

Environmental Samples Holding Time Studies with Alternative Preservation Strategy



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Holding Time (as defined by US EPA) = time period between sample collection and extraction

- PAH in Water samples
 - *7 days after collection with acid preservation and maintained at 0-6°C*
- PAH in Soil/Sediment samples
 - *14 days after collection and maintained at 0-6°C*

Opportunities:

1. Technical basis – analyte loss due to microbial degradation, volatilization, and photo oxidation
2. International sites (re-sampling with high cost)

US EPA Sample Containers, Preservation, and Holding Times for PAHs in Water, Soil/Sediment, and Tissues



Matrix	Container	Preservation	Holding Times
Water	1 Liter glass amber, PTFE lined lid	0 to 6°C	7-Days
Soil / Sediment	4 or 8oz glass, PTFE lined lid	0 to 6°C	14-Days
Tissue	Glass, PTFE lined lid or clean aluminum foil	Frozen -20°C	1 Year

NOAA Deepwater Horizon Project Preservation, and Holding Times for PAHs in Water, Soil/Sediment, and Tissues



Matrix	Preservation	Holding Times
Water	Refrigeration $4^{\circ}\text{C} \pm 2^{\circ}\text{C}$ Optional: Preserved with 1:1 HCL to pH <2	7-Days if not acid preserved; 14-days if acid preserved
Soil /Sediment	Frozen ($-20^{\circ}\text{C} \pm 10^{\circ}\text{C}$)	4 Years
Tissue	Frozen ($-20^{\circ}\text{C} \pm 10^{\circ}\text{C}$)	4 Years

Problem: Condition of samples upon receipt at lab



THL 0072 ✓	17/5/05	1.27 ^{pm}	1	YES	MARICOTE SITE (DAZK)
THL 0073 ✓	✓	1.47 ^{pm}	1	YES	✓
THL 0074 ✓	✓	1.27 ^{pm}	2	YES	✓
THL 0075 ✓	✓	1.47 ^{pm}	3	YES	✓
THL 0076 *	✓	1.27 ^{pm}	1	YES	✓
THL 0077 ✓	✓	1.47 ^{pm}	1	YES	✓
THL 0078 ✓	21/5/05	12.36 ^{pm}	1	YES	Water sample (1000 ml)
THL 0079 ✓	✓	12.52 ^{pm}	1	YES	✓
THL 0080 *	✓	12.40	1	YES	Dark sediment
THL 0081 ✓	✓	1.11 ^{pm}	1	YES	✓
THL 0084 ✓	✓	12.40	4	YES	✓
THL 0082 ✓	✓	1.11 ^{pm}	5	✓	✓
THL 0088 ✓	✓	12.40	1	✓	✓
THL 0089 ✓	✓	1.11 ^{pm}	1	✓	✓
THL 0015 ✓	✓	12.36 ^{pm}	4	✓	Surface water (1000 ml)
THL 0035 ✓	✓	12.05 ^{pm}	4	✓	✓
L. Kabu S. S. S. S.		Date	Time	Received by:	
		28/5/2011	12.25	J. J. J. J.	



Sampling occurred on May 17th and 20th

Samples shipped on May 28th

Samples arrived at an US lab on June 8th

Only have two blue ice package inside the cooler



Findings of literature review on technical basis of US EPA holding times

- No technical bases for the defined holding time requirements- it is more or less defined by the administrative requirements from 1980s

“These holding times are for sediment, water, and tissue based on guidance that is sometimes administrative rather than technical in nature”

Ref: USEPA 1995. QA/QC guidance for sampling and analysis of sediments, water and tissues for dredged material evaluations. EPA 825-B-95-001. April 1995

“Samples should be analyzed as soon as possible after collection. The times listed are the maximum times that samples may be held before the start of analysis and still be considered valid. Samples may be held for longer periods only if the permittee or monitoring laboratory has data on file to show that, for the specific types of samples under study, the analytes are stable for the longer time,”

Ref: Federal Register/Vol 77, No. 97/Friday May 18, 2012/Rules and Regulations 29806-29809.

