Reevaluating the Holding Time Requirements for Acrolein and Acrylonitrile in Aqueous Matrices

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Overview

- This presentation will look at the stability of acrolein and acrylonitrile in aqueous matrices.
- The stability will be compared in samples that were not preserved, that were preserved to a pH of $\leq$2, and that were preserved to a pH of between 4 and 5.
- Since the longest maximum holding time for volatile organics is 14 days, the stability of acrolein and of acrylonitrile was examined over this same time period.

Background

- In 40 CFR 136, Table II and in SW-846 Method 8260, the EPA established aqueous sample preservation and holding time requirements for acrolein and acrylonitrile that differ significantly from those of other volatile organic compounds.

Parameter	Preservation	Holding time
Purgeable Halocarbons	Cool, < 6°C, 0.008% $Na_2S_2O_3$, HCl to pH2[9]	14 days.
2-Chloroethylvinyl ether	Cool, < 6°C, 0.008% $Na_2S_2O_3$	14 days.
Purgeable aromatic hydrocarbons	Cool, < 6°C, 0.008% $Na_2S_2O_3$, HCl to pH2[9]	14 days[9]
Acrolein and acrylonitrile	Cool, < 6°C, 0.008% $Na_2S_2O_3$; Adjust pH to 4-5[10]	14 days[10]

9 If the sample is not adjusted to pH 2, then the sample must be analyzed within seven days of sampling.

10 The pH adjustment is not required if acrolein will not be measured. Samples for acrolein receiving no pH adjustment must be analyzed within 3 days of sampling.

Background

- In November 2010, the former Environmental Laboratory Advisory Board (ELAB) cited data that demonstrated the stability of acrolein and acrylonitrile in both deionized water and groundwater for 16 days, whether preserved to a pH$\leq$2 or unpreserved.
- EPA deemed the information insufficient to justify the requested change.

Background

- In order to improve laboratory productivity and reduce the chance of inadvertent errors, the Environmental Monitoring Coalition (EMC) worked with experts from EPA to design a study to determine whether the more usual preservation and holding time standards are applicable to these analytes.
- This study looked at aqueous samples that represent a more challenging situation with respect to sample stability.

Study Design 1

Samples were collected from six (6) sources representing matrices of interest in the Clean Water Act (CWA) and Resource Conservation and Recovery Act (RCRA) programs.

- Effluent from a publicly owned treatment works (POTW)
- Surface water (SW)
- Two wastewater samples from an industrial facility or influent from a wastewater treatment plant treating industrial wastewater (IW-1 and IW-2)
- Landfill leachate (LL)
- Groundwater with high hardness (GW)

Study Design 2

Upon arriving at the laboratory, an aliquot of each sample was analyzed to determine the “native” level of acrolein and of acrylonitrile and to determine other chemical and physical properties of the water samples.

Study Design 3

- The remaining samples of each matrix were then split into three 2-Liter aliquots.
- One aliquot was immediately preserved with 1:1 HCl to pH ≦ 2.; one to a pH of 4.0 – 5.0; and one aliquot left unpreserved.
- Each of the aliquots was then used to fill, at least, forty-40 mL VOA vials.
- Each VOA vial was then spiked with acrolein and acrylonitrile so that the concentration of acrolein and of acrylonitrile in the vial is approximately 100 ppb.
- Each type of preservation was then analyzed in quintuplicate on Days 0, 3, 7, 10 and 14 using EPA Method 624.1.

Study Design 4

The results of the testing were evaluated by:

(1) Plotting the average results for the subsamples preserved at pH $\leq$2; at pH 4.0 – 5.0; and unpreserved to evaluate relative loss of analyte;

(2) Comparing the concentration of the compound in each sample to the Method 624.1 LCS acceptance criteria of 60 – 140% of the initial (i.e., Day 0) concentration; and

(3) Looking at the concentration of acrolein and of acrylonitrile with all three types of preservation at 14 days.

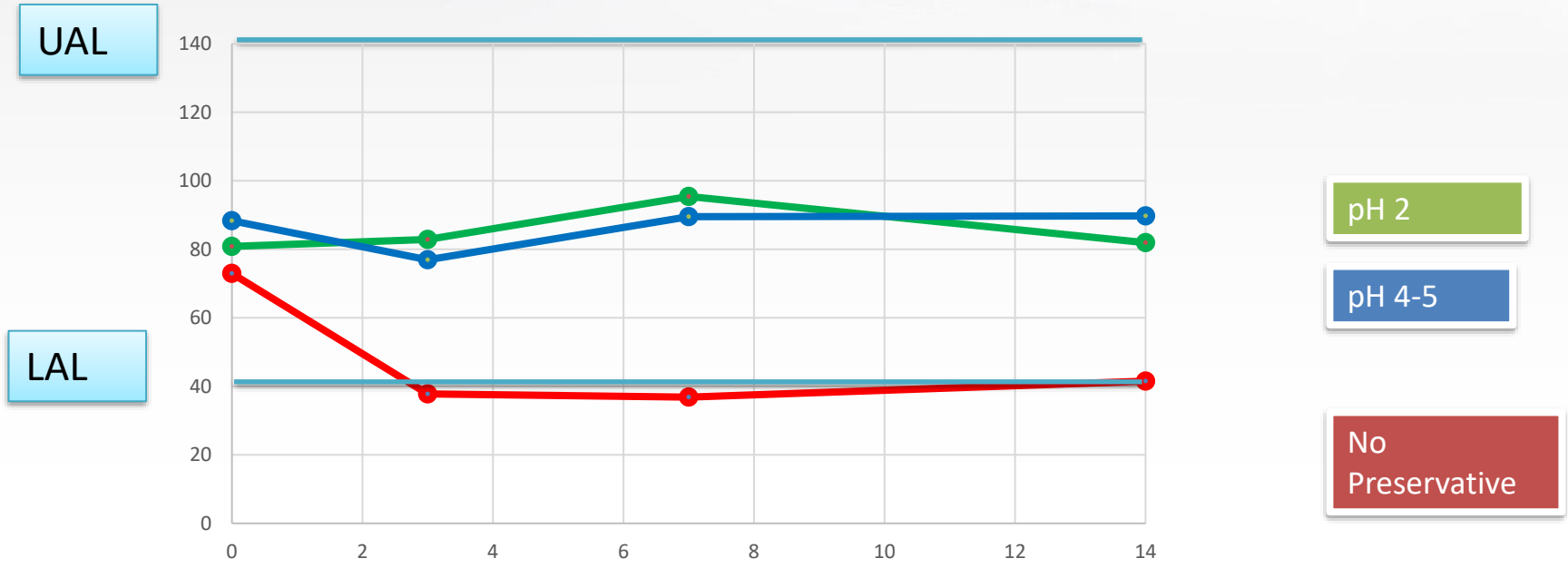
Note: the goal of this study was not to establish holding times, but rather to determine if the preservation and holding time for other volatiles could be used.

