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Via Electronic Mail

Ms. Jodi Howard
U.S. Environmental Protection Agency
Office of Air Quality Planning and
Standards
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Mail Code: E143-01
Research Triangle Park, NC 27711
Howard.Jodi@epa.gov

Re: ***pH Calibration Requirements Under National Emission Standards for Hazardous Air Pollutants for Polyvinyl Chloride and Copolymers Production ("PVC MACT"), 77 Fed. Reg. 22,848 (April 17, 2012)***

Dear Ms. Howard:

As they are finalizing several submissions for the reconsideration of the above-referenced rule, the Vinyl Institute and its PVC MACT Working Group (hereinafter, "Working Group"),[1] have asked that we follow-up with you on an issue of great concern that arose during the March 25, 2015, conference call with the Agency. Specifically, Working Group members were dismayed by the discussion on the pH calibration requirements set out at Table 7 to the final rule. Based on this discussion, it would appear that there is a deep and significant misunderstanding of the industry's processes, which has led to the imposition of an overly burdensome pH calibration requirement in the above-referenced rule. Accordingly, the Working Group seeks to address the apparent misunderstandings below in the hope that the Agency will reconsider the calibration frequency required for pH monitors.

I. Variability in Resin Slate has no Bearing on Scrubbing Media or pH Measurement

Hydrochloric acid ("HCl") is a byproduct of the thermal oxidation of chlorinated organic HAPs, which in the PVC industry is neutralized by using a sodium hydroxide (NaOH) solution or other neutralizing media in the caustic scrubbers. Facilities monitor pH of the caustic liquid,

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[1] In addition to Vinyl Institute ("VI") members Formosa Plastics Corporation, U.S.A., Occidental Chemical Corporation/Oxy Vinyls, LP, Mexichem Specialty Resins Inc. (formerly PolyOne Corporation), Shintech Inc., Westlake Chemical Corporation, Lubrizol Corporation, and Wacker Chemicals, the PVC MACT Working Group has included non-VI members Axiall Corporation. The Vinyl Institute, Inc., founded in 1982, is a U.S. trade association representing the leading manufacturers of vinyl, vinyl chloride monomer, vinyl additives and modifiers, and vinyl compound materials.

using an appropriate probe connected to a continuous analyzer that reads the pH of the caustic liquid at a minimum frequency of once every 15 seconds. The caustic liquid is very effective at neutralizing the HCl gas, and as such the pH of the scrubbing liquid is an excellent parameter for controlling HCl emissions.

Based on the March 25, 2015 discussions, it would appear that Agency staff believe that an HCl continuous emissions monitoring system (CEMS) is a better method of monitoring HCl because it measures HCl emissions directly. The Working Group submits that an HCl CEMS may not be the best parameter to control scrubber performance because it is in effect a lagging indicator of such performance. In contrast, pH monitors provide a more direct measure of the neutralization reaction taking place in the scrubber, and allow for earlier control intervention in the process.

More importantly, Agency staff have argued that the need for frequent pH calibration is due to the variability in PVC resin recipes. The industry has identified variability in product slates as a driver for flexibility of total organic HAPs with the resin and wastewater limits, which EPA appears to have interpreted to extend to the composition of treated process vent streams. The basis for this position is unclear as industry members have never argued that resin recipes affect the composition of treated process vent streams. Rather, Working Group members noted that most emission profiles sought by EPA would have little value because the recovery system causes process vent HAP concentration to have poor correlation with product slate.

