Evaluation of Lead Service Line Lining and Coating Technologies

Stephen J. Randtke, Craig D. Adams, Edward F. Peltier, Rachael F. Lane, Zachary A. Breault, Ray E. Carter, Jr., J. Alan Roberson, and Jonathan D. Cuppett

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Project Personnel

- Water Research Foundation
  - Jonathan Cuppett (Project Manager)
  - Michelle Suazo (Project Coordinator)
  - Traci Case
- Project Advisory Committee (PAC)
  - Clay Commons (Rhode Island)
  - France Lemieux (Health Canada)
  - Mike Schock (EPA)
  - Greg Welter (O'Brien and Gere)

Project Personnel (Cont'd)

- University of Kansas
  - Steve Randtke, PI
  - Ted Peltier, Co-PI
  - Ray Carter, Research Associate
  - Rachael Lane, Graduate Research Assistant
  - Zach Breault, Graduate Research Assistant
- Utah State University
  - Craig Adams, Co-PI
- American Water Works Association
  - Alan Roberson, Co-Investigator

Overview

- Project Objectives
- Regulatory Considerations
- Research Project Tasks & Status
- Lining & Coating Technologies
- Utility Experiences
- Fill-and-Dump Experiments
  - Expt. 1: Epoxy-Coated Pipe Specimens
- Organic Leachates and Byproducts

Research Objectives

- Comprehensively evaluate lead service line (LSL) lining & coating technologies as alternatives to full or partial LSL replacement, and for protecting and repairing lead and copper service lines
- Provide water utilities, consultants, state regulators, consumers, and others with information to make informed decisions regarding lining and coating of lead and copper service lines

Regulatory Considerations

- Lead & copper rule (LCR)
  - Proposed changes expected in 2014
  - LSL replacements
    - Some mandatory, but most voluntary and partial; few homeowners are replacing their LSLs; partial replacement may cause a short-term increase in lead levels
    - Lining & coating not considered “replacement”
- Current and future standards for organic and inorganic contaminants
  - Bisphenol-A (BPA) and other bisphenol compounds
  - Phthalate esters and phthalic acids
  - Antimony & other metals

Research Tasks & Status

- Task 1: Gather and Evaluate Existing Information and Identify Issues
  - Literature
  - Water utilities
  - State, provincial, & other regulatory agencies
  - Manufacturers, contractors, other researchers
  - NSF International
- Status
  - Well underway and still going strong
  - Comprehensive summary → final report
  - Seeking more information internationally

Research Tasks & Status (Cont'd)

- Task 2: Acquire and Evaluate Monitoring Data
  - Acquire data from utilities or other sources
  - Obtain and analyze samples from field, demo, and pilot installations
- Status
  - Limited data obtained (Calgary, DC Water, Providence Water)
  - Few installations available for sampling
  - Sampling efforts put on hold pending methods development and lab test results
  - Seeking data / reports from additional utilities and other parties, especially internationally

Research Tasks & Status (Cont'd)

- Task 3: Conduct Laboratory Studies
  - Examine the most promising technologies
    - Effectiveness for Pb & Cu control
    - Potential to leach organic contaminants
    - Potential to leach other IOCs, e.g., Sb
    - Other water quality effects
    - Installation issues and other issues
- Status
  - Methods development
    - LC-MS/MS methods for bisphenols, bisphenol derivatives, and phthalic acids
    - GC-MS methods for phthalate esters

Research Tasks & Status (Cont'd)

- Status of Task 3 (cont'd)
  - Fill-and-dump experiments
    - Epoxy-coated specimens tested in 2012
    - PET-lined specimens expected momentarily
    - Additional fill-and-dump experiments, including vial studies, in progress or being planned.
  - Other experiments in progress or being planned will examine:
    - Fate of organic contaminants leached from lining and coating materials: hydrolysis, chlorination
    - Liner and coating permeation rates for Pb & Cu, initially and over time
    - Impact of pipe freezing

Research Tasks & Status (Cont'd)

- Task 4: Demonstration Tests
  - Field or pilot tests with ≥3 technologies
  - Closely coordinate with participating utilities
  - Include partial LSL linings & coatings if possible
- Status
  - Providence Water Test (witnessed by A. Roberson)
  - Opportunities limited; assistance offered, but no takers yet; seeking opportunities to "piggy back"
  - Lab experiments, combined with selective sampling and reports by utilities and vendors, especially internationally, may provide better information.

Research Tasks & Status (Cont'd)

- Task 5: Build New Case Studies
  - Focus on system-wide benefits (health & $)
  - ≥3 Utilities likely to benefit
    - Implementation requirements
    - Potential savings & other benefits
    - Disadvantages & additional information needs
- Status
  - Detailed discussions with selected utilities
  - Good cost estimates / data very hard to obtain
  - Weighing value of 3 comprehensive case studies versus a larger number of streamlined case studies

Research Tasks & Status (Cont'd)

- Task 6: Evaluate Lining and Coating Technologies
  - Comprehensive assessment based on Tasks 1-5
- Task 7: Develop Stakeholder Recommendations
  - For utilities, consultants, regulators, consumers, and manufacturers
- Status of Tasks 6 and 7
  - In progress, but at reduced level relative to other tasks until last year of project
  - Primary purpose at this point in time is to inform decisions regarding Tasks 1-5 and keep end result in mind

Lining & Coating Technologies

- Types
  - Epoxy Coatings
    - e.g., Nu Flow, Ace Duraflo, etc.
  - Close-Fit Liners
    - Polyethylene terephthalate (PET) liners (Wavin / Neofit)
    - HDPE (Subline; Polyline)
  - Loose-Fit Liners (e.g., HDPE, PEX)
  - Polyurethane and Polyurea Coatings
    - e.g., 3M Scotchkote 2400
  - Other (Kirmeyer et al., 2000)
    - e.g., Calcite coating, Paltem (PE/epoxy)

PET-Lined LSL Specimen

Lining & Coating Technologies (Cont’d)

- General Considerations
  - Access (typically via pits or interior of home)
  - Surface preparation requirements
    - e.g., scraping, sandblasting, drying
  - Interior obstructions or sharp bends
  - Cost – and difficulty of obtaining accurate cost estimates and installation failure rates
  - Service life
  - Warranties
    - vs service life for a given lining or coating
    - vs service life for Cu (or HDPE) service lines
  - Contaminant leaching

Lining & Coating Technologies (Cont’d)

- General Consideration (cont’d)
  - Degree of flow restriction
  - Tendency to foster biofilm growth
- Coating Considerations
  - Curing time
  - Pooling
  - Holidays
- Lining Considerations
  - Liner stiffness and bending radius vs bends encountered
  - Resistance to damage during installation

Utility Experiences

- Calgary
  - Service lines ~ 10-ft deep
  - Estimated replacement cost ~$10,000
  - Demonstration test of PET liners (5 homes)
- DC Water
  - Epoxy coating demonstration in 2004
  - Coated pipe sections still in use in pilot test
    - Pb < 5 µg/L, but rising in June, 2011
  - Coated pipes not considered replaced (EPA)
  - Reconciliation of cost estimates
  - Estimated service life versus warranty period

Utility Experiences (Cont'd)

- Louisville
  - Demonstration tests in 1990s, but pipes no longer in service
- Madison
  - City-mandated FLSLR program; city matched cost up to $1,500 / connection
- Passaic Valley Water Commission
  - Replaced 193 LSLs in 2010
  - Optimizing treatment

Utility Experiences (Cont'd)