Precision

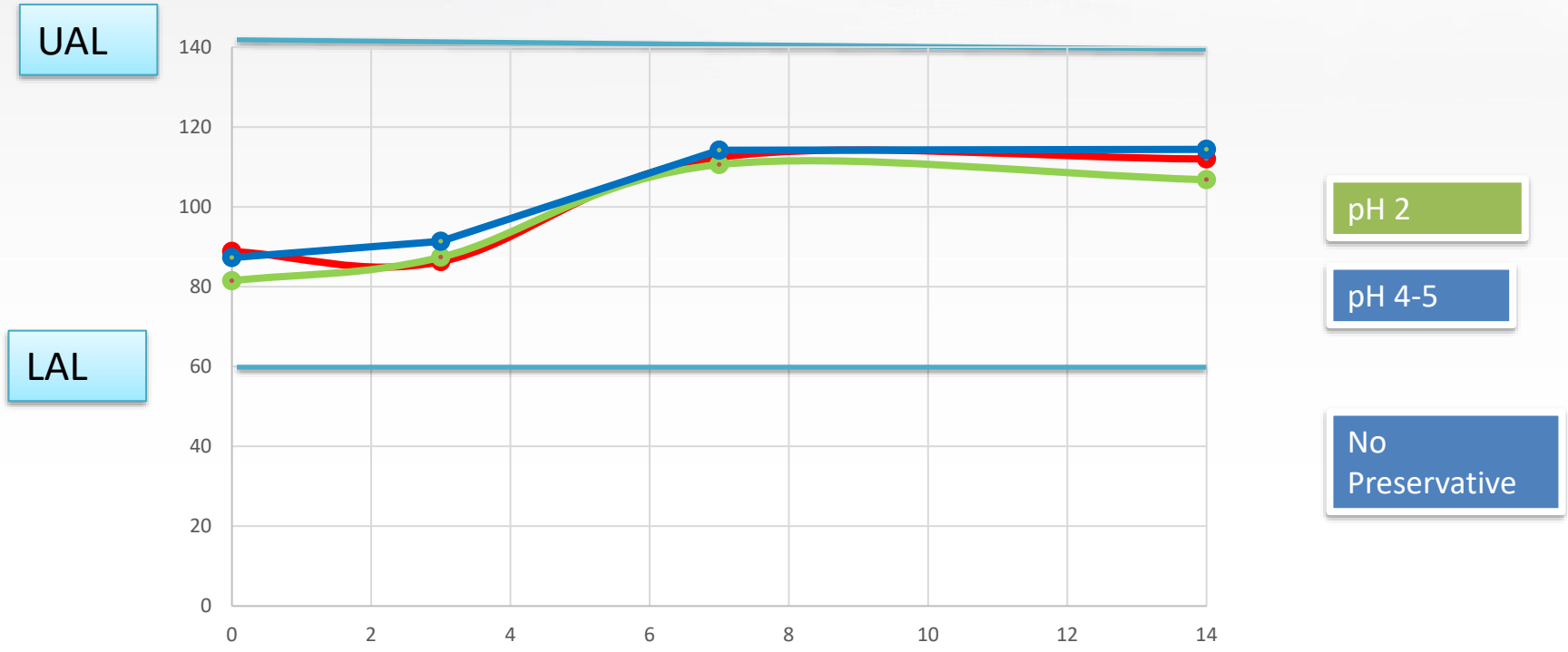
Matrix	Mean Standard Deviation, % (75 Replicates each)	
	Acrolein	Acrylonitrile
POTW Effluent	3.63	2.86
Surface Water	15.3	20.0
Groundwater	3.18	2.76
Leachate	3.16	3.59
Industrial Wastewater 1	0.76	3.36
Industrial Wastewater 2	4.39	4.57

