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The Analysis of Water for BPA and Phthalates in Laboratory & Consumer Water Sources, and Commercial Reusable Drinking Containers

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Phthalates

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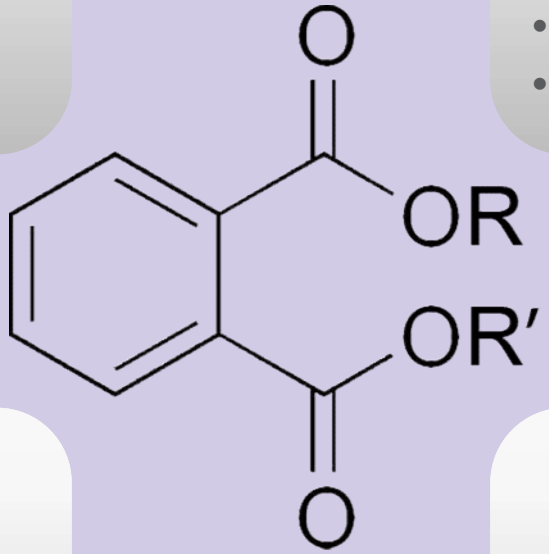
Background

- *Group of esters of 1,2-benzenedicarboxylic acid*
- *Produced since late 1800's*
- *Commercial use in 1920's*

Uses

- *Plastic compounds (10-60% by wt)*
- *Binders*
- *Coatings*
- *Fragrances and pigments*



Health Effects

- *Residue is widespread*
- *Asthma, reproductive disorders, diabetes, obesity and genetic effects*
- *Endocrine disruptor*

Response

- *US ban of DEHP, BBP, DBP in children's toys 2009*
- *Mexico, the EU, and Japan restricted or banned the use of phthalates in children's toys*

Phthalates in Consumer Products

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- Water Bottles
- Bottled Beverages
- Medical tubing and devices
- Cosmetics
- Perfumes
- Health and Beauty Products
- Toys
- Food Packaging
- Baby Mattress Covers
- Plastic Films
- Sunscreens
- Baby Care Ointments & Lotions
- Air Fresheners
- Vinyl flooring

Bisphenol A

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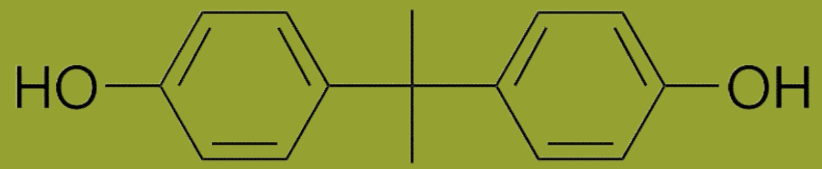
Background

- *2 phenol groups*
- *Produced by condensing acetone + phenol & acid catalyst*
- *3.7 million metric tons/yr*
- *Reported in 1891*

Uses

- *Polymers*
- *Toys*
- *Medical devices*
- *Coatings and epoxy resins*



Health Effects

- *Suggested estrogenic effects the 1930's*
- *Endocrine disruptor*

Regulations

- *The EPA guideline - 50 µg/kg/day*
- *As low as 0.025 µg/kg/day can have adverse effects*

Consumer Products BPA

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- Water Bottles
- Baby Bottles
- Dental Filling Material
- Toys
- Cash Register Receipts
- Food can lining (soda, tomatoes, acidic food)
- Jar lid linings
- Recycled Pizza box lining
- Toilet Paper
- Plastic water piping
- Beer & Wine (fermented in BPA lined vats)
- Currency

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Municipal Water

- US municipal water quality
  - *EPA – Some limits*

Bottled Water

- Bottle water quality
  - *FDA -No guidelines*
  - *Sales (worldwide)*
    - 2012: $168 Billion
    - 2015: $214 Billion
  - *US Consumption*
    - 1979: 1.7 b/g
    - 2012: 8.8 b/g
    - 2014: 11 b/g
  - *2nd most consumed beverage*
  - *Americans drink bottled water:*
    - Substitute for other beverages
    - Concerned over tap water safety
  - *Many sources including tap water*

Sports Bottles

Laboratory Water

Sources of Contamination

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- Many potential sources of organic pollutants in water supplies
  - *Environmental*
  - *Manufacturing or Processing*
  - *Packaging and/or Transport*
  - *Distribution*
- Does processing of water increase BPA & Phthalates?
- Groups raise concern of leaching of chemicals from packaging
  - *Suggestions include: don't reuse, no high temperatures, avoid bottled water*

Consumer Water Sources & Reusable Bottles

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Bottled Water

3 Different brands

Sports Bottles

Traditional
BPA-Free
Jug style
FEP
Squeeze bottle

Tap Water

Straight from Tap
Point of Use Systems (POU)