Indeed, the load of the thermal oxidizer is a function of the production volume, and does not necessarily directly correlate to the variability of the resin product slate. As resin production rates increase, the chlorinated organics load to the thermal oxidizer increases, leading to greater concentrations of HCl in the thermal oxidizer exhaust. As the Working Group noted in its August 16, 2013 letter:

> A PVC facility is designed to prevent inerts and non-condensable materials from entering the process stream. Inerts require increased pressure in the process, increasing the risk of pressure relief device ("PRD") releases or other malfunctions, and interfere with the recovery of VCM in the recovery system. More importantly, PVCPUs are designed to maximize raw material value by recovering unreacted VCM and reusing it in the process…Vent streams collected from process equipment (both continuously and batch-wise) are recovered overhead and reused. The process is engineered to maximize the percent of the stream that is recovered and minimize the amount that is ultimately vented from the recovery system to a control device.[2]

As a result, the load of HCl precursors is a function of the efficiency of the recovery system at each facility, and will not vary significantly by product slate. In addition, the fact that HCl is the

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[2] Docket Document EPA-HQ-OAR-2002-0037-0561 at 52.

only acidic byproduct of thermal oxidation at PVC facilities supports the expectation that non-chlorinated organics are not expected to play a role in the formation of other acidic HAPs. Even if HCl rates do vary, scrubbers at PVC facilities are well designed to compensate. The system continually adds caustic or other neutralizing agent, based on the pH measurement (taken at a minimum of 15 second intervals), to ensure that the HCl is instantly neutralized. As Figure 1 illustrates, pH level will not vary widely at the thermal oxidizer scrubber effluent.[3]. This data shows an actual process unit that is in-control and well-controlled over the two week study period. As long as pH of the scrubber liquid is maintained above a certain level, instantaneous neutralization of incoming steady state loads of HCl will be accomplished.

Calibration data from PVC facilities indicate that pH monitors are unlikely to experience much drift. For example, the chart at **Appendix B** provides 12 weeks of pH calibration data from 4 different continuous pH meters at one PVC facility. As the data indicates, none of the 4 pH monitors was ever adjusted by more than 0.26 pH during its weekly calibration and most of the adjustments were less than 0.10 pH for those three months. This data shows that there is very little drift in the pH measurement. Thus, more frequent than weekly calibration is simply unnecessary.

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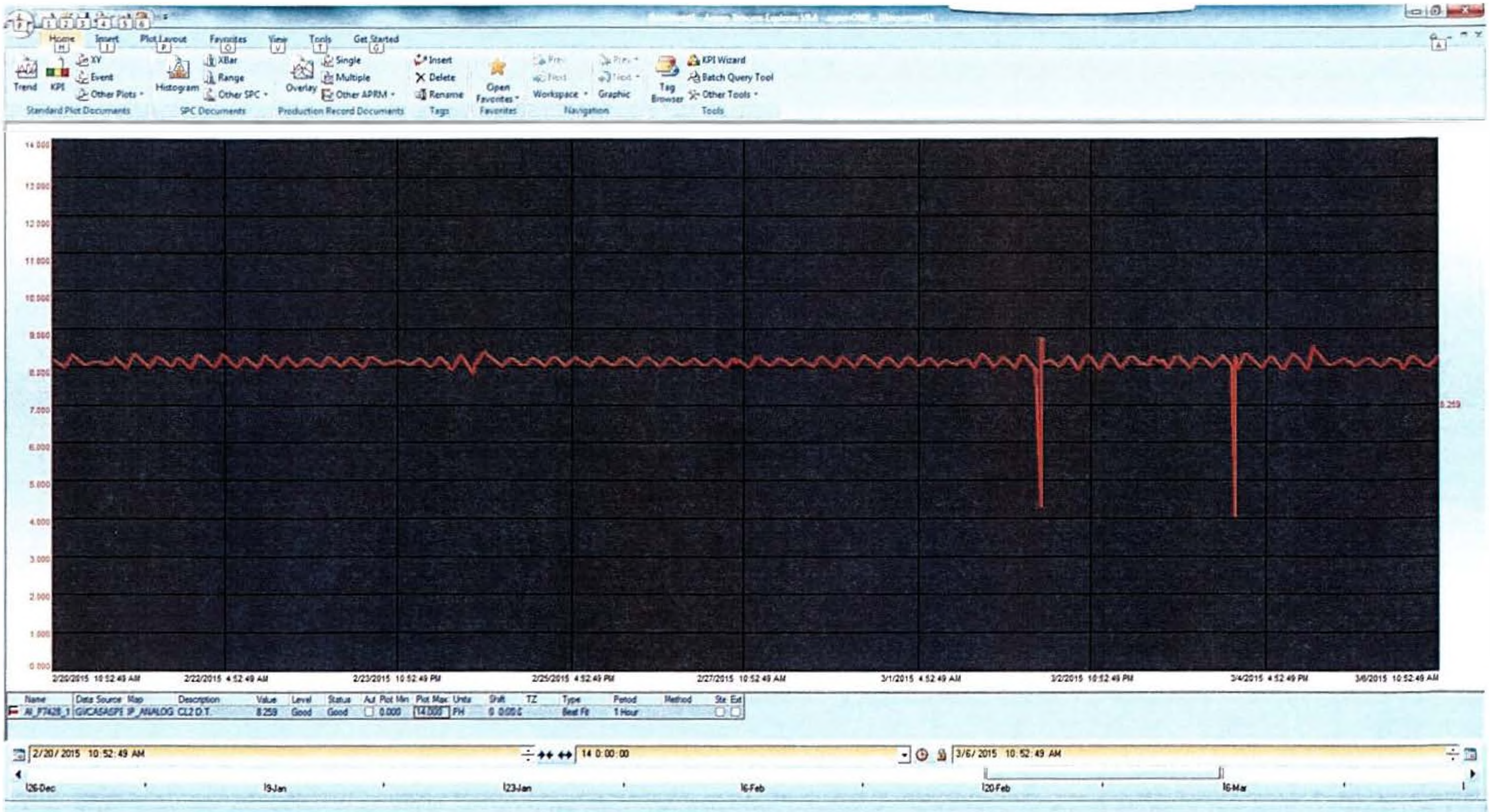
[3] Note that the two dips in Figure 1 for pH on March 2 and March 4 are readings of a test buffer solution, rather than a spike in incoming HCl in the scrubber.



