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A Rapid and Robust Method for Determination of 35 Phthalates in Influent, Effluent and Biosolids from Wastewater Treatment Plants

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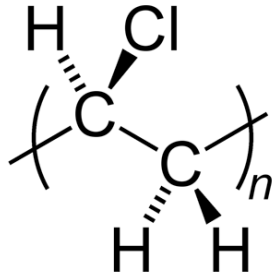
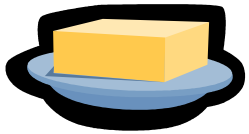
Polyvinyl Chloride (PVC)



- PVC was **accidentally synthesized** in 1835 by French chemist Henri Victor Regnault
- Ivan Ostromislensky and Fritz Klatte both attempted to use PVC in commercial products,
- But difficulties in processing the **rigid, sometimes brittle polymer** blocked their efforts.
- Waldo Semon and the B.F. Goodrich Company developed a method in 1926 to plasticize PVC by blending it with various additives.
- The result was a more flexible and more easily processed material that soon achieved widespread commercial use.

From Wikipedia; accessed Oct, 2014

Plasticizers



- Most vinyl products contain plasticizers which dramatically improve their performance characteristic. **The most common plasticizers are derivatives of phthalic acid.**
- The materials are selected on their compatibility with the polymer, low volatility levels, and cost.
- These materials are usually **oily colorless** substances that mix well with the PVC particles.
- 90% of the plasticizer market is dedicated to PVC
- worldwide annual production of phthalates in 2010 was estimated at 4.9 million tones*

From Wikipedia; accessed Oct, 2014; and Emanuel C (2011) Plasticizer market update. http://www.cpsc.gov/about/cpsia/chap/spi.pdf (accessed March, 2014).

