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# Investigation into Cyanide Levels at the Arcata Wastewater Treatment Facility

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## Abstract

The City of Arcata Wastewater Treatment Facility (AWTF) was issued a new National Pollution Discharge Elimination System (NPDES) permit in 2019, which establishes a water quality objective for cyanide of 1.0 µg/L for the protection of saltwater aquatic life. Since the enactment of the permit, the AWTF has been over the maximum daily effluent limit (MDEL) of 1.0 µg/L and average monthly effluent limit (AMEL) of 0.43 µg/L for cyanide in discharged effluent. However, results show that the concentration of cyanide in the wastewater leaving the plant is on average greater than those measured in the plant influent. This study used distillation and colorimetric analysis to investigate the cyanide formation within the AWTF by comparing the cyanide levels in preserved and unpreserved samples. Samples were taken concurrently with the monitoring samples that were sent to a certified lab. The study, which had an estimated method detection limit (MDL) of 0.55 µg/L, found that unpreserved samples had no detectable levels of cyanide while preserved samples demonstrated a cyanide concentration ranging from no detection to 1.7 µg/L. Results for preserved samples in this study compared well with those from the certified lab, however, the value from our study were consistently lower for each sampling event. The use of field spikes demonstrated that the integrity of the sample was maintained in unpreserved samples. The elevated cyanide levels in preserved samples compared to unpreserved samples suggest that preservation with sodium hydroxide (pH > 12) leads to a positive interference in the analysis.

## Methods

Samples were collected on October 20th and 27th, November 17th, and December 15th in 2021 concurrently with routine monitoring of cyanide. Preserved and unpreserved wastewater effluent samples were collected from Outfall 001. An additional unpreserved sample was spiked with 15 µg/L to determine whether the sample integrity was maintained over the course of the analysis. Samples were taken to Cal Poly Humboldt (CPH) where they were distilled following Standard Method 4500C for cyanide and the concentration was analyzed immediately using an Agilent 8453 diode array spectrophotometer and Standard Method 4500E; a 10 cm quartz-windowed sample cell was used to achieve sufficient sensitivity at detection limits near 0.5 µg/L. Over the course of three months, laboratory control samples spiked with 5 µg/L cyanide were used to establish a method detection limit and bias. All results from CPH were compared to the results from a certified lab where the analysis was performed within the 14-day holding time allowed by EPA protocols.

## Results

For each sampling event, the cyanide concentrations in both the unpreserved and preserved samples from Outfall 001 were analyzed to ascertain whether or not there was an issue with sample preservation method or analysis. As seen below, Figure 2 displays the overlay of spectra for representative standards, a method blank, and samples (preserved and unpreserved).

The MDL reported by a certified lab was 0.70 ug/L, which was similar to the MDL of 0.55 ug/L estimated in this study. The bias of each group's results were calculated using their LCS and LCSD results. Bias calculated for CPH using seven replicate standards was -6%, whereas bias calculated from the certified lab results was +7%.

This study found that there was no detectable amount of cyanide in unpreserved samples during any of the sampling events. Preserved samples that were analyzed 72 hours later showed measurable cyanide during three of the four sampling events. The certified lab found cyanide concentrations exceeding the MDEL of 1.0 ug/L in each of the sampling events. Similar trends were seen by both groups as cyanide concentrations decreased over the testing period, however, certified lab results were consistently higher than CPH results. The results for cyanide concentration in the various samples, by both groups, are listed below in Table 3.



Figure 2: Distillation apparatus for cyanide extraction (left) as compared to specifications in Standard Methods 4500 CN C (right).