Name	Data Source	Map	Description	Value	Level	Status	Aut	Plot Min	Plot Max	Units	Shift	TZ	Type	Period	Method	Ste	Ext
AI_F7428_1	GVCASASPE	IP_ANALOG	CL2 D.T.	8.259	Good	Good	☐	0.000	14.000	PH	0 0:00:0		Best Fit	1 Hour		☐	☐

2/20/ 2015 10:52:49 AM
14 0:00:00
3/6/ 2015 10:52:49 AM

Figure 1: Two Weeks of pH Readings With Two-point Calibration at PVC Facility

II. Calibration Every 8 Hours is Overly Burdensome and Unnecessary

As you know, 40 C.F.R. § 63.11935(c)(5) of the PVC MACT requires that all continuous parameter monitoring systems (CPMS) must comply with the calibration frequency set out at Table 7. For pH monitors, the requirement is every 8 hours of process operation, which can impose significant burdens on facility operations. We understand that most PVC industry facilities use pH monitors with a continuous *in situ* pH probe. The problem is that calibration of these devices can be fairly onerous if performed multiple times within a 24-hour period. The pH analyzer must be taken off-line to remove the pH probe from its holder and perform the calibrations steps summarized at **Attachment A**. According to Working Group members, the calibration can take anywhere from 15 to 40 minutes, depending on how many buffer solutions are used, what kind of probe connectors are in place (probe must be removed to perform calibration), access to the probe, adjustment requirement, instrument manufacturer, and other considerations.

