Envirocleanse Project Report #2

Summary of Findings and Recommendations

Study conducted in the Crawford Lab at the University of Wisconsin Oshkosh, September-November 2021.

Report written by Dr. Kevin Crawford, Professor of Chemistry
December 1, 2021

Executive Summary

At the direction of Envirocleanse personnel, we engaged in a shelf life study of the five different formulations of the Envirocleanse product in two different bottle sizes. The five main questions addressed in this document are:

1. What is the shelf life for the Envirocleanse product in 8-oz and 1-qt bottles?
2. Does salt content affect the shelf life of the product?
3. Does the addition of phosphate buffer increase the shelf life of the product?
4. What is the appropriate Q10 value for shelf life studies?
5. How does the shelf life change once the bottle has been opened?

Findings:

1. The existing Envirocleanse A product has a shelf life (defined as the time to 338ppm FAC) of over one year when the initial FAC is 700ppm and the bottle is stored at 21°C (room temperature). This statement is true for both bottle sizes and all three TDS levels tested.
2. Shelf life of the Enviroclenase A product dramatically decreases as temperature increases. "Conventional Wisdom" is that the rate of a reaction doubles (2x) with every 10°C increase in temperature, but our tests demonstrate that the Envirocleanse A product decays at a higher rate than that (as much as 3.9x faster) with the effect most pronounced in the smaller bottles.
3. Addition of a phosphate buffer to the Envirocleanse A product at bottling helped the solution maintain a stable pH throughout the study. However, the initial FAC in these samples was dramatically lower than the FAC reported by the plant and the FAC continued to drop at a higher rate than that of the un-buffered samples.
4. Repeatedly opened bottles do have an accelerated loss of FAC over time. In the 1-quart bottles the loss was about double of unopened bottles, while in the 8-oz bottles it was triple the rate.

Recommendations:

1. A one-year shelf life (minimum 338ppm FAC on opening) can be claimed for the Envirocleanse A product when it is bottled with an initial FAC of at least 700ppm for both 8oz and 1-quart bottles and within the studied TDS range of 2.6 to 3.4 ppt. Due to the strong temperature dependence for loss of FAC, a note on the label to "store in a cool place" or "protect from heat" may also be desired. Once opened the shelf life is decreased so you may also consider adding something about using the product within a shorter period of time after opening.
2. For additional shelf life studies the appropriate Q-factor for Envirocleanse A was found to be dependent on bottle size and was determined to be 2.4 for the 1-quart bottles and 3.6 for the 8-oz bottles.
3. Though the addition of phosphate buffer controlled the pH drop during aging, it accelerated the loss of HOCl and should not be considered further.

Findings, Conclusions, and Recommendations

During the Fall of 2021, the Crawford lab at the University of Wisconsin Oshkosh analyzed samples of the Envirocleanse A product for the purpose of determining shelf life for two bottle sizes and five compositions. Shelf life here is defined as the time until the Free Available Chlorine (FAC) falls to 338ppm. We were able to hold a set of bottles at room (lab) temperature of 21°C and another set were stored in a climate controlled "warm" room. The bottles in this room were held at 31°C during the entire experiment. Approximately every 7 days we pulled three bottles from each set for each formulation and analyzed the FAC, pH, and TDS. These bottles were then discarded so each data point represents a freshly opened bottle.

Primary objectives as stated in the contract are as follows:

1-A: Establish shelf life for Envirocleanse A in 1-quart HDPE spray bottles and 8 oz. and 100 ml PET white spray bottles. Specifics: Measure FAC, pH, and TDS using a separate bottle each time (3 bottles per time point per bottle type). Half the bottles will be stored at 35C in the Biology warm room, the other half at "room temp" nominally 21 C in the Crawford lab. Client to provide 60 bottles of each type all from the same batch of Texas-produced Envirocleanse A, all starting at approximately 600ppm FAC, 3.6 ppt TDS and pH=6.0.1. What is the impact of salt concentration on the concentration of HOCl? And the impact of salt on HOCl over time?

1-B: Establish shelflife for Envirocleanse A in 1-quart HDPE white bottles, 8-oz white PET bottles and 100 ml white PET bottles. Specifics: Measure FAC, pH, and TDS using a separate bottle each time (3 bottles per time point per bottle type). Half the bottles will be stored at 35C in the Biology warm room, the other half at "room temp" nominally 21 C in the Crawford lab. Client to provide 60 bottles per bottle type, all from the same batch of Texas-produced Envirocleanse A, all starting at approximately 800ppm FAC, 3.6 ppt TDS and pH=6.0.