- EPA Sample Holding Time Re-Evaluation - 2005

<http://www.epa.gov/esd/cmb/tasks/holding.htm>



Methods

Holding Time Study Design (based on ASTM D4815)

- Low and high PAH level holding times for waters will be evaluated at pH<2 and at ambient temperature (~20°C) over a 30-day period.
- Low and high PAH level holding times for sediments will be evaluated preserved with sodium azide and at ambient temperature (~20°C) over a 3 month period.
- The number of replicates required for each time series and for each condition (low and high levels) will be determined by a Precision Study based on the RSD of 3 or 10 replicate analysis - *Standard Practice for Estimation of Holding Time for Water Samples Containing Organic and Inorganic Constituents* (ASTM D4515-85)

Results

BTEX in water



Prescribed Method of Preservation: acidification, refrigeration, or both – 7 days maximum

Experimental Design

Benzene, toluene, ethylbenzene, xylenes (BTEX) water holding time study design matrix.

Matrix	Preservative	BTEX Concentration	Temperature	Measurement Day					
				0	3	7	11	14	21
Water	HCl	Low	4°C	✓	✓	✓		✓	✓
			Ambient	✓	✓	✓	✓	✓	✓
	None	Low	Ambient	✓	✓	✓		✓	✓

✓=Day Analyzed, Gold = Control, Green = Stable, Red = Degraded

Results

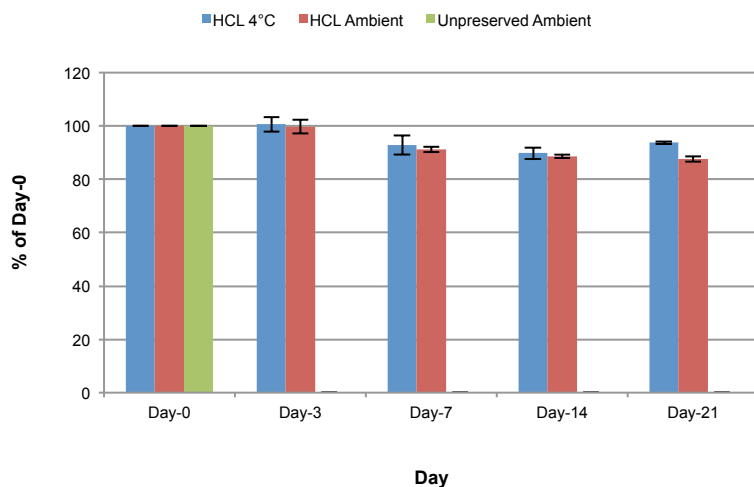
BTEX holding times in water were stable when preserved at ambient temperature for 21 days.



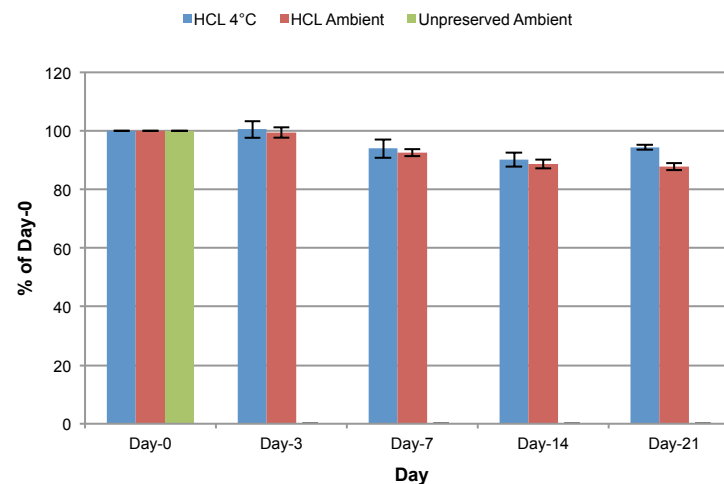
Results

BTEX in water at Day 21 (50ng/ml)