In addition, pH calibration every 8-hours would require facilities to hire up to 4 new instrument technicians to staff a 4-shift operation. By way of background, calibration services at PVC facilities must be performed by employees with specialized training. The instrument technician must have a general understanding and education in mathematics, chemistry and physics, as well as electrical and electronics training and experience. In addition, instrument technicians must attend training offered by instrument manufacturers at each facility. Most PVC facilities use instrument technicians that work 40 hours a week. By requiring calibration every 8 hours, the Agency is essentially compelling facilities to move away from having one or two technicians that work 40-hours per week, to a 4-person shift rotation similar to those for operations that run around the clock.[4]

Calibrating pH monitors every eight hours also is unnecessary. Several factors govern the frequency of calibration, such as types and amounts of contaminants in the liquid stream being analyzed, type of neutralizing media, and concentrations of caustic or acidic components. In the case of the PVC industry, the outflow from the thermal oxidizer consists entirely of gaseous byproducts of combustion, with little if any particulate matter formed during this highly controlled thermal oxidation process. Thermal oxidizer quench and scrubber liquids neutralize the HCl byproduct component to very low residual levels carried out in the exhaust gas leaving the scrubber and vented to the atmosphere. And, as noted above, the process stream is relatively consistent, such that PVC facilities do not experience fouling and other issues that may require more frequent calibration in other industries.

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[4] Although the calibration work would be fairly light duty for a technician, it would be very difficult to train shift employees for this task, and would impose a significant load on them in addition to their other duties.

An informal review of industry facilities indicates that most facilities calibrate their pH monitors at least every two weeks. Specifically, of the nine facilities that responded to the VI, calibration frequency was distributed as follows:

Calibration Frequency	Number of Facilities
Weekly	5
Every Two Weeks	1
Monthly	2
Quarterly	1
Total	9

These calibration intervals appear to be consistent with manufacturer recommendations. For example, Mettler Toledo states that:

> The calibration interval needed for pH is highly application-dependent. The more uniform process conditions are (temperature, pressure, composition, freedom from coating, etc.), the more stable a pH sensor will be and the longer the calibration interval may be. Most pH installations calibrate between once a week and once a month but shorter or longer intervals may be appropriate based on experience. It is a good practice to begin by calibrating frequently and then gradually go to longer intervals, as stability in the installation and accuracy requirements allow.[5]

Similarly, YSI sensors are recommended to be calibrated every two weeks:

> Frequency of calibration for pH and pH/ORP sensors depends on the degree of fouling and the desired level of accuracy. These sensors begin to drift immediately after calibration. While drift occurs within hours, it does not become immediately noticeable for the average user. For most in-situ applications with average conditions and typical accuracy demands (e.g. 0.05 pH units), it's recommended that these sensors are calibrated at least once every two weeks.[6]

III. Frequent Calibration Could Lead to Permit Violations

In addition, the sampling frequency could lead to violation of permit conditions. In this regard, Table 5 to Subpart HHHHHHH requires facilities that use pH monitors as CPMS to monitor and record the pH of the scrubber liquid once every 15 minutes. In addition, the following requirements apply:

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[5] http://us.mt.com/us/en/home/supportive_content/supportive_information/support_faq/FAQ-THOR-ORP-pH.html#question_1

[6] http://www.fondriest.com/pdf/fondriest_calibration_guide.pdf.

- 40 C.F.R. §§ 63.11890(c) and 63.8(c)(4) require the CPMS to be in continuous operation, unless a specific exemption is met.
- 40 C.F.R. § 63.11890(c)(2) prohibits the use of data recorded during specific events, including required monitoring system quality assurance or quality control activities (**including calibration checks and required zero and span adjustments**) when reporting emission levels.
- 40 C.F.R. § 63.11890(c)(2) directs facilities to report any period during which the monitoring system failed to collect required data.
- Obviously, if facilities need to take pH monitors out of service for 30-45 min, three times a day for calibration in accordance with Table 7, these monitors cannot collect pH data at the frequency required by the rule.

The preceding recitation is relevant because the Working Group is aware of at least one facility with a special condition in its permit that makes a deviation any loss of "valid data" due to periods of monitor break down, out-of-control operation, repair, maintenance **or calibration** above 5% in a 24-hour period. Taking a pH monitor out of service for 90 minutes per day would cause the unit to exceed the 5% allowable threshold (over 24 hours).