Laboratory Water

DI Tap
HPLC Grade
LC-MS Grade
DI from HDPE Carboy

Method & Materials: Reagent Contamination

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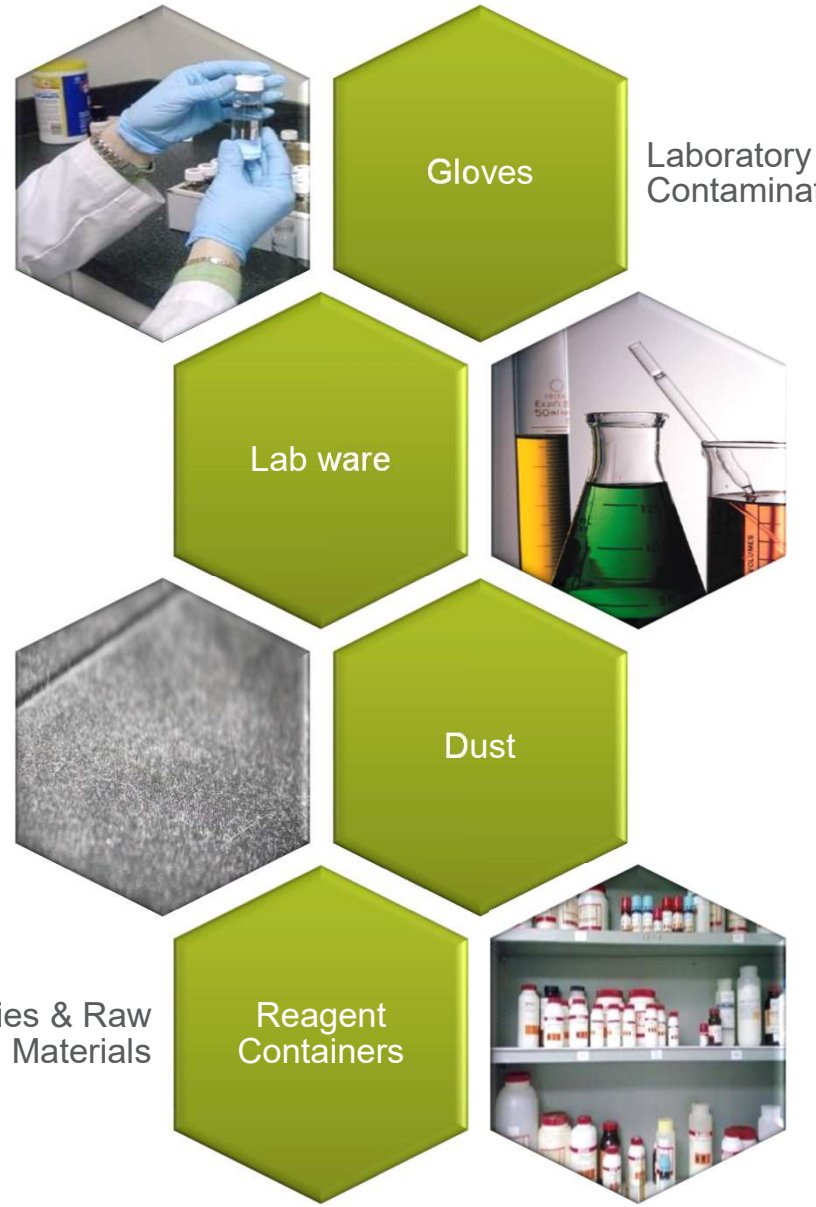

- Difficult to eliminate contamination from samples
- All materials must be tested before use
- Rinse, bake or clean materials when possible before use