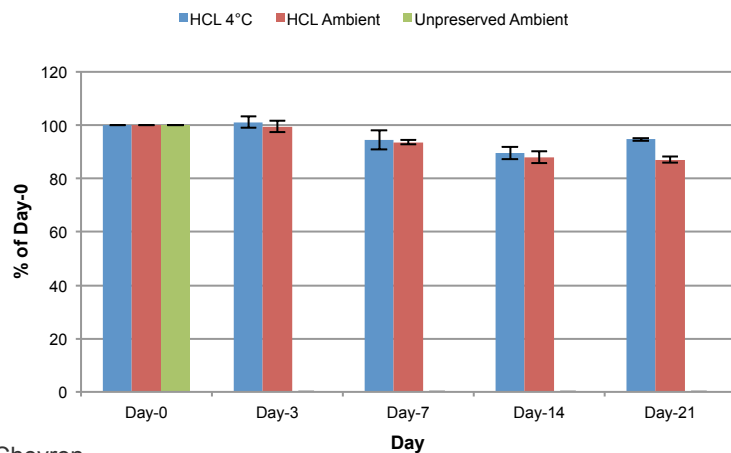
Benzene Holding Time Study



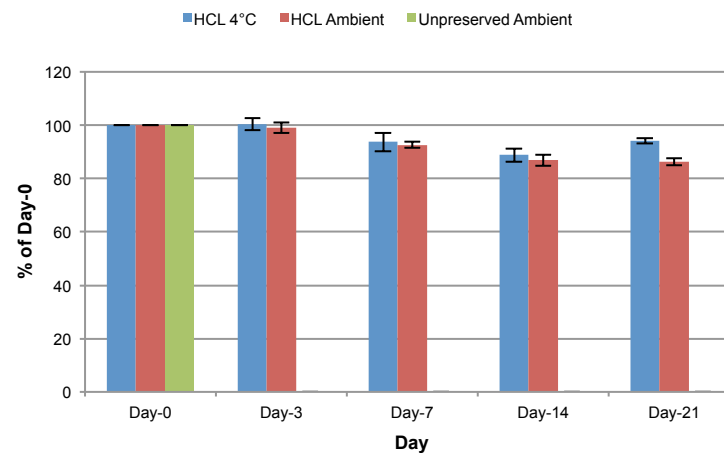
Toluene Holding Time Study



Ethylbenzene Holding Time Study



Total Xylenes Holding Time Study





Results

PAH in Water

Prescribed Method of Preservation: acidification, refrigeration, or both – 7 days maximum

Experimental Design

Polycyclic aromatic hydrocarbon holding time study design matrix.

Matrix	Preservative	PAH Concentration	Temperature	Measurement Day								
				0	1	3	7	11	14	21	30	60
Water	None	Low	Ambient	✓		✓	✓		✓			