The Working Group submits that EPA should reconsider the requirement that facilities using pH monitors as CPMS calibrate these devices every 8 hours. As noted above, the relative consistency of the waste gas stream and cleanliness of the caustic liquid stream are not expected to require calibration of the pH monitor every 8 hours. Consequently, the Working Group submits that requiring weekly calibration or calibration in accordance with manufacturer recommendations should be sufficient to ensure that pH monitors are operating correctly. Making this change would remove an unnecessary regulatory burden, as well as eliminate a potential conflict between this provision and the data recording requirements in the rule and with state air permits.

Cordially yours,

Jean-Cyril Walker

Jean-Cyril Walker

cc: Penny Lassiter, U.S. Environmental Protection Agency
Mark Kataoka, U.S. Environmental Protection Agency
Richard Krock, The Vinyl Institute
The Vinyl Institute PVC MACT Working Group

Enclosure

Appendix A

Typical pH Monitor Calibration Procedure at PVC Facility

1. Record the process pH reading prior to calibration.
2. Place the pH controller in "manual" so that it does not react to calibration activity.

   (Note that putting the controller in manual holds the control valve in its same % open position during the calibration process until the controller is taken off manual control.)
3. Isolate the pH probe and pull the probe from the sampler / holder.
4. Place the probe in lower pH Buffer (typically 4.0) and record result.
5. Place the probe in upper pH Buffer (typically 7.0) and record result.
6. Clean the probe.
7. Place the probe in lower pH Buffer and calibrate as needed to obtain lower result.
8. Place the probe in upper pH Buffer and calibrate as needed to obtain upper result.
9. Place the probe back in the sampler / holder.
10. Re-align the probe to the process stream.
11. Record result of process stream after calibration.
12. Place pH controller back in "automatic" mode.

Appendix B: PVC Facility Incinerator pH Calibration Records – Effluent Streams

Date	Process Prior to Calibration	Buffer 4.01 Prior to Calibration	Buffer 4.01 After Calibration	Buffer 4.01 Adjustment	Buffer 6.86 Prior to Calibration	Buffer 6.86 After Calibration	Buffer 6.86 Adjustment	Process After Calibration
Incinerator A Effluent Stream								
1/5/2015	6.01	4.1	4.01	-0.09	6.76	6.86	0.1	5.99
1/12/2015	6.36	4.04	4.01	-0.03	6.82	6.86	0.04	6.22
1/20/2015	6.1	4.1	4.01	-0.09	6.83	6.86	0.03	6.06
1/26/2015	6.14	4.09	4.01	-0.08	6.75	6.86	0.11	6.12
2/2/2015	6.09	3.93	4.01	0.08	6.8	6.85	0.05	6.2
2/10/2015	6.25	4.08	4.01	-0.07	6.76	6.86	0.1	6.2
2/20/2015	6.09	4.1	4.01	-0.09	6.77	6.86	0.09	6.06
2/25/2015	6.17	4.07	4.01	-0.06	6.81	6.85	0.04	6.17
3/3/2015	6.38	4.14	4.01	-0.13	6.81	6.86	0.05	6.31
3/10/2015	6.21	4.14	4.01	-0.13	6.72	6.86	0.14	6.25
3/18/2015	6.29	4.17	4.01	-0.16	6.67	6.88	0.21	6.47
3/23/2015	6.35	4.1	4.01	-0.09	6.68	6.86	0.18	6.86
Average adjustment to effluent pH Meter 7031A				**-0.08**			**0.10**	
Incinerator B Effluent Stream								
1/5/2015	7.25	4.02	4.01	-0.01	6.87	6.86	-0.01	7.17
1/12/2015	7.6	3.98	4.01	0.03	6.8	6.86	0.06	7.64
1/20/2015	7.45	3.99	4.01	0.02	6.84	6.86	0.02	7.5
1/26/2015	7.36	3.99	4.01	0.02	6.87	6.86	-0.01	8.4
2/2/2015	7.13	4.04	4.01	-0.03	6.93	6.86	-0.07	7.28
2/10/2015	7.2	3.99	4.01	0.02	6.85	6.86	0.01	7.16
2/20/2015	7.24	4.01	4	-0.01	6.87	6.86	-0.01	7.15
2/25/2015	7.46	4.02	4.01	-0.01	6.87	6.86	-0.01	8.25
3/3/2015	7.86	4.03	4.02	-0.01	6.85	6.84	-0.01	7.35
3/10/2015	8.07	3.99	4	0.01	6.84	6.86	0.02	7.75
3/18/2015	7.86	4.03	4.01	-0.02	6.87	6.86	-0.01	6.86
3/23/2015	7.45	4	4.01	0.01	6.81	6.86	0.05	6.86
Average adjustment to effluent pH Meter 7031B				**0.00**			**0.00**	
Orange Highlight indicates maximum adjustment for the period								

