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Phthalates & BPA in Consumer Water Sources

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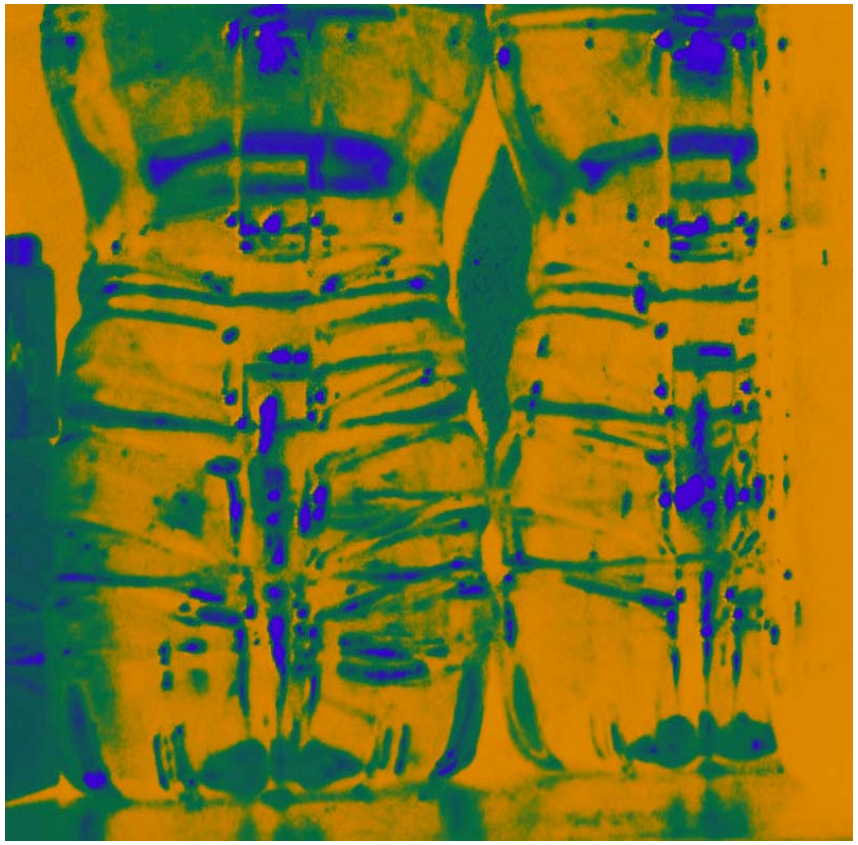

Purpose

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- This study was conducted to determine if consumer water sources and laboratory water sources contained phthalates and/ or bisphenol A.
- Consumer Water Sources studied included:
  - Commercial Bottled Water
  - Municipal Tap Water
  - Filtered and Purified Municipal Water using a Point-of-Use (POU) system
- Laboratory Water Sources Studied included:
  - Bottled HPLC grade Water
  - Bottled HPLC-MS grade Water
  - DI Water from a HDPE carboy
  - DI Water from a DI Water source tap

Background – Bisphenol A & Phthalates

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- Over the past decade, concerns have grown regarding human exposure to phthalates and bisphenol A.
- Focus on these chemicals has called into question what we consume and how we consume it!
- Environmental and Health watchdog groups assert that our food and beverages are being contaminated by phthalates and bisphenol A leaching from plastic packaging.
- New products have been developed in response to these claims which purport to be phthalate and/or bisphenol A free.
- Our study attempted to determine:
  - *1. If consumer water sources contained these target compounds*
  - *2. If the exposure of these consumer water packaging to heat caused increased leaching of these target compounds.*

Background – Bisphenol A

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- Bisphenol A is a building block of several essential polymers and polymer additives.
- BPA is found in various applications including toys, bottles, medical and dental devices, coatings, and epoxy resins.
- 3.7 million metric tons of BPA are produced a year.
- Since the 1930's concerns have grown regarding the safety of bisphenol A and its potential health effects which include reproductive and genetic effects.
- The EPA has set a guideline of 50 ug/kg/day human exposure limit. Some studies indicate levels as low as 0.025 ug/kg/day can have permanent adverse health effects.

Background – Phthalates

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- Phthalates are a group of esters of 1,2-benzenedicarboxylic acid, primarily used in the production of plastic compounds and plastic containing products.
- They are found as binders and coatings for fragrances and pigments.
- Phthalates have been in production since the late 1800's.
- Residue of phthalates is widespread and has been found in human tissues and house dust.
- Studies have linked phthalates to childhood asthma, reproductive disorders, diabetes, obesity and genetic effects.
- Concerns about phthalates has prompted the US to ban certain phthalates from children's toys starting in 2009.
- Many other countries such as Mexico, the EU, and Japan have either restricted or banned the use of certain phthalates in children's toys.

Background – Bottled Water Industry

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- The bottled water industry is predicted to produce over $168 billion a year in sales worldwide by 2012.
- The US consumes over 8.8 billion gallons of bottled water a year.
- Bottled water has become the second largest consumed beverage in the country behind carbonated beverages.
- Americans say they drink bottled water in an effort to substitute water for other beverages and that they were concerned over the safety of their tap water.

Background – Bottled Water Quality

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- In the US municipal water sources are governed by the EPA and bottle water quality is governed by the FDA.
- The EPA has strict guidelines on many potential contaminants in municipal water including bisphenol A and a variety of phthalates
- The FDA does not have any guidelines on the concentration of bisphenol A or phthalates allowable in bottled water.
- Many people in many countries believe that bottled water is a safer alternative to municipal water sources.