		High		✓		✓	✓		✓			
	NaN ₃	Low		✓		✓	✓		✓			
		High										
	HCl	Low		✓	✓	✓	✓	✓	✓	✓	✓	
		High		✓	✓	✓	✓	✓	✓	✓	✓	

✓=Day Analyzed, Gold = Control, Green = Stable, Red = Degraded, White = Undeterminable

Results

Water sample holding time results for the PAH compounds were problematic.

Many exceeded 15% difference criteria in the Day 1- Day 7 low and high level PAH experiments.

Due to potential Day 0 experimental artifact issues.

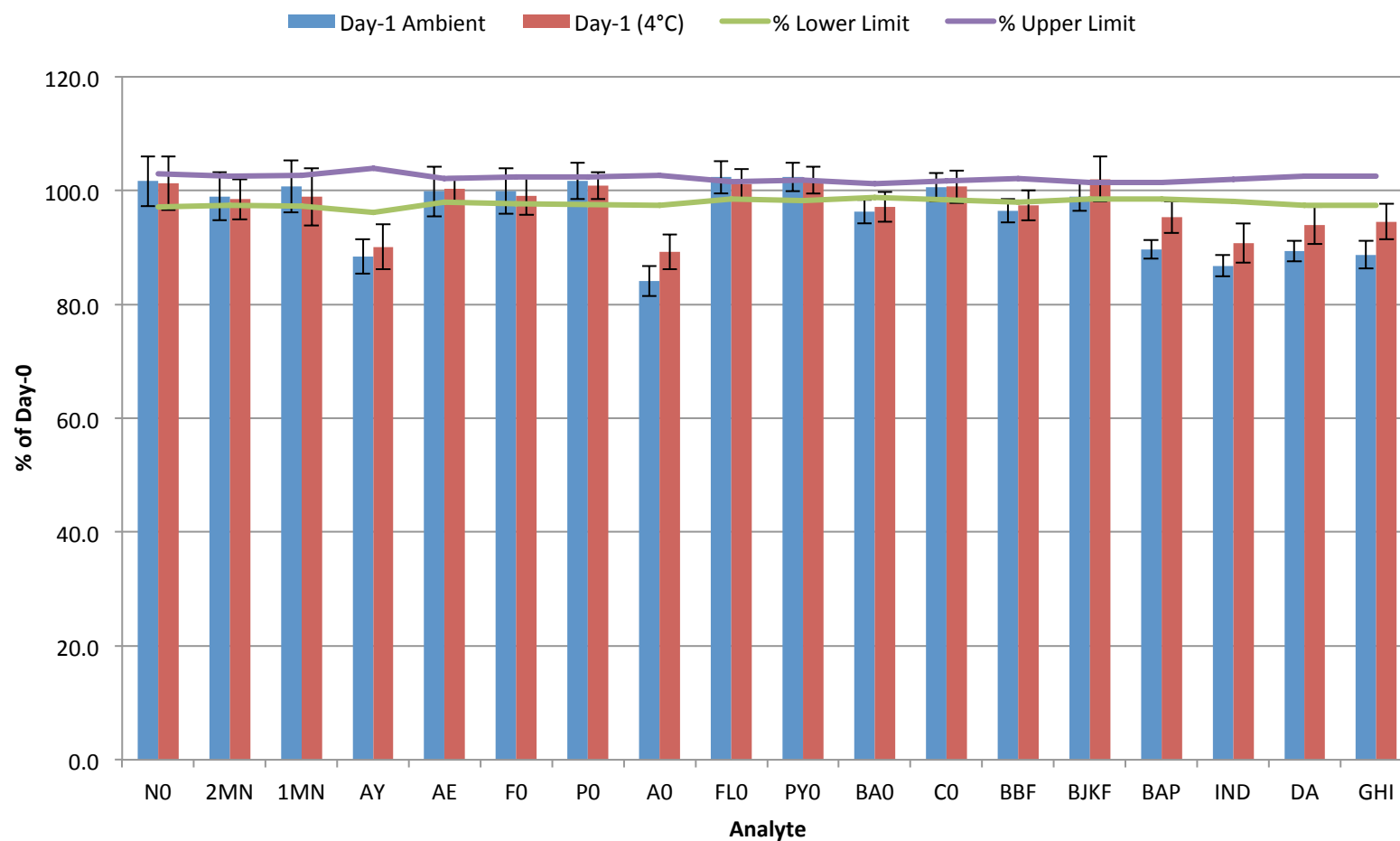
When Day 1 substituted for Day 0, most indicated stable holding times of 10 days.

