# Evaluation of Preservation Recommendations in SW-846 for Volatile Organic Chemicals in Aqueous Sample Matrices

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# All about me

- 2004 to present –US EPA Region 5 laboratory
  - GC/MS
  - Test various media for SVOCs and VOCs


- 2011-2012: 4 month detail to US EPA's Office of Resource Conservation and Recovery in OSWER
  - Worked with SW-846 methods team, Shen-Yi Yang and Kim Kirkland
  - Update V to 3rd edition of SW-846

# Primary Goal of Preserving VOC Samples: Maintain Sample Integrity

## Degradation Mechanisms:

- Biological
- Chemical (oxidation/reduction, hydrolysis)

## Recommended sample preservation techniques:

- Store in low temperature environment ( ≤ 6°C)
- Add pH modifier

# SW-846, 3rd ed., Update IV (2007)

TABLE 4-1
RECOMMENDED SAMPLE CONTAINERS, PRESERVATION TECHNIQUES, AND HOLDING TIMES[a]
(Note: Footnotes are located on the last page of the table.)

| VOLATILE ORGANICS | | |
|---|---|---|
| Sample Matrix | Preservative[1] | Holding Time[1] |
| Aqueous samples with no residual chlorine present | Cool to ≤6 °C and adjust pH to less than 2 with $H_2SO_4$, HCl, or solid $NaHSO_4$ | 14 days |
| | *If carbonaceous materials are present, or if MTBE and other fuel oxygenate ethers are present and a high temperature sample preparative method is to be used, do not acid preserve the samples.* | *7 days* |
| | *If vinyl chloride, styrene, or 2-chloroethyl vinyl ether are analytes of interest, collect a second set of samples without acid preservatives and analyze as soon as possible.* | *7 days* |
| Solid samples (e.g. soils, sediments, sludges, ash) | See the individual methods. | 14 days |
| | *If vinyl chloride, styrene, or 2-chloroethyl vinyl ether are analytes of interest, collect a second set of samples without acid preservatives and analyze as soon as possible.* | 7 days |

# Holding Time / Preservation Table in SW-846 Method 5035A Appendix (2002)

**Table A.1**
**Recommended VOC Sample Preservation Techniques and Holding Times**

| Sample Matrix | Preservative | Holding Time | Comment |
|---|---|---|---|
| Aqueous Samples With No Residual Chlorine Present | Cool to 4 ± 2°C. | 7 days | If MTBE and other fuel oxygenate ethers are present and a high temperature sample preparative method is to be used, do not acid preserve the samples. If aromatic and biologically active compounds are analytes of interest, acid preservation is necessary and the holding time is extended to 14 days. |
| Aqueous Samples With No Residual Chlorine Present | Cool to 4 ± 2°C and adjust pH to less than 2 with HCl or solid $NaHSO_4$. | 14 days[1] | Reactive compounds such as 2-chloroethylvinyl ether readily break down under acidic conditions. If these types of compounds are analytes of interest, collect a second set of samples without acid preservatives and analyze as soon as possible. |

# "PUBLIC COMMENT SUMMARIES AND RESPONSES UPDATE IV TO SW-846"

"Two commenters disagreed with the recommendation in Table 4-1 to collect a second set of samples without acid preservation if vinyl chloride is an analyte of interest. The commenters noted that some studies demonstrate that vinyl chloride is stable for at least 28 days and possibly over 90 days in acidic solution."

**Response:** The Agency agrees that vinyl chloride could be assigned a "highly variable stability" classification …(depending on matrix conditions)… [I]t is also well known that reactive compounds; such as styrene, vinyl chloride, and 2-chloroethyl vinyl ether readily degrade under acidic conditions. For this reason, the current recommendation …is that acid preservation should not be used if these compounds are target analytes.

# Question to answer for Update V:

Does acid preservation during sampling create more problems for quantitative analysis of styrene and vinyl chloride than lack of preservation, or more problems than for other VOCs?

- Sources of information:
  1) Methods from other EPA programs
  2) Literature search for VOC holding time studies
  3) Wastewater holding time studies

# CLP Guidance for Field Samplers, 2011:

Soils: "$NaHSO_4$ preservation creates low pH conditions that will cause the destruction of certain CLP target analytes (e.g., vinyl chloride, trichloroethene, trichlorofluoromethane, cis- and trans-1,3-dichloropropene)." But no similar problems noted for aqueous matrices.

# Drinking water method 524.3:

Styrene and vinyl chloride are target analytes, but no indication that maleic or ascorbic acid preservatives cause stability problems

# Wastewater method 624:

- "Experimental evidence indicates that some aromatic compounds, notably benzene, toluene, and ethyl benzene are susceptible to rapid biodegradation under certain environmental conditions. Refrigeration alone may not be adequate to preserve these compounds in wastewaters for more than seven days. For this reason, a separate sample should be collected, acidified, and analyzed when these aromatics are to be determined."