Preliminary Results by Sample Type

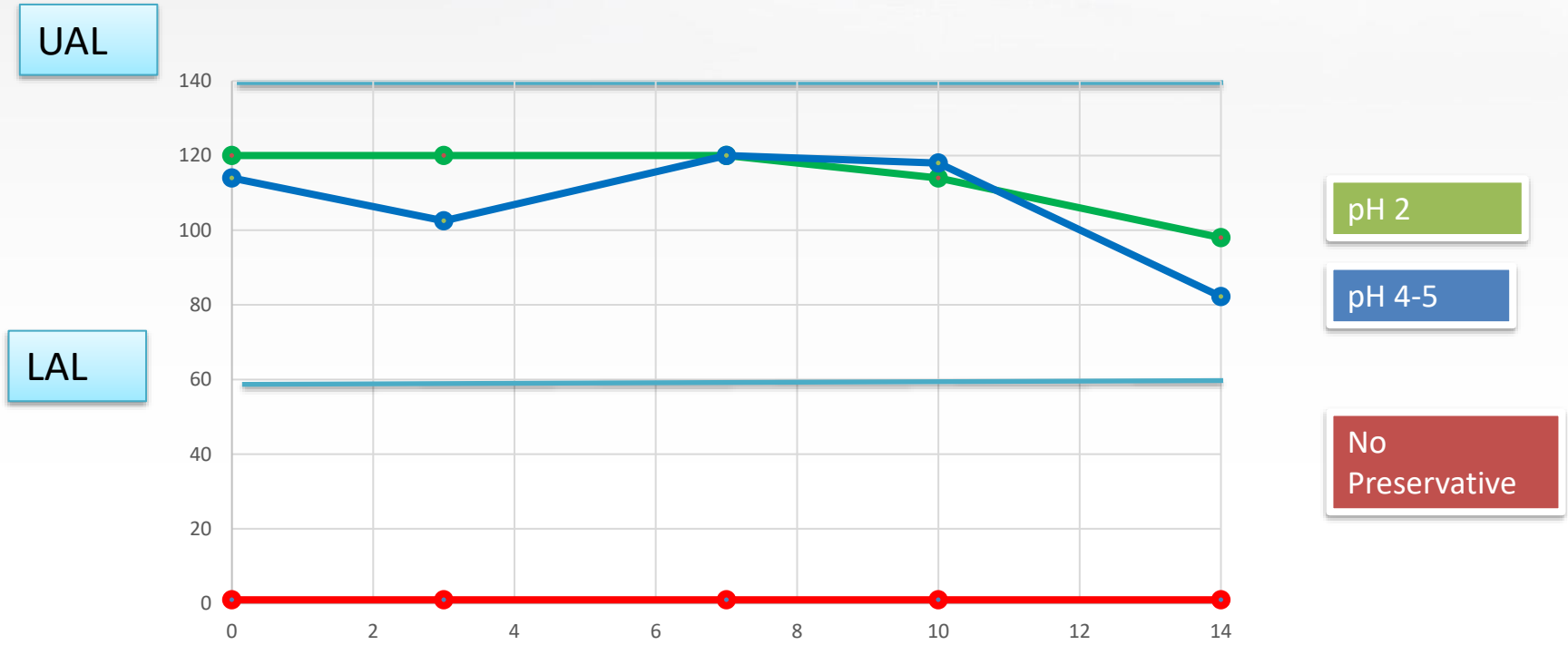
Acrolein – POTW Effluent



Acrylonitrile - POTW Effluent



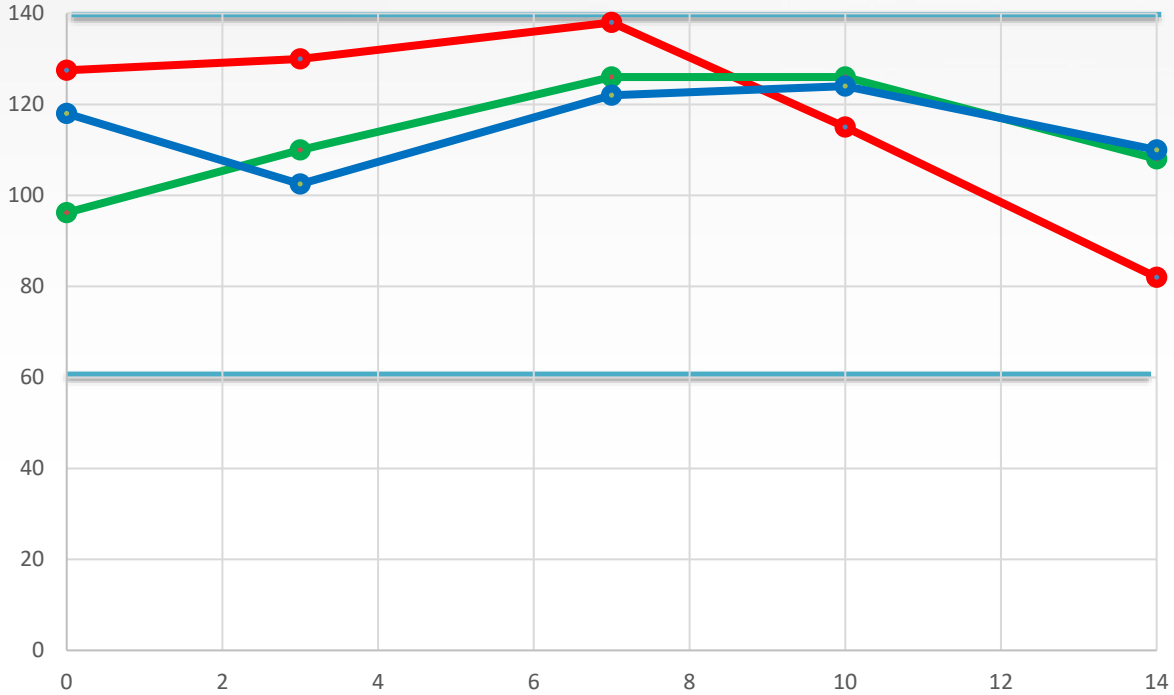
Acrolein – Surface Water



Acrylonitrile – Surface Water

UAL

LAL



pH 2

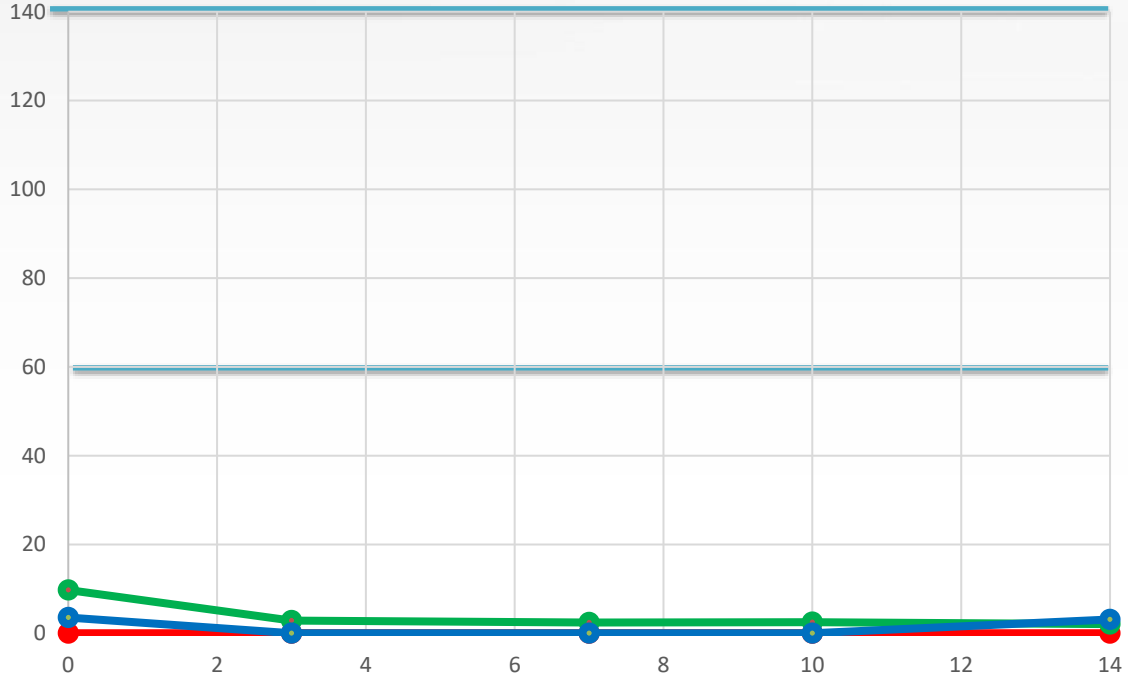
pH 4-5

No Preservative

Acrolein – Wastewater 1

UAL

LAL



pH 2