Results

Spiking anomaly present in both refrigerated and ambient (preserved) results



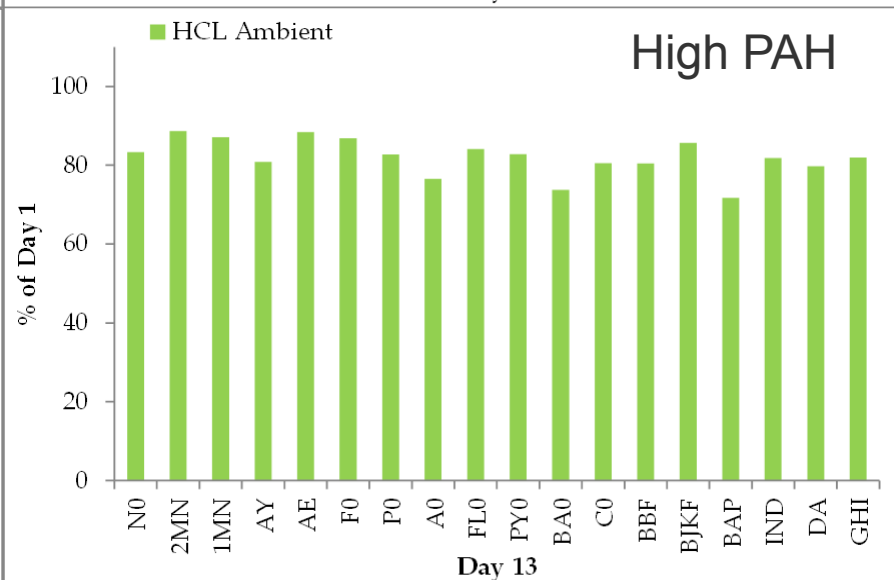
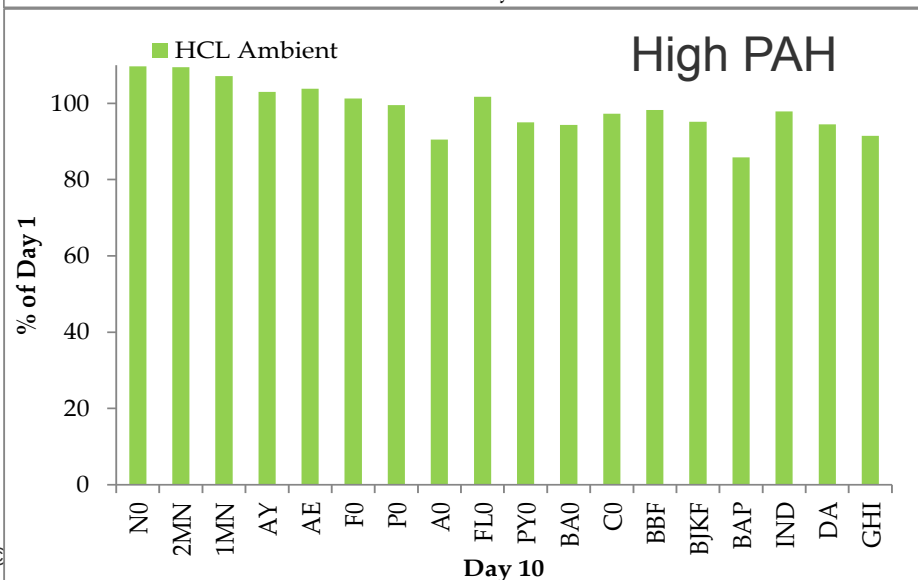
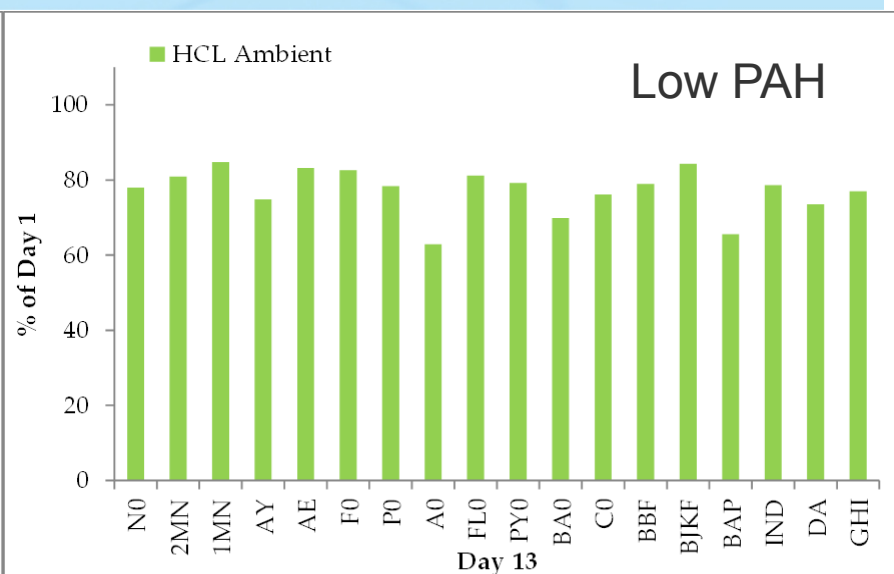
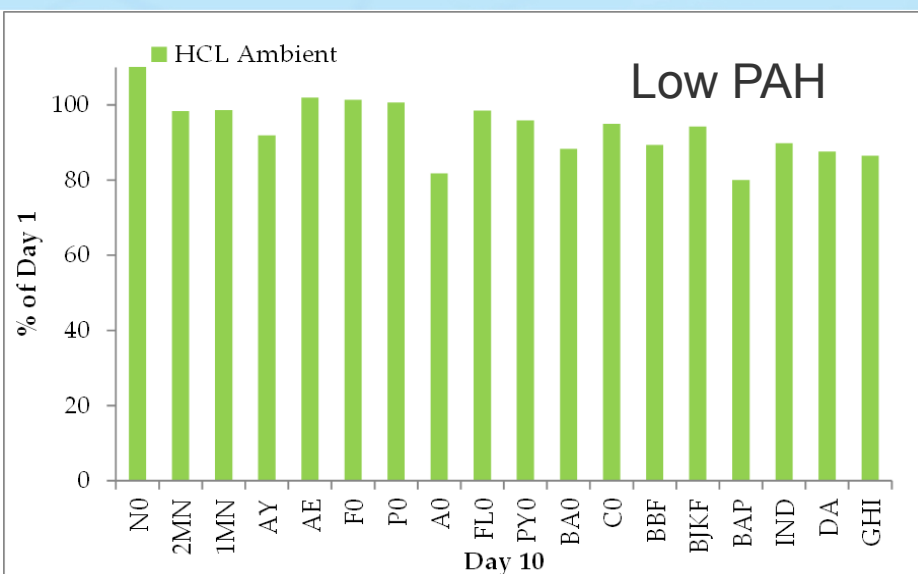
HCL Preserved Waters Day-1 Ambient vs Day-1 (4°C)





Results

PAHs in water (corrected based on Day 1 concentrations)





Results

PAHs in Sediment

Prescribed Method of Preservation: refrigeration, freezing – 14 days maximum

Experimental Design

Polycyclic aromatic hydrocarbon holding time study design matrix.