Background – Concerns & Points of Debate

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- There are potentially many sources of organic pollutants in consumer water supplies.
- Questions have been raised if the additional process of bottling water increases the water's exposure to phthalates and/or BPA.
- Watchdog and consumer groups now warn of potential leaching of chemicals into bottled water.
- These action groups suggest that consumers not reuse disposable plastic water bottles and not to expose bottled water to high temperatures (such as leaving bottles in hot vehicles during the summer).
- Our study attempted to determine if there were phthalates or BPA in various consumer water sources including commercial bottled water.
- We also attempted to determine if the exposure of commercial water bottles would increase the amount of phthalates found in the bottled water.

Method & Materials – Reagent Contamination

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- Phthalates are ubiquitous in the laboratory environment.
- It is difficult if not impossible to eliminate phthalate contamination from samples.
- Many reagents (especially solid compounds) are packaged in plastic or coated containers which potentially may contain phthalate compounds.
- The reagents had to be tested before use to determine their phthalate levels.
- Whenever possible, reagents were rinse or baked to eliminate as much contamination possible.

Methods & Materials – Reagent Contamination

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- In this experiment three solid compounds were used: NaOH, NaCl and Na_2SO_4
- Solids were rinsed with two 60 mL aliquots of methylene chloride. Each aliquot was evaporated to 1mL and run by GCMS. The solids were then allowed to bake in a 210°C oven for 10 to 30 minutes. Two additional 60 mL aliquots of $MeCl_2$ were rinsed through the solids and evaporated to 1 mL prior to GCMS analysis.
- The 'pre-cleaned' and 'cleaned' solids were examined to determine the effectiveness of cleaning.

Methods & Materials – Reagent Contamination

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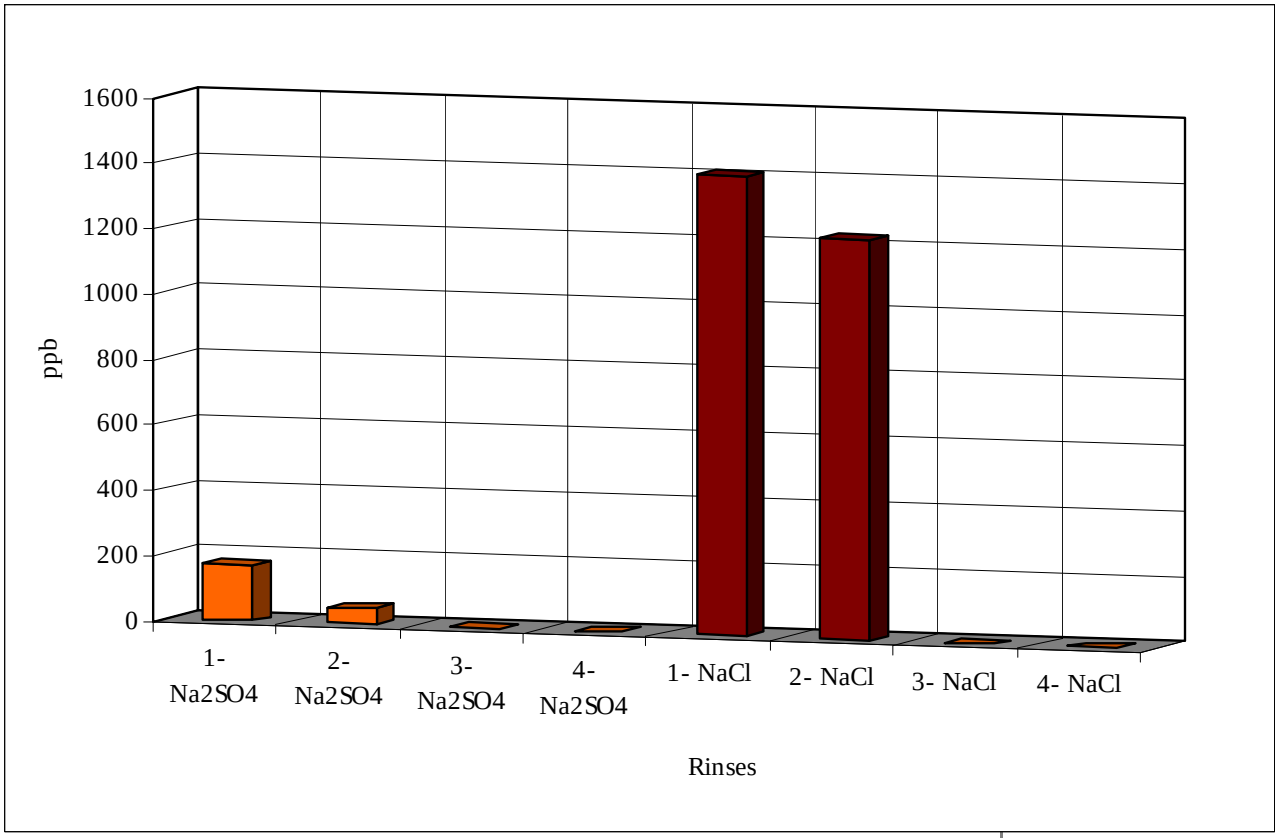
- Significant reduction of total phthalate levels were found in 'post-cleaned' NaCl and Na_2SO_4 reagents.
- The NaOH reagent did not contain any significant amount of phthalates.