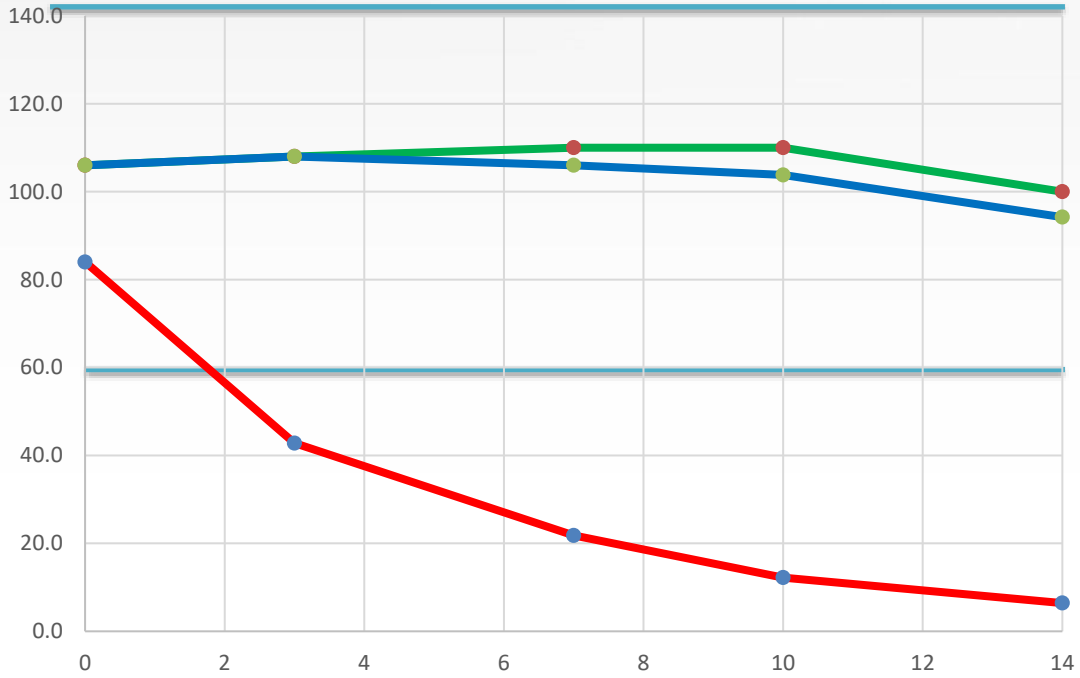
pH 4-5

No Preservative

Acrylonitrile – Wastewater 1

UAL

LAL



pH 2

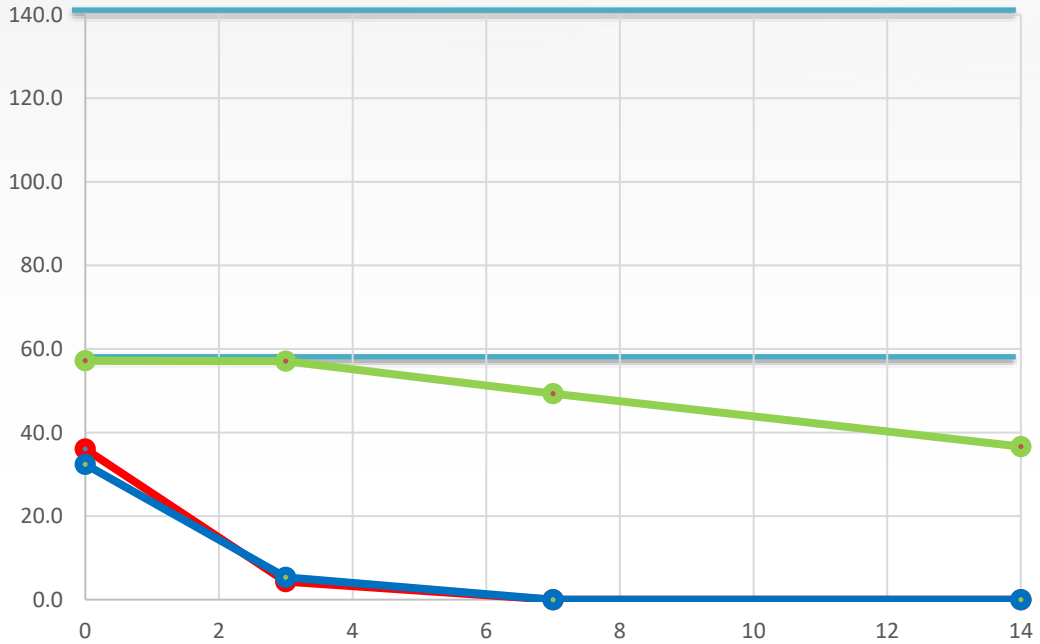
pH 4-5

No Preservative

Acrolein - Leachate

UAL

LAL



pH 2

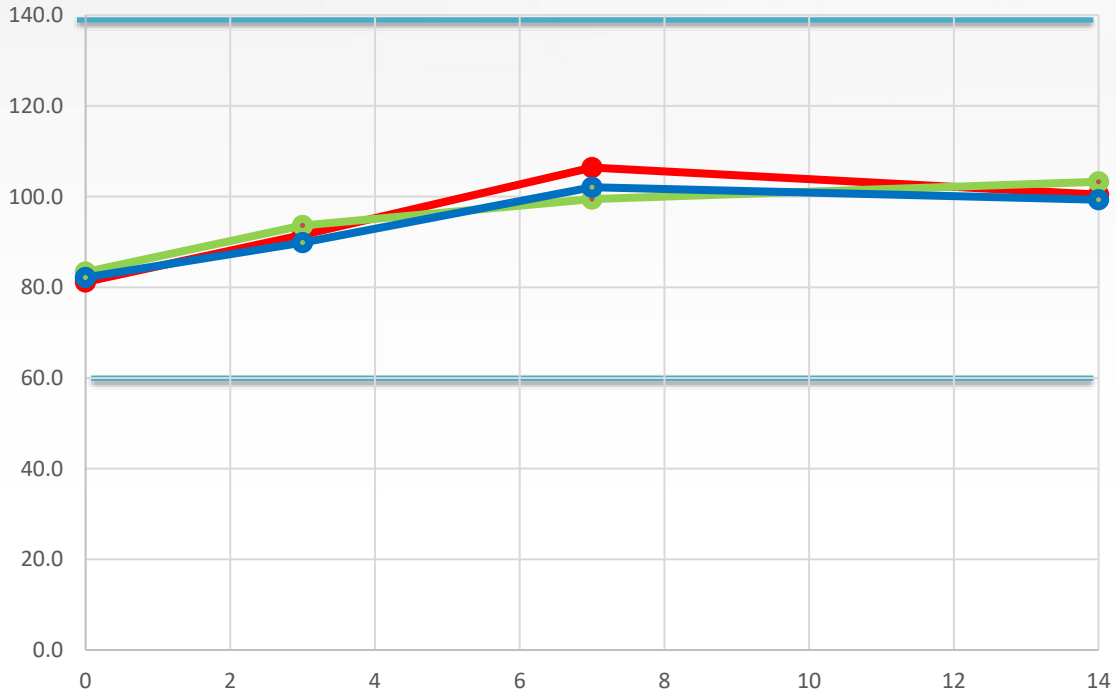
pH 4-5

No Preservative

Acrylonitrile - Leachate

UAL

LAL



pH 2

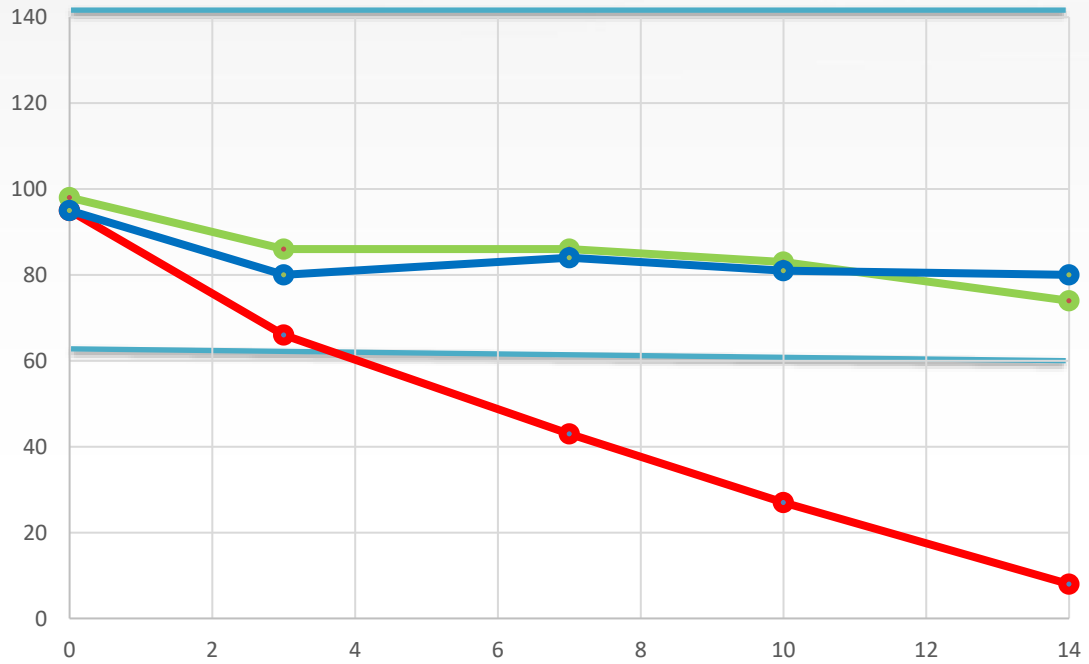
pH 4-5

No Preservative