Appendix B: PVC Facility Incinerator pH Calibration Records – Influent Streams

Date	Process Prior to Calibration	Buffer 4.01 Prior to Calibration	Buffer 4.01 After Calibration	Buffer 4.01 Adjustment	Buffer 6.86 Prior to Calibration	Buffer 6.86 After Calibration	Buffer 6.86 Adjustment	Process After Calibration
Incinerator A Influent Stream								
1/5/2015	8.13	4.07	4.01	-0.06	6.88	6.85	-0.03	8.22
1/12/2015	8.61	4.02	4	-0.02	6.8	6.85	0.05	8.07
1/20/2015	8.35	4.09	4.01	-0.08	7.02	6.86	-0.16	8.99
1/26/2015	8.37	4	4.01	0.01	6.95	6.86	-0.09	8.4
2/2/2015	9.06	4.12	4.01	-0.11	6.76	6.86	0.1	8.21
2/10/2015	9	4.12	4.01	-0.11	6.71	6.85	0.14	8.31
2/20/2015	7.97	4.14	4	-0.14	6.91	6.86	-0.05	8.15
2/25/2015	8.24	4.25	3.99	-0.26	6.95	6.85	-0.1	8.92
3/3/2015	8.4	4.02	3.99	-0.03	6.91	6.83	-0.08	8.46
3/10/2015	8.19	4.11	4	-0.11	6.84	6.85	0.01	8.09
3/18/2015	8.47	4.08	3.99	-0.09	6.97	6.86	-0.11	8.46
3/23/2015	8.2	4.19	4	-0.19	6.98	6.85	-0.13	8.11
Average adjustment to influent pH Meter 7032A				**-0.10**			**-0.04**	
Incinerator B Influent Stream								
1/5/2015	8.6	4.07	4.01	-0.06	6.79	6.86	0.07	7.01
1/12/2015	8.61	4.02	4	-0.02	6.8	6.85	0.05	8.07
1/20/2015	8.43	4.03	4.01	-0.02	6.85	6.86	0.01	8.86
1/26/2015	8.34	4.04	4.01	-0.03	6.99	6.86	-0.13	8.38
2/2/2015	8.83	4.09	4.01	-0.08	6.81	6.86	0.05	8.44
2/10/2015	8.19	4.1	4.01	-0.09	6.93	6.86	-0.07	8.69
2/20/2015	9.14	4.06	4.01	-0.05	6.76	6.87	0.11	8.95
2/25/2015	8.73	4.05	4.02	-0.03	6.79	6.87	0.08	9.18
3/3/2015	9.77	4.1	4.01	-0.09	6.93	6.86	-0.07	8.51
3/10/2015	8.39	4.09	4.01	-0.08	6.75	6.86	0.11	8.22
3/18/2015	8.5	4.09	4.02	-0.07	6.77	6.86	0.09	8.3
3/23/2015	8.35	4.07	4.01	-0.06	6.73	6.86	0.13	8.51
Average adjustment to influent pH Meter 7032B				**-0.06**			**0.04**	
Orange Highlight indicates maximum adjustment for the period								