  Vinyl chloride listed as a target analyte, but not styrene

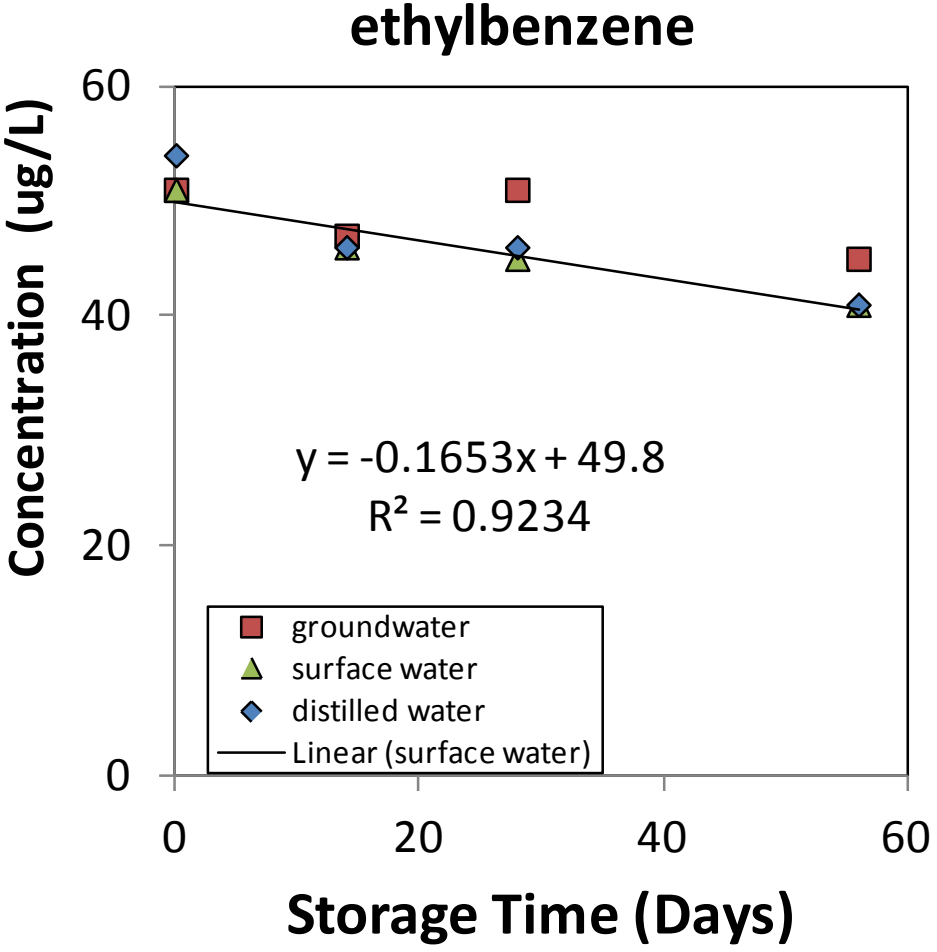
# Refrigerated holding time studies

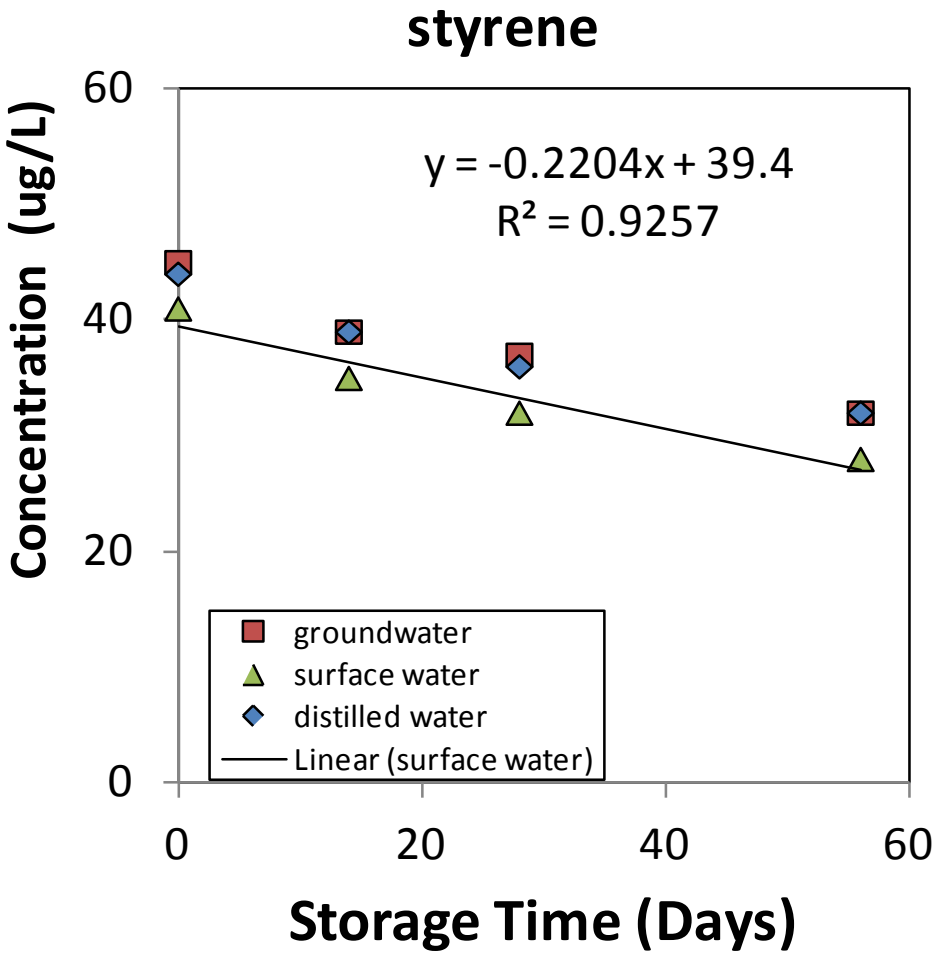
- Department of Energy / Oak Ridge National Lab

