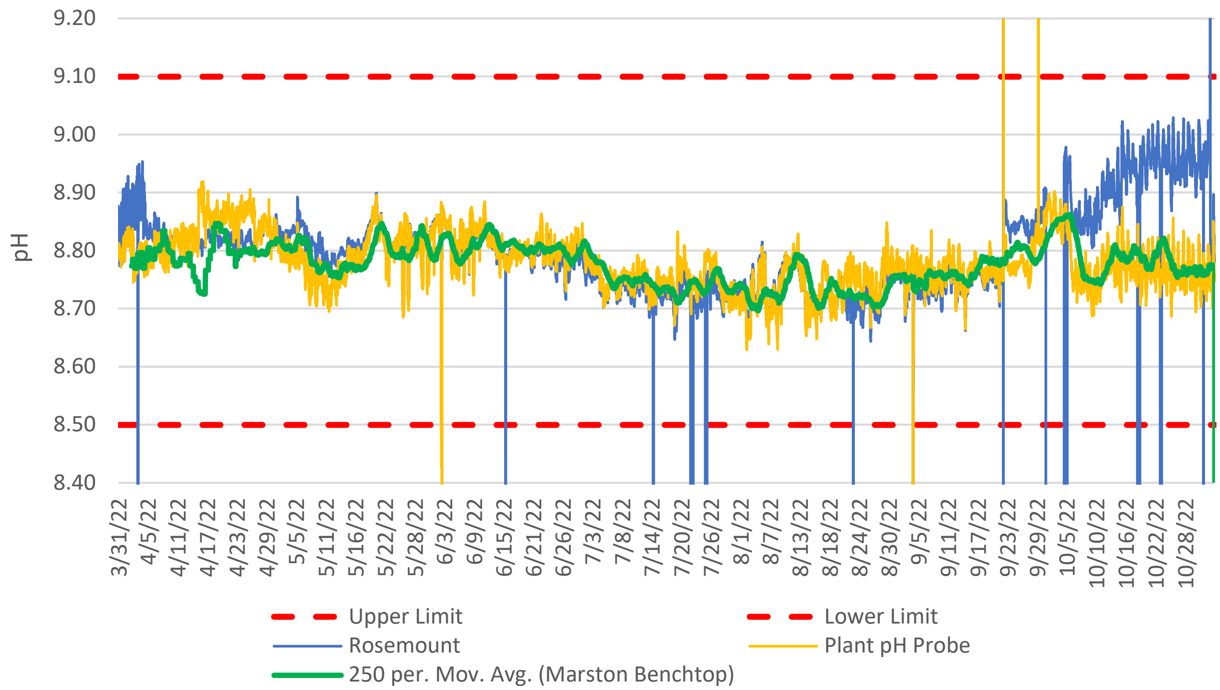


Figure 5. Marston Rosemount data as a function of time.

Figure 6 presents the Yokogawa pH measurements at Marston as a function of time. This probe performed similarly to the Rosemount, but with notable deviation from the benchtop probe occurring at the beginning of the study. The Yokogawa probe improved after a sales representative came onsite May 4 to correct transmitter issues and the probe was recalibrated. It had an RSD of 1.51%, was within limits on 99.92% of data points, and was 85.16% accurate. Besides the initial unplanned maintenance on May 4, no other unplanned maintenance was required.

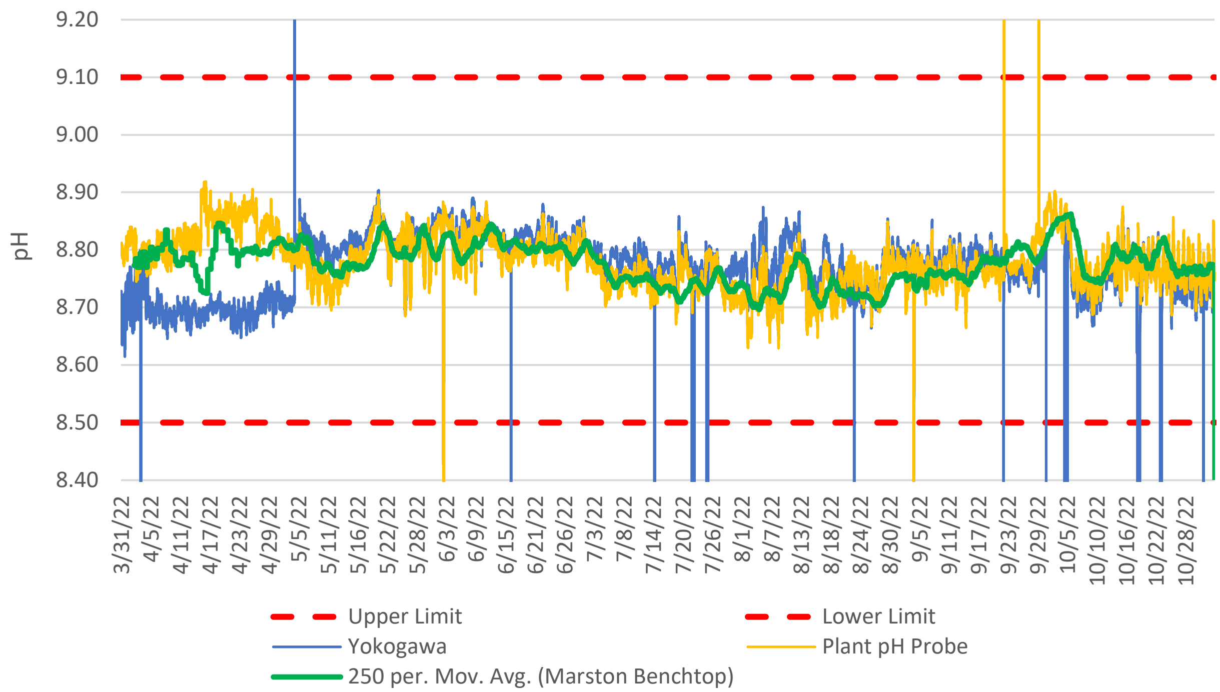


Figure 6. Marston Yokogawa data as a function of time.

Moffat Water Treatment Plant

Following testing at Marston Water Treatment Plant, the pH pilot skid was relocated to the North System at the Moffat Water Treatment Plant. Testing was conducted for approximately three months, compared to the seven month duration at Marston. While there are distinct differences in water quality between the North and South Systems, as summarized in Table 2, this study did not directly assess the impacts of individual water quality parameters on pH probe performance. Grab samples from the benchtop probe, for baseline comparison, were collected at the same four-hour interval as Marston, and quarterly maintenance also continued.

Table 4 summarizes the evaluation criteria for all probes tested at the Moffat Water Treatment Plant, including the RSD, percent of data within the pH 8.5-9.1 limit, and accuracy (± 0.1 SU of the benchtop probe). In general, the probes at Moffat demonstrated a higher RSD (unfavorable), fewer data points within limits, and lower accuracy compared to Marston. There was also a noticeably wider spread in performance between the best (ECD) and worst (ATI) performing probes. Due to such frequent pH swings in all probes, it is difficult to distinguish the top performing probes. Nonetheless, based on the three criteria, the ECD pH probe scored the highest, with minimal difference observed between the S:Can, Yokogawa, Chemtrac, EH, and Mtoledo probes.

Table 4. Summary of evaluation criteria for pH probes at Moffat Water Treatment Plant. Green denotes a high, favorable, score while red is a low score.

Rank	pH Probe	RSD %	Average	Data Points	% within Limits	Accuracy	Maint. Cost
714	ECD	1.50	8.83	9795	98.41	74.59	$136
676	S:Can	1.91	8.82	9795	94.12	66.77	$374
674	Yokogawa	1.57	8.84	9802	98.57	61.37	$204
670	Chemtrac	1.88	8.76	9795	91.48	67.35	$204
665	EH	1.38	8.85	9795	98.45	58.06	$204
650	Mtoledo	1.76	8.86	9795	95.29	56.61	$136
603	Knick	1.89	8.87	9795	94.52	41.99	$272
515	Hach	5.58	8.48	9795	76.68	34.61	$340
511	Rosemount	1.80	8.95	9795	93.03	12.57	$136
245	ATI	1.68	8.37	9795	16.78	0.04	$340
220	ABB	58.35	6.32	9795	62.58	10.72	$850
	Plant pH Probe	2.84	8.77	9802	98.37	-	-

Results showing pH as a function of time for the top four performing probes at Moffat are presented in Figures 7-10. Data from the remaining pH probes is located in the Appendix. Overall, probes tested at Moffat exhibited frequent swings in pH with high amplitude. Similar trends were observed with the grab samples. This was a notable difference between sites that requires further investigation to understand.

In Figure 7, the pH measurements of the ECD probe fluctuate widely, with several deviations outside the defined limits. It tracked higher than the Moffat benchtop and plant pH probes, with an RSD of 1.50%, 98.41% of data within the pH range, and 74.59% accuracy. No unplanned maintenance was performed.

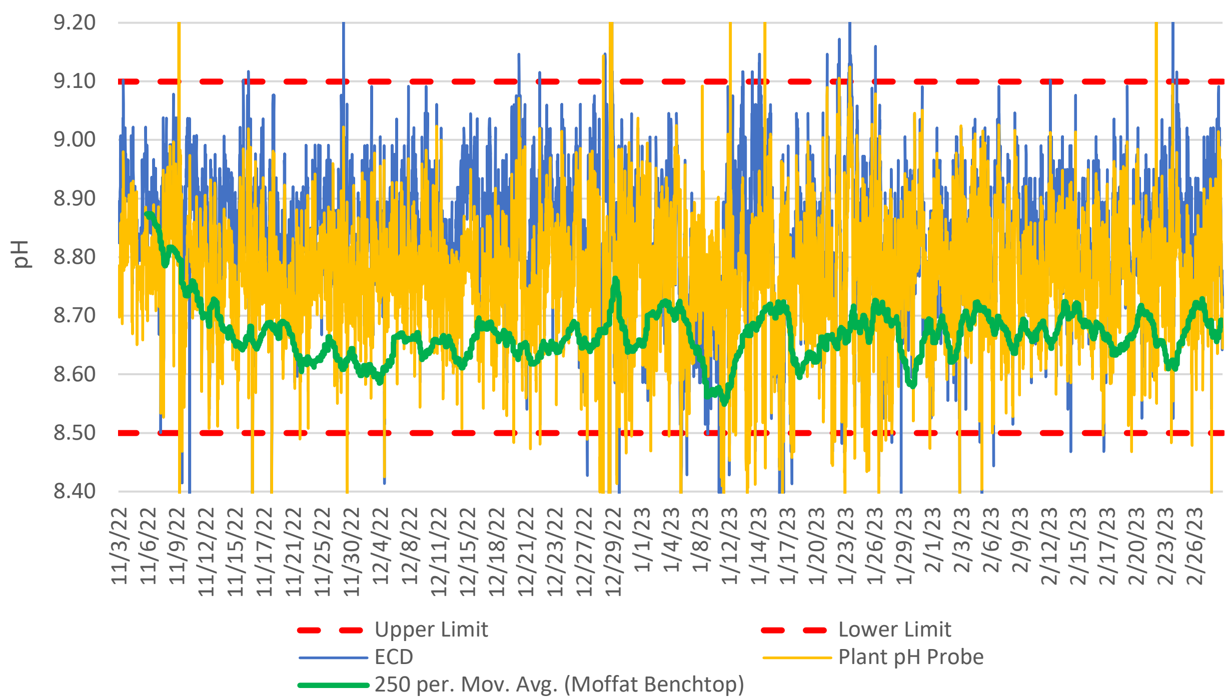


Figure 7. Moffat ECD data as a function of time.

pH measurement data from the S:Can probe at Moffat is presented in Figure 8. It deviated substantially from the benchtop and plant pH probes the first month, then tracked closer to the plant pH probe after a calibration. The RSD was 1.91%; 94.12% of points were within the pH limits, and accuracy was 66.77%.