- Providence Water
  - LSLR program halted in 2012, but still replacing LSLs as part of main replacement / extension projects
  - Providing LSL specimens
  - Demonstration of PET lining (witnessed by Alan Roberson)
  - Demonstration of polyurethane(?) coating (for water main, not LSLs)
- Utilities in the United Kingdom
  - Much recent activity, with parallels to US situation
  - Technologies being demonstrated

Utility Experiences (Cont'd)

- Rochester (NY)
  - 30,000 – 35,000 LSLs; ~99% w/ galvanized interior plumbing
  - Has some polyurethane-lined mains
  - Providing LSL specimens
- WaterOne and Olathe
  - Exceedingly few LSLs; only a few goosenecks
  - WaterOne studying HDPE service lines and conducting trials
  - Providing expert advice and information regarding standard practices, materials, and fittings

Fill-and-Dump Experiments

- LSL Acquisition, Handling, and Preparation
  - Source: Rochester, NY and Providence Water
    - Preferably excavated, not pulled
    - 4-ft lengths with ~5/8-in. ID (sample volume, weight)
  - Outer surfaces cleaned; pipes wrapped in duct tape
  - Volume measured prior to cleaning & coating / lining
  - End Fittings
    - Goals: avoid adsorption or leaching of both metals and trace organics; avoid leaks
    - Wetted surfaces = stainless steel & silicone (Expt. 1)
    - 316 SS pipe nipples threaded into LSL specimens and secured with hose clamps

Fill-and-Dump Experiments (Cont'd)

- Acquisition, Handling, and Preparation of Copper Pipe Specimens
  - Source: Home Depot
    - 50-ft roll of 1/2-in. Type L (soft) potable-water-grade tubing
    - Straightened, then cut into 4-ft lengths (to match LSLs)
  - End Fittings
    - Wetted surfaces: same as for LSLs
    - 316 SS stubs connected with compression fittings (can't be threaded in; PEX tubing also available)
- Lining Installation or Coating Application
  - Preferably by manufacturer or their representative
  - Unlined / uncoated specimens used as controls

Fill-and-Dump Experiments (Cont'd)

- **Extraction Water Preparation**
  - Dechlorinated Lawrence tap water (pH 8.0)
    - Cold tap water drawn 24-48 hours prior to experiment
    - Dechlorinated with sodium bisulfite
    - Adjusted to pH 8.0 with 0.1 N HCl and 0.1 M NaOH
  - Chlorinated extraction water (pH 8.0)
    - Deionized water amended with 1 mM $NaHCO_3$ + 1 mM $CaCl_2$
    - NaOCl added to produce free Cl_2 residual of 2.0 $\pm$ 0.2 mg/l
    - Adjusted to pH 8.0 with 0.1 N HCl
  - Low pH metal extraction water (pH 6.5)
    - Deionized water amended with 1 mM $NaHCO_3$ + 1 mM $CaCl_2$
    - Adjusted to pH 6.5 with 0.1 N HCl

Fill-and-Dump Experiments (Cont'd)

- Test Protocol
  - Remove end caps and inspect specimens
  - Rinse and wipe off exterior surfaces of end fittings
  - Flush 15 min. with Lawrence tap water (NH_2Cl)
  - Rinse with 100 mL extraction water, then fill with extraction water and insert silicone stopper
  - After specified holding time, dump sample into clean glass beaker and collect subsamples for:
    - pH & alkalinity (determined immediately)
    - Metals, TOC, and organic chemicals
    - Residual chlorine (when applicable)
  - Determine post-lining/coating specimen volume

Fill-and-Dump Experiment No. 1: Epoxy-Coated Pb & Cu Pipes

- Overview
  - LSLs (Rochester) and CSLs – 8 each (+ controls)
  - Coated by Nu Flow Technologies
    - Witnessed by Zach Breault
    - Returned by overnight carrier
  - Specimens flushed and filled with extraction water on 9/14/12
  - Selected results presented below
  - Follow-up experiments pending

Fill-and-Dump Experiment No. 1: Epoxy-Coated Pb & Cu Pipes

- Procedure for Epoxy Coating the Pipe Specimens
  - Sandblast
  - Flush
  - Dry
  - Apply epoxy
  - Cure

Fill-and-Dump Experiment No. 1: Epoxy-Coated Pb & Cu Pipes

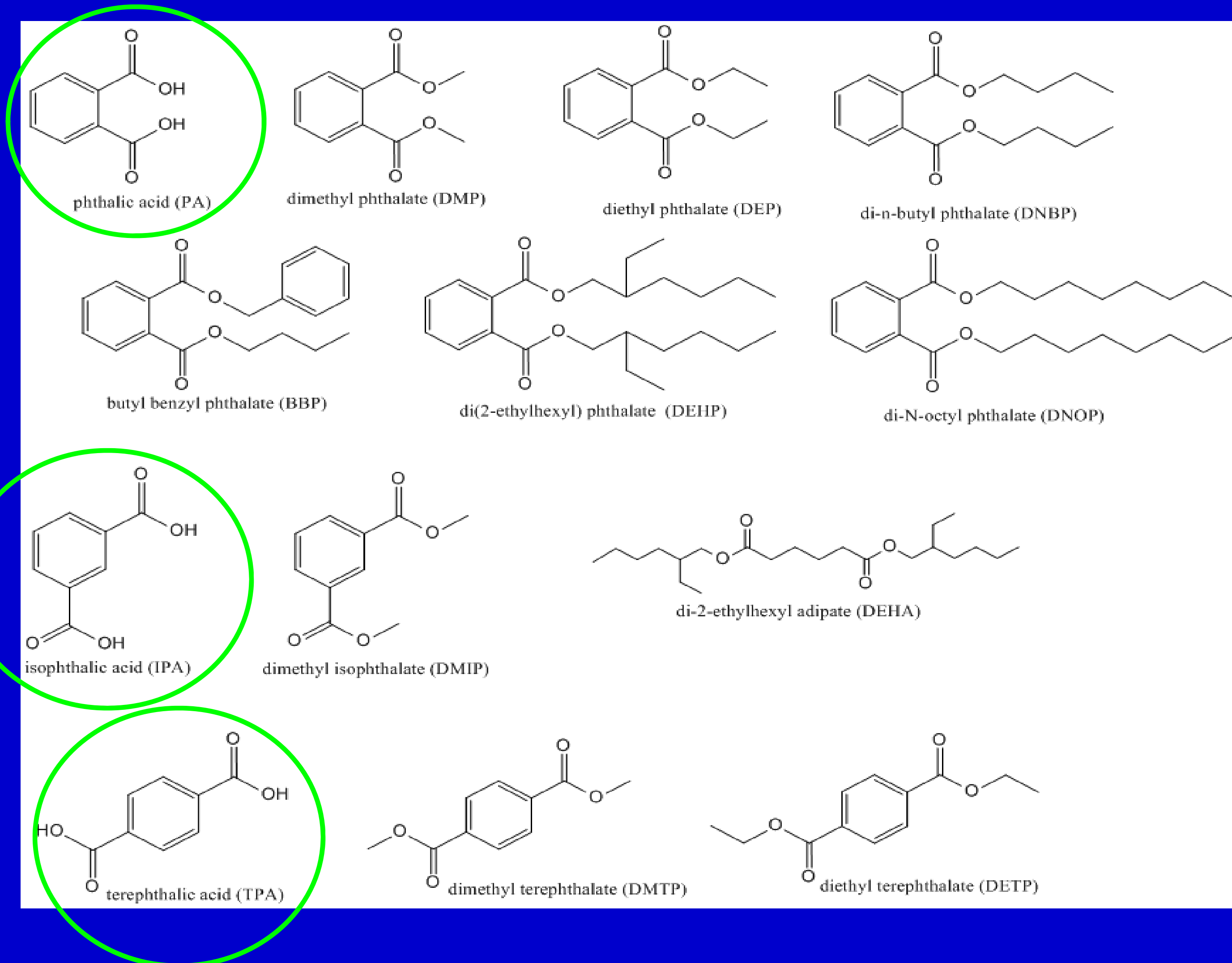
- **Lead Results**
  - Uncoated controls: Pb >1,000 μg/L
  - Extraction waters prior to extraction: Pb <MDL
  - Chlorinated and low-pH waters: <MDL in 8 of 10 samples; maximum = 1.2 μg/L
  - Pb > 5 μg/L in one tap-water sample, but <MDL when later re-extracted with low pH water
- **Copper Results**
  - Dechlorinated tap: Cu = 5.7 μg/L
  - Uncoated copper-pipe controls: 390 – 830 μg/L
  - Extraction waters: 8 of 30 ≥ 10 μg/L, 0 > 20 μg/L