  -Maskarinec et al (1989), unpreserved or preserved with bisulfate, HCl

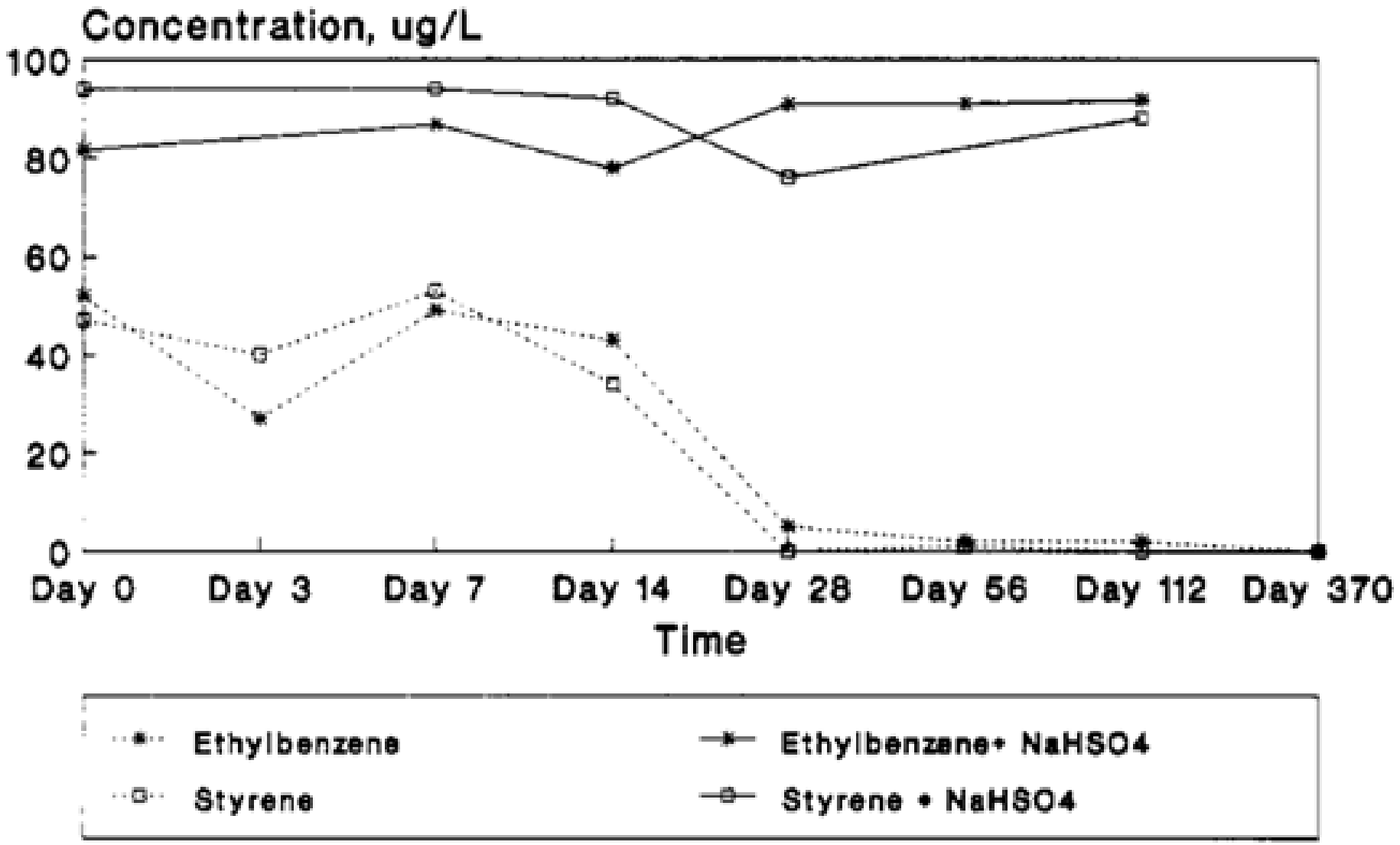
  - West et al (1996), preserved with bisulfate
- USGS (1999), surface water and groundwater preserved with HCl
- Groundwater – US EPA ORD Lab in Ada
  - preserved with HCl or trisodium phosphate
- Wastewater: Hampton Roads Sanitation District (VA)
  - Municipal and Industrial WWTP influent, unpreserved or preserved with HCl
- Wastewater - Test America
  - Hydrofracking wastewater unpreserved or preserved with HCl