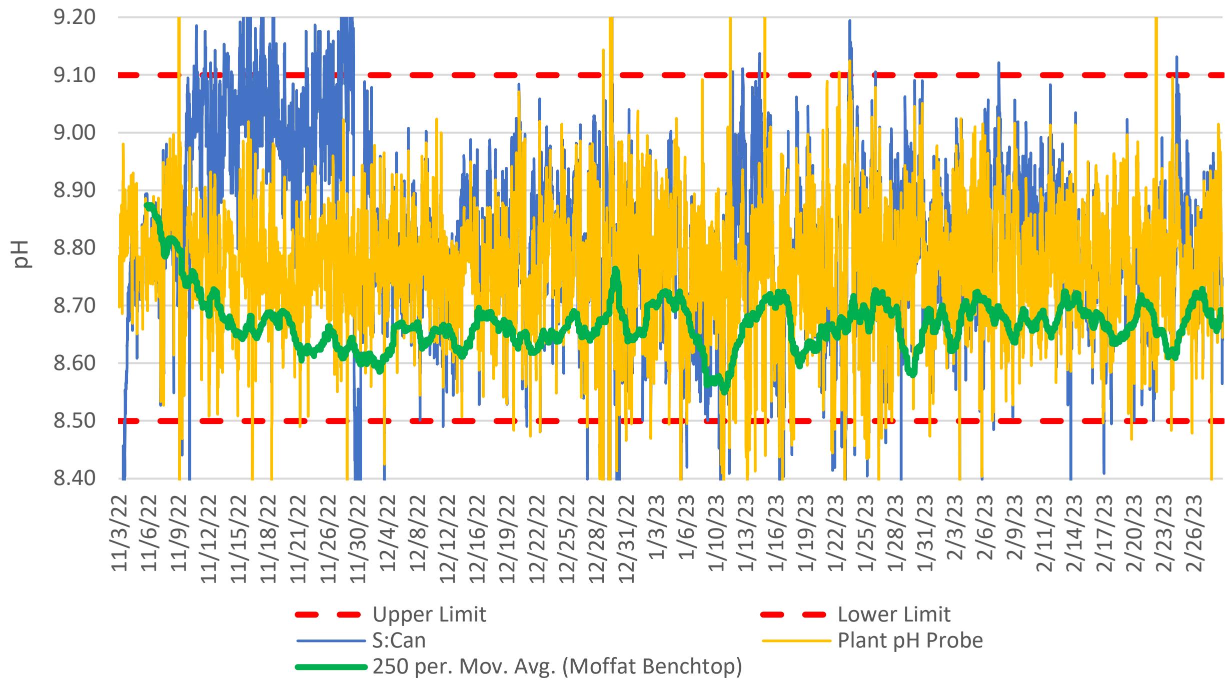


Figure 8. Moffat S:Can data as a function of time.

Figure 9 presents pH measurement as a function of time for the Yokogawa probe at Moffat. The Yokogawa pH probe tracked similar to the ECD probe, but with a slightly lower accuracy of 61.37%.

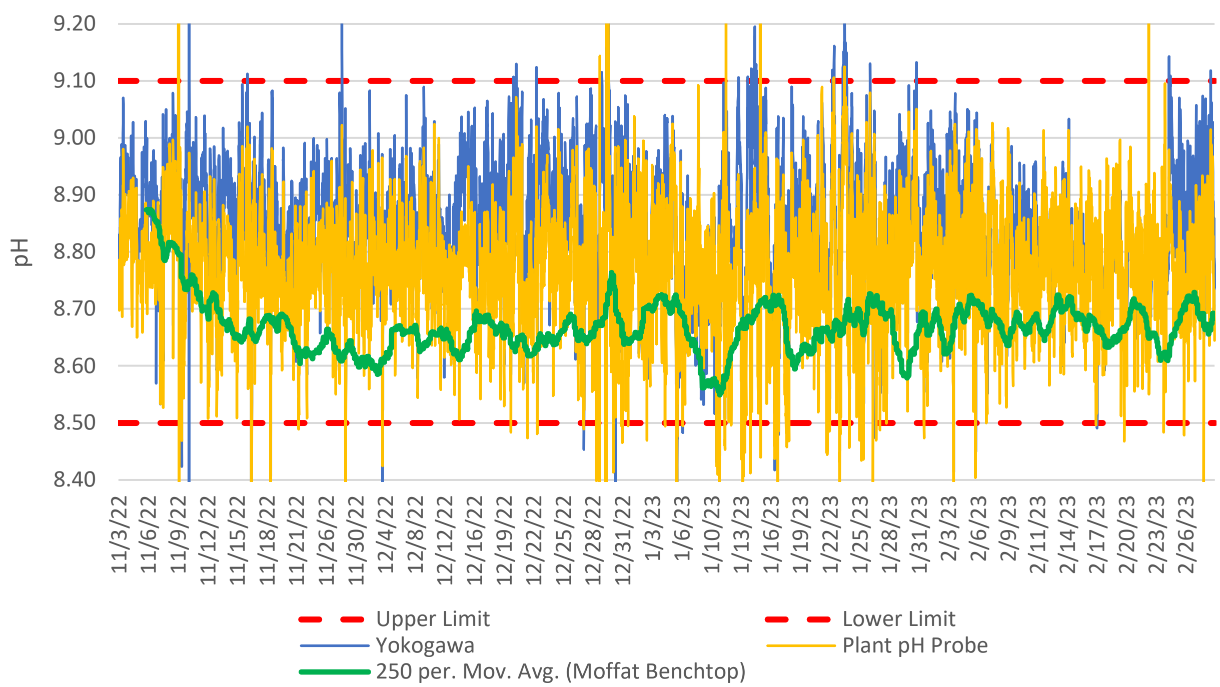


Figure 9. Moffat Yokogawa data as a function of time.

Figure 10 presents the Chemtrac data. It tracks fairly well with the plant pH probe but still exhibits the continuous swings of high amplitude. It had an RSD of 1.88%, 91.48% of data points were within the target pH range, and it was 67.35% accurate.

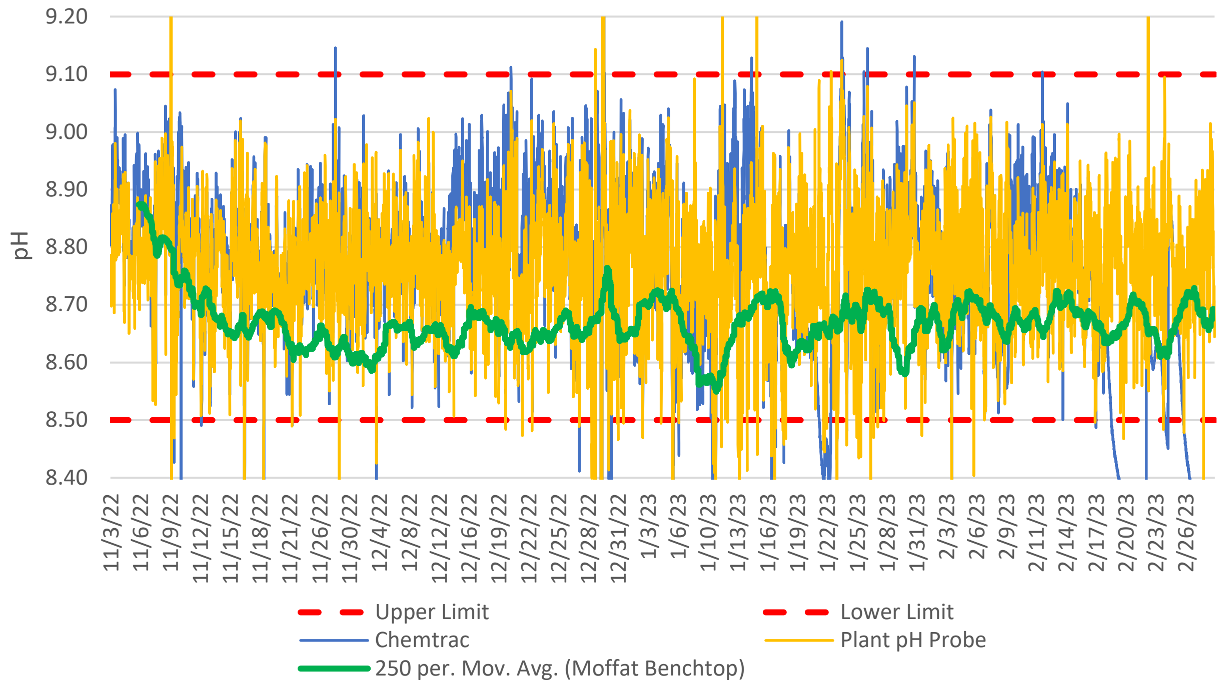


Figure 10. Moffat Chemtrac data as a function of time.

Combined Ratings

The evaluation criteria for all 11 probes tested at Marston and Moffat is combined and summarized Table 5. The ECD probe performed the best at both plants and is reflected clearly as the top with the combined data. Mtoledo and Yokogawa scored the same in the combined data, followed by Rosemount.

Table 5. Combined summary of evaluation criteria for pH probes at Marston and Moffat Water Treatment Plants. Green denotes a high, favorable, score while red is a low score.

Rank	pH Probe	RSD %	Average	Data Points	% within Limits	Accuracy	Maint. Cost
763	ECD	1.03	8.81	30117	99.45	89.97	$136
723	Mtoledo	1.29	8.82	30117	98.45	78.10	$136
723	Yokogawa	1.58	8.79	30124	99.48	77.54	$204
671	Rosemount	1.47	8.85	30117	97.70	61.77	$136
656	Chemtrac	1.57	8.72	30117	97.13	57.62	$204
637	Knick	1.63	8.76	30079	98.16	50.14	$272
635	Hach	3.49	8.64	30117	92.36	58.40	$340
619	S:Can	3.04	8.79	30117	90.94	53.83	$374
556	EH	21.72	9.36	30117	92.23	62.31	$204
419	ABB	40.35	8.25	30117	82.78	56.94	$850
378	ATI	1.79	8.51	30117	55.18	7.10	$340
	Plant pH Probe	20.04	8.79	30629	99.42	-	

Conclusion

In this study, the ECD pH probe demonstrated the best performance out of the 11 probes tested at the Marston and Moffat Water Treatment Plants. After ECD, several probes performed similarly but cannot necessarily be distinguished from each other, including the Mtoledo, Yokogawa, and Rosemount probes.

There was an obvious difference in pH measurement between the Marston and Moffat sites; however, it is not clear what caused such variation. Potential impacts could include water quality or other seasonal variations. The study was conducted exclusively during winter at Moffat, versus spring/ summer/ fall at Marston. The conductivity, alkalinity, and temperature of the water at Moffat were all lower than at Marston, likely contributing to water stability challenges. Another impact could be the plant flow rate at Moffat. There are perceived challenges with chemical mixing in the disinfection contact basin (DCB) at lower flow rates. During this study, Moffat was operated at 20 MGD, rather than 80 MGD during load season. The dosing application point of sodium hydroxide (i.e., caustic) changes depending on the plant flow. The pH of finished water at Moffat also tends to be slightly higher in the distribution than in the DCB, suggesting potential water quality stability challenges that are currently under review. The drastic swings observed in every pH probe at Moffat implies that pH instrumentation is not the problem.

While the data collected from Marston is conclusive, with clear distinctions in performance between pH probes, more work is needed in the North System to identify the most appropriate probe. Next steps include continued pH pilot testing into the summer load season (80 MGD) at Moffat and revisiting the *Moffat pH A3* that was conducted in 2021.

With the top pH probes identified for Marston, the next steps in the South System and Distribution include confirming instrument availability for procurement. An implementation plan to begin replacement of known trouble probes and compliance probes in the distribution system will be prepared. Installation of new pH probes works towards the goal of standardizing downstream distribution probes to the treatment plants.

Appendix

Standard Operating Procedures (SOPs)

Denver Water PH SOP

Denver Water Water Treatment Section Water Treatment Plants Standard Operating Procedure	Revised: 05/30/2020

Benchtop pH Analysis

Purpose

The pH of drinking water reflects how acidic it is. pH stands for "potential of hydrogen", referring to the amount of hydrogen found in a substance (in this case water). pH is measured on a scale of 0 – 14. Seven is neutral, meaning there is a balance between acid and alkalinity. A measurement below 7 means acid is present, and a measurement above 7 is basic. Operations will be monitoring online analyzers throughout the treatment plant and comparing results with benchtop analyzers. The pH must not drop below 8.5. Denver Water is targeting a pH of 8.8+\-0.2 for corrosion control requirements.