Acrolein - Groundwater

UAL

LAL



pH 2

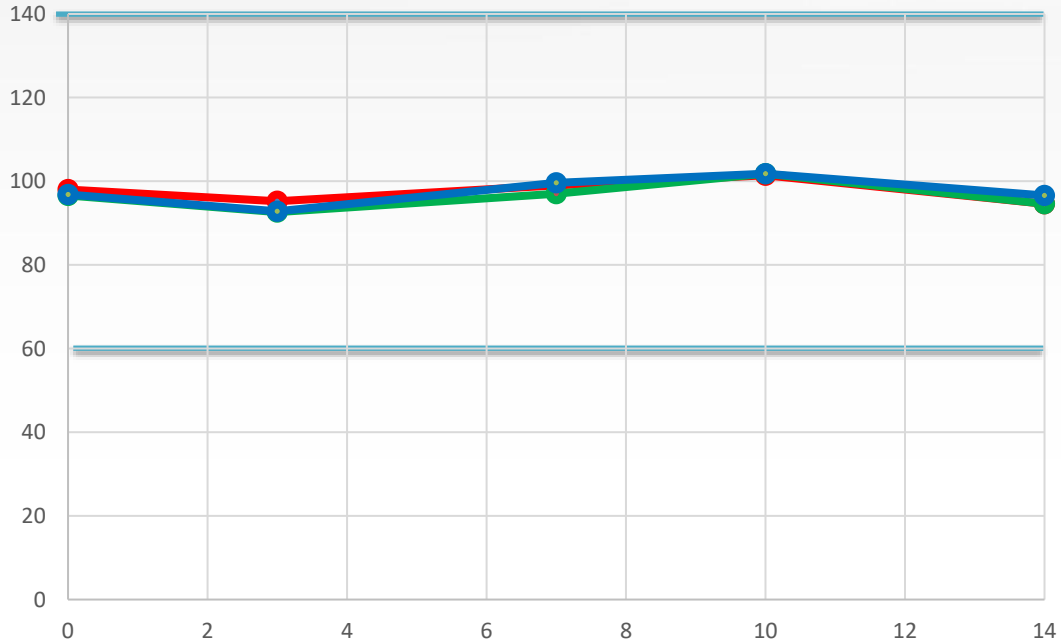
pH 4-5

No Preservative

Acrylonitrile - Groundwater

UAL

LAL



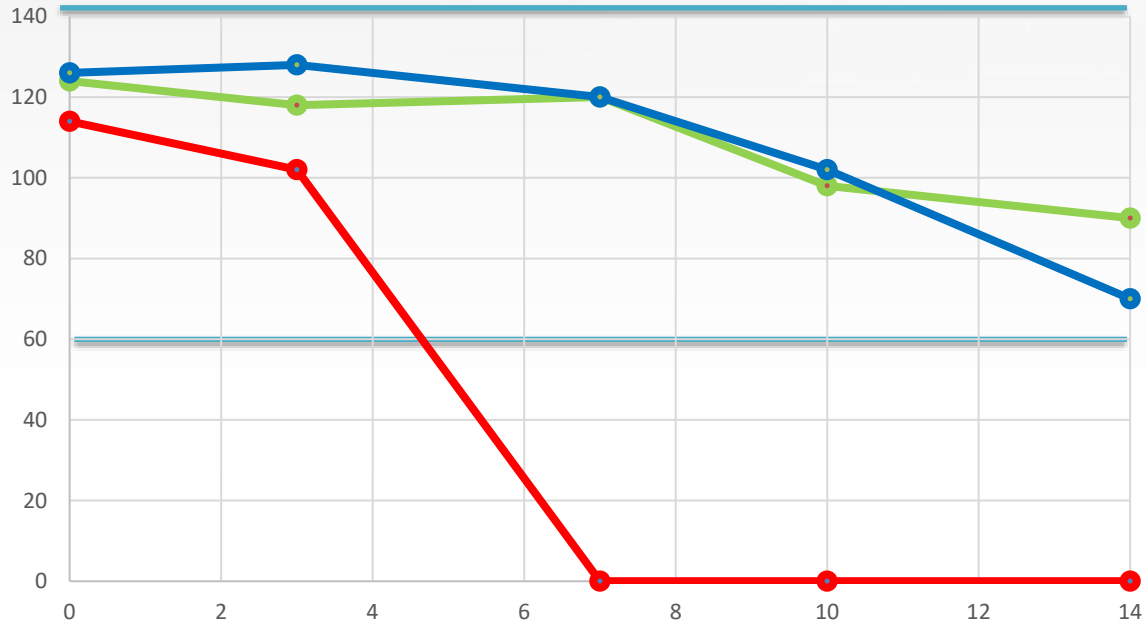
pH 2

pH 4-5

No Preservative

Acrolein – Wastewater 2

UAL



LAL

pH 2

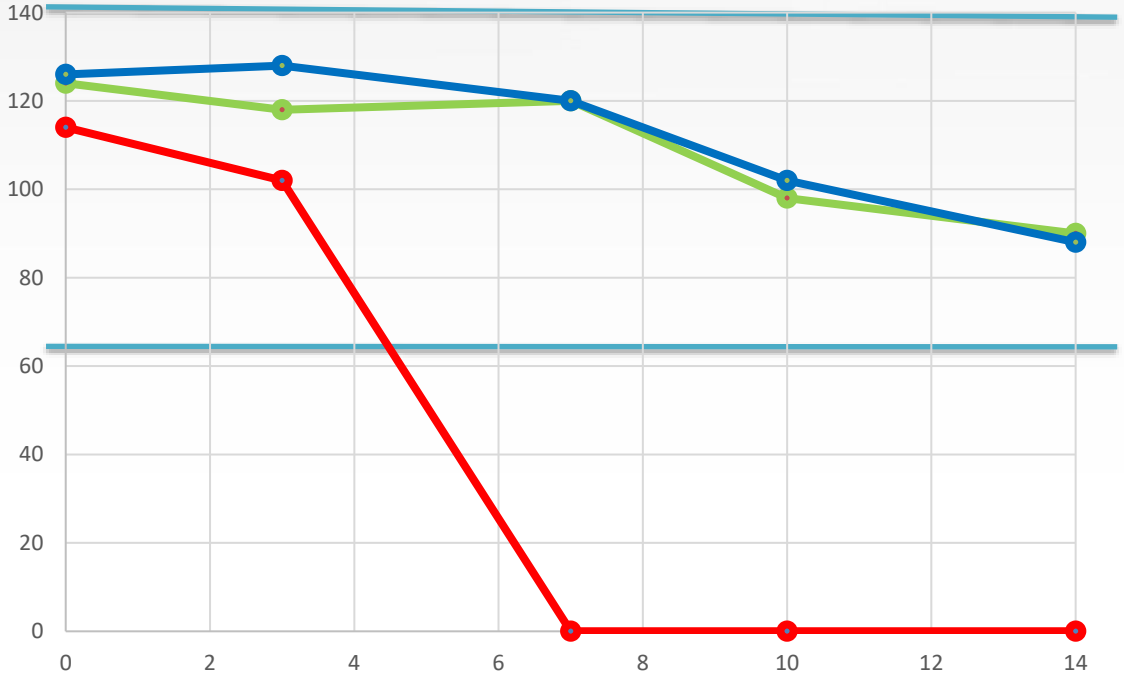
pH 4-5

No Preservative

Acrylonitrile – Wastewater 2

UAL

LAL



pH 2