Methods & Materials – Sample Collection

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- 500 mL samples of each laboratory and consumer water source.
- One set of commercial bottled water bottles were placed in an oven at 60°C for one week to simulate exposure to summer temperatures inside a vehicle.
- Water taken from a DI water system and Point-of-Use (POU) water filtration and sanitization systems were taken from a stationary system where the water had remained static for over 12 hours and from a flushed system where at least 2 L of water had been flushed through the system prior to obtaining the sample.
  - *POU-A was a Point-of-Use water dispensing system without a visible filter and no sanitization system*
  - *POU-B was a UV sanitization and carbon fiber filtration system.*

Methods & Materials – Extraction

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- Liquid – Liquid extraction
- 15 gm of 'cleaned' NaCl added to 500 mL of sample
- Acid extraction: 3-10 drops of ACS grade HCl until pH was below 3.
- Base extraction: 1 mL – 5 mL of 50% NaOH added until pH was above 9.
- 30 mL of Methylene chloride added at a time to a total of 60 mL for each extraction.
- Extracts were dehydrated using 'cleaned' Na_2SO_4.
- The acid and base extracts were combined and dried to 1 mL final volume.

Methods & Materials – Instrument Conditions

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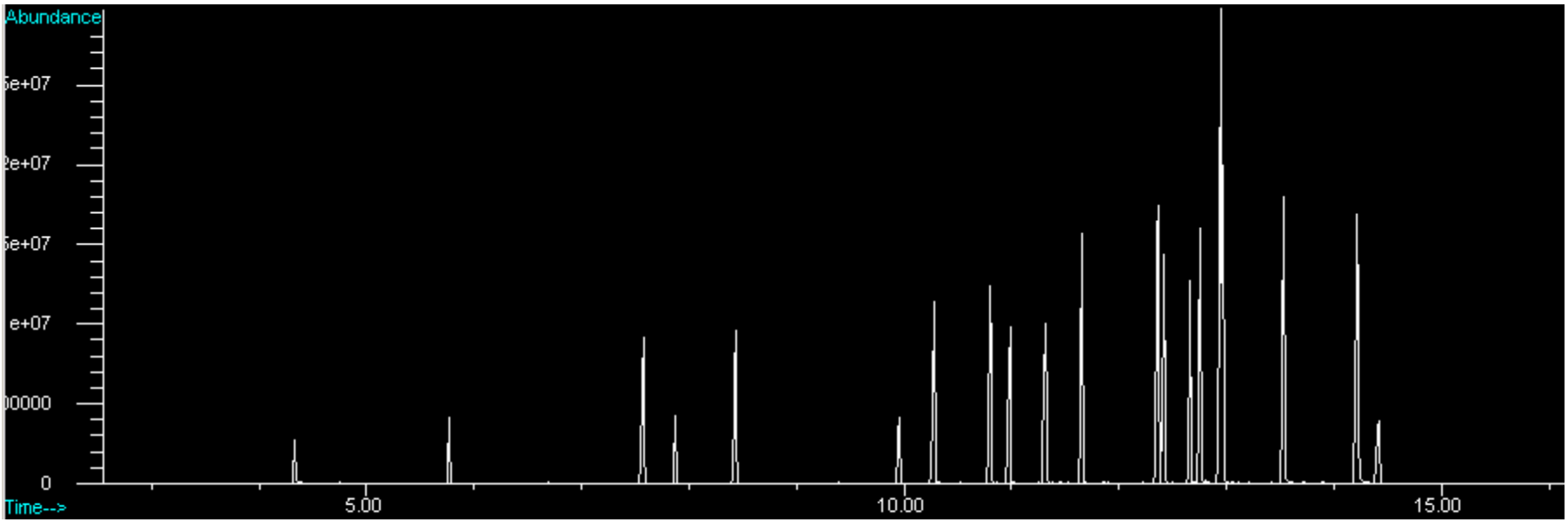
- GC-MS in scan mode, scan range 35-450 m/z
- Sample injection volume 1 uL
- CV-5 capillary column (3.0 m x 0.25 mm x 0.25 um)



Results – Target Compounds

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Name	Abbreviation	RT	Ions	Structural formula	CAS No.
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	Bisoflex DNP	14.22	149, 293, 71, 57, 43	C26H42O4	84-76-4

Results – Laboratory Water Samples

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- Highest concentration and total number of phthalate and BPA contaminates found in HPLC grade water tested. (91 ppb)
- Lowest concentration of phthalate and BPA contamination found in LCMS grade water tested. (1 ppb)
- Lowest total number of different phthalate and BPA contaminates found in municipal tap water. (2 identified phthalates)
- The phthalates with the highest concentration in the laboratory water sources were DEHP and BBP.
- The HPLC grade water was the only laboratory water source with detectable amounts of BPA. (3 ppb)