Note: A link to the USEPA electrode method is below.
https://denverwater-my.sharepoint.com/:b:/r/personal/jvaler_denverwater_org/Documents/Documents/Projects/pH%20Analyzer%20Transition/pH%20USEPA%20electrode%20method%20(1).pdf?csf=1&web=1&e=BkRc2p

Materials List

1. pH probe and multi meter (probe should already be connected to meter)
2. HACH pH Singlets 4.01, 7.00, 10.01
3. pH probe filling solution
4. Magnetic plate for sample and stir bars for mixing
5. Deionized water
6. Glass beakers

Calibration/Verification

Calibration defines the accuracy and quality of measurements recorded using a specific piece of equipment. Over time there is a tendency for the results and accuracy to drift. Ideally, a product would produce test results that exactly match the sample value, with no error at any point within the calibrated range. However, without calibration, an actual product may produce test results different from the sample value, with a potential error. Calibrations are performed at each shift change.

To calibrate the pH probe, perform the following steps:

https://denverwater.sharepoint.com/OM/watertreatment/Standard Operating Procedures/Authorized SOP's/Laboratory Testing SOPs- Authorized/Water Treatment Section Benchtop pH SOP.docx

***Note:** Singlet 4.01, 7.00 and 10.01 buffers are meant for a 1-time use and then should be discarded. Since finished water pH is the most critical parameter for reporting purposes, place your Singlet buffers in a finished water water bath. The buffers need to be brought up to a temperature representative of your samples before calibrating.*

1. Push Calibrate on the multi meter.
2. Rinse the pH probe with DI water and blot dry.
3. Remove your Singlet 4.01 buffer from the water bath open cut open the buffer packet.
4. Place the pH probe in the Singlet 4.01 buffer, ensuring that the reference junctions are completely submerged.
5. Push Read. The display on the multi meter will show "Stabilizing" and a progress bar as the probe stabilizes in the standard. The display shows the buffer that has been read, and shows the temperature and corrected pH value when the reading is stable.
6. Repeat steps 3 – 6 for the 7.00 and 10.01 Singlet buffers.
7. Push Done when calibration is complete.
8. View the calibration summary. Record the % slope, mV range (typically –58 mV (±3) at 25 °C) and the verified pH value on the Denver Water calibration log. Enter in LIMS or equivalent data base.
9. Push Store, the display will return to the regular pH screen.
10. Verify the calibration using the 7.00 Singlet buffer.

Procedure

To perform a water analysis on a calibrated probe, perform the following steps:

1. Rinse your sample beaker 3 times with water from whatever sample point you intend to analyze, and collect your sample.
2. Rinse the pH probe with deionized water.
3. Put the pH probe in the sample water.
4. Place a magnetic stir bar in the sample and turn on the magnetic stir plate, ensuring that the reference junctions are completely submerged.
5. Depending upon how your pH probe is set up, the sample will stabilize and be read automatically. If it is not set up for the "float" mode, press Read on the multi meter.

Note: pH must be analyzed within 15 minutes of collection. If the pH test cannot be completed within 15 minutes, a new sample must be collected.

6. Compare results with online analyzer. If your reading differs by more than 0.2, retest the sample following the above steps before proceeding to the trouble shooting section of this SOP.

7. Store pH probe in 7.00 buffer.
8. Rinse sample glassware three times with DI and store on drying rack.
9. Record result on lab sheet and enter in LIMS or equivalent data base.

Troubleshooting

Calibration:

1. Calibration not done correctly > Recalibrate using freshly prepared pH Singlet buffers.
2. Contaminated glass sensor > Clean the probe. *Note: refer to pH USEPA electrode method (pg.4)*
3. Check the age of the electrode. Benchtop probes will last at most up to two years. After six months of usage, the HACH warranty for benchtop probes is expired. If the probe is old, as a last resort, try the cleaning method detailed in HACH's user manual or call tech support.
4. Reference HACH pH probe manual.

Results:

1. Check for adequate flow at the sample tap and online analyzer.
2. Ensure your sample is from the proper sampling point.
3. Check for error messages on online analyzer.
4. Run analysis again. If results are still out of spec, proceed to the Treatment Section Analyzer Sampling Form For Out Of Range Analyzers on page four of this SOP. This form can also be found at https://denverwater.sharepoint.com/OM/watertreatment/Standard%20Operating%20Procedures/Forms/AllItems.aspx?RootFolder=%2FOM%2Fwatertreatment%2FStandard%20Operating%20Procedures%2FAuthorized%20SOP%27s%2FLaboratory%20Testing%20SOPs%2D%20Authorized&FolderCTID=0x012000D4556E2ED222E04389E4E5EF8693375D&View=%7B05872637%2DEAC0%2D428D%2D894C%2D516A391AAD6A%7D
5.

Identifying an out of spec Finished Water pH result- Bench top reading from lab sample tap is **> ± 0.2 SU** from online Finished Water analyzer

Troubleshooting Steps

Step 1- Verify pH meter was calibrated within 12 hours and verify probe is clean or has been cleaned and that the KCL solution hasn't crystalized, is fresh and meter has met required parameters. If it was not done or did not meet specified parameters, re-calibrate

Step 2- Pull and re-run sample from lab sample tap. If still out of spec go to Step 3

Step 3- Pull and re-run sample pulled from online instrument tap. If still out of spec go to step 4

Step 4- Re-calibrate bench top meter and re-run the sample. If still out of spec go to step 5

Step 5- Run Samples and document results on chart. Draft Maximo workorder and attach chart. Online pH meter should be considered out of service and bench top results should be documented a minimum of every two hours.

Call a Supervisor to determine whether and on call Process Control Instrumentation Water Treatment Technician (PCIWT) call out is necessary

Date	Time	Operator/s Initials			
Analyzer in Question	**Online pH SCADA**	**Grab from Online**	**In the Field**	**Process pH meter #1**	**Process pH meter #2**
Analyzer Up or Downstream of the Analyzer in Question					

Samples should be run as close together as possible

This data sheet should be attached to any analyzer out of range work orders

Key

Online pH SCADA	*Online analyzer reading in SCADA*
Grab from Online	*Grab sample from the effluent of the analyzer in the field. Read in the process lab on the main/#1 pH meter*
In the Field	*Transporting bench analyzer main/#1 on battery power in to the field and reading online analyzer effluent*
Process pH meter #1	*Reading from Lab sample sink from main/#1 pH benchtop meter*
Process pH meter #2	*Reading from Lab sample sink from alkalinity/#2 pH benchtop meter*
Notes	

Moffat should use online pH analyzer___________________________for validation (usually downstream location)

Foothills should use online pH analyzer of Reservoir Influent 1&2 when validating/checking Finished Water pH values.

Marston should use the online pH analyzer at the Ranger box wen validating/checking Finished Water pH values

Team, (04/05/2022)

The pH probe pilot is collecting data from Marston Ranger Box 1 water. Treatment operations have been asked to collect pH readings on a periodic basis from the vicinity of the pH probe pilot.

The reason that Ranger Box 1 water is being supplied to the pH probe panel is to keep (regulatory) finished water line free of any additional monitoring roles in the Marston treatment process. Changing the panel supply water to the Ranger Box alleviates any ambiguities related to what may or may not be reportable finished water data.

The pH probe pilot is now being supplied with water from Ranger Box 1. Grab samples are now collected at the Ranger Box 1 running tap. All grab sample results will be compared to the pH controller output at Ranger Box 1. Figure 3 has been updated below to show where the sample supply to the pH probe pilot is being supplied from, where the grab sample shall be collected, and the pH controller that grab samples shall be compared to.

Continue with the standard process control monitoring. The second bench pH probe is still located in the pipe gallery by the Ranger Box panel.

IN ADDITION TO the current process, treatment operations will collect a pH grab sample from the Ranger Box 1 sample tap and analyze that sample on the spot. A bench pH meter and the necessary materials to carry out analysis is located in the immediate area. A supply of buffer singlets are also located in the immediate area. Please make a best-faith effort to collect the finished water grab sample close to the usual monitoring times of 03:00, 07:00, 11:00, 15:00, 19:00, and 23:00.

- Collect grab samples from the running sample tap for Ranger Box 1
- Triple rinse the glass beaker and then collect the grab sample
- Recorded the pH grab sample result and the display value of the Ranger Box 1 pH probe controller on the sheet located in the area
- Calibrate the bench pH probe as usual (once per shift)

This is a pilot and we are learning things as we move along. It is likely that sampling and monitoring procedures will change frequently as we move forward. The pH data from grab sampling and the display value is needed to help monitor the performance of the pH probe panel. Treatment operations have a large stake in this pilot as we are the end-users of these instruments. Please be generous with ideas that will improve and support this process.

Please reach out to Craig McGonagill (361-548-1324) with questions, comments, and/or suggestions.

Figure 1 Bench-top pH Probe and log sheet

Figure 2 pH probe panel

Figure 3 Ranger Box 1 pH probe and grab sample location

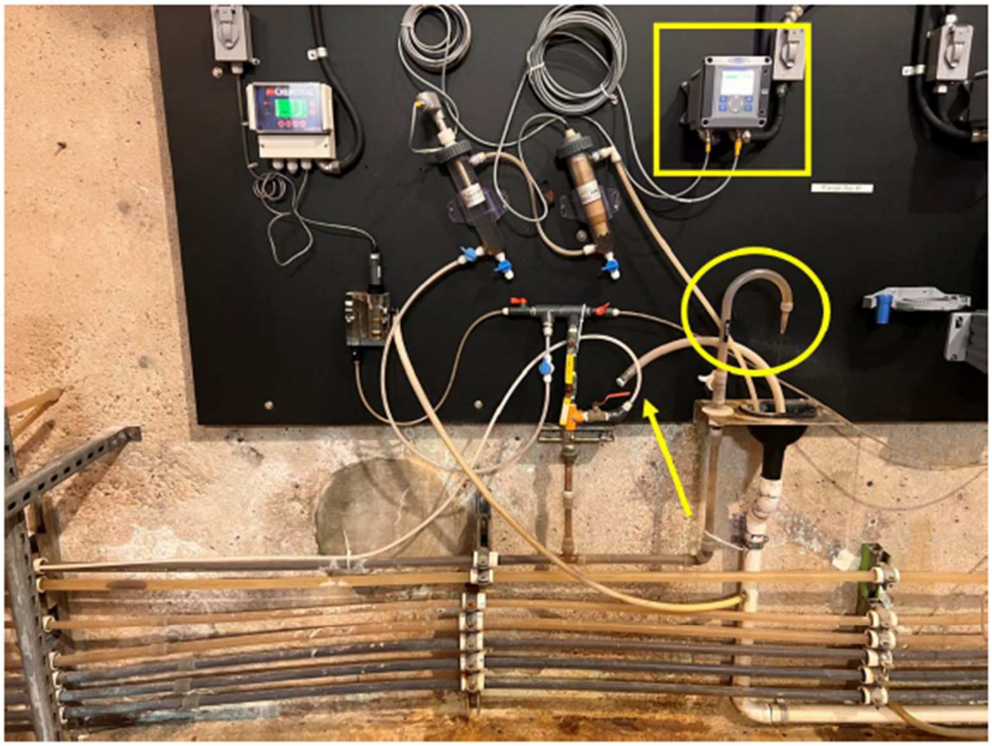
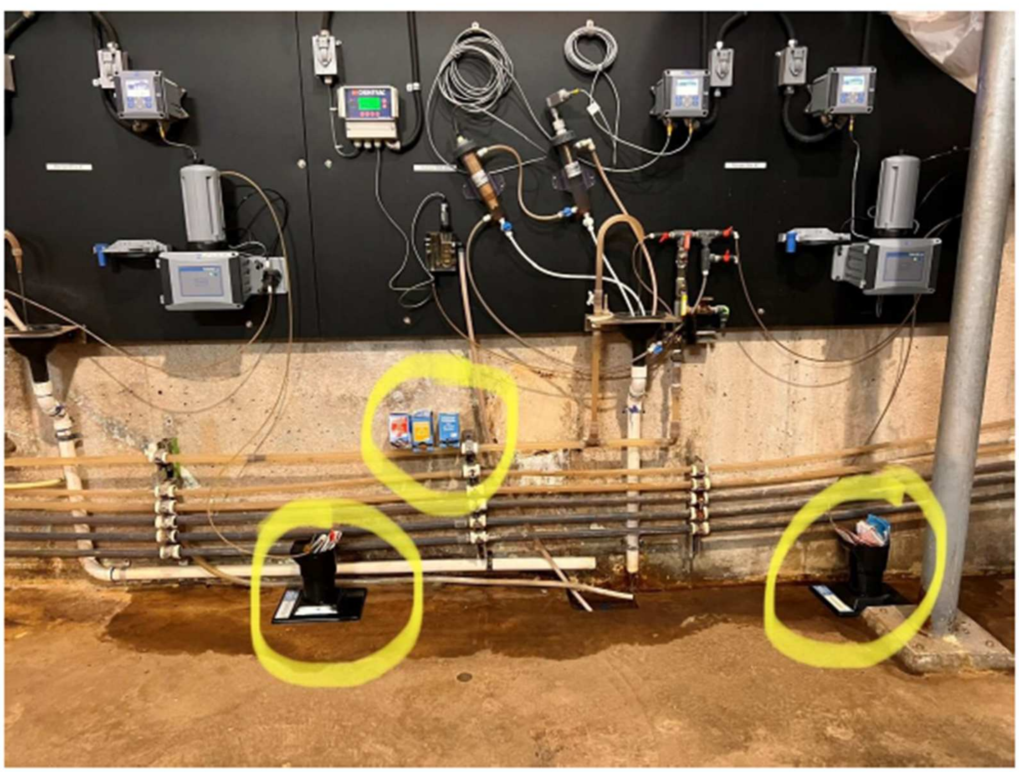


Figure 4 Buffer singlets for bench-top pH probe calibrations



Team, 11/03/2022

The pH probe pilot is collecting data from Moffat DCB 5 water. Treatment operations have been asked to collect pH readings on a periodic basis from the vicinity of the pH probe pilot.