pH 4-5

No Preservative

Summary of Results

Acrolein

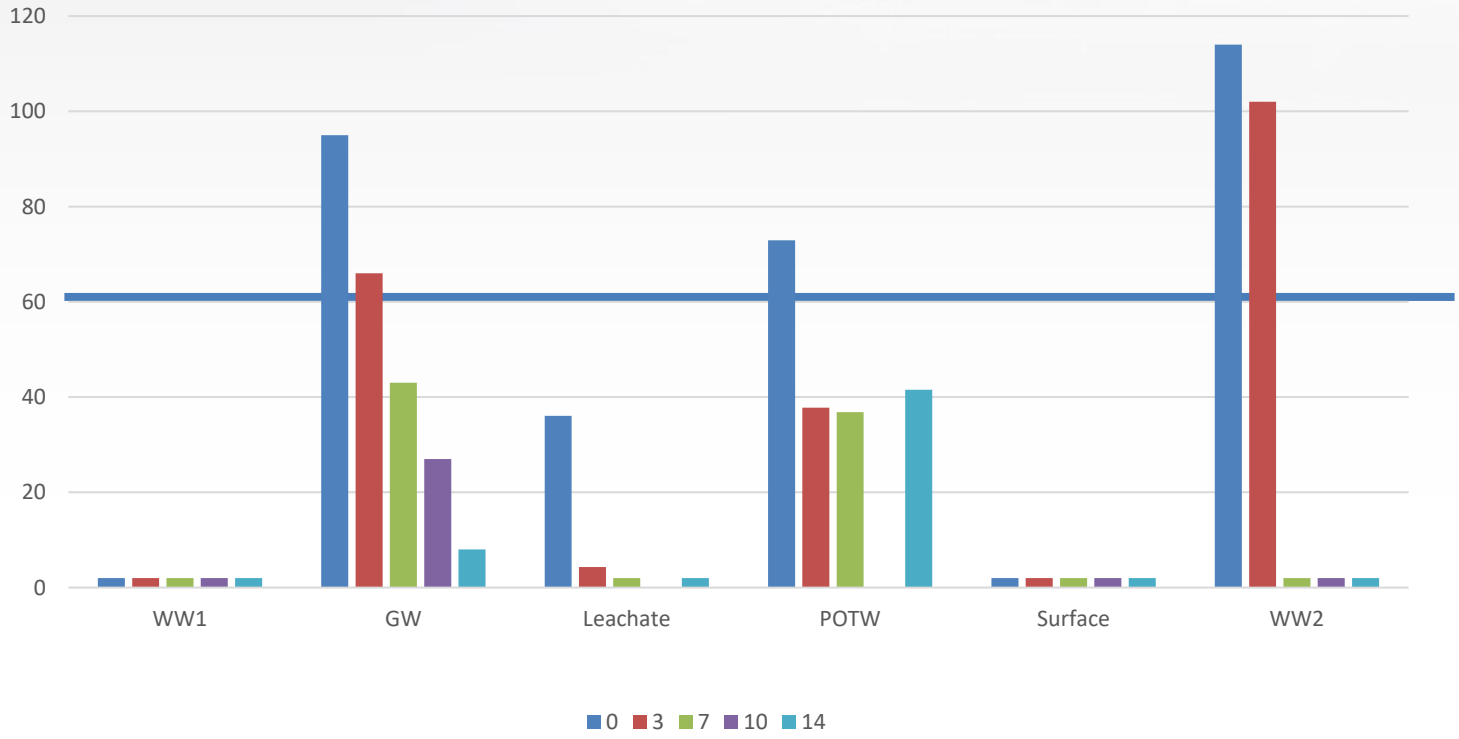
- Unpreserved samples have at best a 3-day holding time.
- Except for the leachate sample, both pH 2 and pH 4-5 had acceptable recoveries at 14 days, with pH 2 providing the best performance.
- Wastewater 1 has a significant matrix effect with poor recoveries at all preservation types.