Methods & Materials: Reagent Contamination

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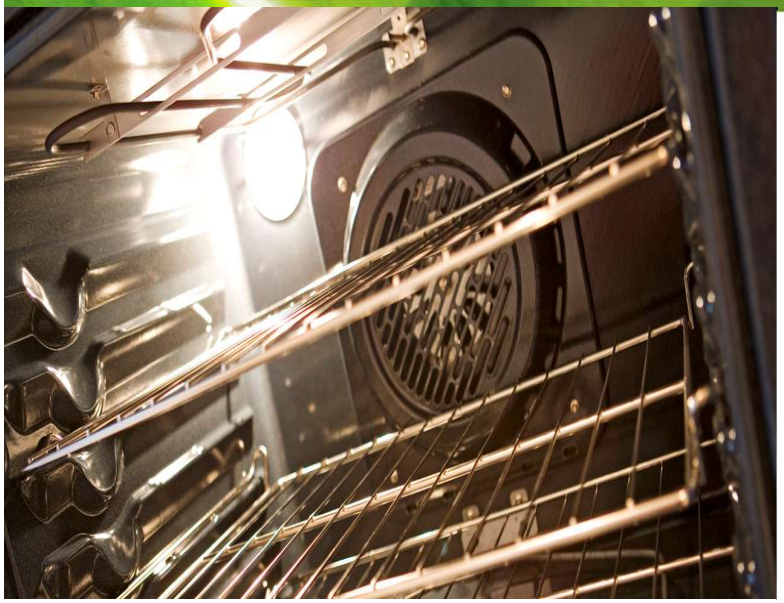
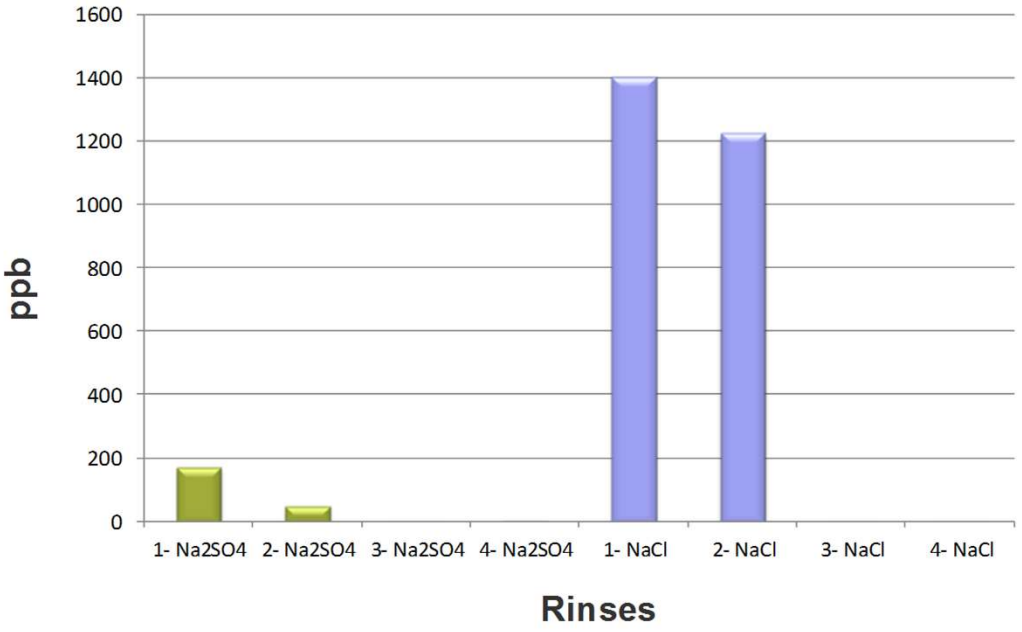


- NaOH, NaCl & Na_2SO_4
  - *2-60 mL $MeCl_4$ rinses*
    - Reduced to 1mL – GC/MS
  - *Baked 210°C, 30 min*
  - *2-60 mL $MeCl_4$ rinses*
    - Reduced to 1mL – GC/MS



- Phthalates reduced after rinse & baking
- NaOH did not contain phthalates

Methods & Materials: Water Sample Collection

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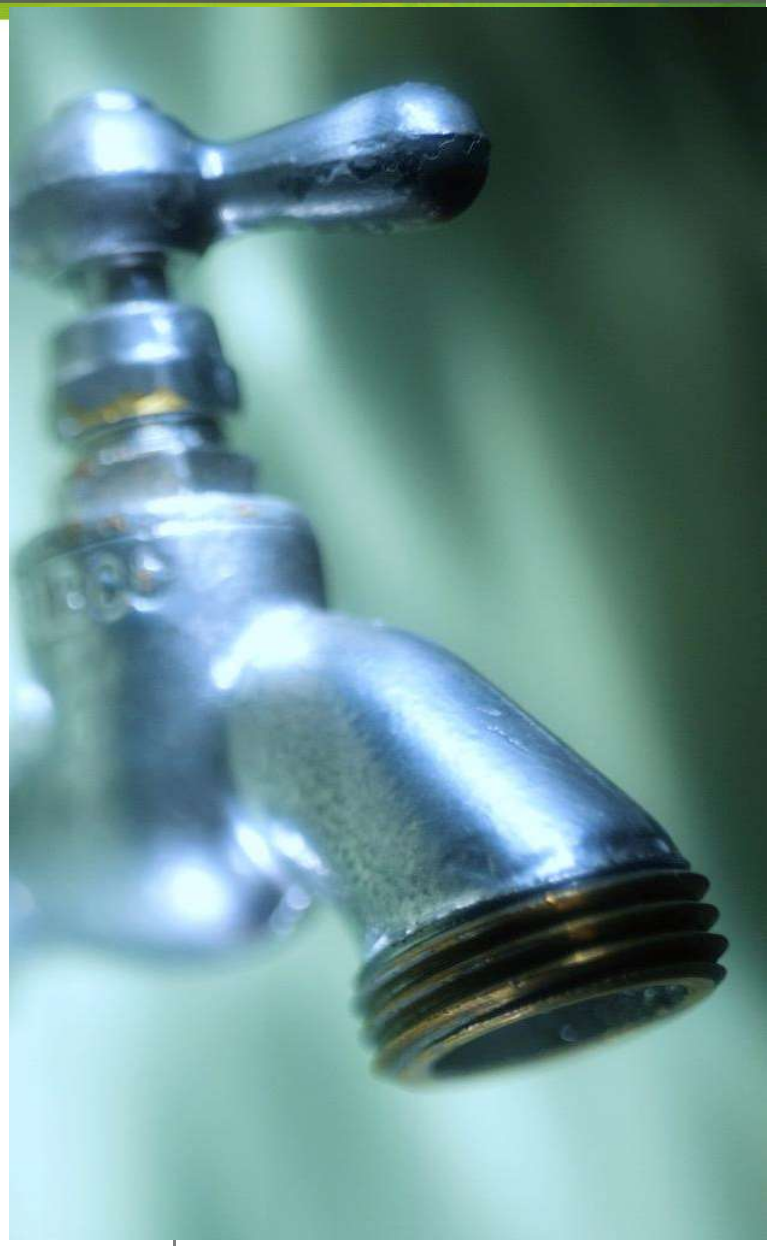
Laboratory & Municipal Water