IN ADDITION TO your current process, treatment operations will collect a pH grab sample and perform a bench analysis onsite. Samples are to be collected at the end of sample line after all regulatory analyzers. Figure 3 is where the pH probe pilot will be supplied from, and where the grab sample shall be collected. The Bench top pH probe will be located on the table in the center of the analyzer area. All necessary materials to carry out analysis will be in the immediate area. A supply of buffer singlets will also be located under the table. Please make a best-faith effort to collect the finished water grab sample close to the usual monitoring times of 03:00, 07:00, 11:00, 15:00, 19:00, and 23:00.

- Collect grab samples from the sample tap for DCB 5
- Triple rinse the glass beaker and then collect the grab sample
- Recorded the pH grab sample result and the display value of the DCB 5 pH probe controller on the sheet located in the area
- Calibrate the bench pH probe as usual (once per shift)
- Minimum once per day enter sample data into LIMS **(currently Under Marston Tab but will be moved to Moffat)**

This is a pilot, and we are learning things as we move along. The pH data from grab sampling and the display value is needed to help monitor the performance of the pH probe panel. Treatment operations have a large stake in this pilot study as we are the end-users of these instruments. Please be generous with ideas that will improve and support this process.

Please reach out to Alvin Johnson (720-273-2099) with questions, comments, and/or suggestions.

Link to SOP for calibration of bench top pH analyzer
https://denverwater.sharepoint.com/:w:/r/OM/watertreatment/Standard%20Operating%20Procedures/Authorized%20SOP%27s/Laboratory%20Testing%20SOPs-%20Authorized/pH%20SOP.docx?d=w7a2c43f7d1a84f88a27e6c0db5e259f0&csf=1&web=1

Figure 1 Bench-top pH Probe and log sheet

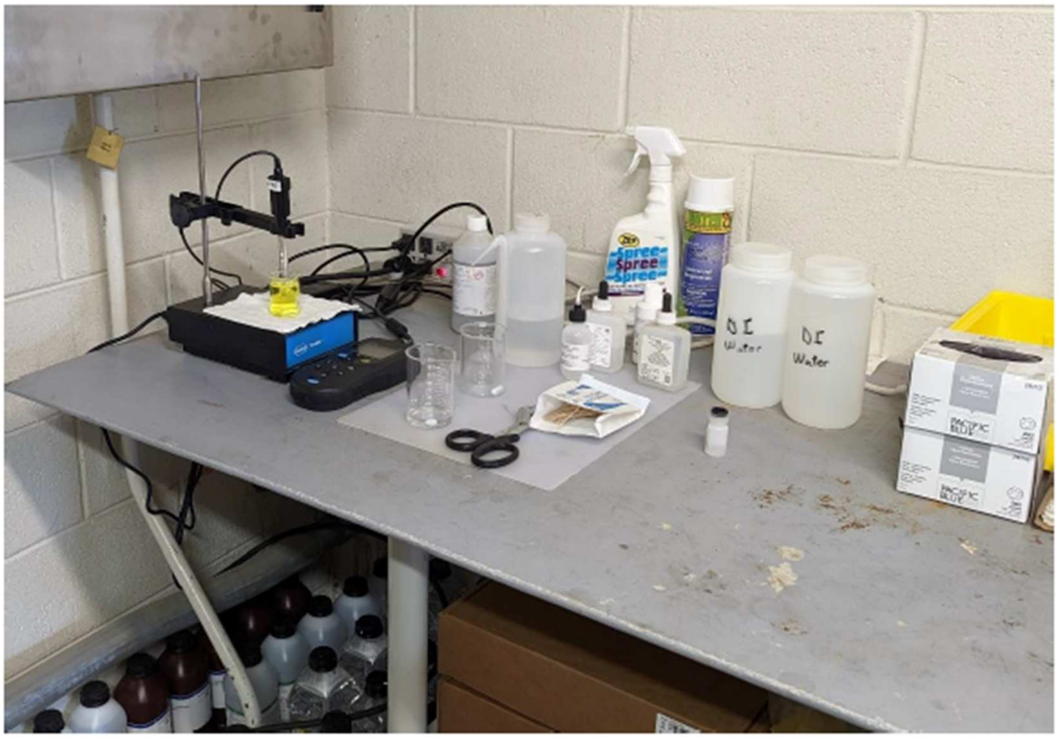
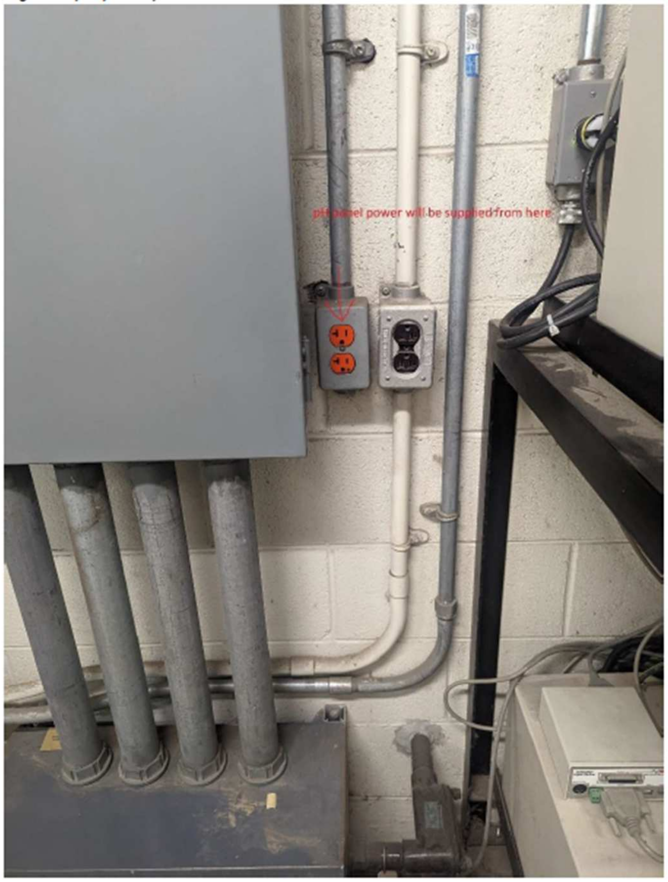


Figure 2 pH probe panel

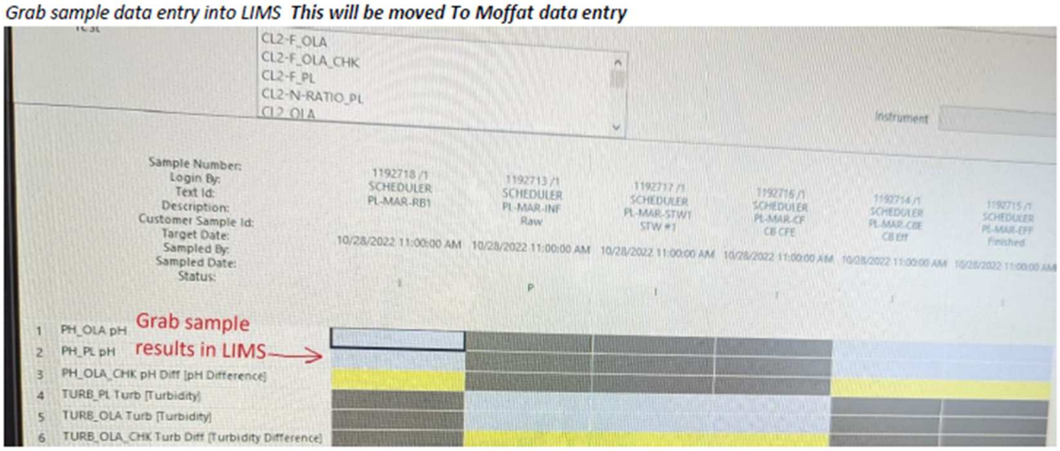
Figure 3 DCB 5 sample tap and location for grab sample

Figure 4 SCADA connection

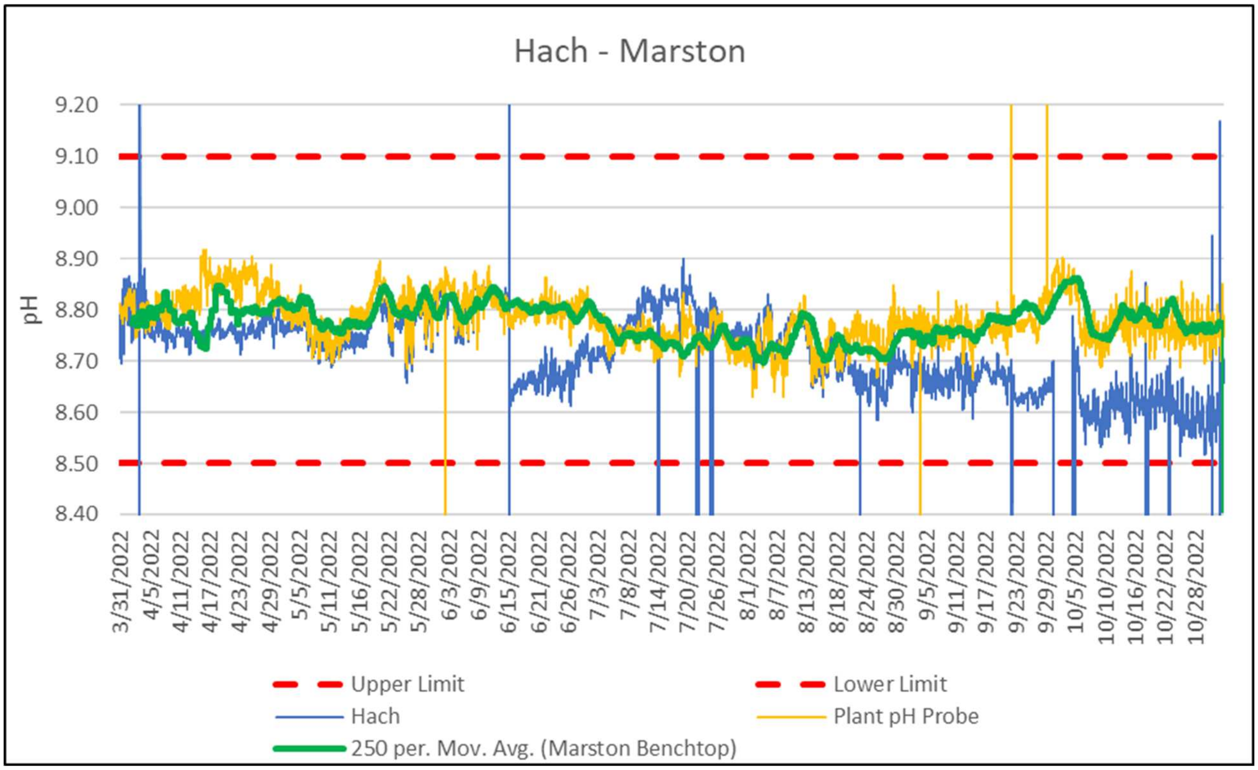
Figure 6 pH panel power connection will be here.