Acrylonitrile

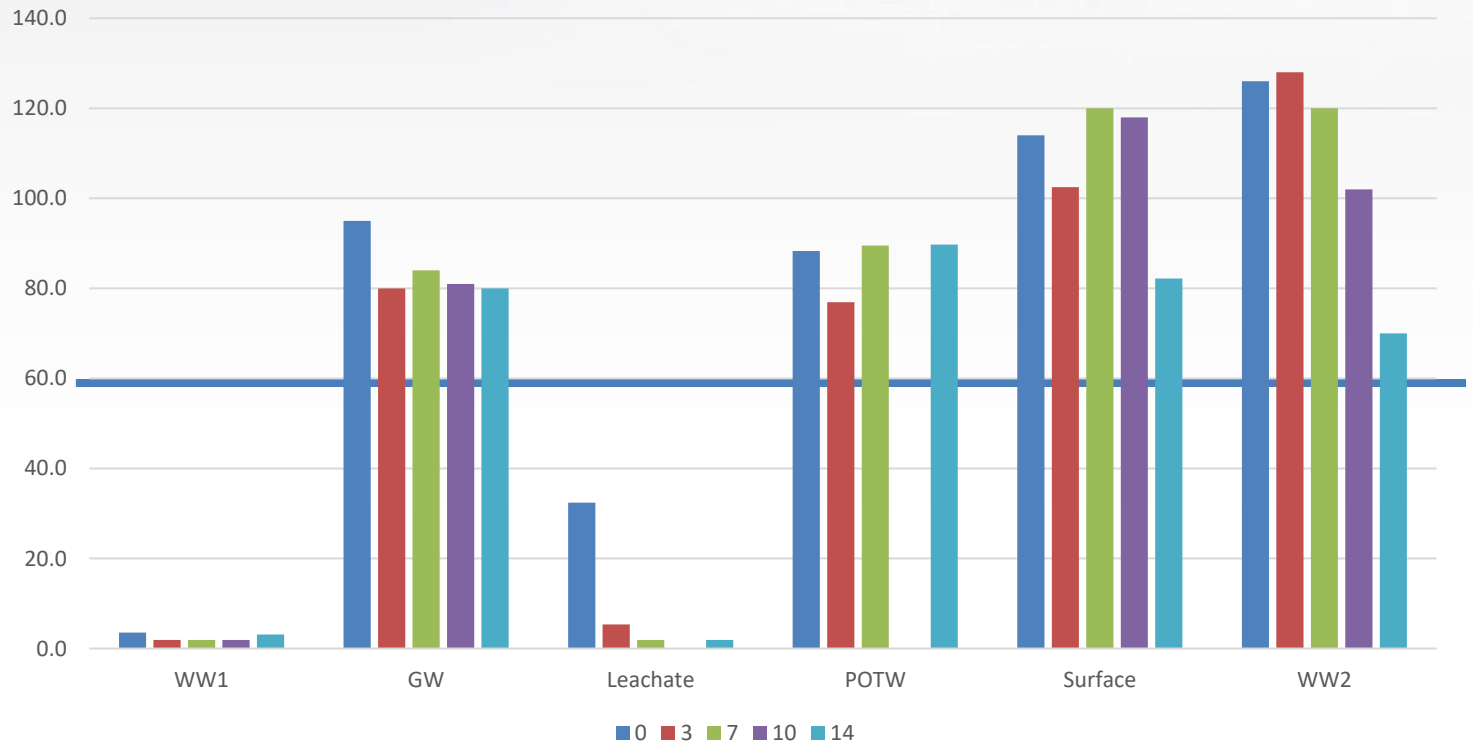
- For the most part, any of the preservatives provided acceptable results.
- Both of the unpreserved wastewater samples showed poor recoveries after 3 days.