Stationary: Static > 12h

Flushed: >2L Rinsed

- POU: Dispenser
- DI System
- Tap: Municipal Water

- **POU A: Dispense only**
- **POU B: UV & Carbon Filter**



Methods & Materials: Reusable Bottle Testing

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Rinsed 500 mL LC/MS Water (retained)

Dishwasher with Soap & Heat

Rinsed 4x DI water,
2x LC/MS Water (last retained)

500 mL in each bottle

One set 60 C
&
Second set RT – one week

Methods & Materials: Bottled Water

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- Two sets of each brand
- One set placed at 60°C - one week
- Second set placed at RT - one week

Methods & Materials: Extraction

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- Liquid – Liquid extraction
  - *15 gm NaCl*
  - *Acid extraction:*
    - HCl (pH <3)
  - *Base extraction:*
    - 50% NaOH (pH >9)
  - *60 mL DCM*
  - *Dried with 'cleaned' Na_2SO_4*
  - *Extracts combined & evaporated to 1 mL*

Methods & Materials: Standards

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- S-509 Bisphenol A Standard
- 8061-X Phthalate Mix
- 8060-QC Phthalate Mix
- CLPS-1 Internal Standards

Target Compounds

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Name	Abbreviation	RT	Ions	Structural formula	CAS #
Dimethyl phthalate	DMP	7.57	163, 77, 164, 76	C10H10O4	131-11-3
Diethyl phthalate	DEP	8.43	149, 177, 150, 65, 29	C12H14O4	84-66-2
Diisobutyl phthalate	DIBP	10.28	149, 57, 29, 41, 223	C16H22O4	84-69-5
Di-n-butyl phthalate	**DBP**	**10.8**	**149, 150, 29, 41, 57**	**C16H22O4**	**84-74-2**
Di(2-methoxyethyl) phthalate	DMEP	10.98	59, 58, 45	C14H18O6	117-82-8
Diisohexyl phthalate	DIHxP	11.33	149, 43, 85, 150	C20H30O4	146-50-9
Di-n-pentyl phthalate	DNPP	11.66	149, 43, 150, 41, 29	C18H26O4	131-18-0
Bisphenol A	**BPA**	**11.83**	**213, 228, 119, 214, 91**	**C15H16O2**	**80-05-7**
Di-n-hexyl phthalate	DNHP	12.36	149, 43, 41, 29, 150	C20H30O4	84-75-3
Butyl benzyl phthalate	**BBP**	**12.42**	**149, 91, 206, 65, 104**	**C19H20O4**	**85-68-7**
Hexyl 2-ethylhexyl phthalate	H2EHP*	12.66	149, 43, 251	C22H34O4	75673-16-4
Di(2-n-butoxyethyl) phthalate	DBEP	12.75	149, 57, 56, 101, 85	C20H30O6	117-83-9
Di(2-ethylhexyl) phthalate	**DEHP**	**12.95**	**149, 167, 279, 71**	**C24H38O4**	**117-81-7**
Dicyclohexyl phthalate	DCP	12.96	149, 167, 55, 150, 249	C20H26O4	84-61-7
Di(n-octyl) phthalate	**DNOP**	**13.53**	**149, 279, 43, 57**	**C24H38O4**	**117-84-0**
Dinonyl phthalate	**DINP**	**14.22**	**149, 293, 71, 57, 43**	**C26H42O4**	**84-76-4**