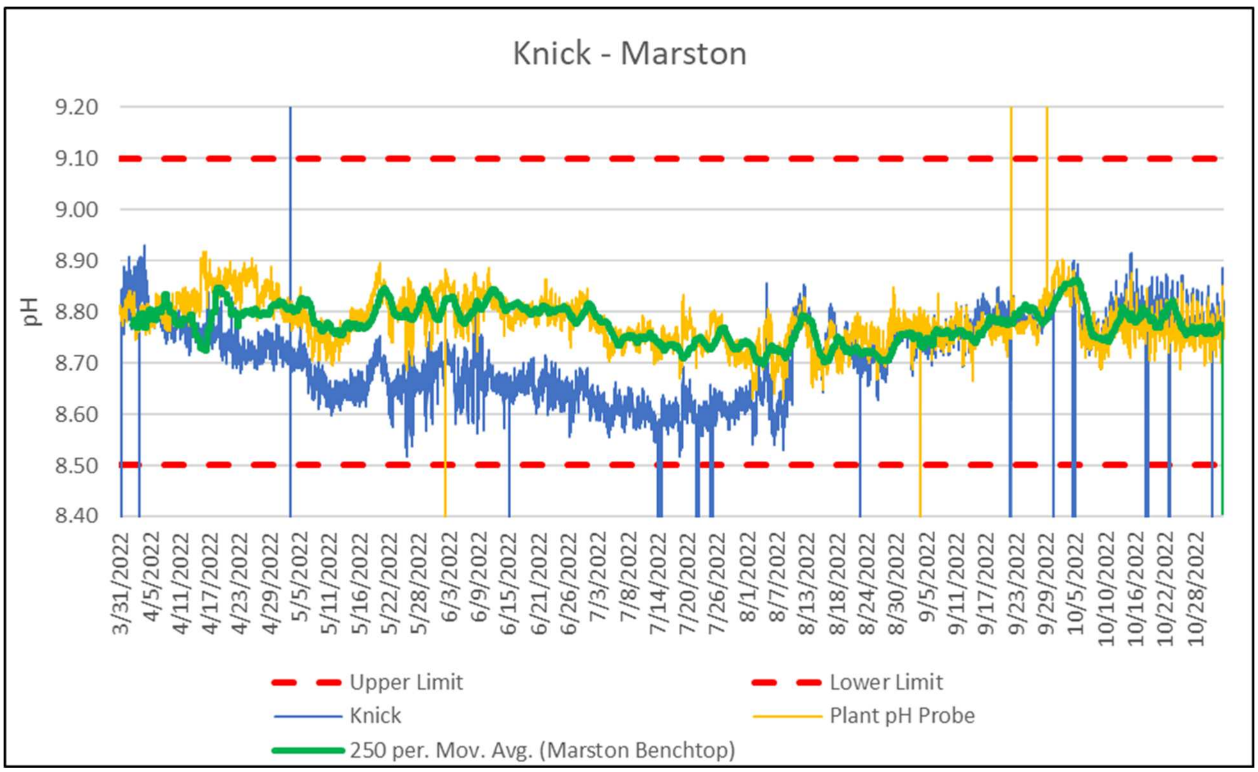


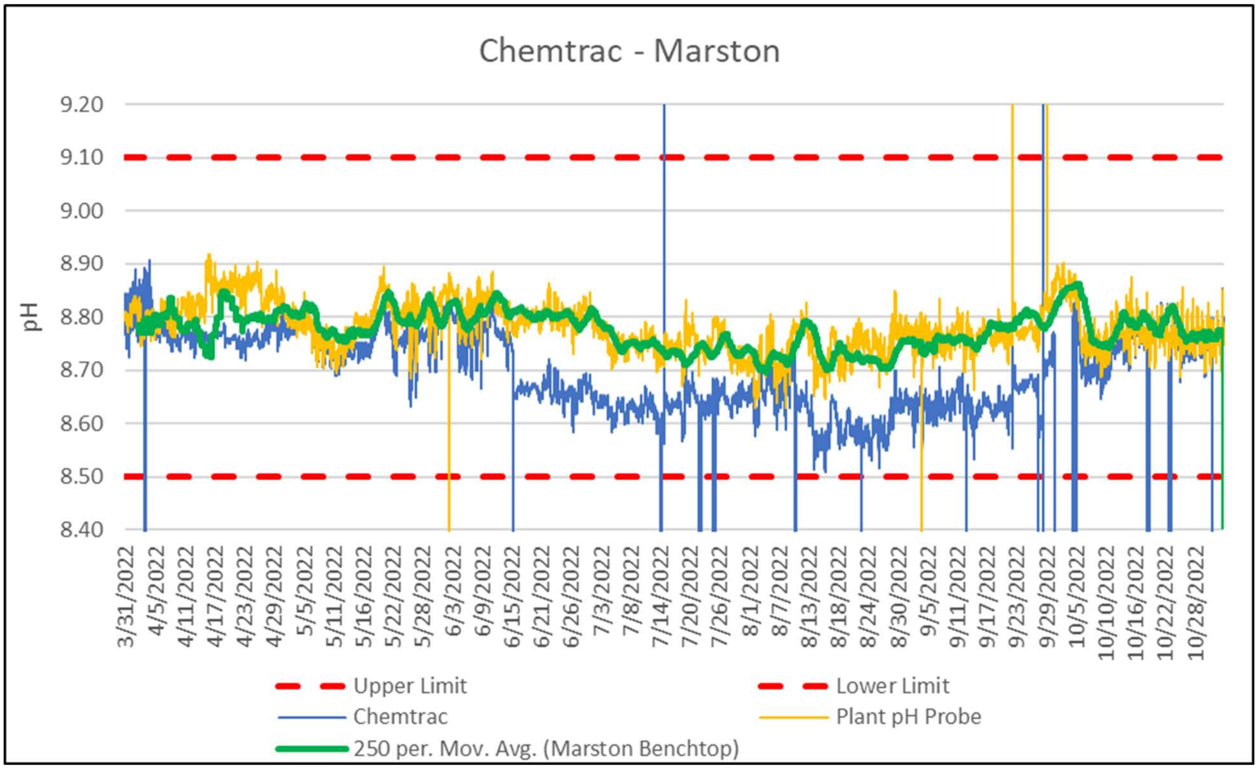
Grab sample data entry into LIMS This will be moved To Moffat data entry



Marston Water Treatment Plant Results






Chemtrac - Marston
pH
9.20
9.10
9.00
8.90
8.80
8.70
8.60
8.50
8.40
3/31/2022
4/5/2022
4/11/2022
4/17/2022
4/23/2022
4/29/2022
5/5/2022
5/11/2022
5/16/2022
5/22/2022
5/28/2022
6/3/2022
6/9/2022
6/15/2022
6/21/2022
6/26/2022
7/3/2022
7/8/2022
7/14/2022
7/20/2022
7/26/2022
8/1/2022
8/7/2022
8/13/2022
8/18/2022
8/24/2022
8/30/2022
9/5/2022
9/11/2022
9/17/2022
9/23/2022
9/29/2022
10/5/2022
10/10/2022
10/16/2022
10/22/2022
10/28/2022
Upper Limit
Lower Limit
Chemtrac
Plant pH Probe
250 per. Mov. Avg. (Marston Benchtop)

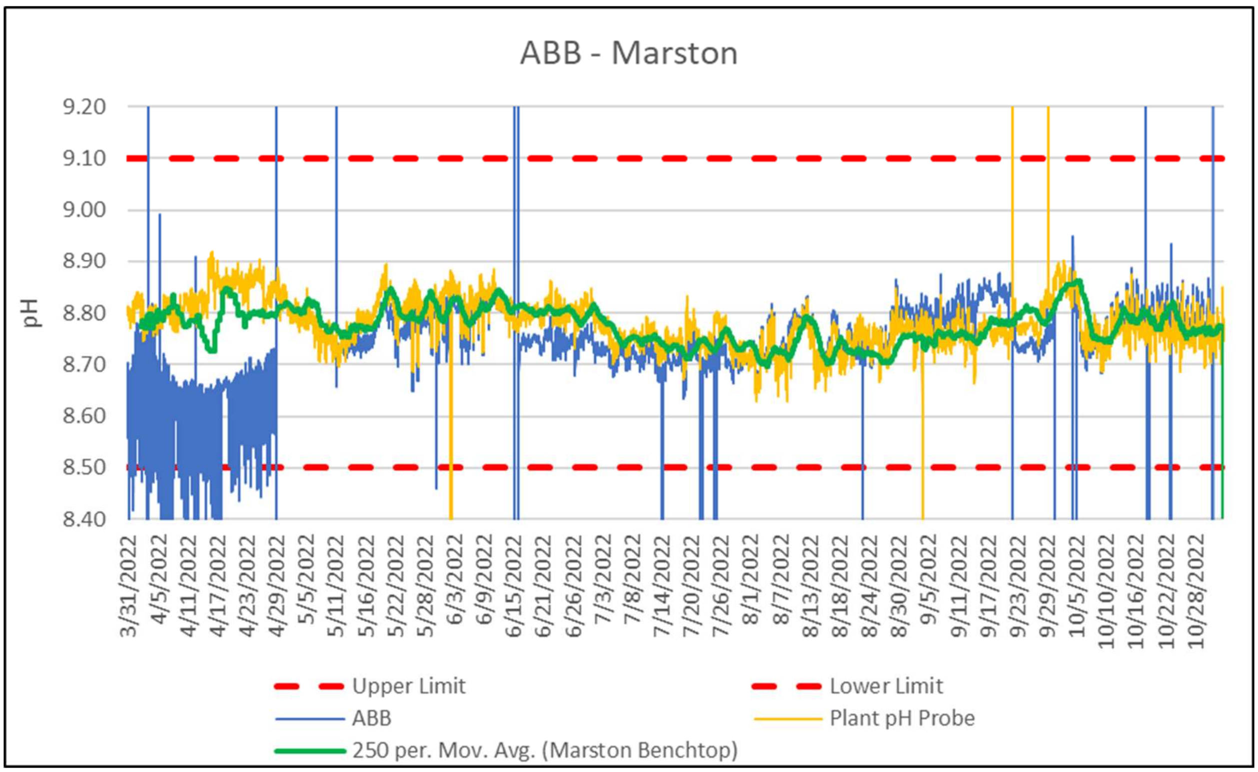
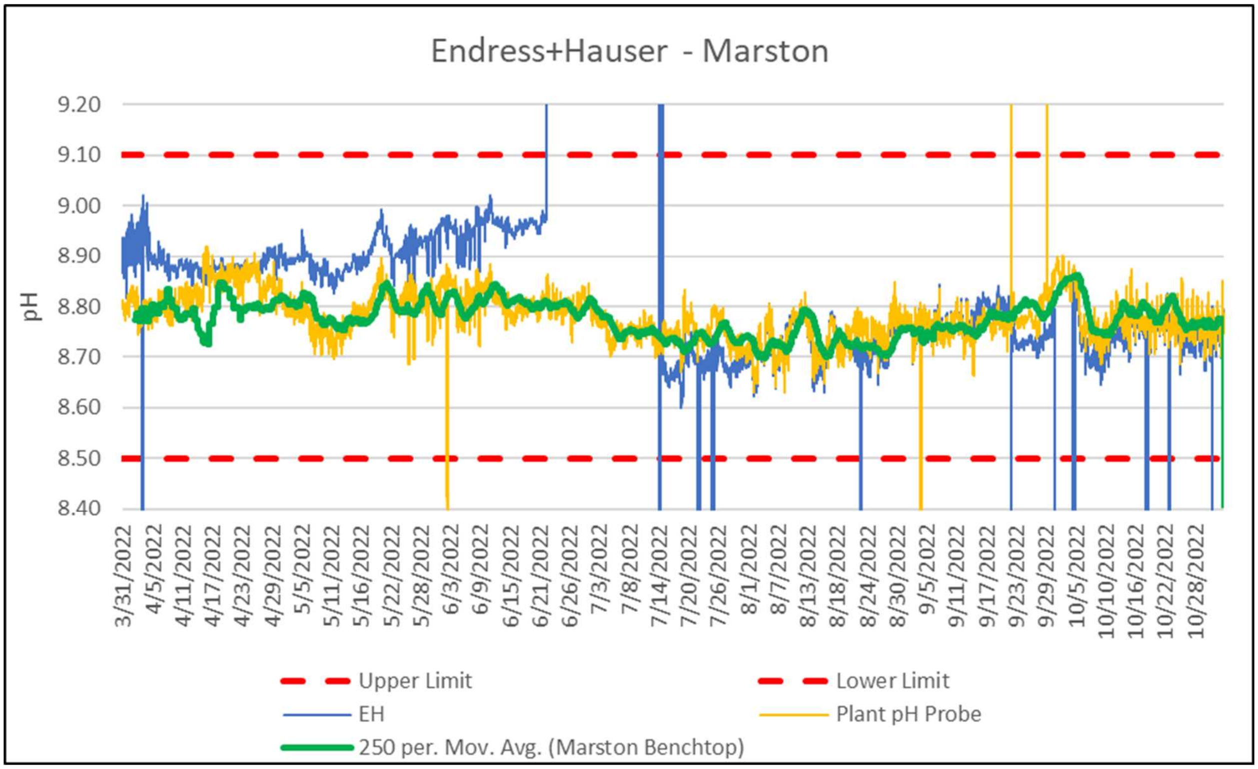