Matrix	Preservative	PAH Concentration	Temperature	Measurement Day								
				0	1	3	7	11	14	21	30	60
Sediment	None	Low	Ambient	✓			✓		✓		✓	
		High		✓			✓		✓		✓	
	NaN ₃	Low		✓			✓		✓	✓	✓	✓
		High		✓			✓		✓	✓	✓	✓

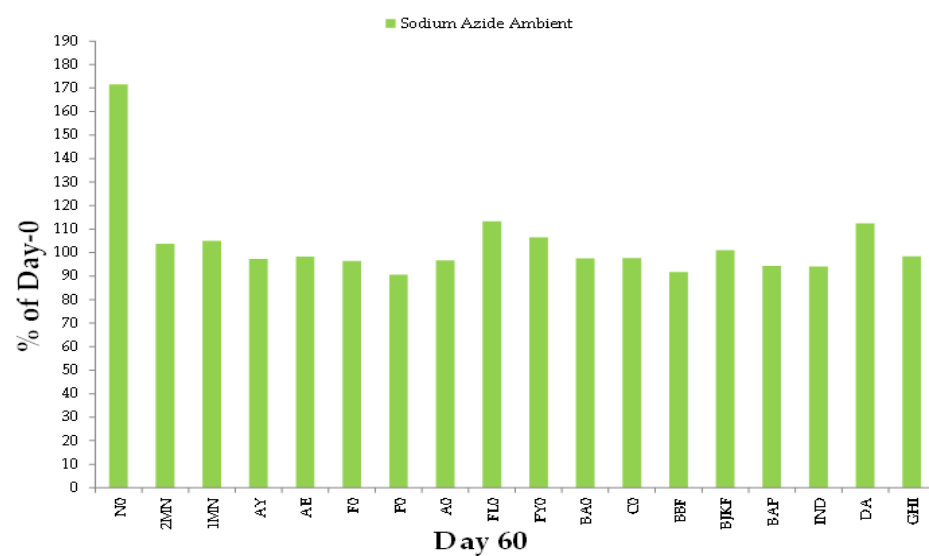
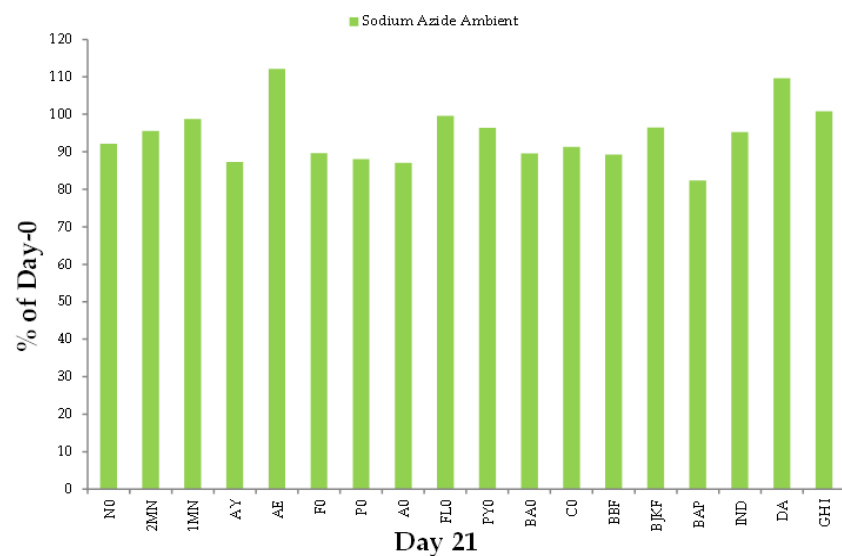
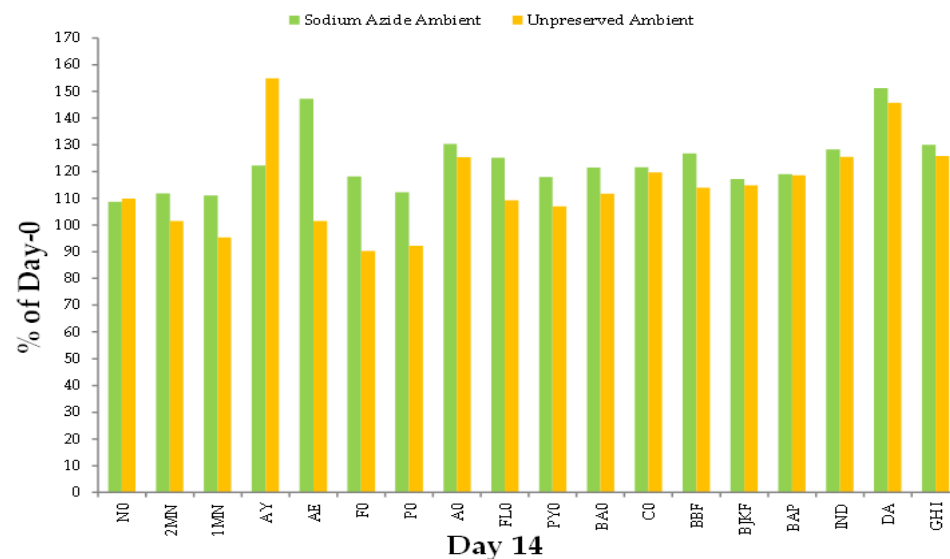
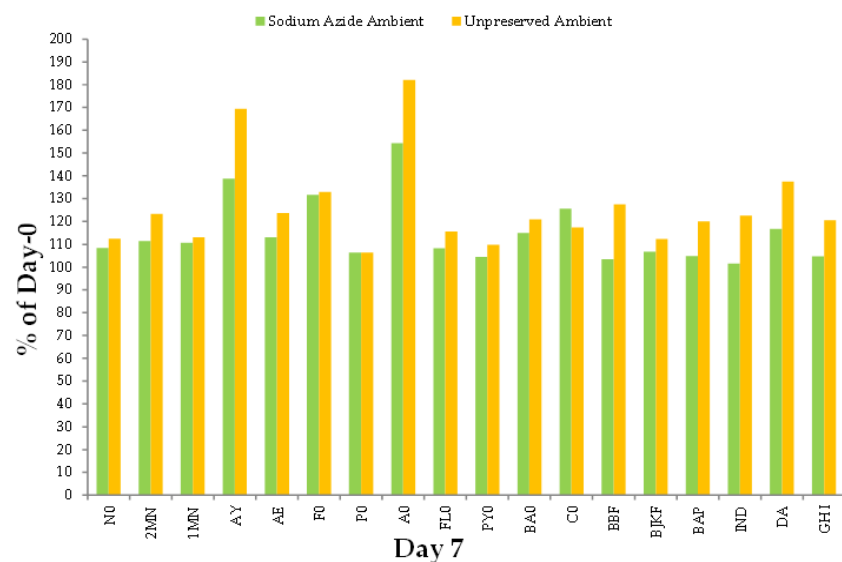
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Results