Methods & Materials: Instrument Conditions

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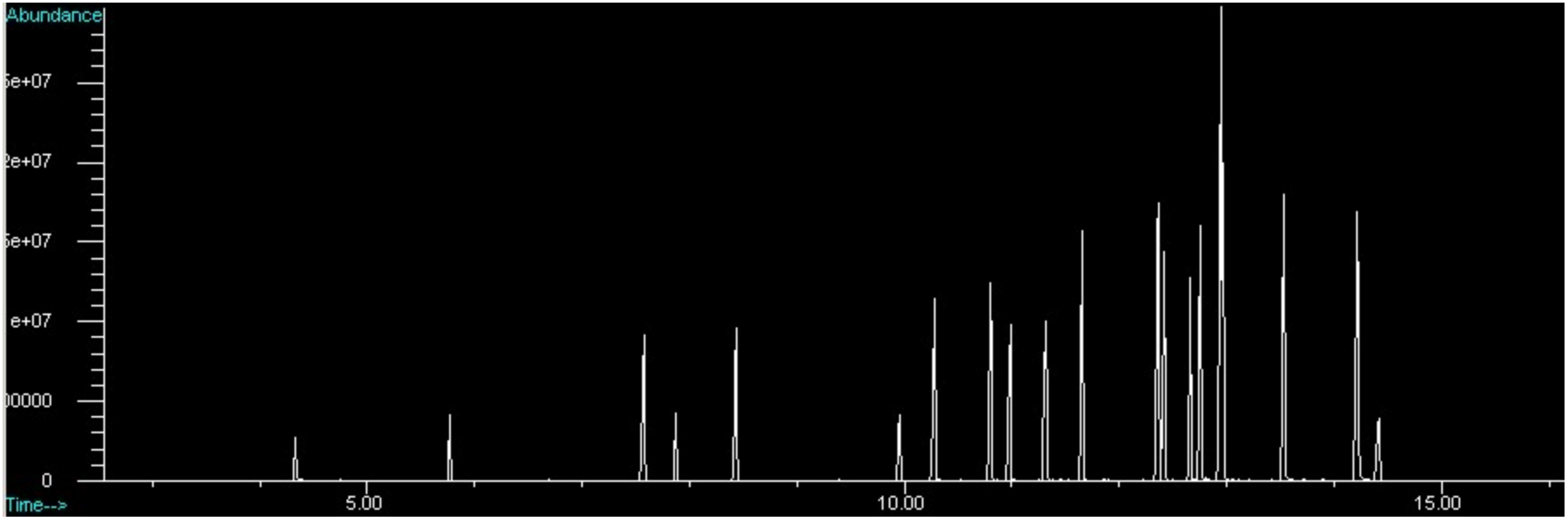
- GC-MS in scan mode
- scan range 35-450 m/z
- Injection volume 1 µL
- CV-5 capillary column (3.0 m x 0.25 mm x 0.25 µm)



Chromatogram of SPEX CertiPrep Phthalate Standard 8061-X & Internal Standard Mix CLPS-I90

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Laboratory Water

Results: Laboratory Water Samples

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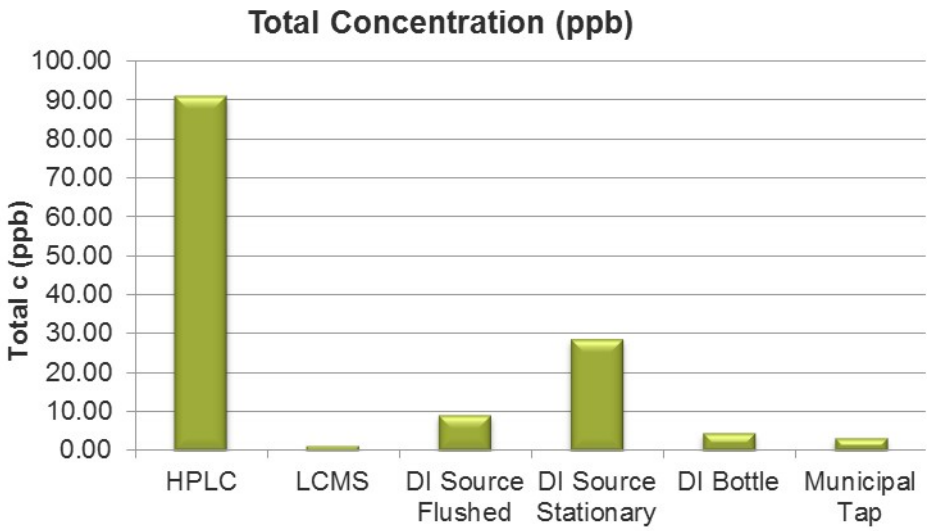
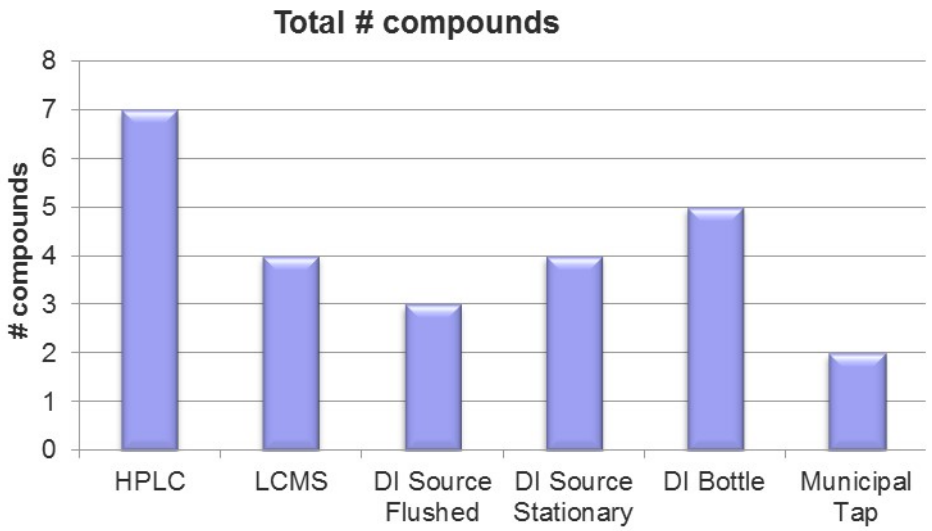
	HPLC	LCMS	DI Source Flushed	DI Source Stationary	DI Bottle	Municipal Tap
DEP	6.28	0.18	0.00	0.30	0.50	0.00
DIBP	3.52	0.16	0.88	1.36	0.52	0.00
DBP	16.72	0.00	0.00	0.00	0.54	0.00
BPA	3.16	0.00	0.00	0.00	0.00	0.00
BBP	44.74	0.20	2.32	0.63	0.47	1.29
DCP	1.00	0.00	0.00	0.00	0.00	0.00
DEHP	15.60	0.63	5.92	26.41	2.44	1.94
Total c (ppb)	**91.02**	**1.17**	**9.12**	**28.70**	**4.47**	**3.23**
Total # compounds	**7**	**4**	**3**	**4**	**5**	**2**