2-A: Determine the effect of high salt concentration on Envirocleanse A shelf life (1-quart HDPE white bottles, 8-oz white PET bottles and 100 ml white PET bottles). Specifics: Measure FAC, pH, and TDS using a separate bottle each time (3 bottles per time point per bottle type). Half the bottles will be stored at 35C in the Biology wann room, the other half at "room temp" nominally 21 C in the Crawford lab. Client to provide 60 bottles of each type all from the same batch of Detroit-produced Envirocleanse A, all starting at approximately 600ppm FAC, >8.0ppt TDS and pH=6.0.

2-B: Determine the effect of low salt concentration on Envirocleanse A shelflife (1-quart HDPE white bottles, 8-oz white PET bottles and 100 ml white PET bottles). Specifics: Measure FAC, pH, and TDS using a separate bottle each time (3 bottles per time point per bottle type). Half the bottles will be stored at 35C in the Biology warm room, the other half at "room temp" nominally 21 C in the Crawford lab. Client to provide 60 bottles of each type all from the same batch of Texas-produced Envirocleanse A, all starting at approximately 600ppm F AC, <2.75ppt TDS and pH=6.0.

3-A: Determine effects of phosphate buffer additive on Envirocleanse A shelf life in 32-oz HDPE white bottles, 8-oz white PET bottles and 100 ml white PET bottles. Specifics: Measure

FAC, pH, and TDS using a separate bottle each time (3 bottles per time point per bottle type). Half the bottles will be stored at 35C in the Biology warm room, the other half at "room temp" nominally 21 C in the Crawford lab. Client to provide 60 bottles per bottle type all from the same batch of Texas-produced Envirocleanse A, all starting at approximately 600ppm FAC, 3.6 ppt TDS, starting pH between 5.5 and 6 with lM phosphate buffer (pH=5.0) added at a rate equivalent to 20mL per gallon at bottling.

3-B: Determine effects of phosphate buffer additive on Envirocleanse A shelf life in 32-oz HDPE white bottles, 8-oz white PET bottles and 100 ml white PET bottles. Specifics: Measure FAC, pH, and TDS using a separate bottle each time (3 bottles per time point per bottle type). Half the bottles will be stored at 35C in the Biology warm room, the other half at "room temp" nominally 21 C in the Crawford lab. Client to provide 60 bottles per bottle type all from the same batch of Texas-produced Envirocleanse A, all starting at approximately 600ppm FAC, 3.6 ppt TDS, starting pH between 5.5 and 6 with lM phosphate buffer (pH=5.0) added at a rate equivalent to 60mL per gallon at bottling.

4: Selected bottles from each of #l-A through 3-B will be retained and monitored AFTER opening for FAC, pH, and TDS to determine relative decay rates in opened bottles.

5. For each of 1-3 above, data will be used to estimate a shelf-life for the product in each container type as-received. The data will also be used to determine an appropriate Ql0 value for further shelf-life studies of HOCl-containing products.

Envirocleanse personnel chose to eliminate the 100mL white PET bottles from our tests, so all results are for the 1 quart and 8 oz bottles only. We received four different sets of samples from the Houston plant covering high and low FAC with the low FAC also having a lower TDS. The lower FAC sample was also used to produce the two phosphate-added samples. We also received one set of samples from the Detroit plant with higher TDS and lower FAC.

Shelf Life for Houston-produced Envirocleanse A Formula

Our experiment was set up to test bottles of Envirocleanse A formula at both room temperature and at an elevated temperature over at least 10 weeks. Weekly testing involved removing three unopened bottles from both temperature environments and immediately testing FAC, pH, and TDS. Average room temperature was 21°C and held within 2 degrees throughout the study. The elevated temperature room was set to 35°C, but testing of the temperature of the Envirocleanse A samples showed the temperature of the samples was actually 31°C, so that is the temperature used throughout the results analysis.

The length of time covered by this study allowed us to use room temperature results to calculate a shelf life and also to compare those results to the elevated temperature results and determine an appropriate accelerated aging factor (Q10) value for the Envirocleanse A product.

Envirocleanse A (Houston) products:

Sample 1 was a set of 1-quart and 8-oz PET spray bottles containing Envirocleanse A produced at the Houston plant. For the 1-quart samples we measured initial (as received) values of: FAC = 693ppm, pH = 4.97 and TDS = 2.99ppt. The 8-oz samples had initial values of: FAC = 707ppm, pH = 5.12, and TDS = 2.95ppt.