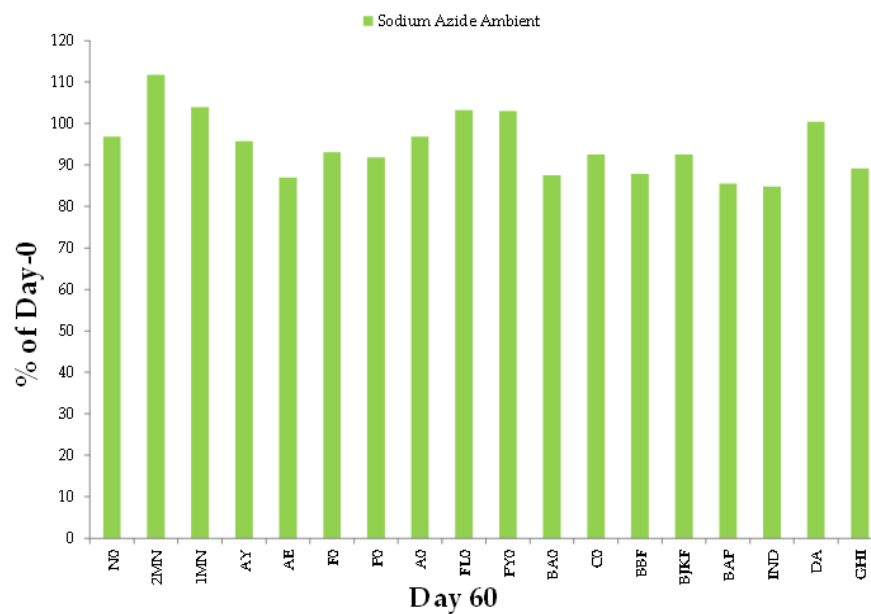
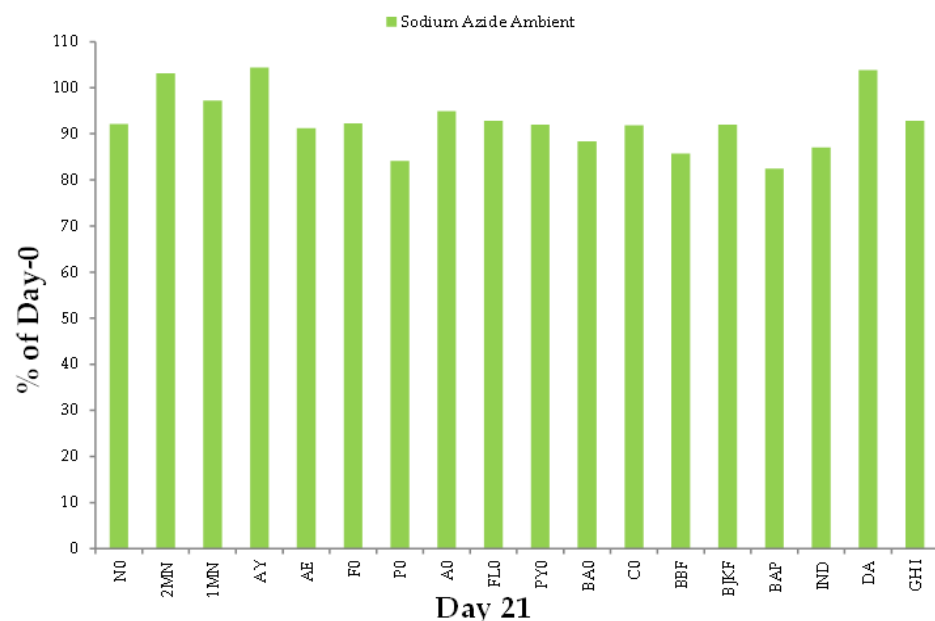
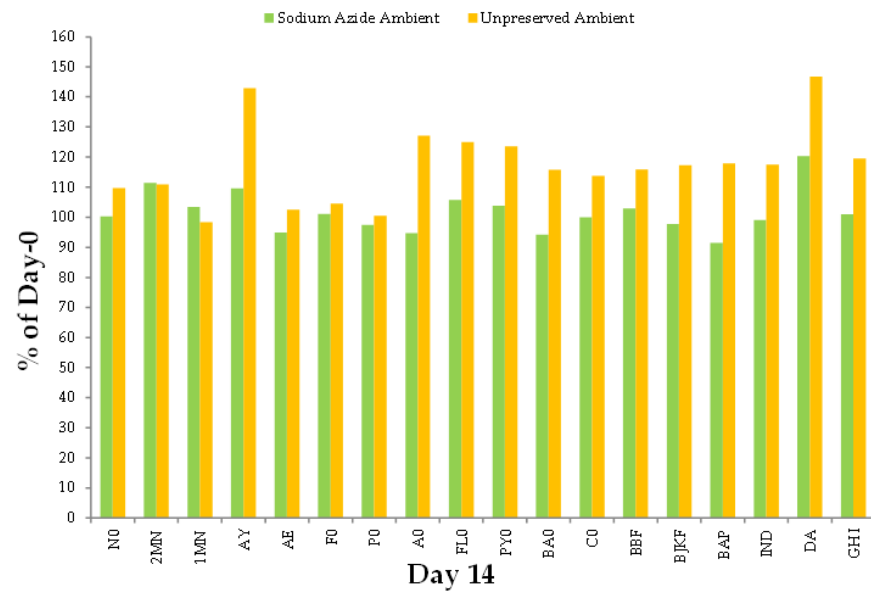
No statistical difference up to 60 days when preserved with sodium azide

No statistical difference up to at least 14-days with no preservative.

Low concentration PAHs in Sediment



High Concentration PAHs in Sediment





Conclusions

Technically supportable holding times at ambient temp

- BTEX holding time in water were stable up to 21 days at pH < 2 at ambient temperature
- PAHs holding time in water were stable up to 10 days at pH < 2 at ambient temperature
- PAHs holding time in sediment were stable up to 60 days with sodium azide at ambient temperature
- Even without preservation, PAHs in sediments can be stable up to 14 days at ambient temperature

Q&A