Conclusions: Lab Reagents & Water

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- Phthalate contamination- widespread in laboratory
- Many materials may contain significant phthalates
- Rinses & baking reduce phthalate residue
- Large variability of phthalate in lab water
- All laboratory water sources had contamination
  - *1 to 91 ppb*
  - *Lowest level: LCMS grade water*
  - *Highest level: LC grade water*

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Consumer Drinking Water

Results:
Room Temperature Samples

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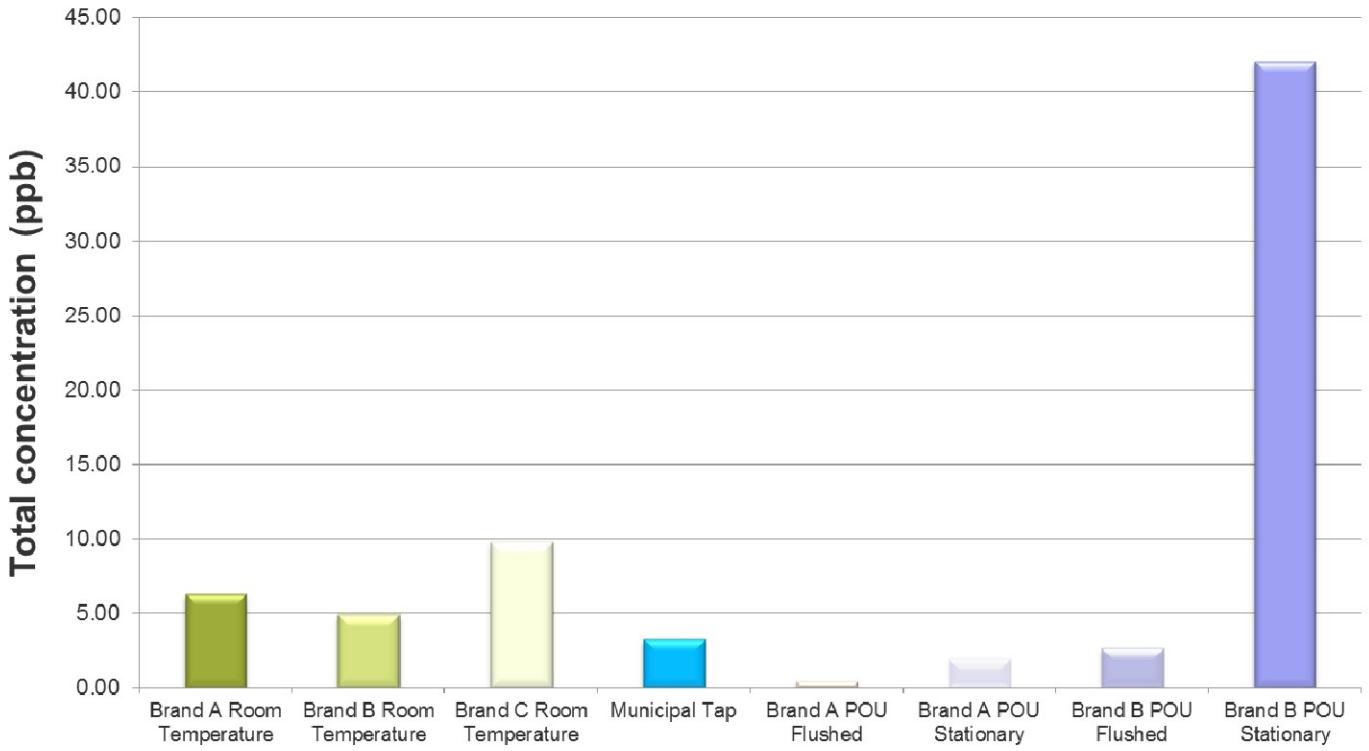