Sample 2 was a set of 1-quart and 8-oz PET spray bottles containing Envirocleanse A produced at the Houston plant. For the 1-quart samples we measured initial (as received) values of: FAC = 587ppm, pH = 5.09 and TDS = 2.61ppt. The 8-oz samples had initial values of: FAC = 607ppm, pH = 5.16, and TDS = 2.60ppt.

Together these two samples represent a high initial FAC (Sample 1) and a lower initial FAC (Sample 2) with Sample 2 also having a lower TDS (about 12% lower) than Sample 1.

Data analysis:

All FAC data was converted to HOCl molarity (moles per liter). This conversion made the assumption that all FAC measured was in the form of HOCl and used the molar mass of HOCl (52.46 g/mole) to convert ppm (mg/L) to M (mole/L).

In sealed bottles the loss of HOCl from the samples may occur through two likely routes: it may permeate the plastic or it may decompose by reacting with itself or other components of the formulation. In first-order kinetics systems the rate of decay is described by Equation 1. When both sides are integrated (Equation 2 and 3) then a linear function between the natural log, ln, of concentration and time results. This is the basis for the graphs produced (ln [HOCl] versus time, an example is in Figure 1), and the slope of the graphs represents the k-factor. When the k-factor is larger it represents a faster rate, so a direct comparison of the k-factors allows you to decide whether one reaction (or set of conditions) yields a faster or slower reaction than another.

$$Rate = \frac{-d[HOCl]}{dt} = k[HOCl]$$

Equation 1: Rate equation for first order kinetics

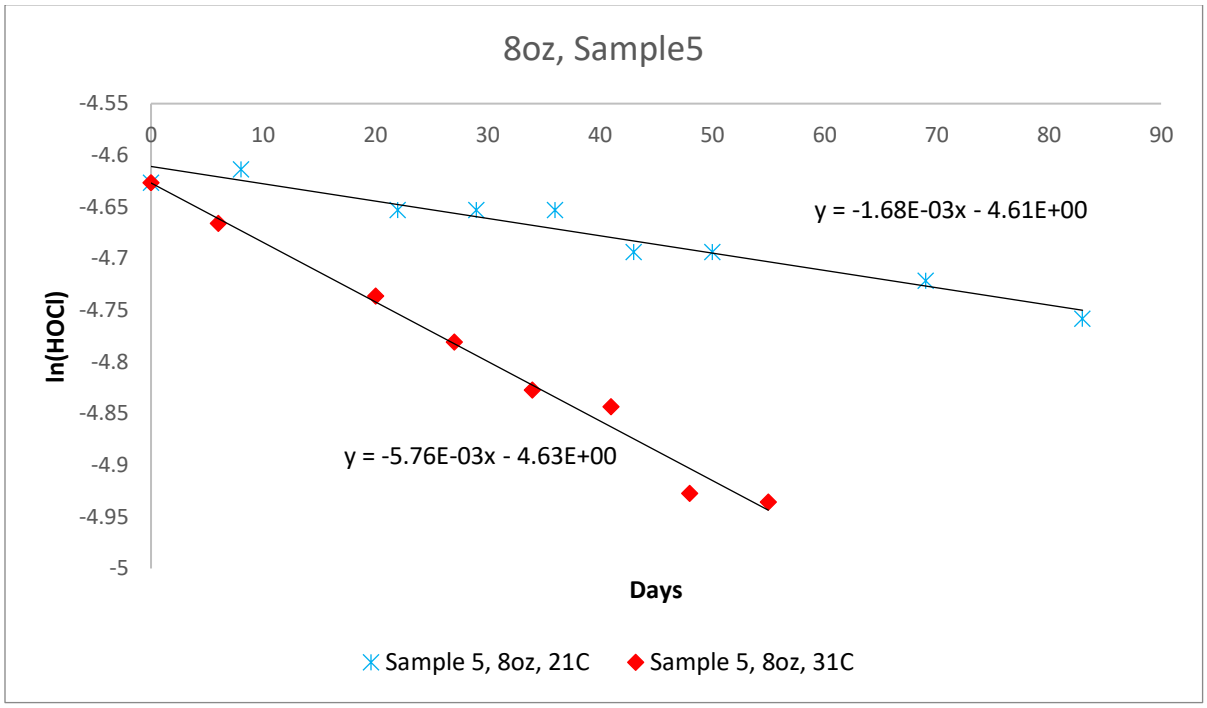
$$\frac{1}{[HOCl]} d[HOCl] = -kdt$$

Equation 2: Rate equation rearranged for integration

$$\ln[HOCl] = -kt + \ln [HOCl]_0$$

Equation 3: Integrated first order rate equation (subscript zero indicates initial concentration)

Figure 1: An example of a first order rate law graph for Envirocleanse A. This graph shows the results for Sample 5 in the 8-oz bottles at 21 and 31C. The linear fit equation is shown on the graph for each data set.