Objectives of Organics Studies

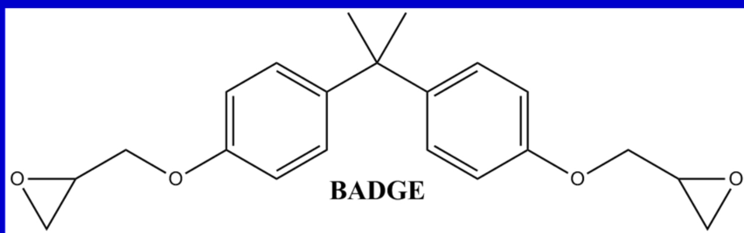
- Determine "likely" leachates, develop methods, and determine primary leachates
- Evaluate leachate stability and reactivity as a function of pH, hydrolysis, free chlorine, monochloramine, and partitioning properties.
- For reactive compounds:
  - 1) model reaction kinetics,
  - 2) determine hydrolysis and/or oxidation byproducts,
  - 3) determine sorption characteristics
- Examine relevance of leaching, reaction rates, and toxicity of degradates (e.g., estimate concentrations for consumers under varied scenarios)

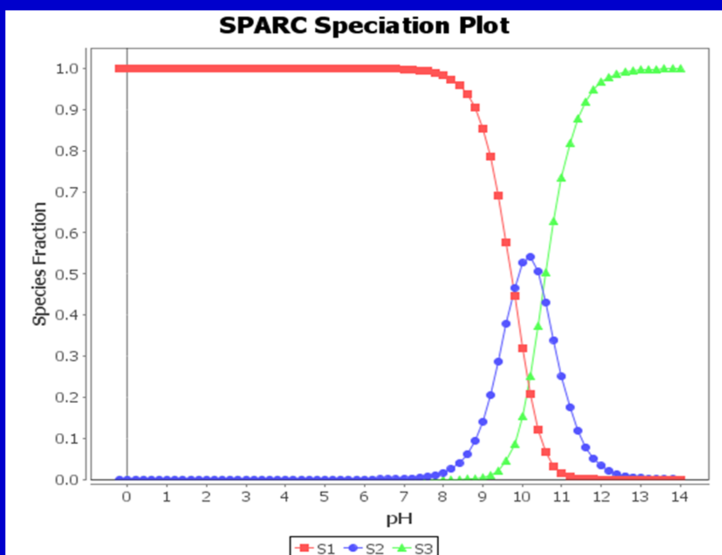
Phthalate Ester and Phthalic Acid Methods

- Phthalates may leach from various plastics (e.g., PET and VC)
- Three phthalic acids (via LC-MS/MS; MRM mode)
- Ten phthalate esters (via GC-MS)