Results: Exposure to Heat

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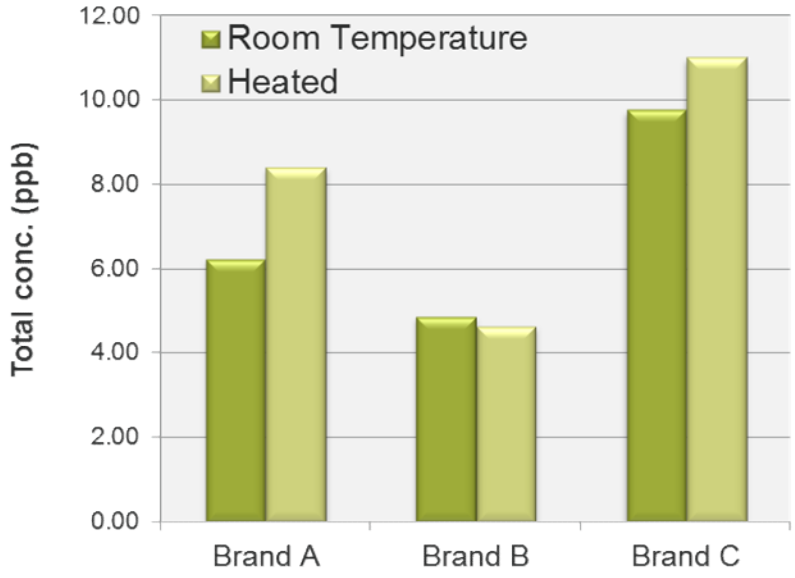
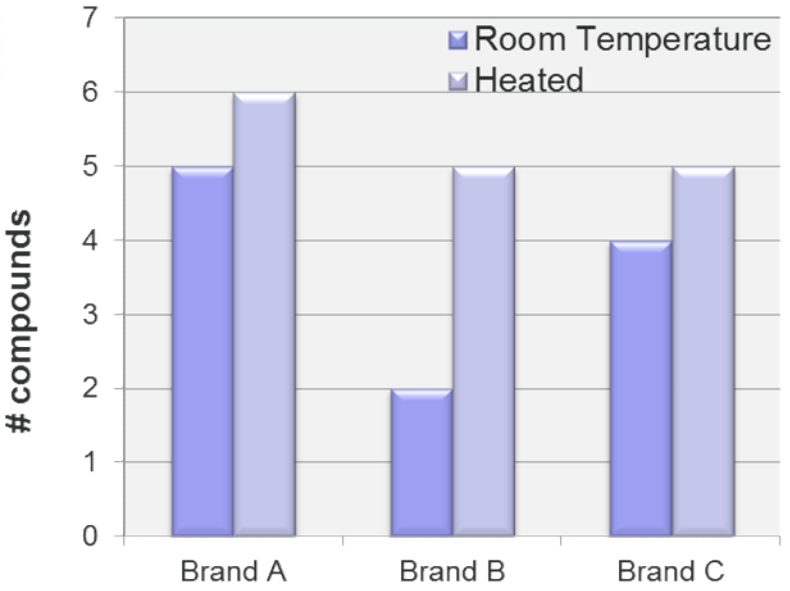
- Heated samples no significant increase (< 2 ppb increase)
- Number of phthalates increased (largest from 2 to 5) between heated and RT samples





Results: Bottled Water Comparison

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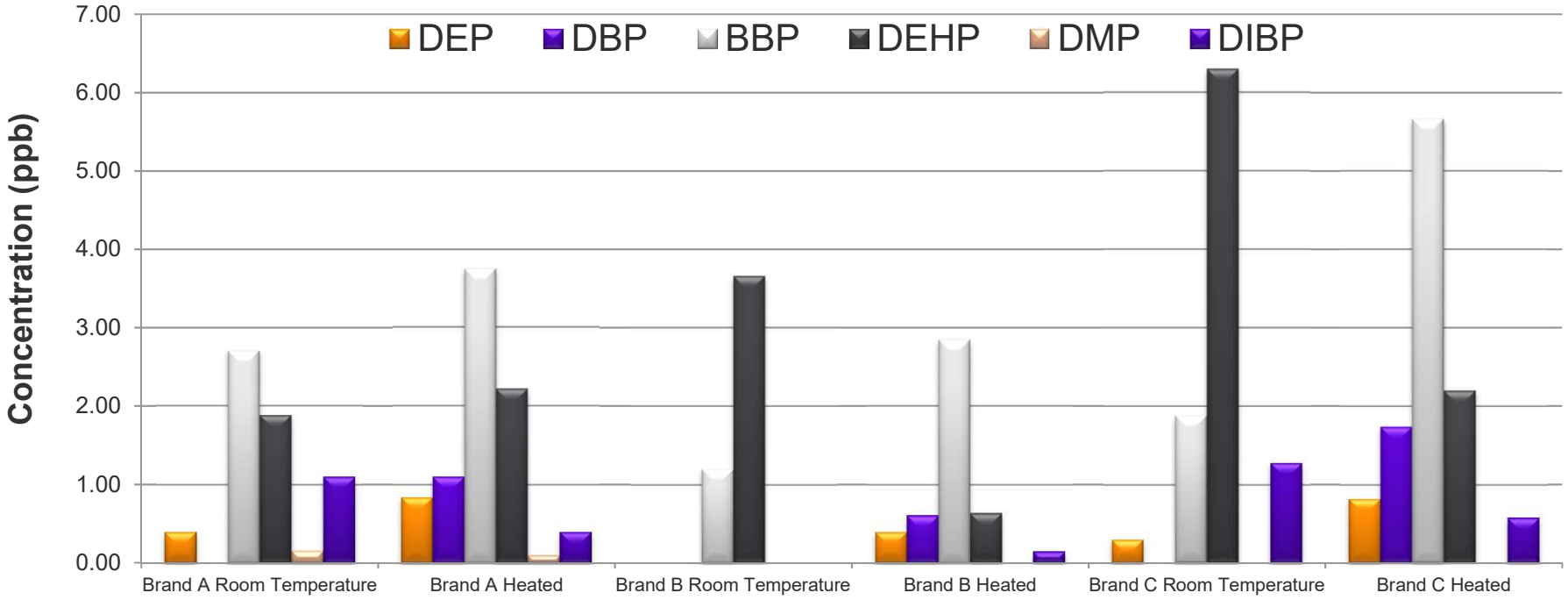
Compounds Found in Bottled Water Samples