Room Temperature Results:

Rate constants (k-values) for both bottle sizes and Samples 1 and 2 ranged from 0.00148 to 0.00170 day^{-1}, and with the uncertainty of the linear regressions, these values are essentially equivalent. In other words, the starting FAC and TDS concentrations and bottle size did not substantially change the room temperature decay rate.

Using these k-values and extrapolating to 365 days, Sample 1 would have a remaining FAC of 394ppm in 1-quart bottles and 409ppm in 8-oz bottles (nearly the same result). Sample 2 would have a remaining FAC of 339 and 344ppm in the 1-quart and 8-oz bottles respectively. Again, these values are essentially the same and bottle size does not strongly impact shelf life at room temperature.

For both Sample 1 and 2, this model predicts that a starting FAC of over 600ppm yields at least 338ppm FAC at 365 days of room temperature storage. Production of 700ppm Envirocleanse A would give an additional safety factor to ensure a 1-year shelf life at room temperature.

Elevated Temperature Results:

Accelerated aging at 31°C demonstrated a faster rate of decomposition as expected. Rate constants (k-values) for both bottle sizes and Samples 1 and 2 ranged from 0.00297 to 0.00643 day^{-1} with the 8-oz bottles having the higher values (0.00514 and 0.00643).

The k-factors at two different temperatures can be used in Equation 4 to determine the Q_{10} value. A Q_{10} value of 2 is most common and in shelf life studies represents the typical case that a 10-degree increase in temperature doubles the rate of a reaction. With a Q_{10} value of 2 then a 31°C accelerated aging test requires 183 days to be equivalent to a year at 21°C, and at 45°C only 70 days are required.

$$Q_{10} = \left(\frac{k_2}{k_1}\right)^{\frac{10}{(T_2 - T_1)}}$$

Equation 4: Formula for calculating a Q_{10} value from rate factors

The Q_{10} values we calculated from our data for Samples 1 and 2 range from 1.7 to 4.3. The 1-quart bottles had values of 1.7 (Sample 2) and 2.6 (Sample 1) while the 8-oz bottles were 3.3 (Sample 2) and 4.3 (Sample 1). Two conclusions come from these results: first, Sample 2 with a lower initial FAC and TDS has a slower decay rate at elevated temperature compared to Sample 1 and second, the smaller 8-oz bottle has a much faster decay rate at elevated temperature than the 1-quart bottle. Taken together these results also show that a Q_{10} factor of 2 is too small for this kind of sample in 8-oz bottles and it is very dependent on container size.

Shelf Life for Detroit-produced Envirocleanse A Formula

Sample 5 was a set of 1-quart and 8-oz PET spray bottles containing Envirocleanse A produced at the Detroit plant. For the 1-quart samples we measured initial (as received) values of: FAC = 560ppm, pH = 4.92 and TDS = 3.52ppt. The 8-oz samples had initial values of: FAC = 470ppm, pH = 5.05, and TDS = 3.50ppt. These bottles were treated in the same manner as Samples 1 and 2 with some stored at an elevated temperature and unopened bottles sampled in triplicate over 10 weeks. These samples have about an 18% higher TDS than Sample 1 with a starting FAC below that of Sample 2.

Room Temperature Results:

Rate constants (k-values) were nearly identical between the two bottle sizes: 0.00161 and 0.00168 day^{-1}, indicating no effect of bottle size on HOCl loss at room temperature. These values are also consistent with Samples 1 and 2, indicating no impact of elevated salt and differing initial FAC on the decay rate.

These samples started with an FAC of 513ppm (8oz) and 560ppm (1qt) so with the k-values above and extrapolating to 365 days both the 8oz and 1qt bottles would have less than 338ppm FAC remaining. However, if the samples started with at least 625ppm FAC then they would have at least 338ppm FAC at one year. As with Samples 1 and 2, the Detroit-produced

Envirocleanse A should have at least 700ppm FAC at production in order to ensure a 1-year shelf life.