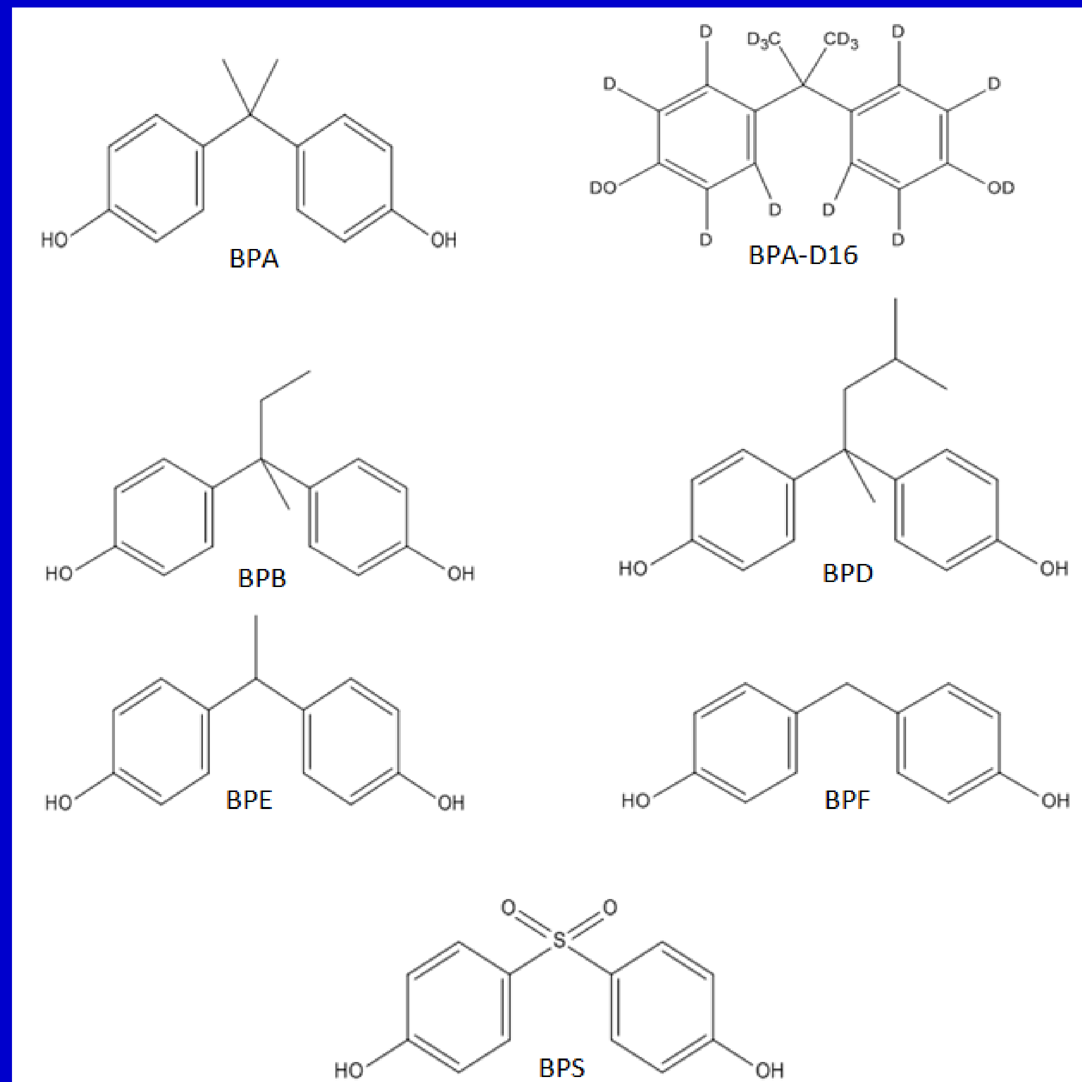


Structures of Bisphenols and BADGE



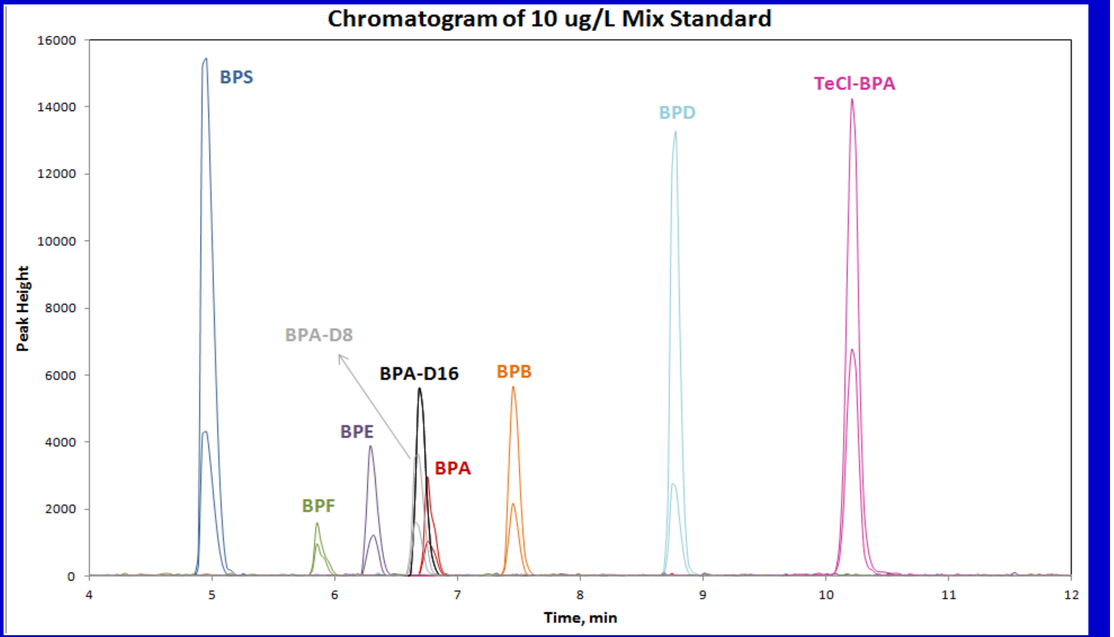


pK1 BPA = 10.08
pK2 BPA = 10.2
Similar for BPB, BPD, BPE
Ref (SPARC v. 4.6)



Bisphenols Method

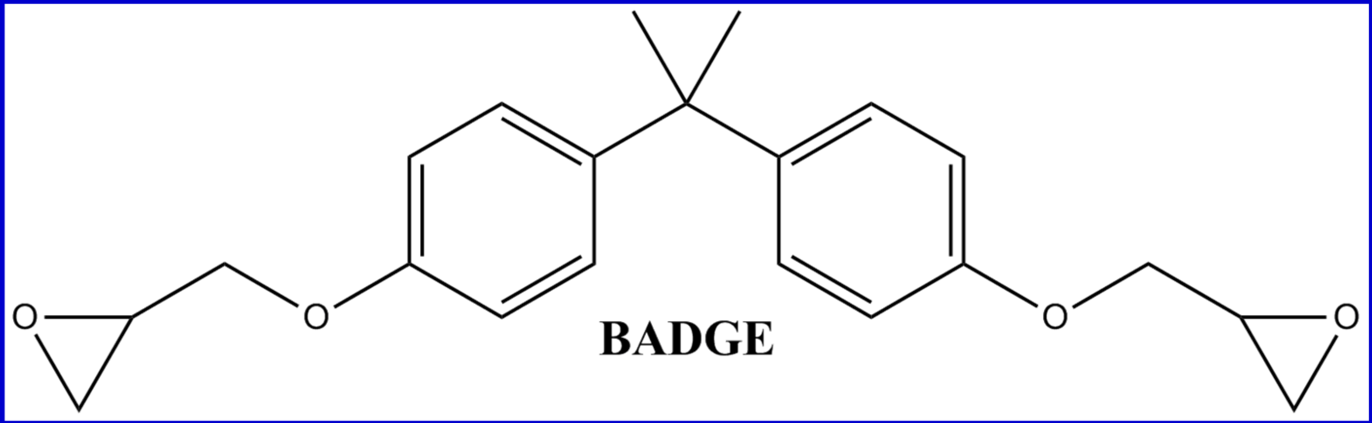
- BPA-D8 = surrogate (recovery standard)
- BPA-D16 = internal standard (IS)
- Filter = mixed cellulose ester (MCE) syringe filter
- Analyzed using MRM mode on AB Sciex AB4000Q LC-MS/MS
- Tetrachloro-BPA (TeCl-BPA) also included in the analysis



Analyte	MDL, µg/L
BPA	0.057
BPB	0.18
BPE	0.070
BPF	0.18
BPD	0.10
BPS	~1
TeCl-BPA	-

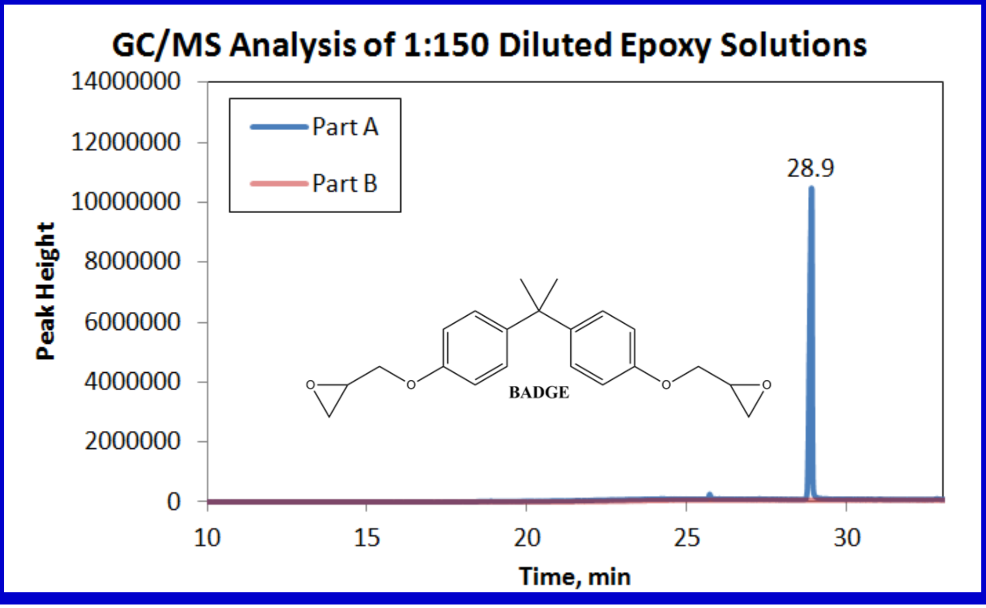
BADGE & BFDGE Method

- BFDGE is bisphenol-F diglycidyl ether
- BADGE & BFDGE not ionized by electrospray
- Ammonium adducts are stable, however (+18)
- Sulfamethoxazole-D4 = internal standard (IS)
- MRM mode on AB Sciex AB4000Q LC-MS/MS (ion trap)