ABB - Marston
pH
9.20
9.10
9.00
8.90
8.80
8.70
8.60
8.50
8.40
3/31/2022
4/5/2022
4/11/2022
4/17/2022
4/23/2022
4/29/2022
5/5/2022
5/11/2022
5/16/2022
5/22/2022
5/28/2022
6/3/2022
6/9/2022
6/15/2022
6/21/2022
6/26/2022
7/3/2022
7/8/2022
7/14/2022
7/20/2022
7/26/2022
8/1/2022
8/7/2022
8/13/2022
8/18/2022
8/24/2022
8/30/2022
9/5/2022
9/11/2022
9/17/2022
9/23/2022
9/29/2022
10/5/2022
10/10/2022
10/16/2022
10/22/2022
10/28/2022
Upper Limit
Lower Limit
ABB
Plant pH Probe
250 per. Mov. Avg. (Marston Benchtop)


Endress+Hauser - Marston
pH
9.20
9.10
9.00
8.90
8.80
8.70
8.60
8.50
8.40
3/31/2022
4/5/2022
4/11/2022
4/17/2022
4/23/2022
4/29/2022
5/5/2022
5/11/2022
5/16/2022
5/22/2022
5/28/2022
6/3/2022
6/9/2022
6/15/2022
6/21/2022
6/26/2022
7/3/2022
7/8/2022
7/14/2022
7/20/2022
7/26/2022
8/1/2022
8/7/2022
8/13/2022
8/18/2022
8/24/2022
8/30/2022
9/5/2022
9/11/2022
9/17/2022
9/23/2022
9/29/2022
10/5/2022
10/10/2022
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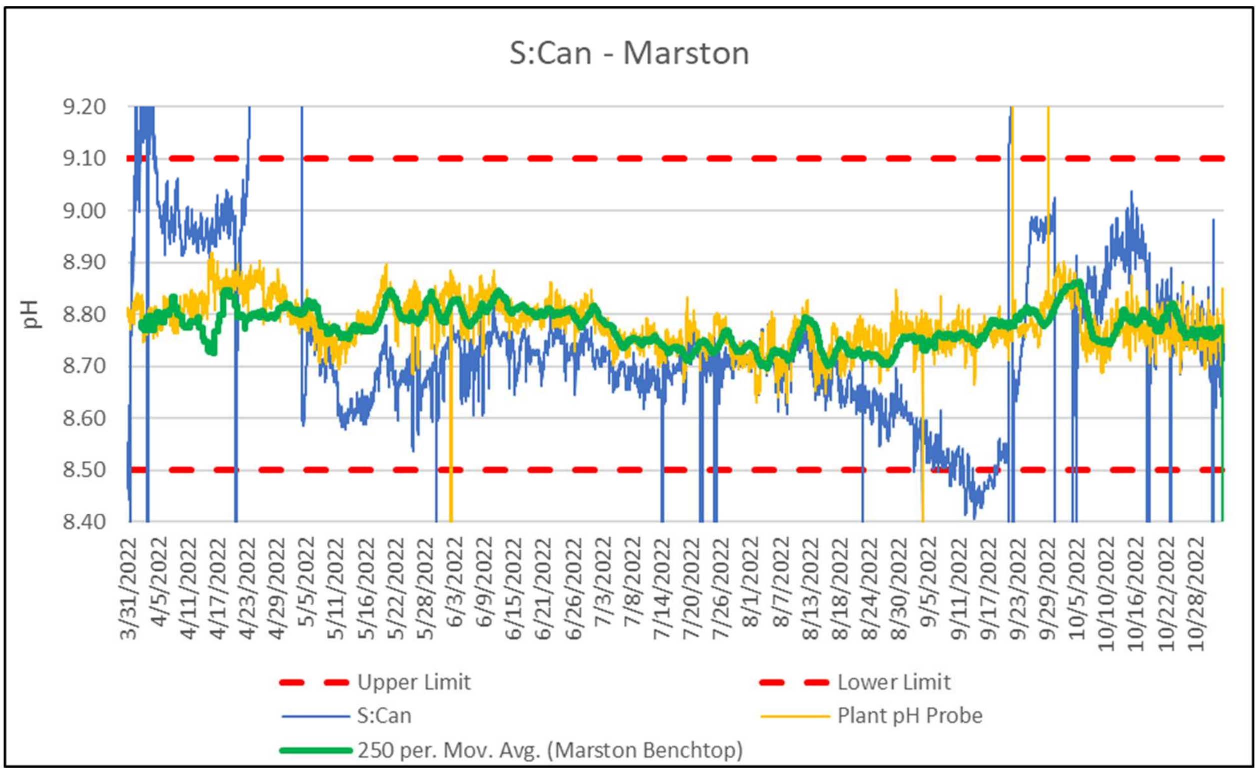
Upper Limit
Lower Limit
EH
Plant pH Probe
250 per. Mov. Avg. (Marston Benchtop)


S:Can - Marston
pH
9.20
9.10
9.00
8.90
8.80
8.70
8.60
8.50
8.40
3/31/2022
4/5/2022
4/11/2022
4/17/2022
4/23/2022
4/29/2022
5/5/2022
5/11/2022
5/16/2022
5/22/2022
5/28/2022
6/3/2022
6/9/2022
6/15/2022
6/21/2022
6/26/2022
7/3/2022
7/8/2022
7/14/2022
7/20/2022
7/26/2022
8/1/2022
8/7/2022
8/13/2022
8/18/2022
8/24/2022
8/30/2022
9/5/2022
9/11/2022
9/17/2022
9/23/2022
9/29/2022
10/5/2022
10/10/2022
10/16/2022
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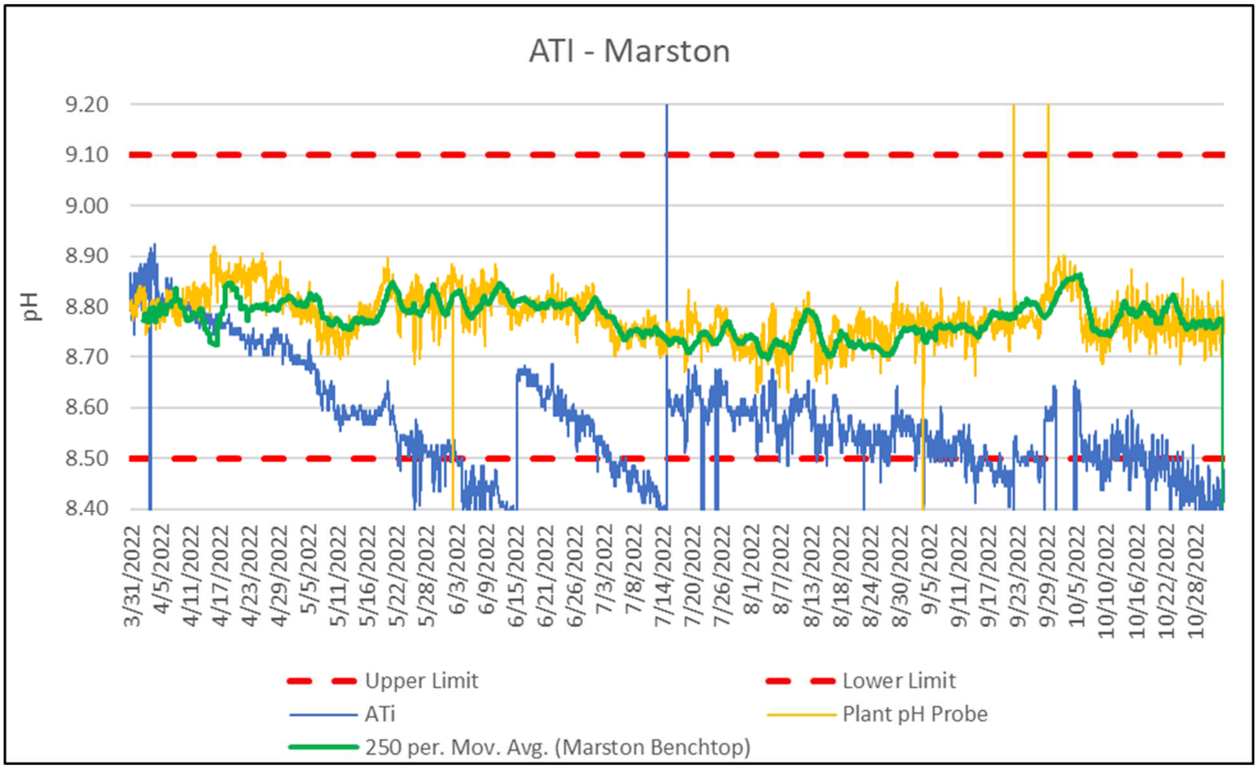
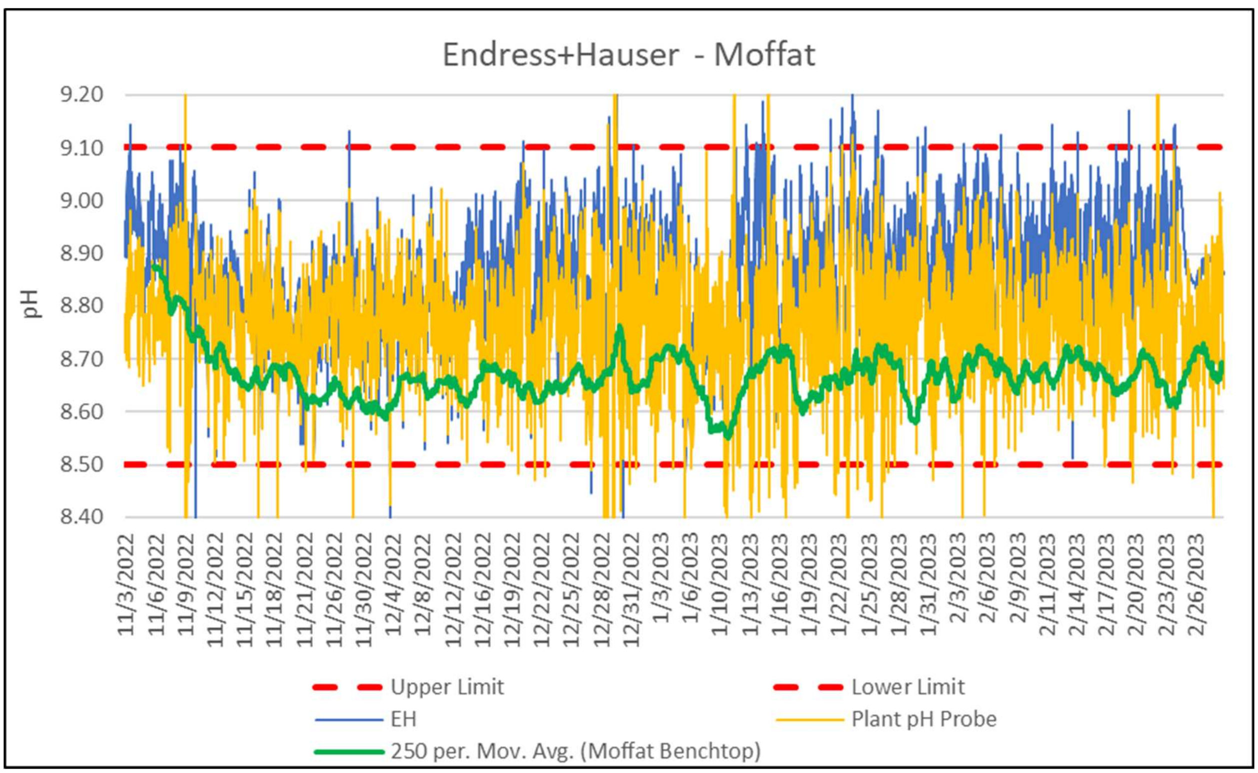
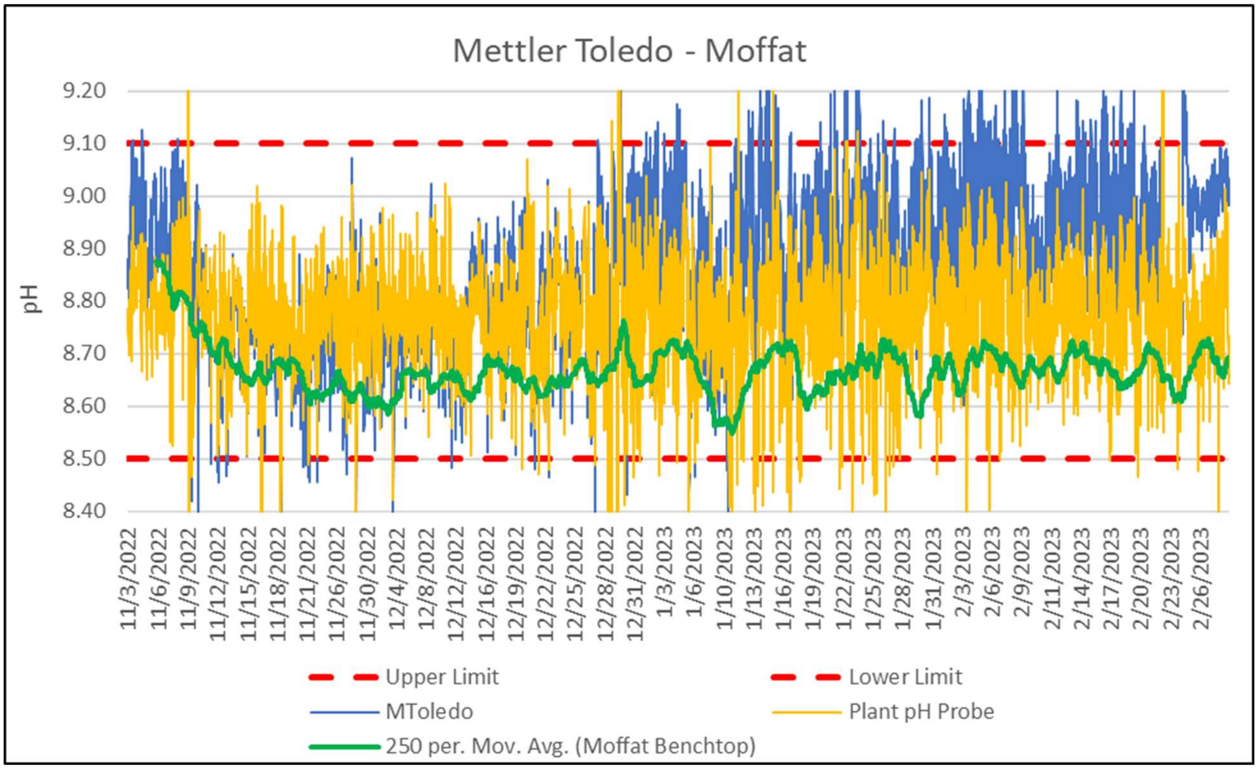
10/28/2022
Upper Limit
Lower Limit
S:Can
Plant pH Probe
250 per. Mov. Avg. (Marston Benchtop)