Results – Laboratory Water Samples

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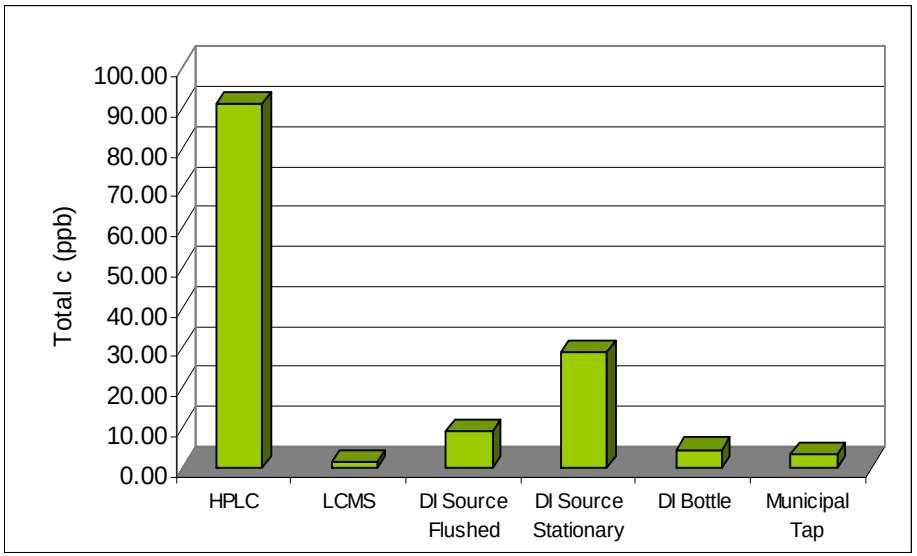
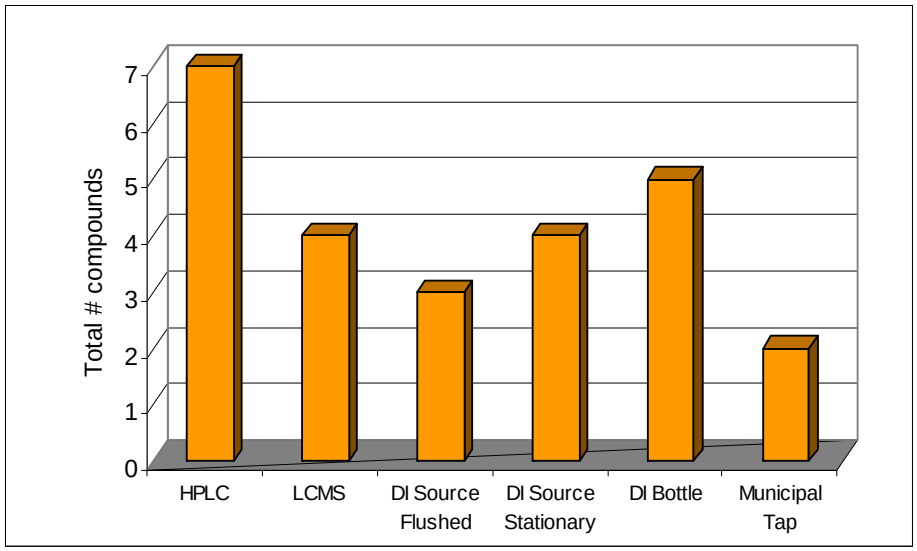
	HPLC	LCMS	DI Source Flushed	DI Source Stationary	DI Bottle	Municipal Tap
DEP	6.28	0.18	0.00	0.30	0.50	0.00
DIBP	3.52	0.16	0.88	1.36	0.52	0.00
DBP	16.72	0.00	0.00	0.00	0.54	0.00
BPA	3.16	0.00	0.00	0.00	0.00	0.00
BBP	44.74	0.20	2.32	0.63	0.47	1.29
DCP	1.00	0.00	0.00	0.00	0.00	0.00
DEHP	15.60	0.63	5.92	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**





Results – Room Temperature Samples

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- All the brands of bottled water had less than 10 ppb of total phthalates.
- Municipal Tap Water had less than 4 ppb to total phthalates.
- None of the municipal tap water or bottled water brands contained measurable BPA.
- The greatest variability between samples was seen in the POU systems.
- Stationary or unused systems had higher levels of phthalates than flushed systems.
- Samples from the POU system which had sanitization and filtration components were the only consumer samples to contain BPA.

Results – Room Temperature Samples

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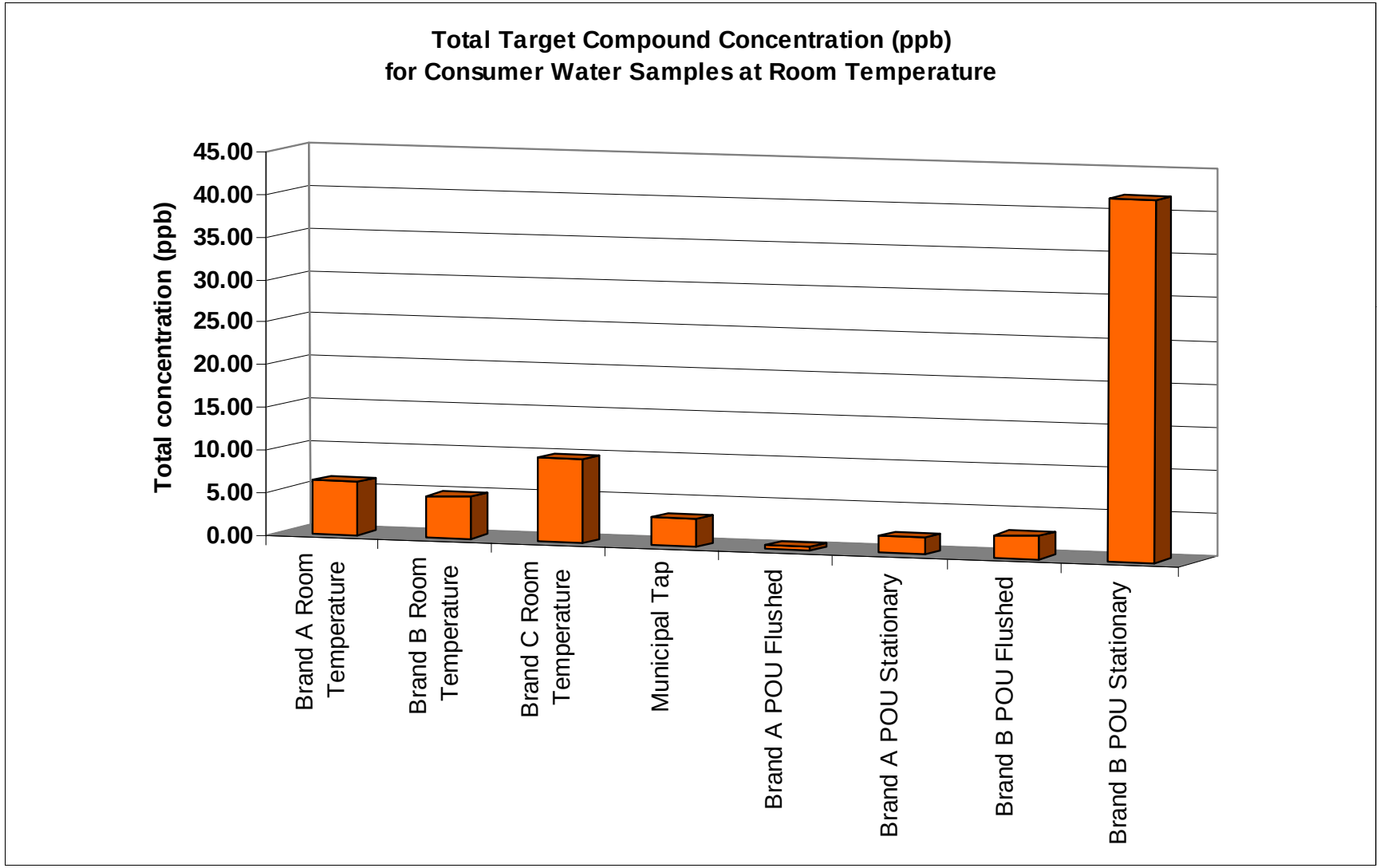