# HCl preserved DI water, surface water, and groundwater



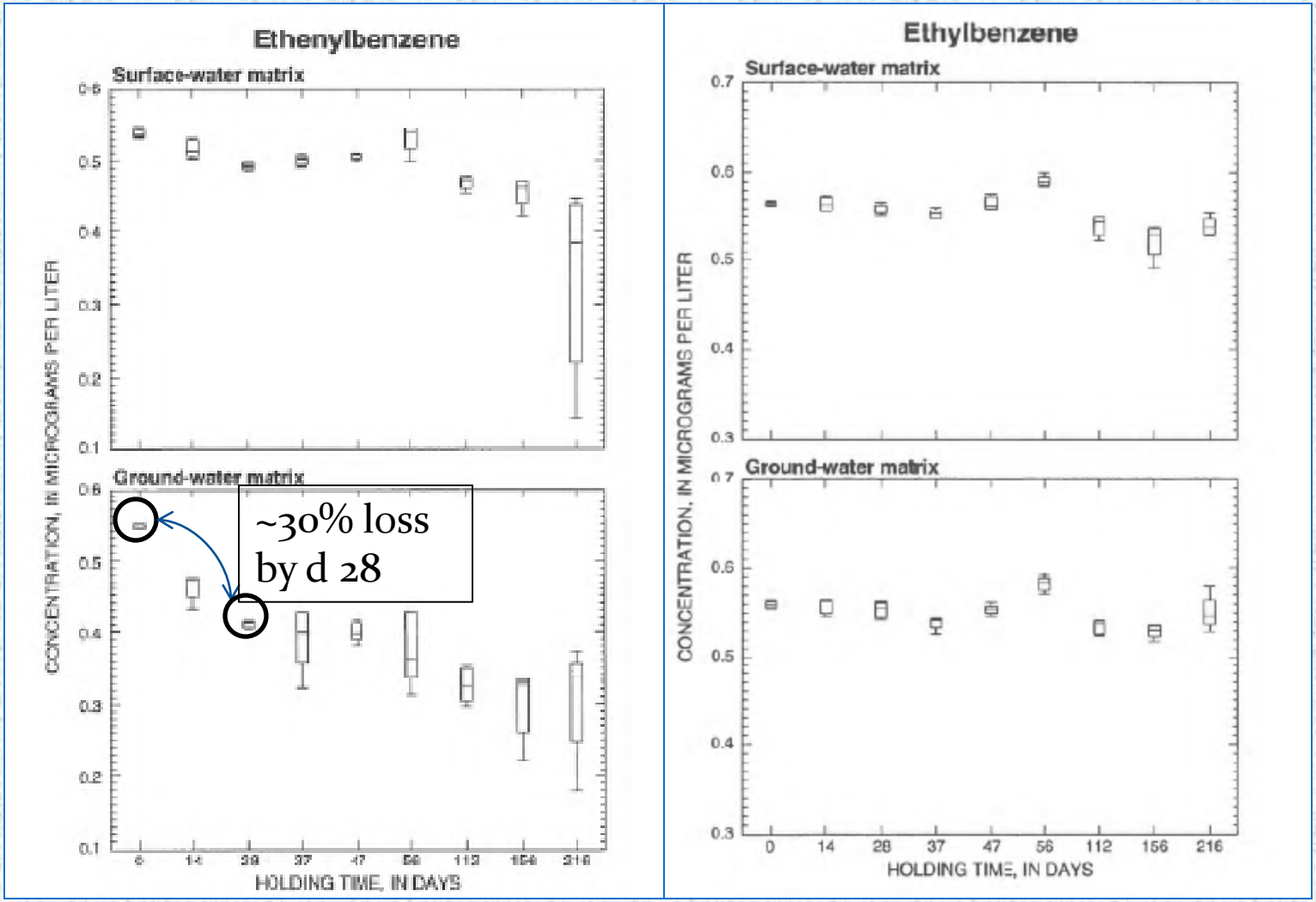




Maskarinec et al., 1989




Maskarinec et al., 1989

# 216 Day Surface and Groundwater Holding Time Study – Styrene




Love, et al., 1999.

# Styrene Stability during 28 days refrigerated storage

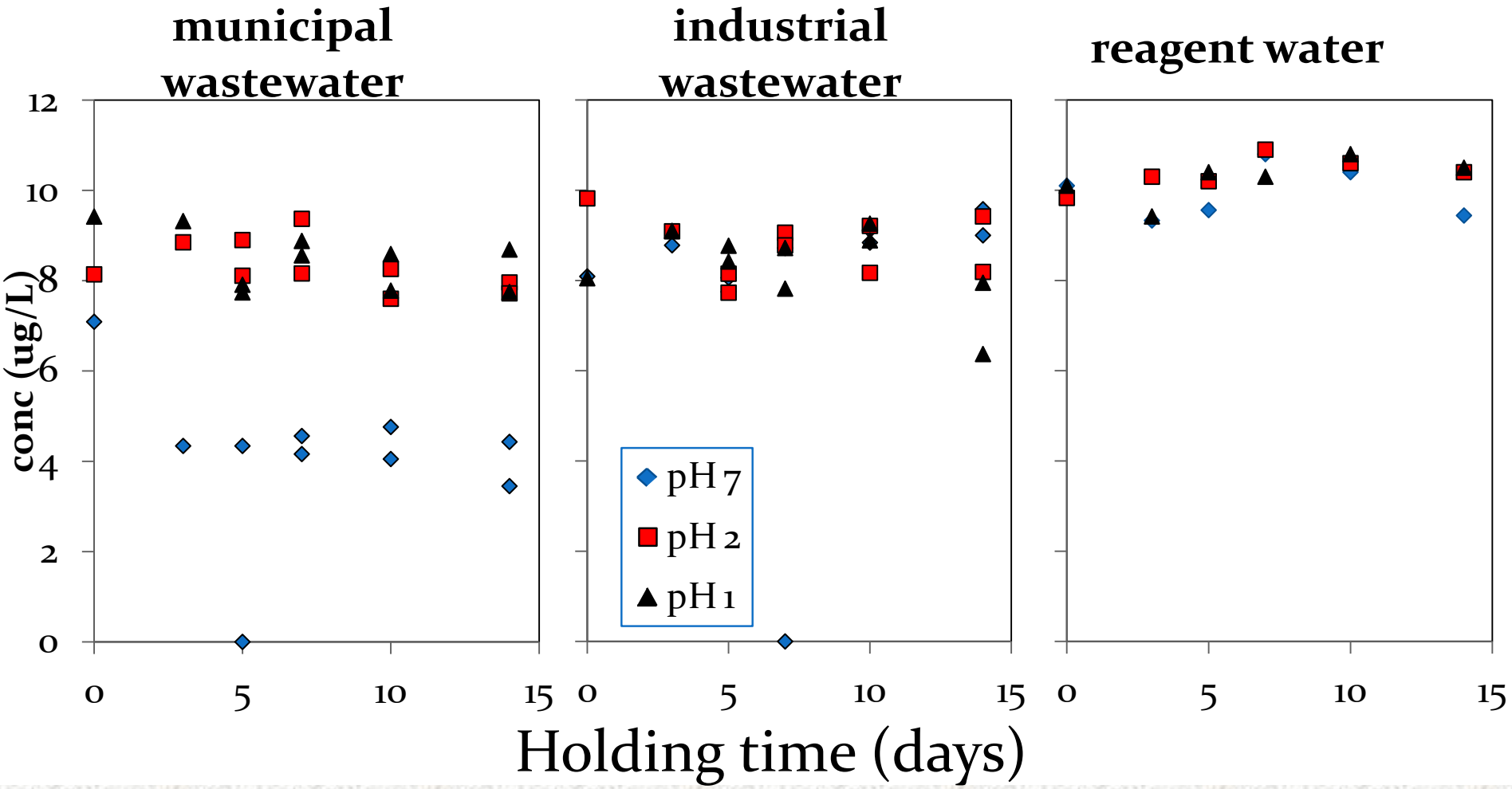
Groundwater from hazardous waste site investigation