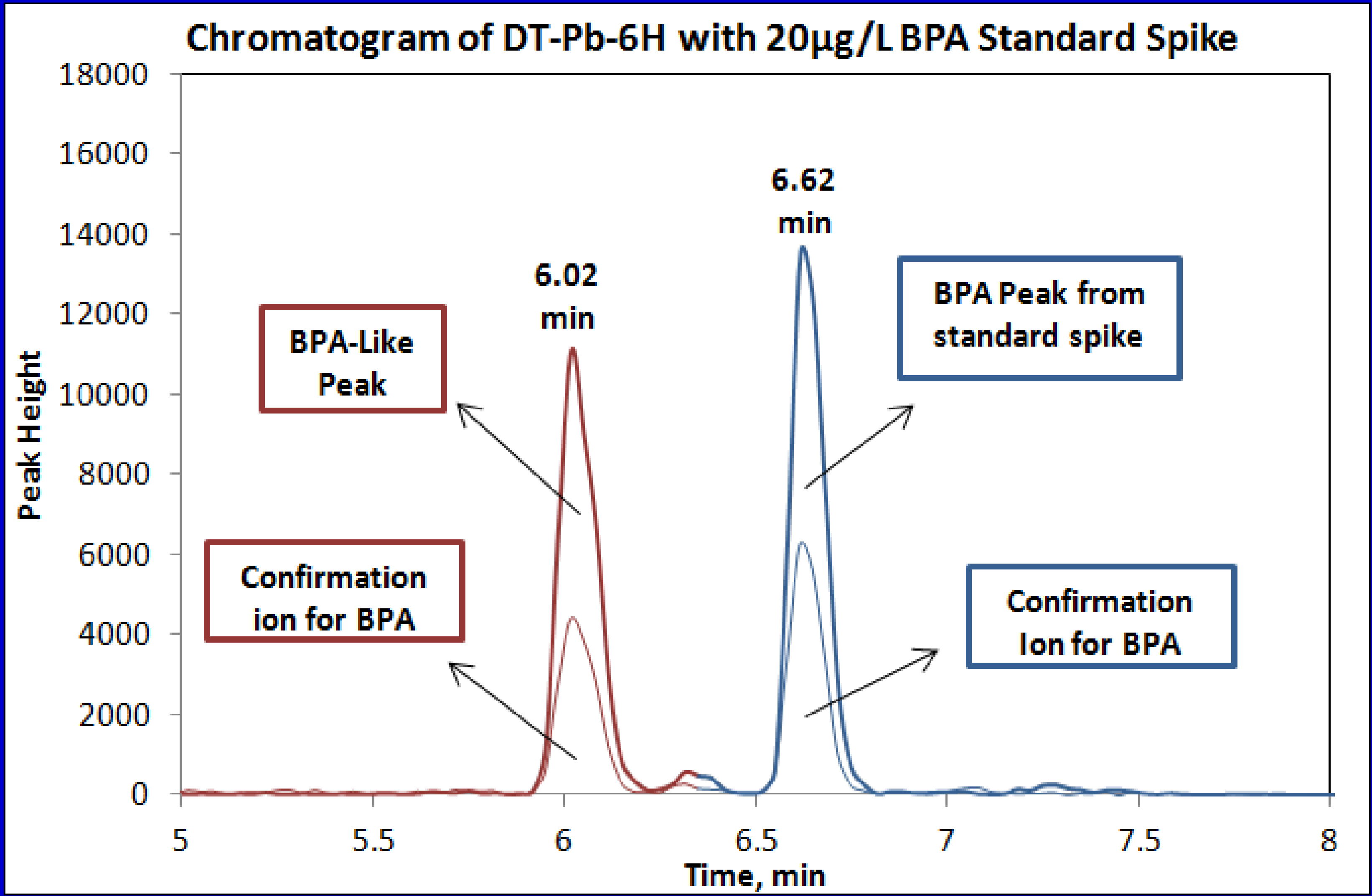
Epoxy Analysis

- **Bisphenols**
  - Analyzed for BPA, TeCl-BPA, BPB, BPD, BPE, BPF, and BPS
  - No bisphenols observed
- **BADGE & BFDGE**
  - NIST Spectral Library matched peak at 28.9 min to BADGE
  - No BFDGE (bisphenol F diglycidyl-ether) observed



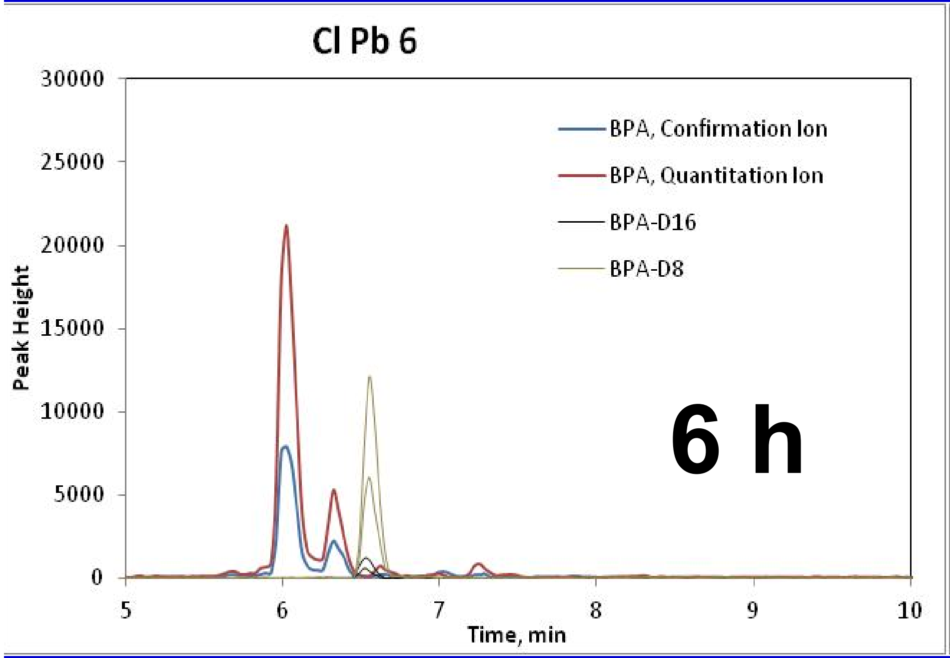
Fill-and-Dump Experiment No. 1: Epoxy-Coated Pb & Cu Pipes

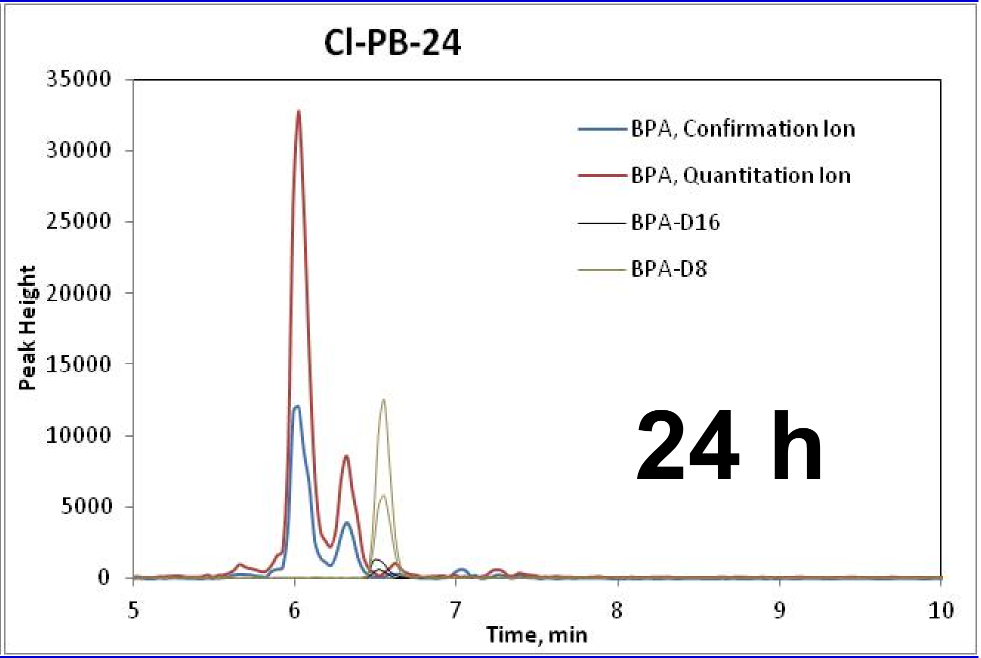
- Organic compounds
  - BPA detected (< 2 μg/L) in 5 of 36 samples
  - Other bisphenols non-detectable, except for traces of bisphenol-S (<5 μg/L) in 4 samples;
  - BADGE (bisphenol-A diglycidyl ether) detected (but well below 0.5 mg/L) in 9 of 36 samples with extraction times up to 24 hours
  - BADGE not detected in samples with longer extraction times (4-10 days)
  - “BPA-Like” compounds detected in many samples (all <0.1 mg/L, assuming a response equivalent to that for BPA)