Results – Room Temperature Samples

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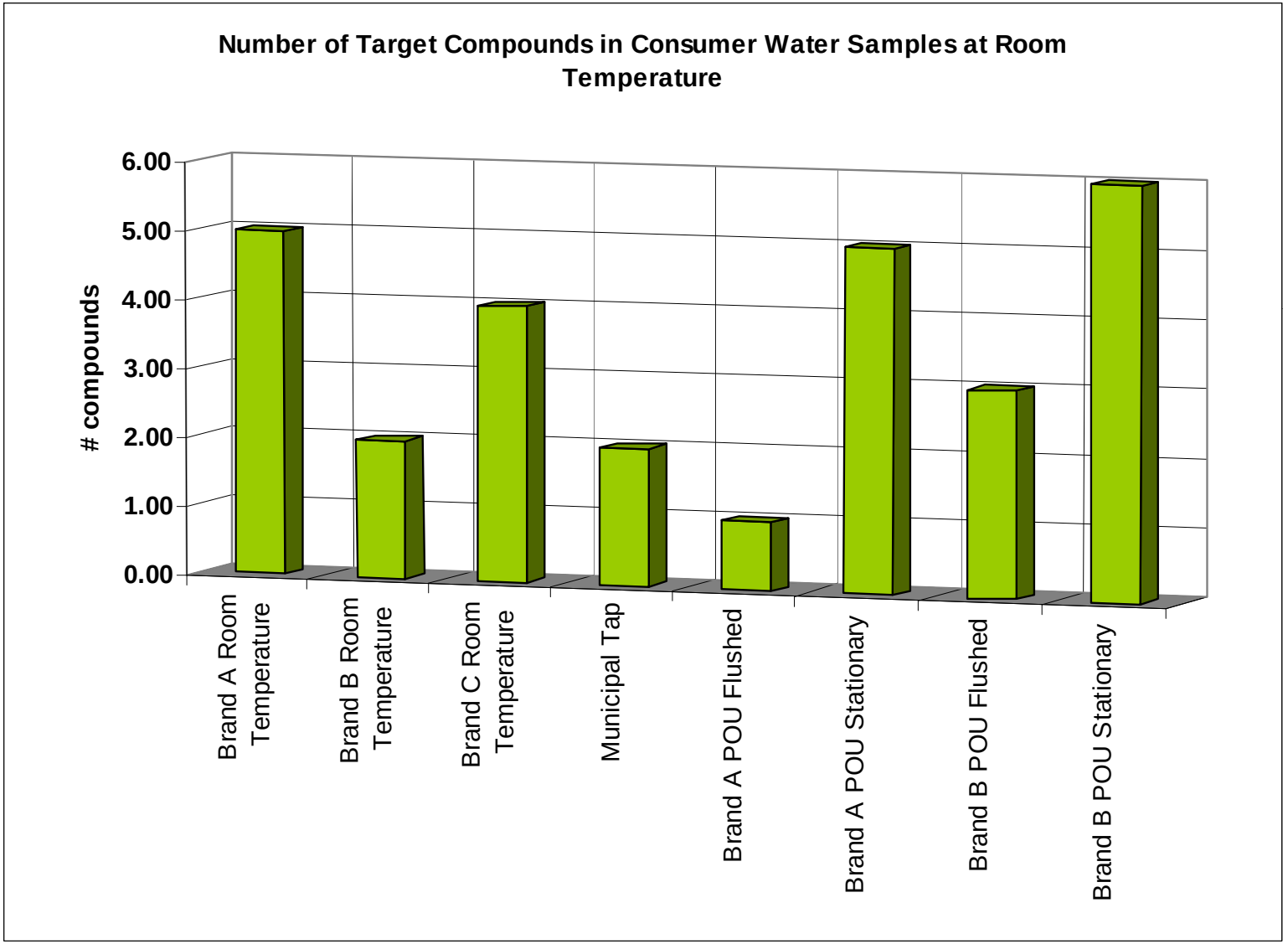