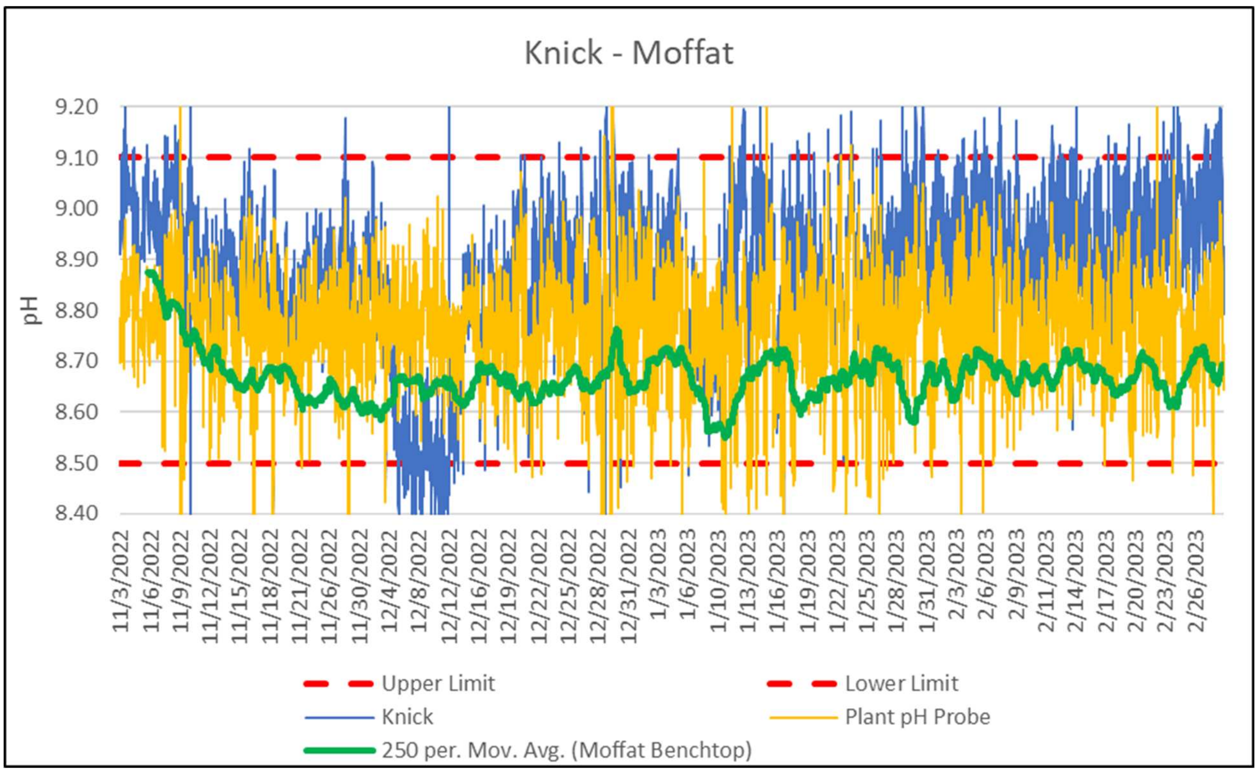


Moffat Water Treatment Plant Results

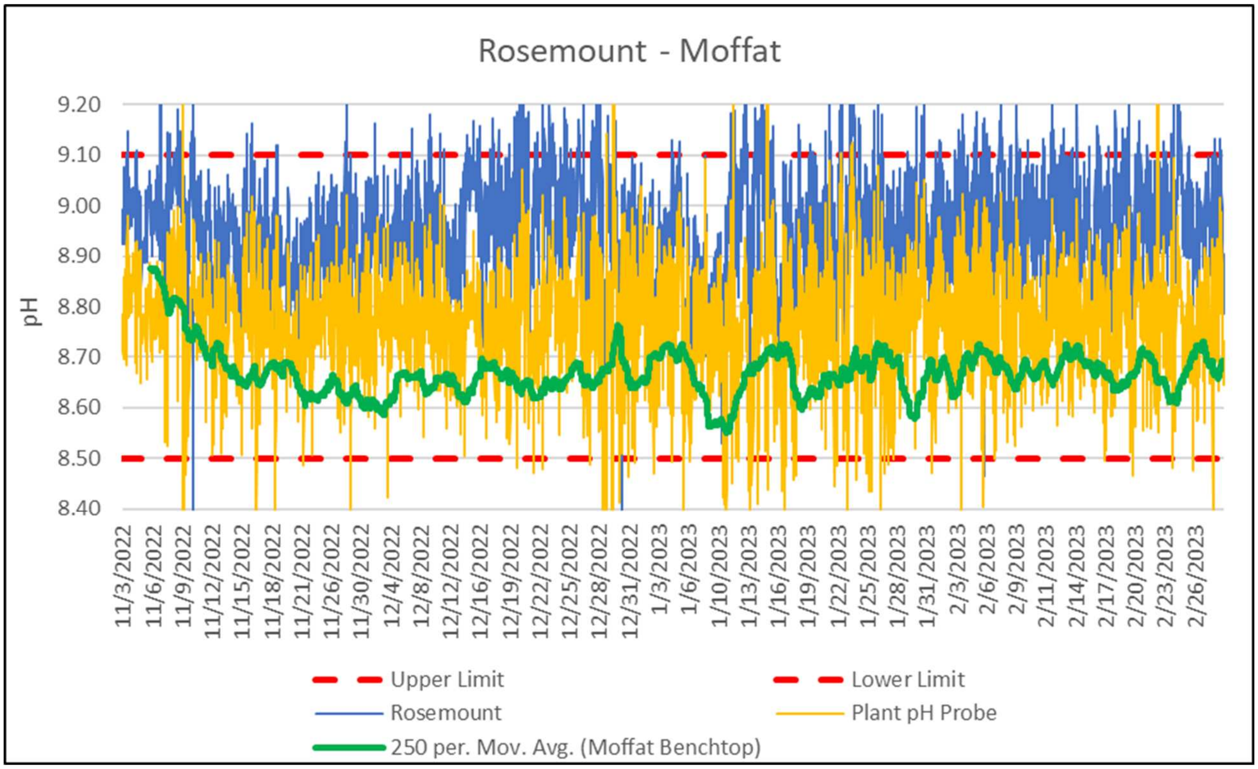




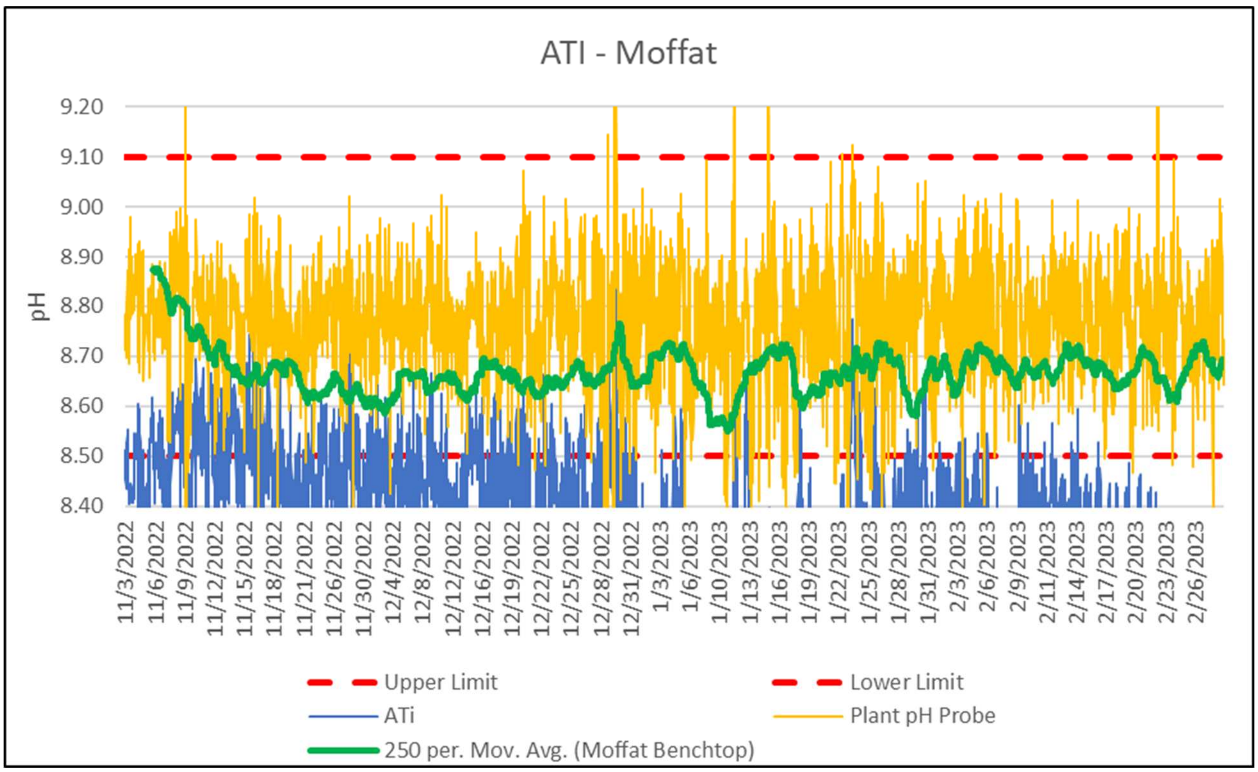
Mettler Toledo - Moffat
pH
9.20
9.10
9.00
8.90
8.80
8.70
8.60
8.50
8.40
Upper Limit
Lower Limit
MToledo
Plant pH Probe
250 per. Mov. Avg. (Moffat Benchtop)