Preliminary Results Across Sample Types

Acrolein – No Preservative

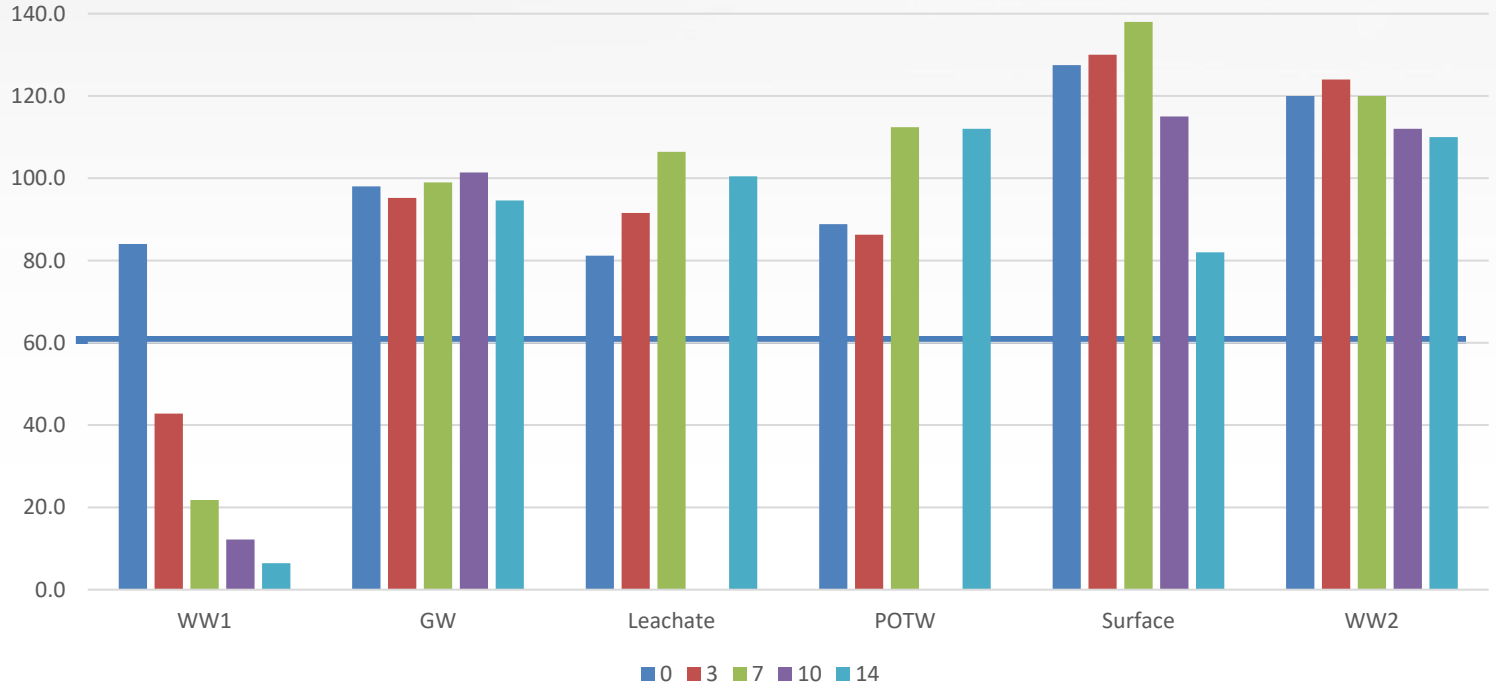


Acrolein – pH 4-5

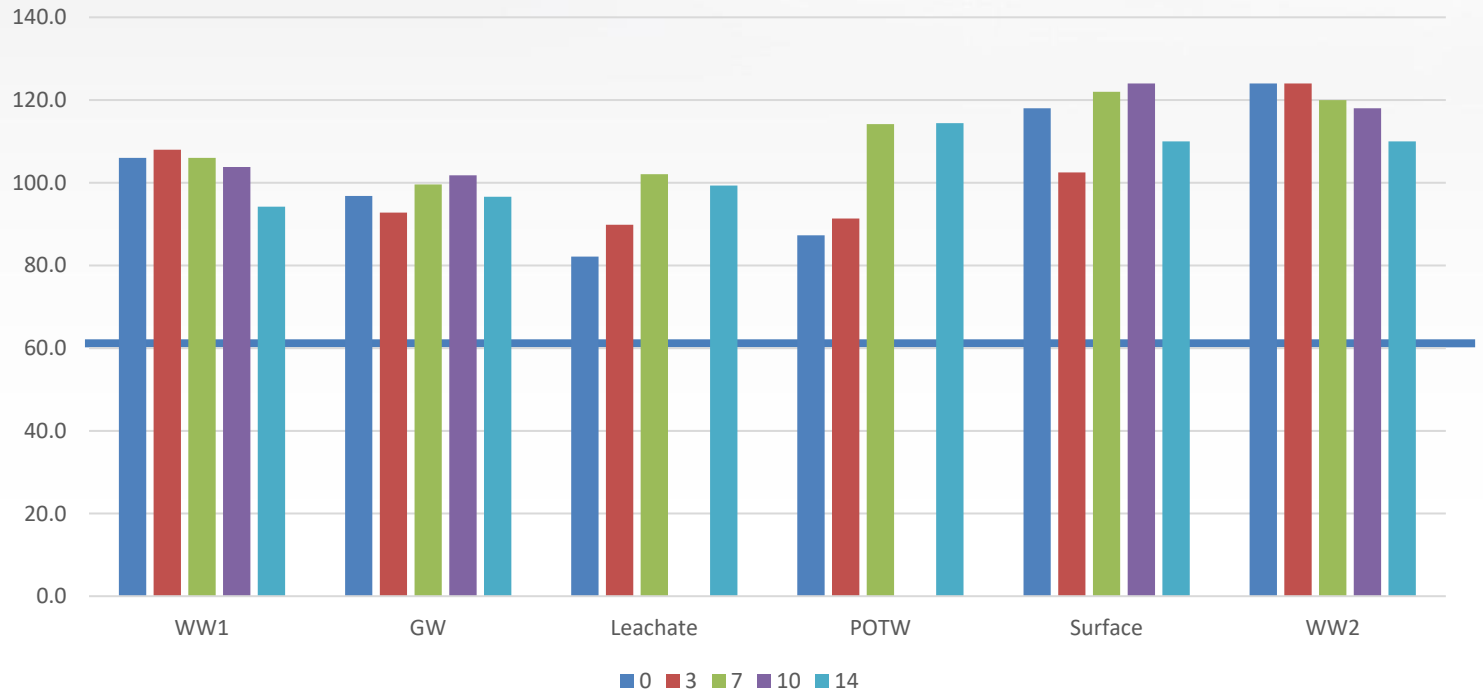


Acrolein – pH 2

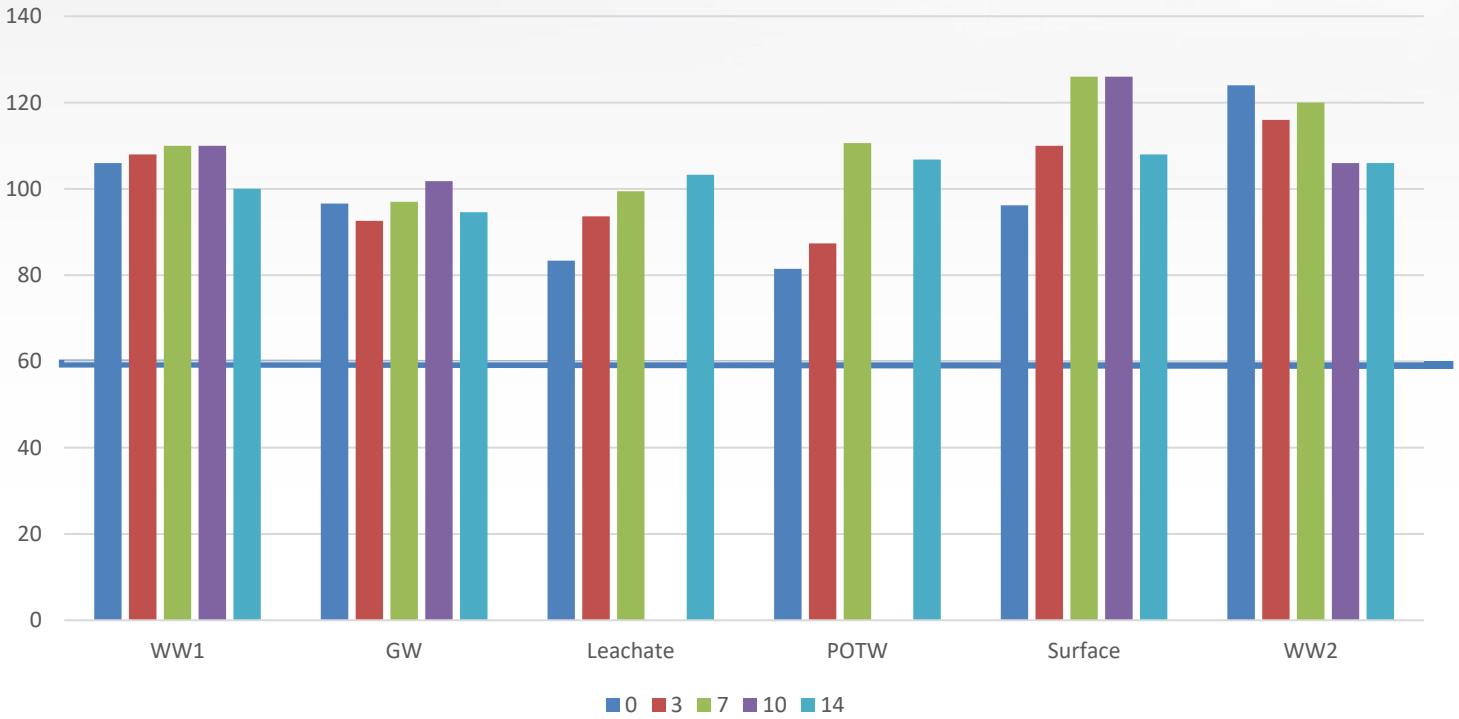
Acrylonitrile – No Preservative



Acrylonitrile – pH 4-5



Acrylonitrile – pH 2



Summary of Results

Acrolein

- 23 of the 28 unpreserved samples were below 60% with <2% for the WW1 and Leachate samples at all times.
- 19 of the 28 samples had acceptable recoveriesat both pH 2 and pH 4-5, with pH 2 slightly better.
- Wastewater 1 has a significant matrix effect with poor recoveries at all preservation types.

Acrylonitrile

- Except for IW1, the unpreserved samples had acceptable recoveries.
- Recoveries at both pH 2 and pH 4-5 were above 80% for all 28 samples.

Conclusions

- Preservation
  - pH $\leq$ 2 preserves the acrolein and acrylonitrile as well as, if not better than, the current pH 4 – 5 requirement.
  - For acrolein, even the pH 4 - 5 acidification is better than non-acidification.
- Holding Time
  - For acrolein, with pH < 2 acidification, after a 14 day holding time recoveries are at least 80%, with the exception of one of the industrial wastewaters, where the acrolein was lost almost immediately, with all the preservatives.
  - For acrylonitrile, with pH <2 acidification, there was little or no loss of analyte during a 14-day holding time.

Conclusions

- This study showed that in a variety of water matrices, changing the required sample preservation and holding time requirements would not compromise the resulting analyses.
- Samples preserved to a pH <2 and held for 14 days before analysis would generally meet the current EPA Method 624.1 recovery criteria of 60 – 140%.
- Samples must be acidified to a pH of <5 if the values at 14 days are to be valid.

Next Steps

- Try and determine why the IW1 and leachate samples had poor recoveries.
- Investigate the cause of the imprecision of the Surface Water sample.
- Prepare a detailed Study Report.
- Provide to OW and ORCR with a request to change preservation to pH <2 and a 14 day holding time.

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Participating Laboratories

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For review of the Study Plan

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