- Earlier studies found DEHP in water decreased in samples above 20°C – possible breakdown of DEHP

Results: Consumer Water Comparison

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Municipal Water

Lowest Phthalates:
Municipal Tap & POU After Flushing

Highest Phthalates:
Static POU-B
(also only BPA; <1 ppb)

Bottled Water

Slightly higher phthalate concentration than tap

No BPA

All Water <10 ppb

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Reusable Drinking Bottles

Results: Sports Bottles (PC)

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	Sports Bottle			BPA Free Sports Bottle			
	Unrinsed RT	Rinsed RT	Rinsed Heated	Unrinsed RT	Rinsed RT	Rinsed Heated	Old Bottle Rinsed Heated
Dimethyl phthalate	10.74	0.00	0.00	0.00	0.00	0.00	0.00
Diethyl phthalate	0.25	0.00	0.00	0.00	0.13	0.00	0.00
Diisobutyl phthalate	0.08	0.00	0.00	4.62	0.13	7.89	2.04
Di-n-butyl phthalate	**0.35**	**0.07**	**0.12**	**0.00**	**0.17**	**0.00**	**0.00**
Bisphenol A	**0.17**	**0.00**	**0.12**	**0.00**	**0.00**	**0.00**	**0.00**
Butyl benzyl phthalate	**0.13**	**0.33**	**0.00**	**0.72**	**0.00**	**1.06**	**0.98**
Bis(2-ethylhexyl) phthalate	**0.34**	**0.00**	**0.00**	**4.00**	**0.00**	**4.16**	**3.53**
Total Phthalates	**12.06**	**0.40**	**0.25**	**9.34**	**0.43**	**13.11**	**6.55**
# of Phthalates	**7**	**2**	**2**	**3**	**3**	**3**	**3**

- BPA was found in PC Sports Bottle
  - *BPA found in Heated PC Bottle*
  - *No BPA in BPA-Free Bottle*
- Unrinsed bottles had larger amounts of phthalates
- All rinsed or heated bottles <15 ppb

Results: Sports Bottles

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	Squeeze Reusable Bottle			Plastic Jug Type Bottle		
	Unrinsed RT	Rinsed RT	Rinsed Heated	Unrinsed RT	Rinsed RT	Rinsed Heated
Dimethyl phthalate	0.00	0.00	0.00	0.00	0.00	0.00
Diethyl phthalate	0.00	0.33	0.37	0.10	0.11	0.28
Diisobutyl phthalate	0.00	32.14	0.03	0.09	15.90	0.09
Di-n-butyl phthalate	**0.05**	**4.15**	**0.00**	**0.26**	**2.38**	**0.43**
Bisphenol A	**0.00**	**0.00**	**0.00**	**0.18**	**0.00**	**0.11**
Di-n-hexyl phthalate	0.00	0.00	0.00	0.00	0.00	0.00
Butyl benzyl phthalate	**0.01**	**1.41**	**0.00**	**0.00**	**0.95**	**0.22**
Hexyl 2-ethylhexyl phthalate	0.00	0.00	0.00	0.00	0.00	0.00
Bis(2-ethylhexyl) phthalate	**0.00**	**3.98**	**0.04**	**0.00**	**1.97**	**0.32**
Total Phthalates	**0.06**	**42.00**	**0.44**	**0.63**	**21.30**	**1.44**
# of Phthalates	**2**	**5**	**3**	**4**	**5**	**6**

- BPA was found in Jug type Bottle & FEP
- BPA found in Heated Bottles not RT
- No BPA in Squeeze Bottle
- Less phthalates came from rinse than Sports bottles
- More phthalates in RT bottles than in Sports bottles
- Major phthalates at RT from DIBP

Conclusions: Sports Bottles

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BPA

- Found PC Bottle & Plastic Jug (unrinsed & heated)
- No BPA in BPA-Free Bottle
- BPA <1 ppb PC & Plastic Jug

Phthalates

- PC Bottles = highest unrinsed & heated
- Soft plastics = Highest rinsed RT
- Highest >40 ppb Squeeze bottle

Conclusions: Sports Bottles

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	BPA	Phthalates
Municipal	None	3 ppb
POU	BPA <1 ppb	Static System with Filters: >40 ppb Rest: <3 ppb
Bottled Water	None	2 – 11 ppb; heating little effect
Reusable Bottles	BPA <1 ppb PC & Plastic Jug	Highest >40 ppb (Squeeze bottle) Washing increases phthalates

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Thank You for Your Time