Results – Exposure to Heat

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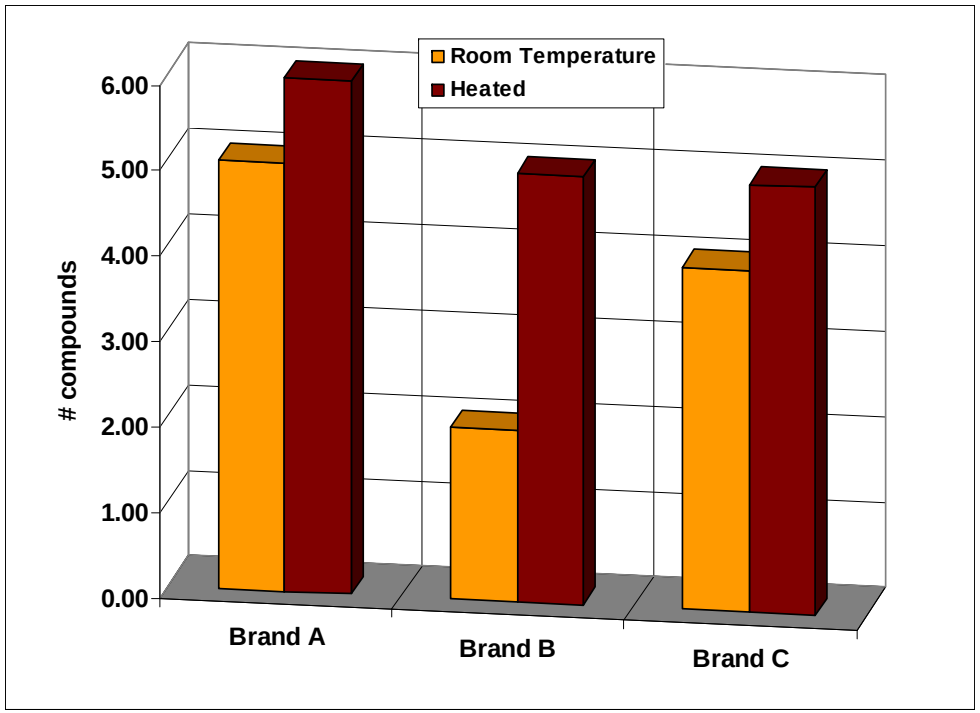
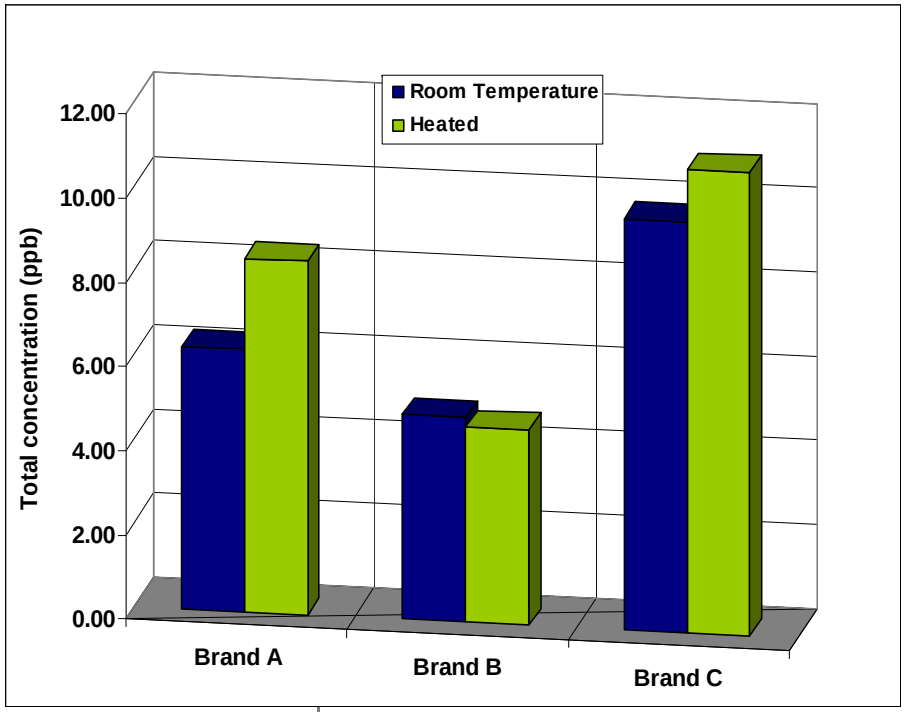
- Bottled water samples which were exposed to heat for a week did not have significant increases in total phthalate concentrations (< 2ppb increase)
- There were some increases in the number of identified phthalates (largest increase was from 2 to 5 identified phthalates) between heated and room temperature samples.





Results – Bottled Water Comparison

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- The largest differences between heated and room temperature samples was seen in the concentrations of individual phthalates, especially DEHP and BBP.
- BBP and DEHP decreased after heating in two out of three brands.
- A prior study of DEHP in water found that DEHP levels decreased in samples held above 20°C suggesting DEHP may degrade at higher temperatures.