Matrix spike recovery in pH 2 HCl preserved groundwater samples at d 0 and d 28

| Spike level (ug/L) | d 0 mean % recovery | d 28 mean % recovery | $S_{pool}$ (%) | % diff (d28 - d0) | Significant loss? (α=0.05) |
|---|---|---|---|---|---|
| 20 | 93 | 69 | 6 | 24 | Y |
| 200 | 92 | 79 | 12 | 13 | N |

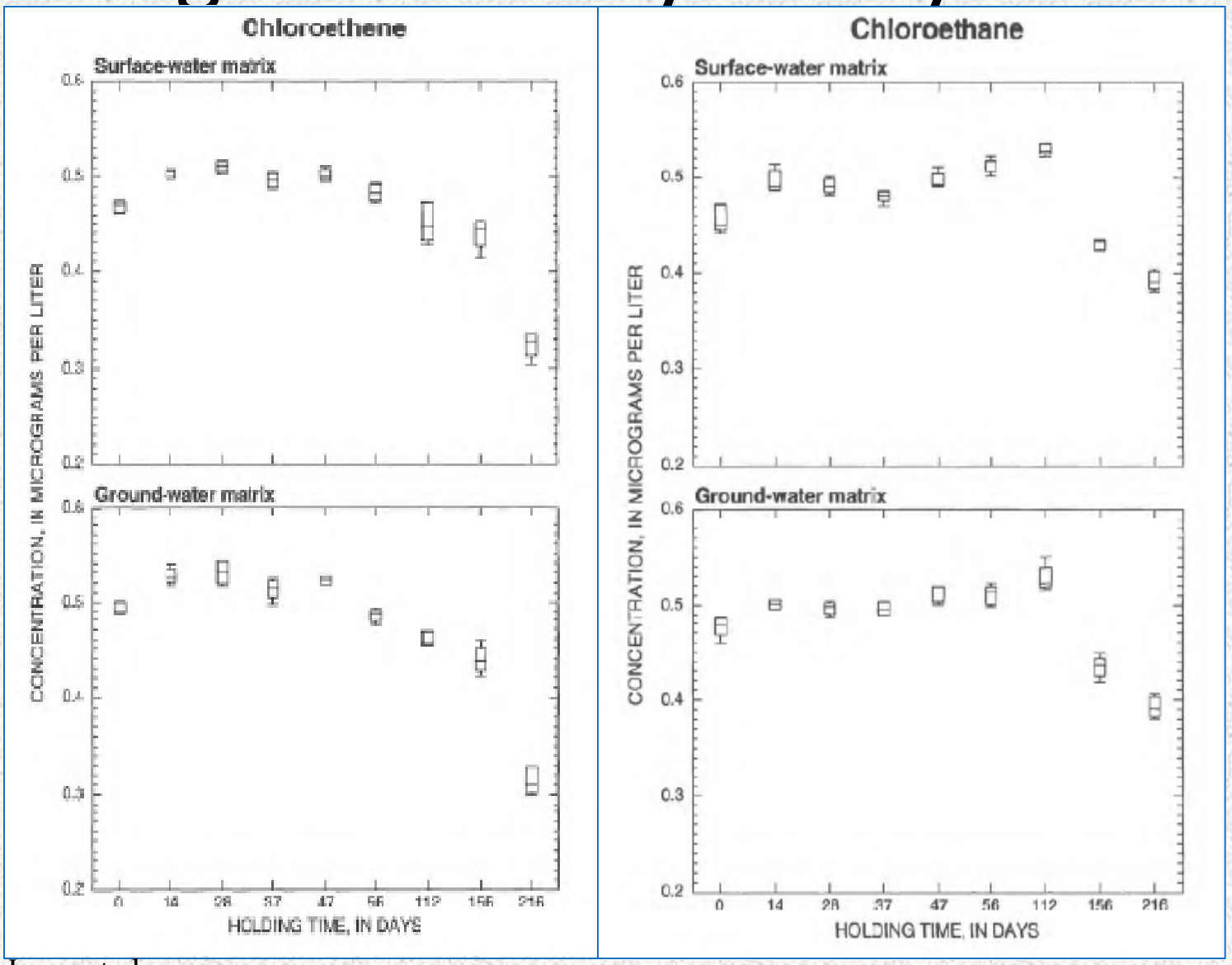
Data adapted from: Wilson, Fine, and Beach, 2008.

# Municipal and Industrial Wastewaters Holding Time Study: Styrene




Data provided by Hampton Roads Sanitation District

# 216 Day Surface and Groundwater Holding Time Study – Vinyl Chloride




Love, et al., 1999.