Elevated Temperature Results:

As with Samples 1 and 2, Sample 5 also had a greatly accelerated decay rate at elevated temperature. Rate constants were 0.00467 day^{-1} in the 1-quart bottles and 0.00576 day^{-1} in the 8oz bottles. The Q_{10} values calculated for Sample 5 are 2.9 (1-quart) and 3.4 (8oz) again indicating a strong temperature dependence for loss of FAC. Any future shelf life studies with this formulation should use a Q_{10} value of 3.

Shelf life for Houston-produced Envirocleanse A with Phosphate Buffer additive:

Sample 3 consisted of a set of 1-quart and 8-oz PET spray bottles containing Envirocleanse A produced at the Houston plant (as Sample 2 above) with the addition of 20mL of a 1 Molar phosphate buffer (pH=6.0) per gallon of product. Sample 4 consisted of a set of 1-quart and 8-oz PET spray bottles containing Envirocleanse A produced at the Houston plant (as Sample 2 above) with the addition of 60mL of a 1 Molar phosphate buffer (pH=6.0) per gallon of product.

Our previous report provided initial results on the effect of a phosphate additive on the Envirocleanse A product. It provided pH stability over several weeks but our results then did not show any change in the rate of loss of HOCl. This current study had a longer time period and used new unopened bottles at room and elevated temperature, while our first study was for only a 2-week period and used 1-gallon opened bottles only held at room temperature.

Upon receiving the samples we tested the FAC, pH, and TDS as a time=0 point. We noted that the FAC was already much lower than the as-prepared FAC. At the Houston plant Sample 3 and 4 were measured as 620ppm FAC but upon receipt we found Sample 3 had only 540ppm FAC and Sample 4 had only 512ppm FAC. The loss could be attributed to losses during mixing of the phosphate buffer before bottling if the FAC was measured before the addition of the phosphate, but you will see in our results that the phosphate buffer also accelerated the loss of FAC. We noted that the pH values were also lower than measured at the plant (Sample 3: 6.35 → 6.10, Sample 4: 6.46 → 6.31) while TDS remained very close to the original values.

Room Temperature Results:

Rate constants (k-values) were again similar across bottle sizes for each sample. Sample 3 had a rate constant of 0.00287 in the 1 quart bottles and 0.00304 in the 8-oz bottles. The rates were even higher for Sample 4 with a rate constant of 0.00549 in the 1 quart bottles and 0.00494 in the 8-oz bottles.

The rate for Sample 3 is almost 2 times faster than Sample 2 (Envirocleanse A with no phosphate added) and Sample 4 is over 3 times faster than Sample 2. The much faster rates means that the Envirocleanse A with 20ml phosphate buffer per gallon would need to have an initial FAC of

1000ppm to achieve a 1-year shelf life and at 60mL per gallon it would need an initial FAC of over 2000ppm. These results demonstrate that the FAC is more rapidly lost when a phosphate buffer is present. The buffer did help control the pH however, starting at pH of 6.10 and ending at 5.31 for Sample 3 while starting at pH of 6.31 and ending at 6.00 for Sample 4 (the higher buffer concentration is more effective).

Elevated Temperature Results:

As expected, Sample 3 and 4 had higher rates of loss of FAC at elevated temperature. Sample 3 was 0.00411 day^{-1} for the 1-quart bottles and 0.00631 day^{-1} for the 8-oz bottles. Sample 4 was 0.00785 day^{-1} for the 1-quart bottles and 0.00981 day^{-1} for the 8-oz bottles. The rates for Sample 3 were similar to the rates for Sample 1 at elevated temperature, so the Q_{10} factor is not as large since Samples 3 and 4 had faster rates than Sample 1 at room temperature. Our results showed Q_{10} values for Sample 3 of 1.4 (1-quart) and 2.1 (8-oz) and for Sample 4 of 1.4 (1-quart) and 2.0 (8-oz). These values are more aligned with the "expected" value of 2.0 but there does seem to be an effect of bottle size on the value.

Open Bottles: Effect of opening on shelf life:

One set of samples was set aside after initial shelf life testing for further testing over time. This allowed us to determine the effect of opening and closing a bottle on its loss of FAC. These bottles were stored at room temperature and sampled throughout the study period. Table 1 below shows the comparison between room temperature unopened bottle decay rates and room temperature opened bottles decay rates. In each case the opened bottles lost FAC more quickly with the effect most pronounced in the smaller 8-oz bottles which decayed by a factor of 3 faster.