Results – Bottled Water Comparison

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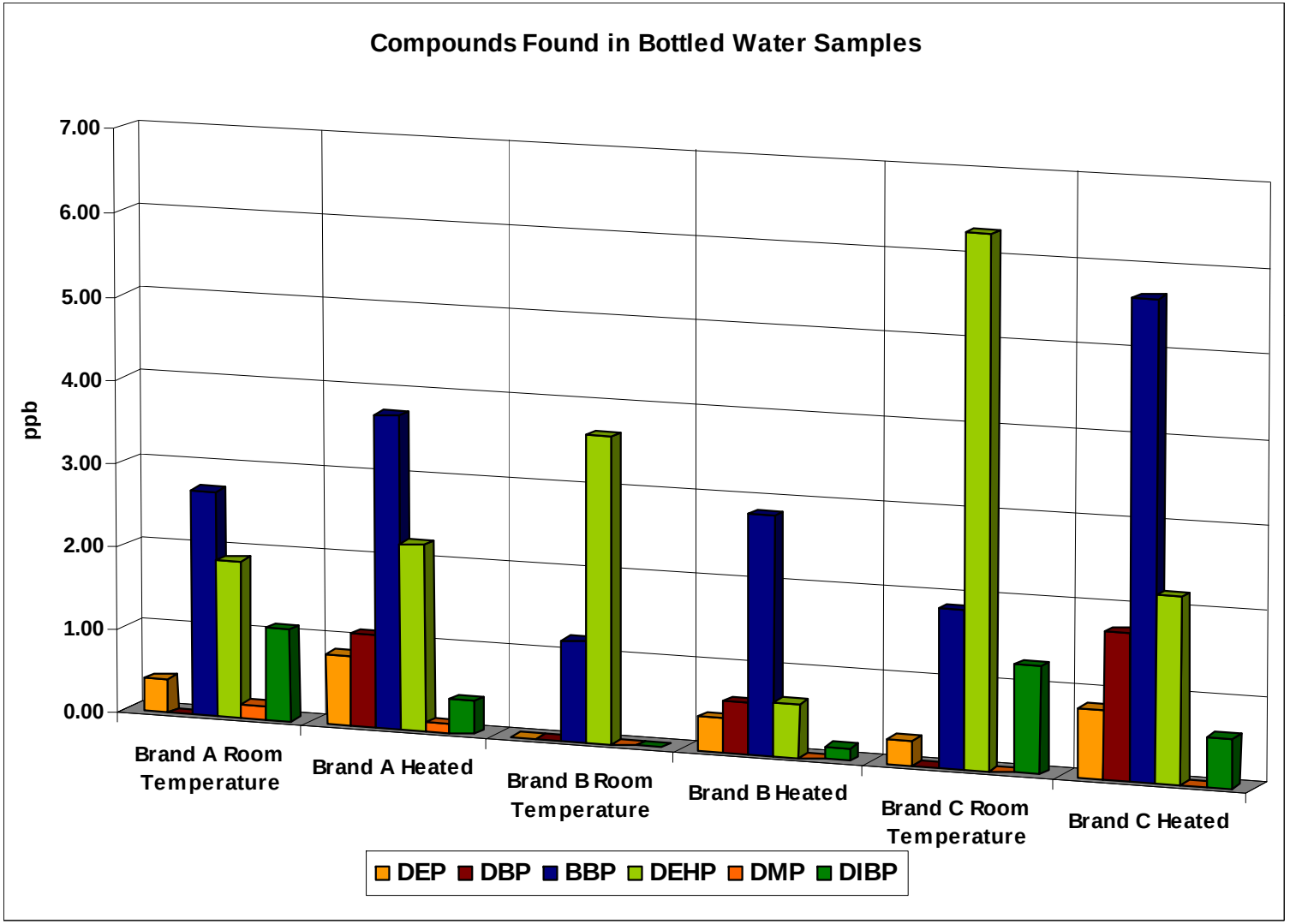

Results – Bottled Water Comparison

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	DMP	DEP	DIBP	DBP	BPA	BBP	DEHP	Bisoflex DNP	Total (ppb)	Total # Compounds
Brand A Room Temperature	0.16	0.40	1.10	0.00	0.00	2.70	1.88	0.00	**6.24**	**5**
Brand A Heated	0.10	0.84	0.40	1.10	0.00	3.74	2.22	0.00	**8.40**	**6**
Brand B Room Temperature	0.00	0.00	0.00	0.00	0.00	1.20	3.66	0.00	**4.86**	**2**
Brand B Heated	0.00	0.40	0.15	0.61	0.00	2.84	0.64	0.00	**4.64**	**5**
Brand C Room Temperature	0.00	0.30	1.28	0.00	0.00	1.88	6.30	0.00	**9.76**	**4**
Brand C Heated	0.00	0.82	0.58	1.74	0.00	5.66	2.20	0.00	**11.00**	**5**
Municipal Tap	0.00	0.00	0.00	0.00	0.00	1.29	1.94	0.00	**3.23**	**2**
Brand A POU Flushed	0.00	0.00	0.00	0.00	0.00	0.00	0.42	0.00	**0.42**	**1**
Brand A POU Stationary	0.00	0.18	0.18	0.25	0.00	0.60	0.74	0.00	**1.95**	**5**
Brand B POU Flushed	0.00	0.00	0.00	0.00	0.09	0.14	2.38	0.00	**2.61**	**3**
Brand B POU Stationary	0.00	0.27	0.00	0.33	0.04	0.04	4.41	36.95	**42.04**	**6**

Results – Comparison Consumer Water

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- The lowest total concentrations of target compounds were found in the municipal tap source and the POU sources obtained after flushing the system.
- All sources (with the exception of the POU-B stationary sample) had less than 10 ppb total concentration of target compounds.
- The highest total concentration of target compounds were found in the POU-B samples taken after the system had been unused for several hours (stationary samples).
- Bottled water samples had slightly higher concentrations of target compounds compared to municipal tap sources.
- None of the bottled water samples or the municipal tap water sample contained BPA. The POU-B system had a small amount of BPA observed in both the flushed and stationary samples (0.04 to 0.09 ppb)