# Vinyl Chloride Stability during 28 days storage of acid or base preserved samples

Matrix spike recovery in pH 2 HCl preserved groundwater samples at d 0 and d 28

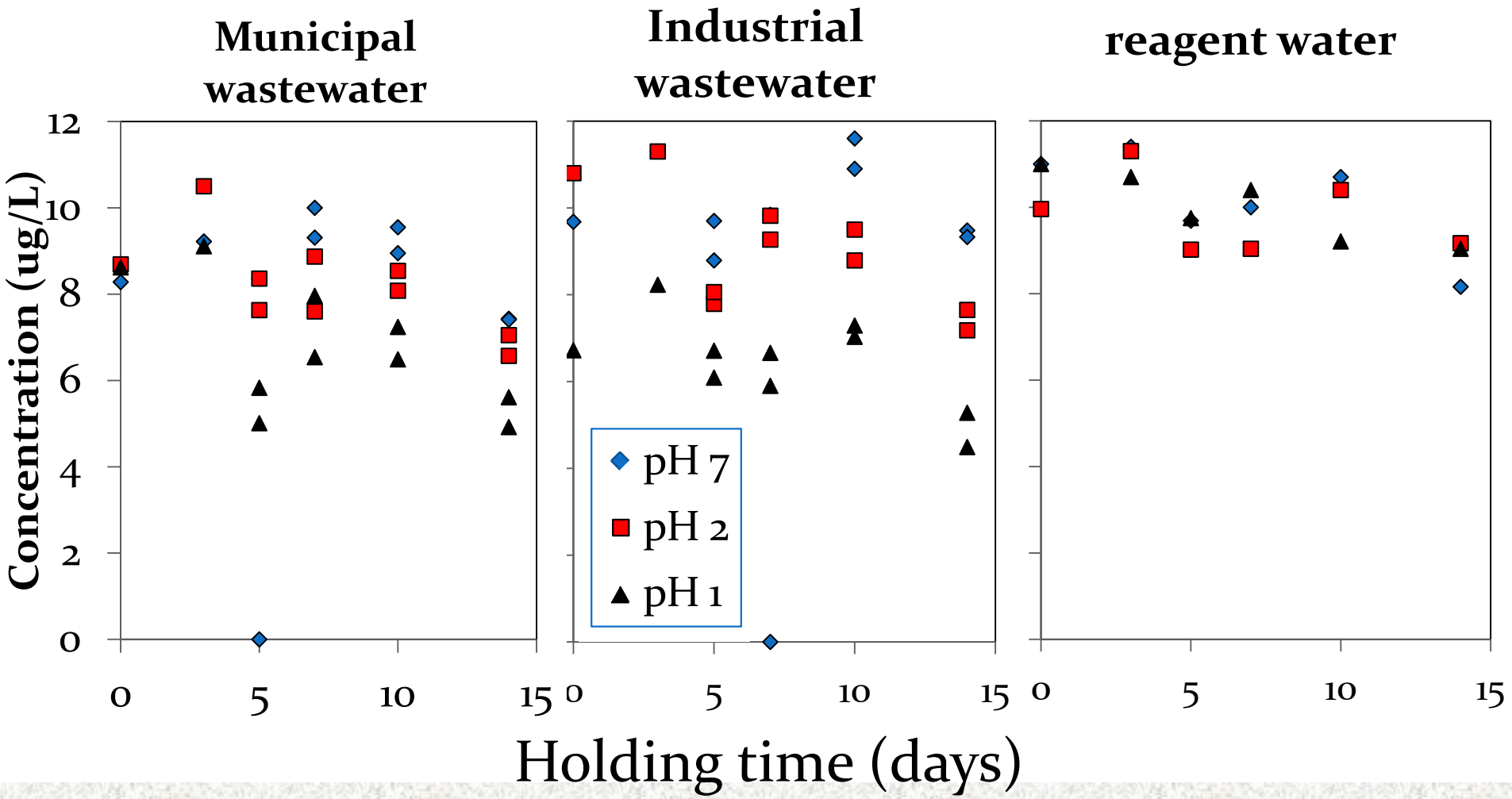
| Spike level (ug/L) | d 0 mean % recovery | d 28 mean % recovery | $S_{pool}$ (%) | % diff (d28 - d0) | Significant loss? (α=0.05) |
|---|---|---|---|---|---|
| 20 | 81 | 71 | 16 | 10 | N |
| 200 | 89 | 74 | 7 | 15 | Y |

Measured concentrations of select VOCs in acid or base preserved replicate samples after 28 days refrigerated storage.

| Chemical | Mean sample conc (ug/L) | preservative | conc ratio (VC / cisDCE) | conc ratio in different preservatives (HCl / TSP) |
|---|---|---|---|---|
| vinyl chloride | 7480 | HCl | 0.92 | 0.94 |
| | 7980 | TSP | 0.95 | |
| cis-1,2-DCE | 8170 | HCl | | 0.97 |
| | 8400 | TSP | | |