Epoxy-Coated LSL Specimen Extracted with Dechlorinated Tap Water for 6 Hours

BPA-Like Degradates in Chlorinated Water After 6h in Pipe Freshly Coated with Epoxy

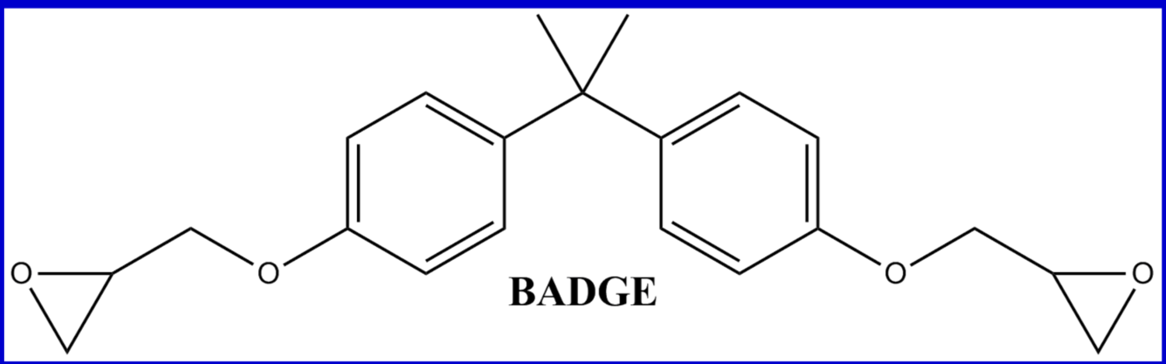


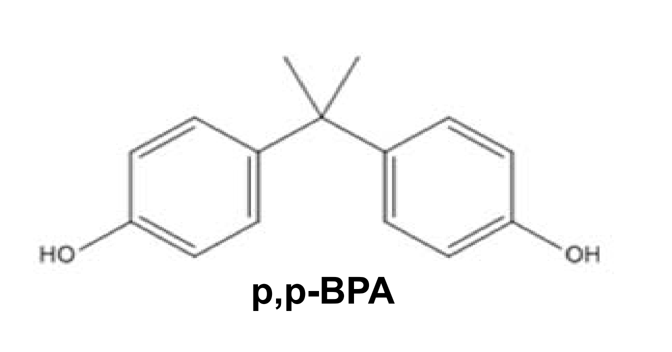


- BADGE (not shown) found after 6h, decreased at 24 h, not found at 4 or 10 days
- BPA-Like compounds (shown) found when analyzing for bisphenols

BADGE and Degradates (cont'd)

- **BADGE appeared to degrade to three degradates with the same ion pair as BPA (two with a shorter retention time than BPA)**
  - **A hypothesis is being tested**
  - **Relative toxicity?**