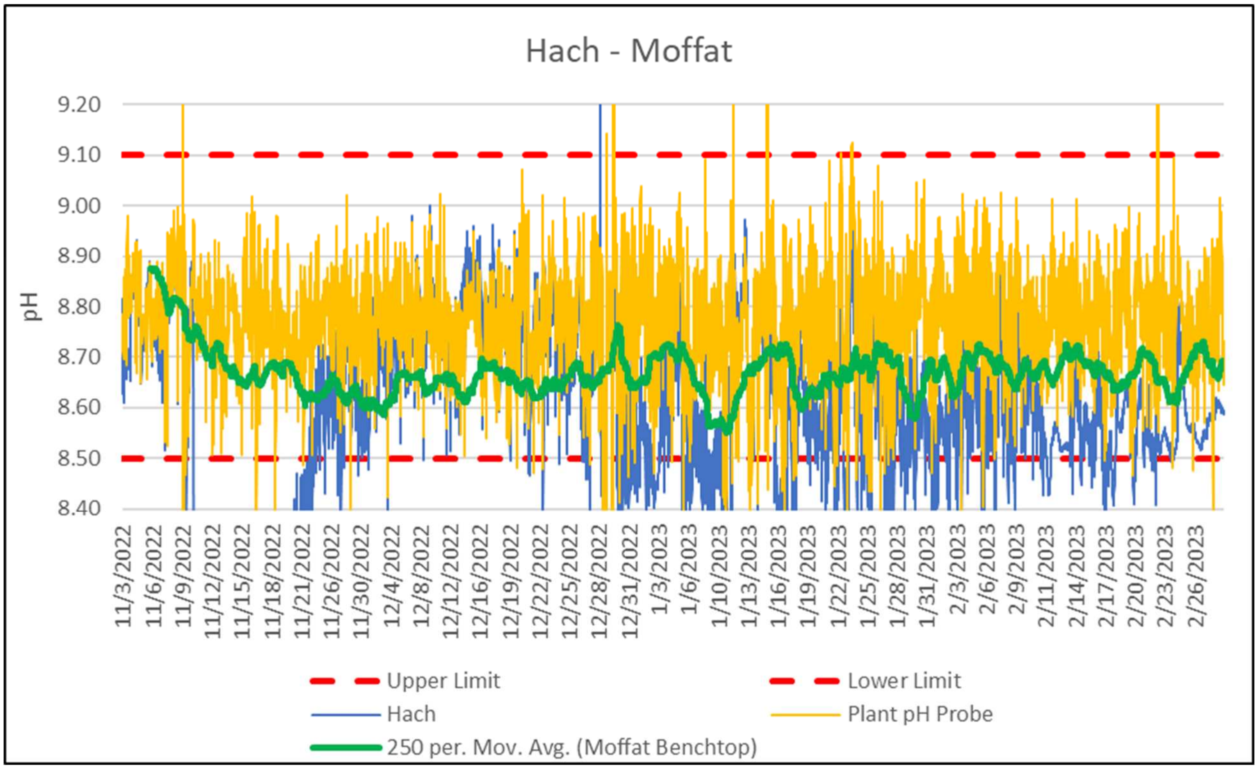
Knick - Moffat
pH
9.20
9.10
9.00
8.90
8.80
8.70
8.60
8.50
8.40
Upper Limit
Lower Limit
Knick
Plant pH Probe
250 per. Mov. Avg. (Moffat Benchtop)



Rosemount - Moffat
pH
9.20
9.10
9.00
8.90
8.80
8.70
8.60
8.50
8.40
11/3/2022
11/6/2022
11/9/2022
11/12/2022
11/15/2022
11/18/2022
11/21/2022
11/26/2022
11/30/2022
12/4/2022
12/8/2022
12/12/2022
12/16/2022
12/19/2022
12/22/2022
12/25/2022
12/28/2022
12/31/2022
1/3/2023
1/6/2023
1/10/2023
1/13/2023
1/16/2023
1/19/2023
1/22/2023
1/25/2023
1/28/2023
1/31/2023
2/3/2023
2/6/2023
2/9/2023
2/11/2023
2/14/2023
2/17/2023
2/20/2023
2/23/2023
2/26/2023
Upper Limit
Lower Limit
Rosemount
Plant pH Probe
250 per. Mov. Avg. (Moffat Benchtop)



ATI - Moffat
pH
9.20
9.10
9.00
8.90
8.80
8.70
8.60
8.50
8.40
11/3/2022
11/6/2022
11/9/2022
11/12/2022
11/15/2022
11/18/2022
11/21/2022
11/26/2022
11/30/2022
12/4/2022
12/8/2022
12/12/2022
12/16/2022
12/19/2022
12/22/2022
12/25/2022
12/28/2022
12/31/2022
1/3/2023
1/6/2023
1/10/2023
1/13/2023
1/16/2023
1/19/2023
1/22/2023
1/25/2023
1/28/2023
1/31/2023
2/3/2023
2/6/2023
2/9/2023
2/11/2023
2/14/2023
2/17/2023
2/20/2023
2/23/2023
2/26/2023
Upper Limit
Lower Limit
ATi
Plant pH Probe
250 per. Mov. Avg. (Moffat Benchtop)



Hach - Moffat
9.20
9.10
9.00
8.90
8.80
8.70
8.60
8.50
8.40
pH
11/3/2022
11/6/2022
11/9/2022
11/12/2022
11/15/2022
11/18/2022
11/21/2022
11/26/2022
11/30/2022
12/4/2022
12/8/2022
12/12/2022
12/16/2022
12/19/2022
12/22/2022
12/25/2022
12/28/2022
12/31/2022
1/3/2023
1/6/2023
1/10/2023
1/13/2023
1/16/2023
1/19/2023
1/22/2023
1/25/2023
1/28/2023
1/31/2023
2/3/2023
2/6/2023
2/9/2023
2/11/2023
2/14/2023
2/17/2023
2/20/2023
2/23/2023
2/26/2023
Upper Limit
Lower Limit
Hach
Plant pH Probe
250 per. Mov. Avg. (Moffat Benchtop)

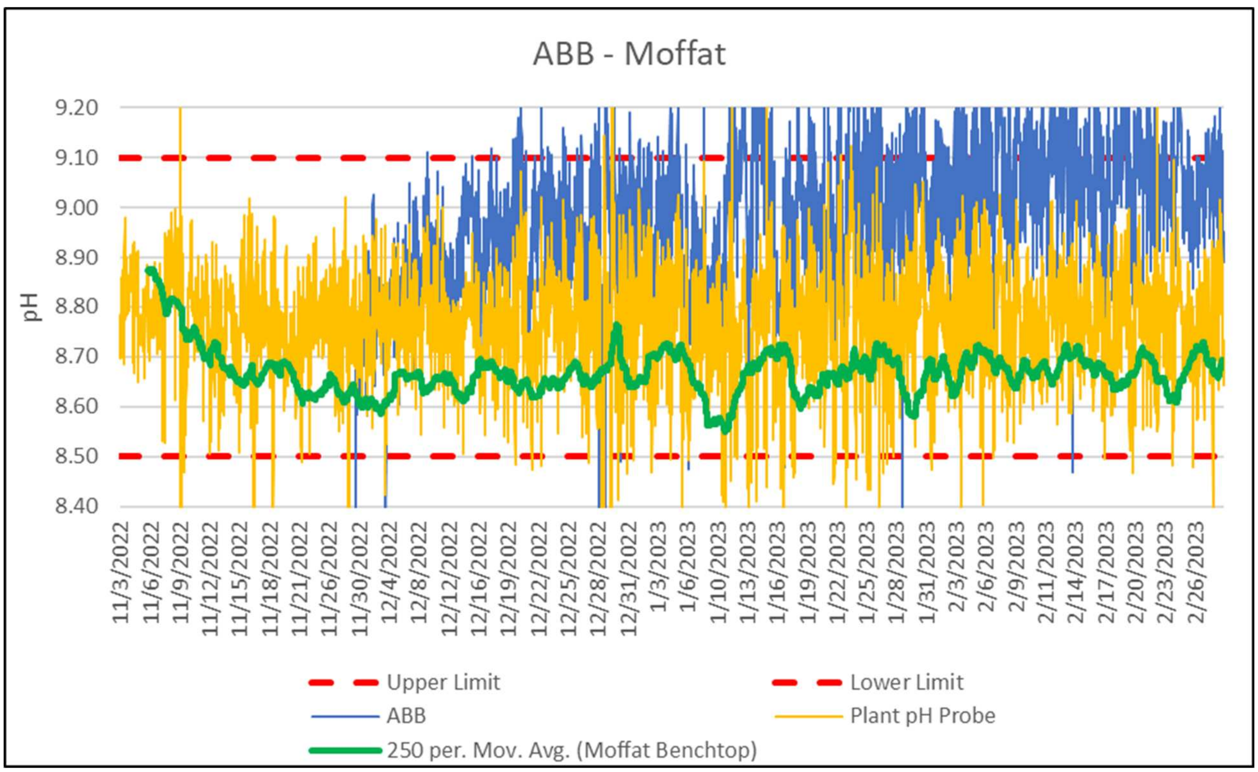


ABB - Moffat
9.20
9.10
9.00
8.90
8.80
8.70
8.60
8.50
8.40
pH
11/3/2022
11/6/2022
11/9/2022
11/12/2022
11/15/2022
11/18/2022
11/21/2022
11/26/2022
11/30/2022
12/4/2022
12/8/2022
12/12/2022
12/16/2022
12/19/2022
12/22/2022
12/25/2022
12/28/2022
12/31/2022
1/3/2023
1/6/2023
1/10/2023
1/13/2023
1/16/2023
1/19/2023
1/22/2023
1/25/2023
1/28/2023
1/31/2023
2/3/2023
2/6/2023
2/9/2023
2/11/2023
2/14/2023
2/17/2023
2/20/2023
2/23/2023
2/26/2023
Upper Limit
Lower Limit
ABB
Plant pH Probe
250 per. Mov. Avg. (Moffat Benchtop)

Maintenance Logs

Date	pH Sensor ID	Work type
30-Mar	Chemtrac	Calibration
30-Mar	ABB	Calibration
30-Mar	M4 Knick	Calibration
30-Mar	ECD	Calibration
30-Mar	Yokogawa	Calibration
30-Mar	Rosemount	Calibration
30-Mar	Chemtrac	Calibration
30-Mar	Hach	Calibration
30-Mar	Endress	Calibration
30-Mar	Mettler	Calibration
30-Mar	ATI	Calibration
29-Apr	ABB	Probe Broken
30-Mar	S:can	Calibration
11-May	ABB	New Probe
14-Jun	ECD	Calibration
15-Jun	Chemtrac	Calibration
15-Jun	ABB	Calibration
15-Jun	Hach	Calibration
15-Jun	S:Can	Calibration
15-Jun	M4 Knick	Calibration
15-Jun	Emerson/Rosemont	Calibration
20-Jun	ATI	Calibration
23-Jun	Endress	Probe dropped
23-Jun	Mettler	Calibration
15-Jul	Endress	New Probe installed
10-Nov	Chemtrac	Calibration
10-Nov	M4 Knick	Calibration
10-Nov	Rosemount	Calibration
10-Nov	ATI	Calibration
10-Nov	Yokogawa	Calibration
10-Nov	Mettler	Calibration
10-Nov	Endress	Calibration
10-Nov	s:CAN	Calibration
10-Nov	ECD	Calibration
10-Nov	Hach	Calibration
1-Dec	S:CAN	Calibration
1-Dec	Hach	Calibration
28-Dec	Rosemount	Calibration
28-Dec	Hach	Calibration
28-Dec	ABB	Calibration