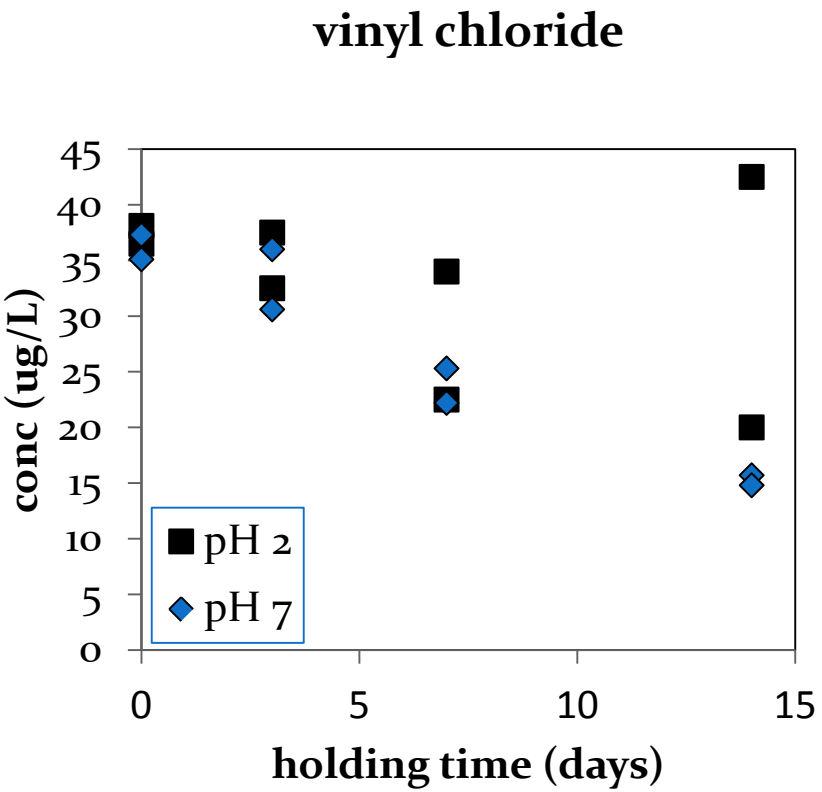
TSP – Trisodium Phosphate, HCl – Hydrochloric Acid
Data adapted from: Wilson, Fine, and Beach, 2008.

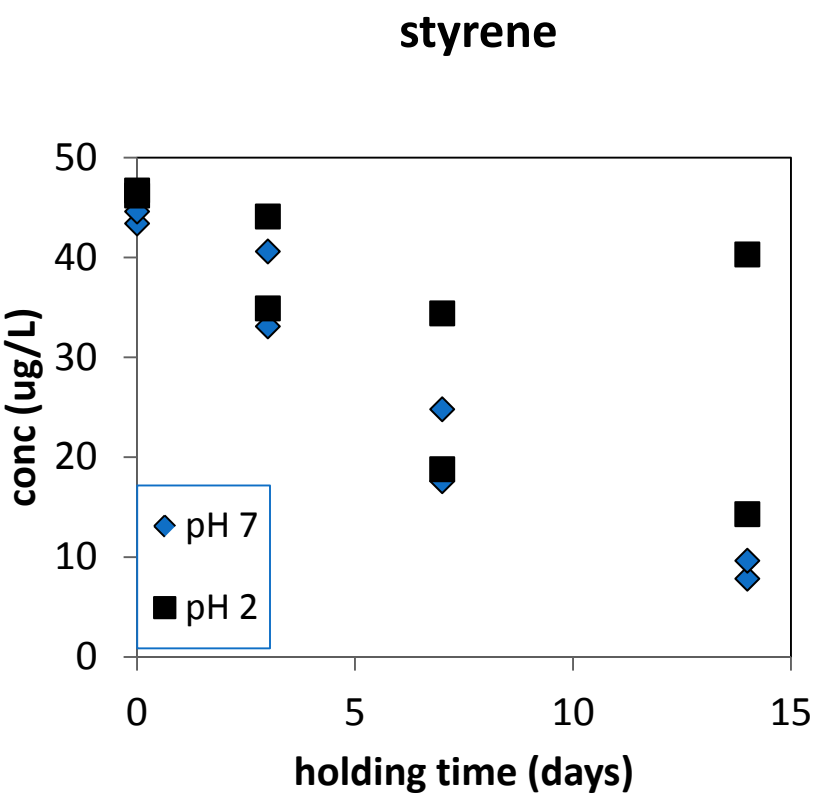
# Municipal and Industrial Wastewaters Holding Time Study: Vinyl Chloride