Table 1: Comparison of Rate Constants for unopened and opened bottles stored at room temperature.

Opened 1qt room temp bottles			
Sample:	1	2	5
Unopened bottles rate	1.59E-03	1.70E-03	1.61E-03
Opened bottles rate	3.24E-03	2.37E-03	2.84E-03
Ratio open/un-opened	2.0	1.4	1.8
Opened 8oz room temp bottles			
Sample:	1	2	5
Unopened bottles rate	1.49E-03	1.58E-03	1.68E-03
Open bottle rate	4.96E-03	4.65E-03	5.24E-03
Ratio open/un-opened slopes	3.3	2.9	3.1

Summary

Overall results of our shelf life studies for each bottle size are summarized in the tables below.

Summary table of results for 1-quart bottles:

Sample:	1	2	3	4	5
21°C HOCl slope (rate, day^{-1})	0.00159	0.00170	0.00287	0.00549	0.00161
31°C HOCl slope (rate, day^{-1})	0.00420	0.00297	0.00411	0.00785	0.00467
Q_{10}	2.6	1.7	1.4	1.4	2.9
Starting FAC (ppm)	693	587	547	507	560
Predicted ppm FAC at 365D, 21°C	394	339	187	71	293
Predicted ppm FAC at 365D, 31°C	152	209	119	30	96

Summary table of results for 8-ounce bottles:

Sample:	1	2	3	4	5
21°C HOCl slope (rate, day^{-1})	0.00149	0.00158	0.00304	0.00494	0.00168
31°C HOCl slope (rate, day^{-1})	0.00643	0.00514	0.00631	0.00981	0.00576
Q_{10}	4.3	3.3	2.1	2.0	3.4
Starting FAC (ppm)	707	607	540	520	513
Predicted ppm FAC at 365D, 21°C	409	344	176	87	286
Predicted ppm FAC at 365D, 31°C	67	94	53	14	64

Findings:

1. The existing Envirocleanse A product has a shelf life (time to 338ppm FAC) of over one year when the initial FAC is 700ppm and the bottle is stored at 21°C (room temperature). This statement is true for both bottle sizes and all three TDS levels tested. See Summary Tables above, "Predicted FAC at 365D, 21°C" for Samples 1, 2, and 5.
2. Shelf life of the Enviroclenase A product dramatically decreases as temperature increases. "Conventional Wisdom" is that the rate of a reaction doubles (2x) with every 10°C increase in temperature, but our tests demonstrate that the Envirocleanse A product generally decays at a higher rate than that (1.7-3.9x faster, averaging 2.4 in 1-quart bottles, averaging 3.6 in 8-oz bottles) with the effect most pronounced in the smaller bottles. See Summary Tables above, Q_{10} results for Samples 1, 2, and 5.
3. Addition of a phosphate buffer to the Envirocleanse A product at bottling helped the solution maintain a stable pH throughout the study. However, the initial FAC in these samples was dramatically lower than the FAC reported by the plant and the FAC continued to drop at a higher rate than that of the un-buffered samples. See Summary Tables above, Samples 3 and 4.

4. Repeatedly opened bottles do have an accelerated loss of FAC over time. In the 1-quart bottles the loss was about double of unopened bottles, while in the 8-oz bottles it was triple the rate. See Table 1 for results.

Recommendations:

1. A one-year shelf life (minimum 338ppm FAC on opening) can be claimed for the Envirocleanse A product when it is bottled with an initial FAC of at least 700ppm for both 8oz and 1-quart bottles and within the studied TDS range of 2.6 to 3.4 ppt. Due to the strong temperature dependence for loss of FAC, a note on the label to "store in a cool place" or "protect from heat" may also be desired. Once opened the shelf life is decreased so you may also consider adding something to the label about using the product within a shorter period of time after opening.
2. For additional shelf life studies the appropriate Q-factor for Envirocleanse A was found to be dependent on bottle size and was determined to be 2.4 for the 1-quart bottles and 3.6 for the 8-oz bottles.
3. Though the addition of phosphate buffer controlled the pH drop during aging, it accelerated the loss of HOCl and should not be considered further.

This report would not have been possible without the extensive lab work and contributions of Thomas Cisler.

Submitted December 1, 2021