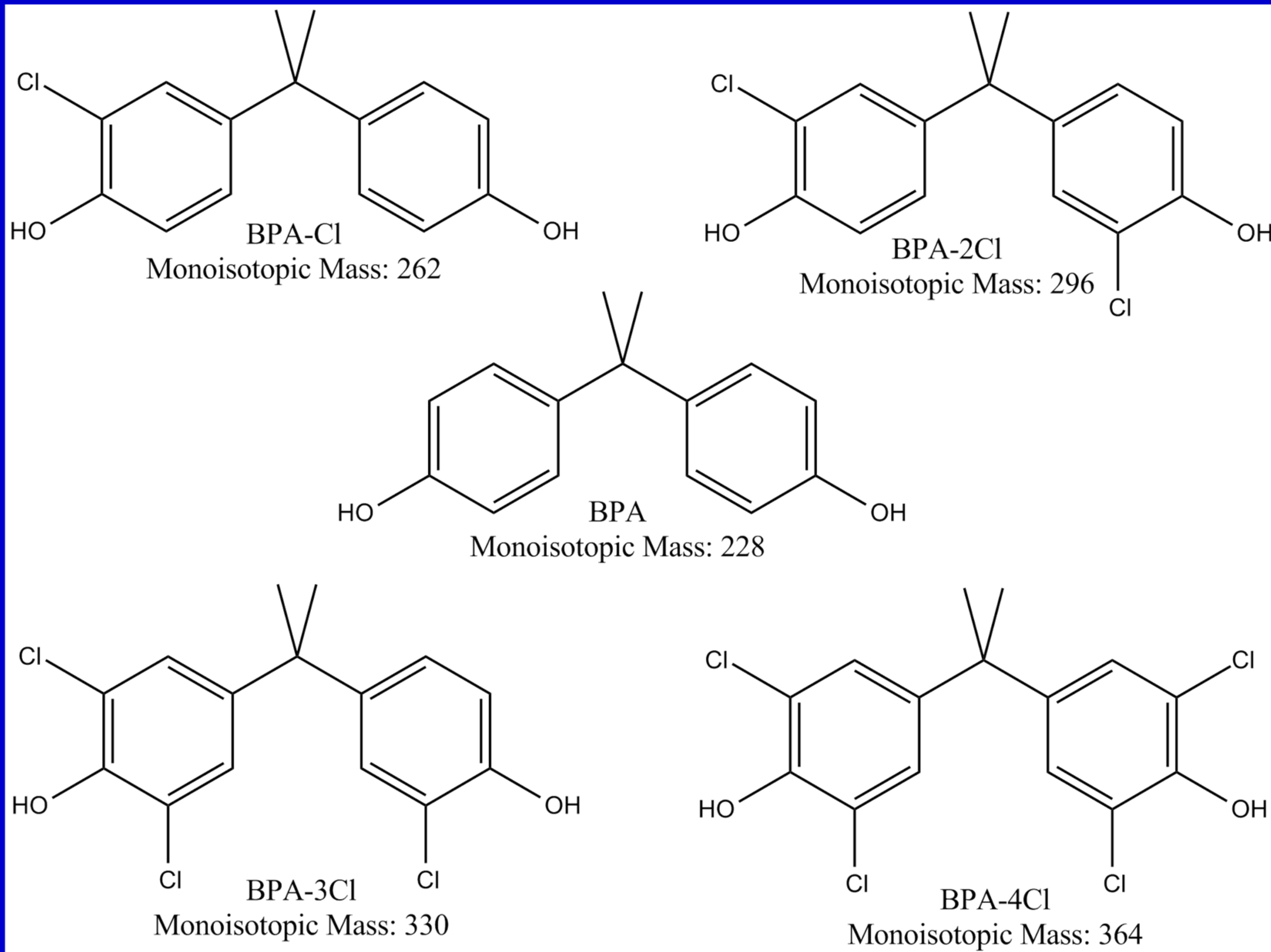


Degradates – Ongoing & Planned Work

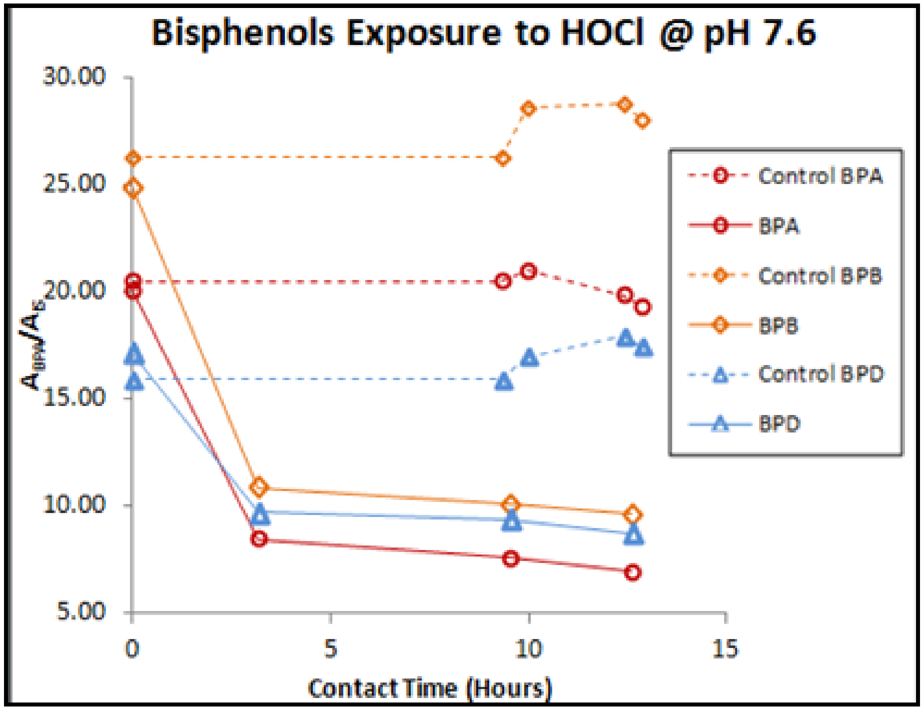
- Degradates to be determined using TOF, Agilent 6490 Q1 library match, and other methods
- Various standards available (esp. for BPA and BADGE hydrolysis and chlorination products)
- Pathways and kinetics to be modeled and experimentally calibrated/validated
  - Hydrolysis, chlorination, and chloramination
  - With speciation of chlorine & and compounds as f(pH)

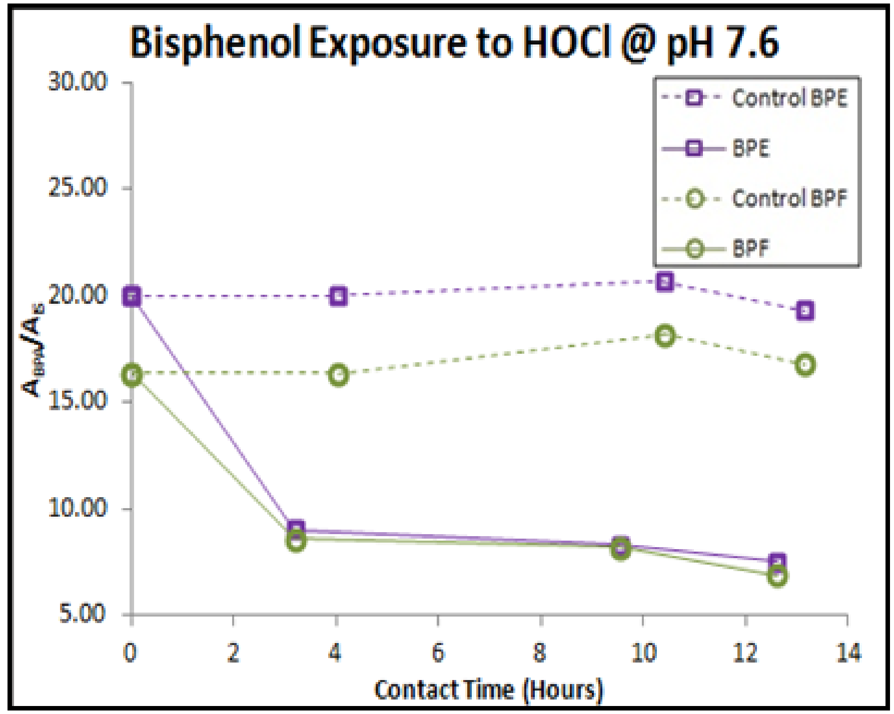
$$\frac{dA}{dt} = \underbrace{-k_A[A][H^+]}_{\text{Acid hydrolysis}} - \underbrace{k_N[A]}_{\text{Neutral hydrolysis}} - \underbrace{k_B[A][OH^-]}_{\text{Basic (alkaline) hydrolysis}}$$

- Partitioning to be estimated computationally
- Toxicity to be estimated from literature & computationally
  - Computational toxicity estimation approach, e.g.:
    - > DEREK (expert system, looks for toxiphores)
    - > TOPKAT (mol files from ChemDraw) to Quantitative Structure Activity Relationships (QSAR) to multivariate approach