Data provided by Hampton Roads Sanitation District

# Hydraulic fracturing wastewater holding time study from Test America



# Stability in NaHSO4 preserved soil

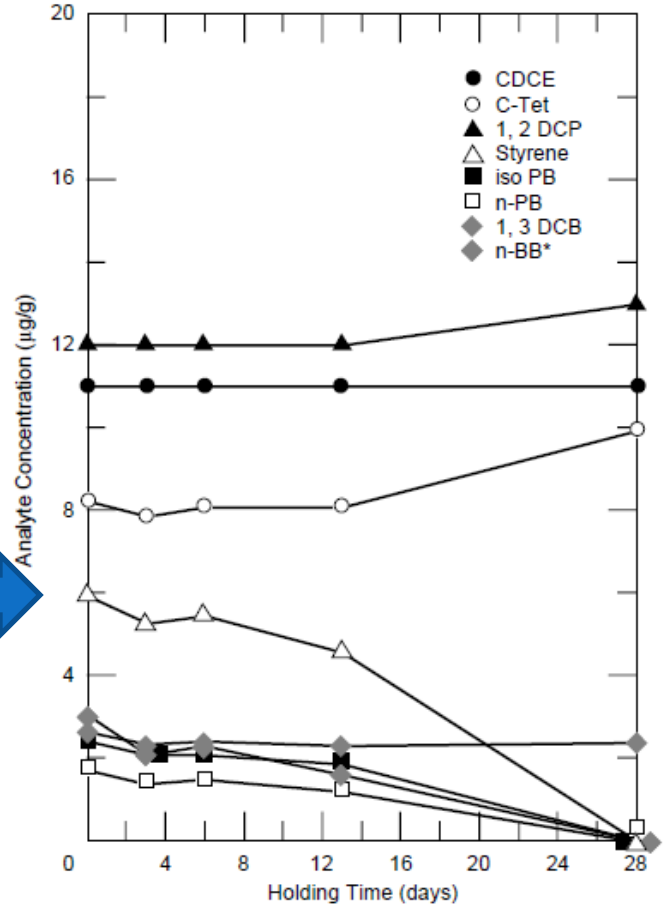



*Figure 13. Set 3/trial 3. Contaminated soil stored at 4°C.*

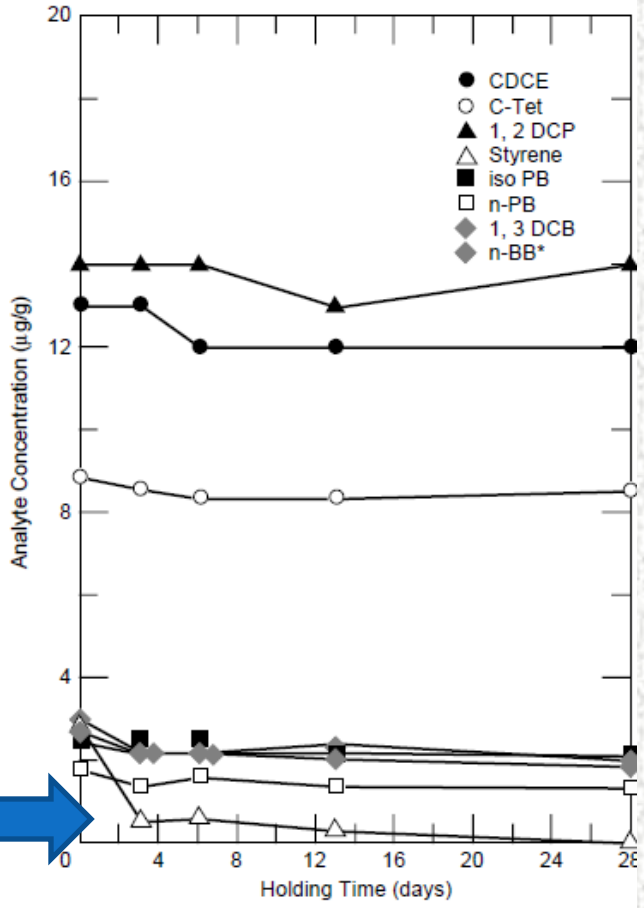



*Figure 15. Set 3/trial 3. Contaminated soi preserved with $NaHSO_4$ and stored at 22°C.*

"Styrene was not stable in the soil preserved with NaHSO4… The chemical reaction that transforms styrene most likely is catalyzed by the soil. Clearly, soil sample preservation by NaHSO4, or perhaps any acid, would not be compatible for investigations where styrene is a constituent of interest." A. Hewitt, 1995.

# Observations from Study Data

- Styrene
  - Some loss observed over extended holding times in acidified waters, but generally ≤ 30% over 28 days
  - Significant losses of styrene in some unpreserved samples
- Vinyl chloride
  - Similar stability seen with acidic and basic preservative
  - No rapid losses resulting from acid preservation in sample matrices tested

# Revised Table 4-1 in Update V

TABLE 4-1 (continued)
RECOMMENDED SAMPLE CONTAINERS, PRESERVATION TECHNIQUES, AND HOLDING TIMES*

| VOLATILE ORGANICS (continued) | | | |
|---|---|---|---|
| Sample Matrix | Container[1] | Preservative[2] | Holding Time[3] |
| Aqueous samples WITH residual chlorine present | Methods 5021, 5030, 5031, and 5032:<br>2 x 40-mL vials with PTFE-lined septum caps | Collect sample in a 125-mL container which has been pre-preserved with 4 drops of 10% sodium thiosulfate solution. Gently swirl to mix sample and transfer to a 40-mL VOA vial. Cool to ≤6 °C and adjust pH to less than 2 with $H_2SO_4$, HCl, or solid $NaHSO_4$. | 14 days |
| | | If carbonaceous materials are present, or if MTBE and other fuel oxygenate ethers are present and a high temperature sample preparative method is to be used, do not acid preserve the samples. | 7 days |
| | | If compounds that readily degrade in acidified water (e.g., 2-chloroethyl vinyl ether[4]) are analytes of interest, collect a second set of samples without acid preservatives and analyze as soon as possible. | 7 days |
| Acrolein and Acrylonitrile<br>Aqueous samples | Methods 5021, 5030, 5031, and 5032:<br>2 x 40-ml vials with PTFE-lined septum caps | Adjust to pH 4-5. Cool to ≤6 °C.<br>These compounds are highly reactive and should be analyzed as soon as possible. | 7 days |
| Solid samples (e.g. soils, sediments, sludges, ash) | Method 5035: See the method.<br>Method 5021: See the method.<br>Methods 5031 and 5032: See the methods. | See the individual methods. | 14 days |
| | | If compounds that may be reactive in acidified soils (e.g., vinyl chloride, styrene, 2-chloroethyl vinyl ether) are analytes of interest, collect a second set of samples without acid preservatives and analyze as soon as possible. | 7 days |

# A word about preservation

"If a preservative functions as intended, the concentrations of the analyte of concern will not change during storage. Science can not be used to prove a negative. Experimental trials with preservatives can not be used to prove that a preservative is universally effective."

- John T. Wilson, microbiologist at EPA ORD NRMRL, in "A Guide for Assessing Biodegradation and Source Identification of Organic Ground Water Contaminants using Compound Specific Isotope Analysis", EPA 600/R-08/148, 2008

# Thanks

- Workgroup
  - Chemists from USEPA Regions 3, 4, 6, 10
  - Jessie DeLuna, Paula Hogg, HRSD
  - Richard Burrows, Test America
  - Chung-Rei Mao, US ACE
- John Wilson USEPA ORD NRMRL

# References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