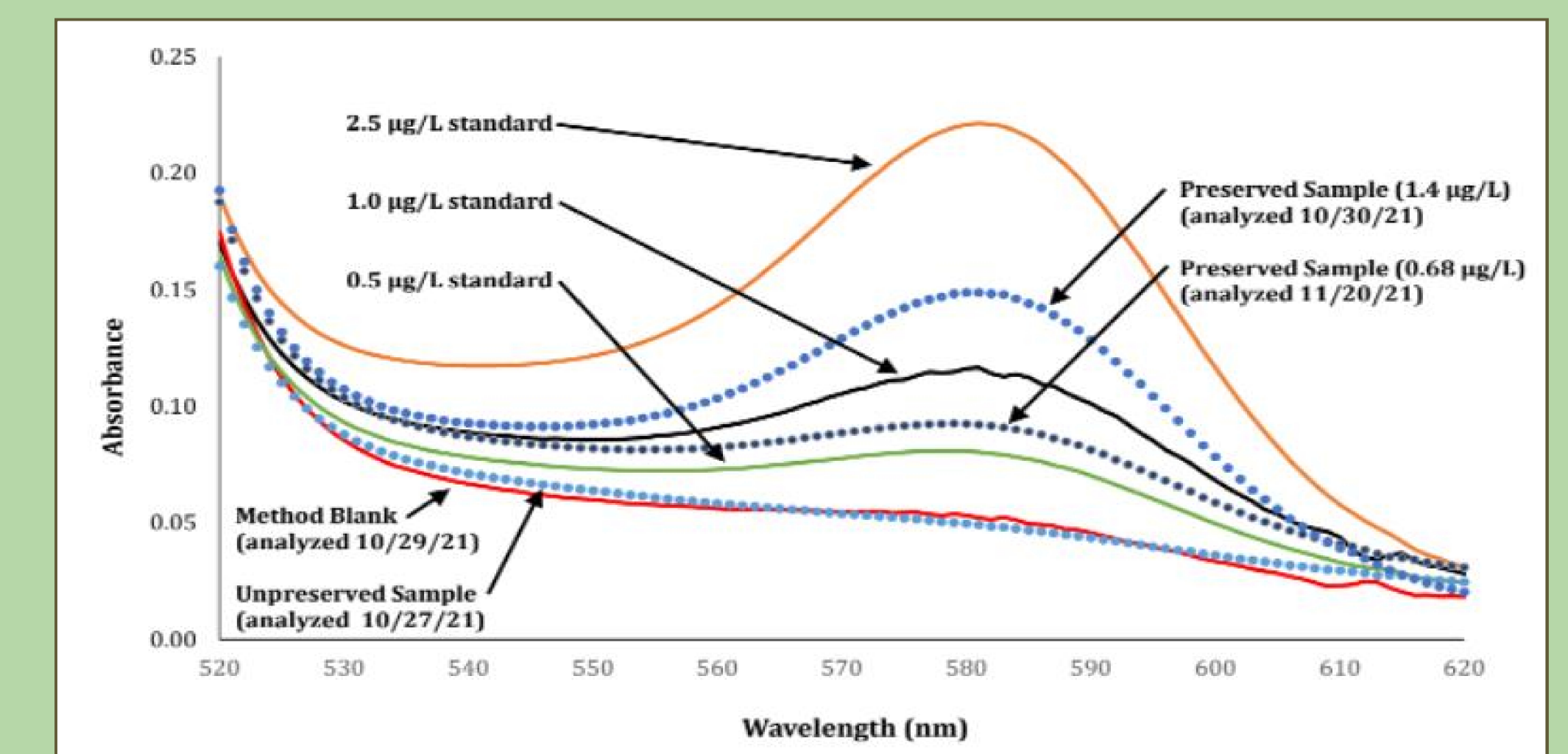


Figure 3: Spectra of standards and method blank (solid lines) and samples (dotted lines) generated from the colorimetric analysis for cyanide in Standard Methods 4500 CN E.

Date of Sample Collection	Unpreserved Sample (CPH)	Preserved Sample + Duplicate (CPH)	Preserved Sample (Certified Lab)
10/20/21	ND	1.2   1.7	2.9
10/27/21	ND	1.4   1.3	2.0
11/17/21	ND	(0.68)   (0.69)	1.8
12/15/21	ND	ND   ND	1.1

Table 3: Results for the cyanide (in ug/L) measured in plant effluent (Outfall 001). The concentrations in parentheses are below the reporting limit but above the MDL.

## Experiment

Day 1: (Wednesday)

- § Begin distillation and analysis of unpreserved sample within 15 minutes of sample collection
- § Distill and analyze the unpreserved field spike sample within 2.5 hours of sample collection or immediately after the processing of the initial sample to show that sample integrity was maintained.

Day 2: (Friday)

- § Process the method blank and LCS for the sample set

Day 3: (Saturday)

- § Process the preserved sample after a holding time of 72 hours
- § Perform a duplicate analysis of the preserved sample
- § Process the matrix spiked preserved samples

Date of Sample Collection	LCS (CPH)	LCS and LCSD (Certified Lab)
10/20/21	93%	105%   115%
10/27/21	100%	108%   114%
11/17/21	91%	100%   109%
12/15/21	94%	104%   104%

Table 1: Recoveries (in percent) for laboratory control samples (LCS) and duplicates samples (LCSD) performed at CPH and the certified lab..

Date of Sample Collection	Field Spike on Unpreserved Sample (CPH)	Matrix Spike on Preserved Sample (CPH)	Matrix Spike + Duplicate on Preserved Sample (Certified Lab)
10/20/21	95%	76%	107%   107%
10/27/21	102%	100%	104%   103%
11/17/21	100%	96%	87%   98%
12/15/21	101%	84%	101%   103%

Table 2: Recoveries (in percent) for field spikes on unpreserved samples and matrix spikes on preserved samples analyzed by CPH and a certified lab.

## Objective

Since using a new method to detect low-level concentrations of cyanide, all samples being sent to a certified laboratory have reported cyanide concentration above the AMEL in discharged effluent to Humboldt Bay on a regular basis, triggering accelerated monitoring requirements and fines. This was presumed to be due to cyanide formation in the wetlands, positive interferences caused by the wastewater sample matrix, or with the new analytical methodology. The objective of this study was to determine the source of the cyanide in the plant effluent by performing on-site analysis for cyanide at Cal Poly Humboldt, which was used to determine whether the preservation method for the cyanide test was causing false positives in plant effluent (Outfall 001). The cyanide results from the on-site analysis of unpreserved and preserved samples were compared to results from a certified laboratory.

## Conclusion

It was determined that the unpreserved wastewater samples collected and analyzed immediately (within 15 minutes) showed no detectable levels of cyanide. Furthermore, the preservation of the sample with sodium hydroxide was shown to produce a false positive for cyanide at low-level reporting limits analyzed after 3 days. The results were found to be highly dependent on the analyst and the distillation set-up.

In future work, a lower cyanide concentration should be used in field spikes when determining whether the sample integrity of unpreserved samples is maintained. Lastly, the method detection limit for the analysis of cyanide at CPH should be further developed in order to define the reporting limit.

This study provides evidence that there is an issue with the sampling procedure for cyanide required by the NPDES permit. The North Coast Regional Water Quality Control Board have reviewed these findings and it is allowing the City of Arcata to perform a holding time study to show that the analysis of cyanide at AWTF can be performed using unpreserved samples.

## Acknowledgements

We would like to thank the City of Arcata for funding this project. We would also like to thank the staff in the Chemistry Department Stockroom at Cal Poly Humboldt for providing assistance with laboratory logistics and supplies.



Figure 1: Map of Arcata Marsh Wastewater Treatment Facility featuring sampling site (Outfall 001)