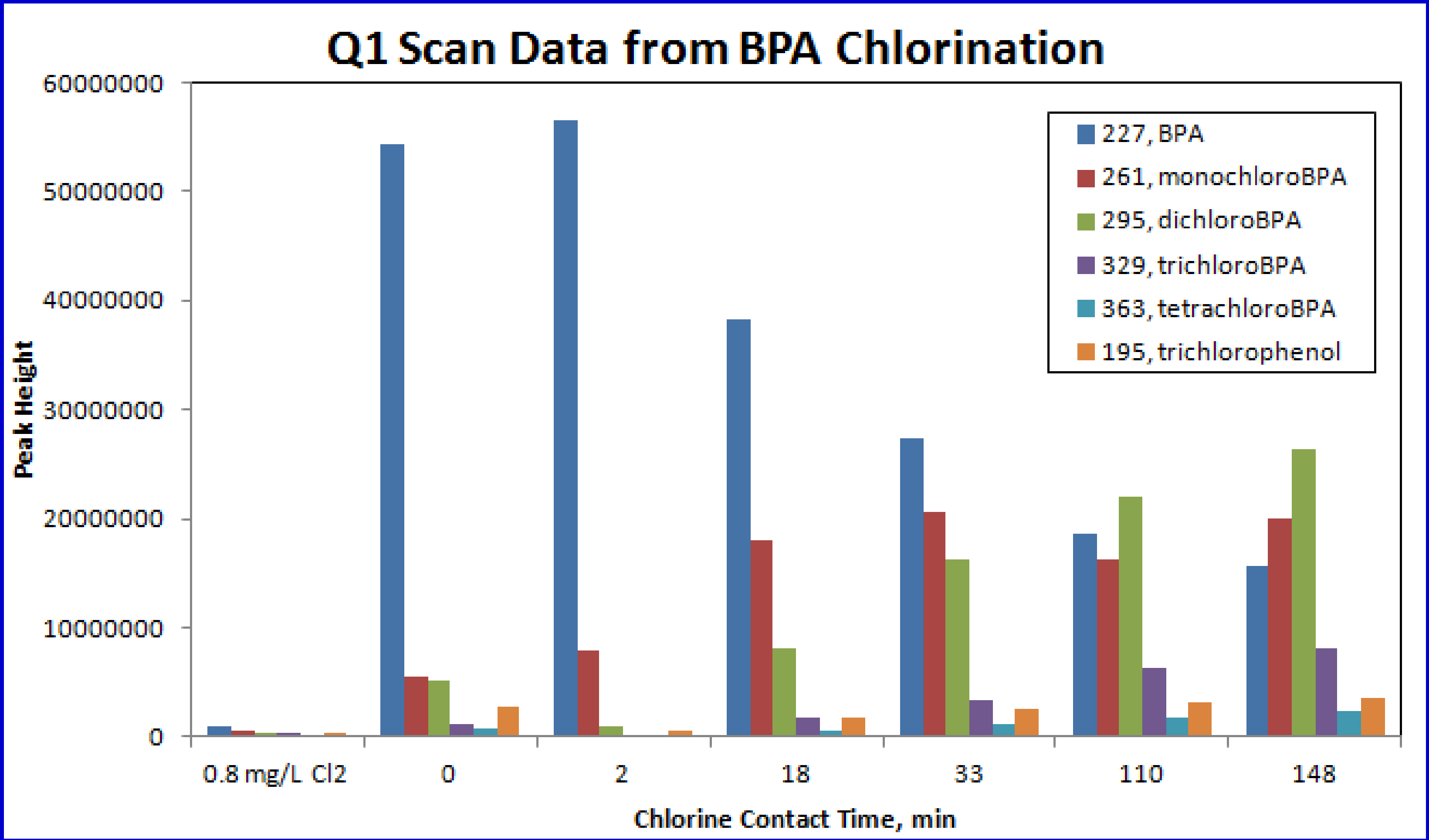


Structures of BPA and Chlorinated Byproducts of BPA





Oxidation of Bisphenols by Free Chlorine at pH 7.6



Formation of Chlorinated Products of Bisphenol-A (BPA)

Chlorination kinetic model for BPA degradation

$$\text{rate}\,(M^{-1}\cdot s^{-1}) = \frac{dC_{Tot,BPA}}{dt} = -kC_{Tot,Cl}C_{Tot,BPA}$$

Six separate reactions: 2 chlorine and 3 BPA species

$$C_{Tot,Cl} = [HOCl] + \left[OCl^{-}\right] = C_{Tot,Cl}\left(\alpha_{HOCl} + \alpha_{OCl^{-}}\right)$$

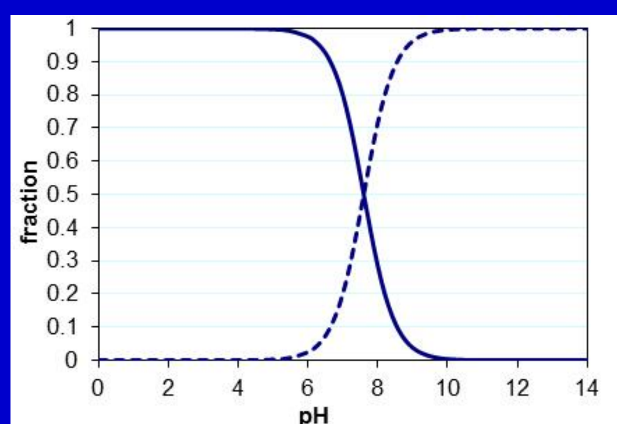
$$C_{Tot,BPA} = [H_2A] + \left[HA^{-}\right] + \left[A^{2-}\right] = C_{Tot,BPA}\left(\alpha_{BPA^{0}} + \alpha_{BPA^{-1}} + \alpha_{BPA^{-2}}\right)$$

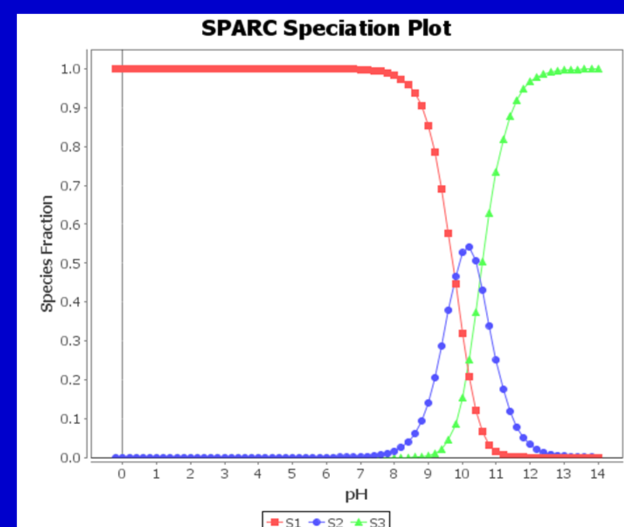
$$\alpha_{BPA^{0}} = \frac{1}{1 + \frac{K_1}{\left[H^{+}\right]} + \frac{K_1 \cdot K_2}{\left[H^{+}\right]^2}}$$

$$\alpha_{BPA^{-1}} = \frac{1}{1 + \frac{\left[H^{+}\right]}{K_1} + \frac{K_2}{\left[H^{+}\right]}}$$

$$\alpha_{BPA^{-2}} = \frac{1}{1 + \frac{\left[H^{+}\right]}{K_2} + \frac{\left[H^{+}\right]^2}{K_1 \cdot K_2}}$$

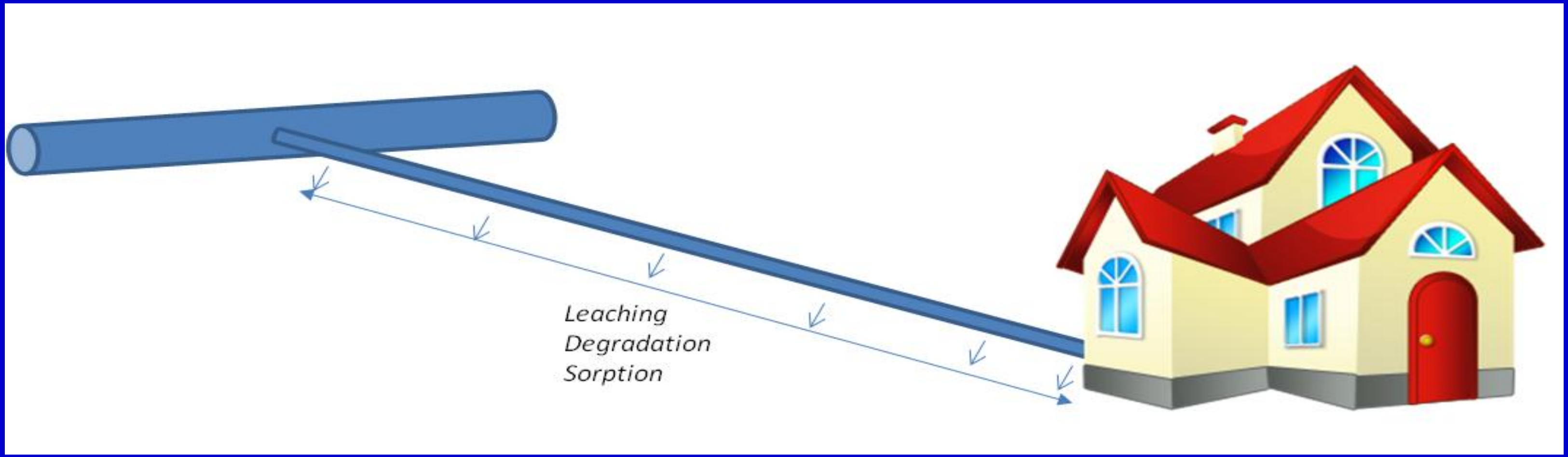
Most important reactions likely to be HOCl with phenolates





Modeling fate and exposure pathways

- **DIFEQ/numerical model for each relevant reaction, e.g., formation of chlorinated and hydrolysis byproducts**
- **Plug flow kinetics ($C = C_0e^{-kT}$)**
- **Allows estimation of tap-water concentrations as function of time and initial concentration, to assess relevance of various degradates and associated risks**



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That’s all folks!!

Questions?