Results – Comparison Consumer Water

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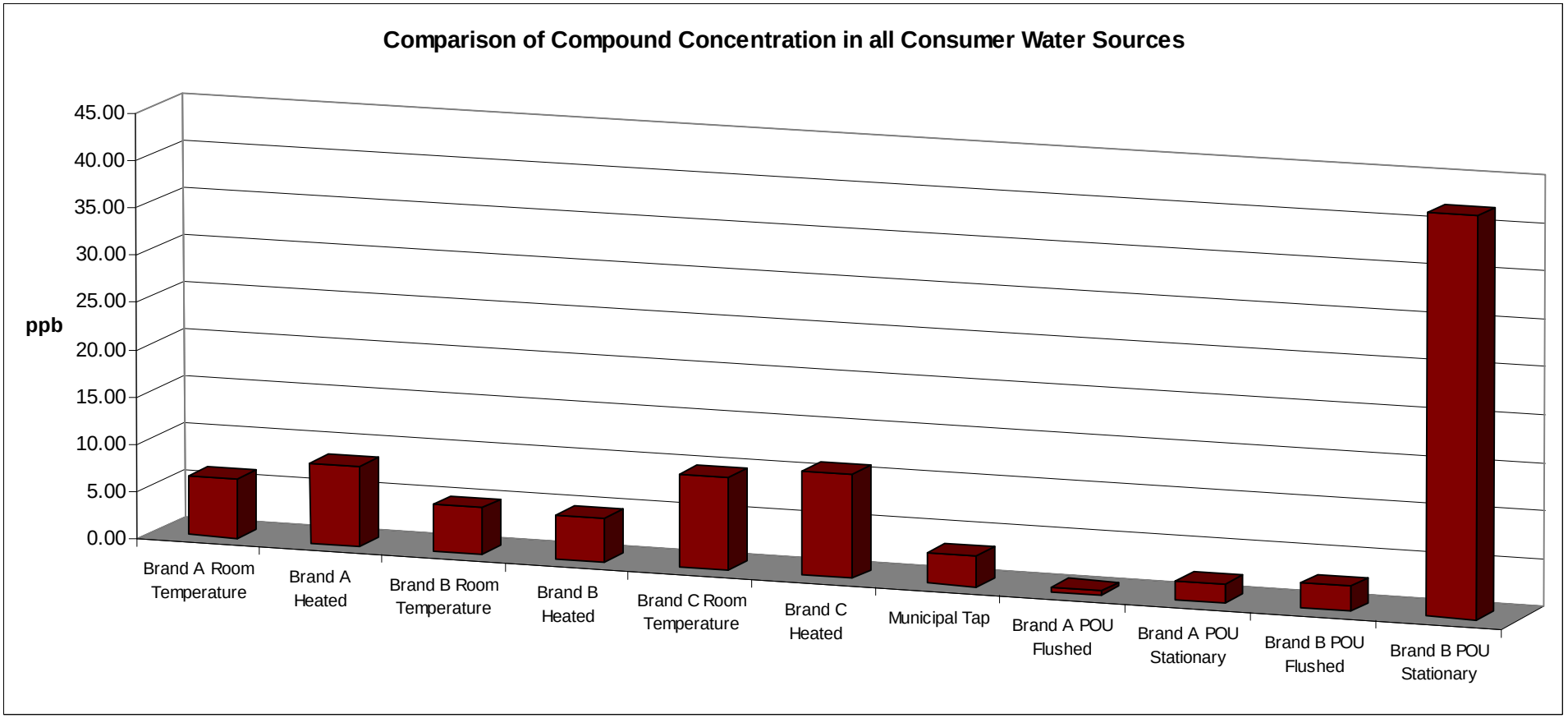

Conclusions – Laboratory Reagents & Water

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- Most of the solid reagent material used in the extraction of samples had significant phthalate contamination and had to be cleaned before use.
- Methylene chloride rinses and baking of material greatly reduced the amount of phthalate residue.
- There was large variability in the phthalate levels between the different laboratory water sources.
- All laboratory sources had contamination ranging from 1 to 91 ppb of phthalates and BPA.
- The lowest level of phthalates for laboratory sources was the LCMS grade water.

Conclusions – Bottled Water

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- All the different brands of bottled water had less than 10 ppb of total phthalates.
- There were no significant differences observed in the levels of phthalates between the different brands of water.
- Heated bottled water samples had insignificant increases in phthalate levels and the number of different phthalates observed in comparison with room temperature samples.
- Two of the three brands of heated bottled water samples had a reduction the concentration of DEHP and BBP when compared with their room temperature counterparts.

Conclusions – Consumer Water Sources

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- The municipal tap water and water from the POU-A filtration system (flushed samples) had the lowest levels of BPA and phthalates.
- The highest level of phthalates were observed in the stationary POU-B system. The levels were significantly lower in that POU system after the system had been flushed with up to 2 L of water.
- All the stationary water samples (POU and laboratory DI water) had higher target compound concentrations compared to flushed water samples, showing that water should be allowed to rinse through a system before use.

Disclaimer

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This study was not intended to determine the safety or purity of any water source. Only the compounds listed in this study were examined and quantified. It is possible that there are other compounds contained in these water sources that were not covered by this study. The types and sources of water studied were just representative samples of different types of water and not all-encompassing in water types or brands. This study was not intended to advise or warn against any particular brand or water purification method.

References

- All references available by request
  - *Call 1-800-LAB-SPEX*
  - *Or email crmsales@spexcsp.com*
- For more information, see our whitepaper

'The Analysis of Laboratory and Consumer Water Sources for the Presence of BPA and Phthalates'