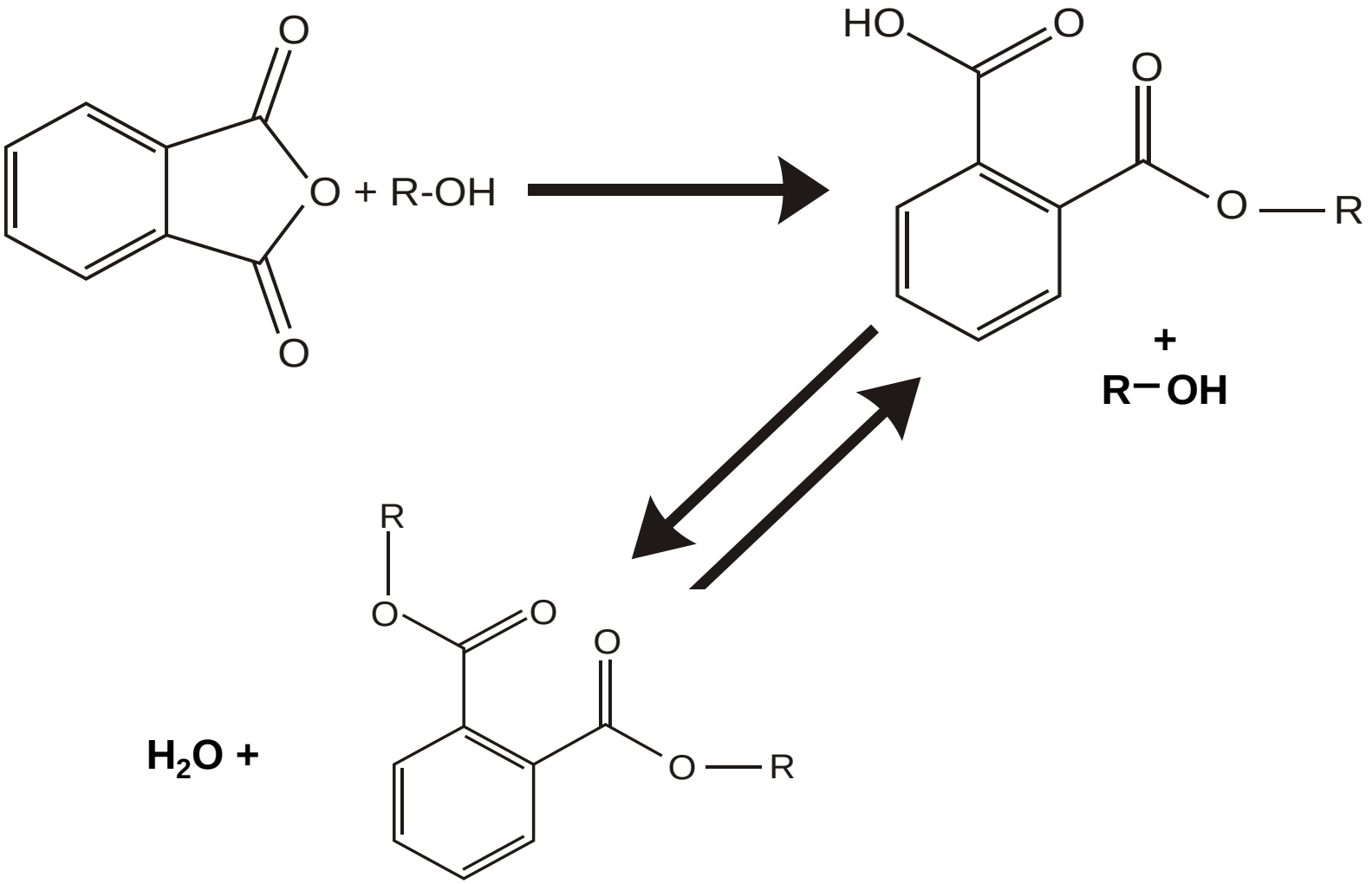
Phthalate Uses

- Plasticizers:
  - Wire and cable, building and construction, flooring, medical, automotive, household etc.,
- Solvents:
  - Cosmetics, creams, fragrances, candles, shampoos etc.

Why Study Phthalates?

- Since they are only mixed with polymeric materials they can be easily released into the environment.
- They have been detected in household dust, food, etc.
- Phthalate metabolites have been detected in human urine
- Phthalates have been shown to have EDR in laboratory animals

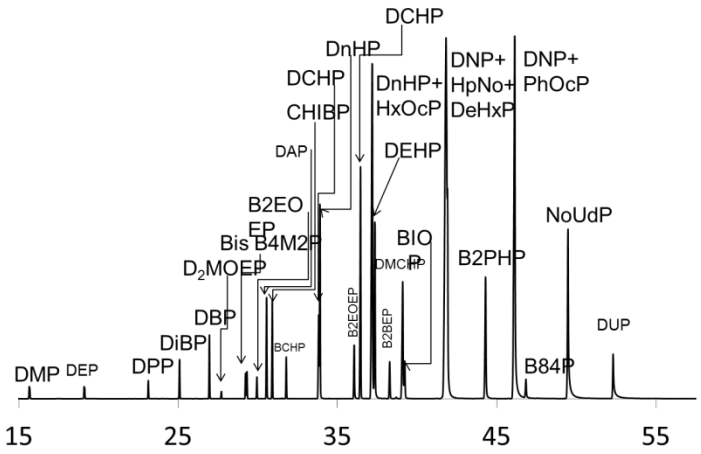
Synthesis of Phthalate Esters:

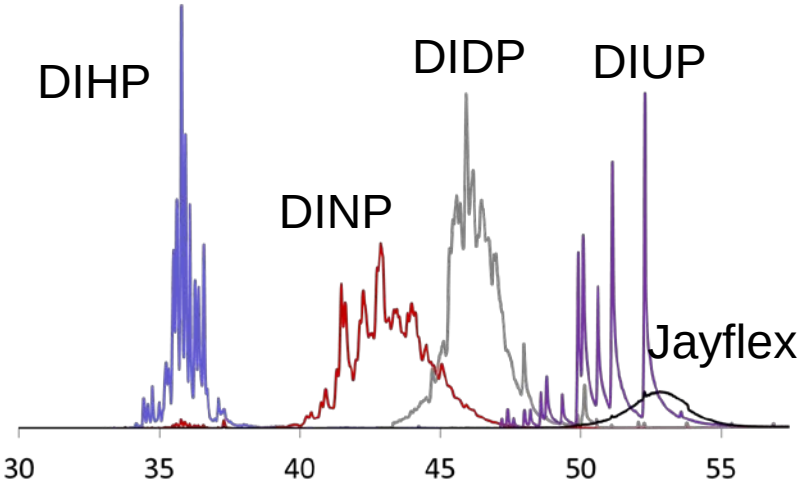


Abbreviation	CAS RN	Substance Name	Abbreviation	CAS RN	Substance Name
DMP	131-11-3	Dimethyl phthalate	DEHP	117-81-7	Diethylhexyl phthalate
DEP	84-66-2	Diethyl phthalate	NH	1929-81-9	Heptylnonyl phthalate
DAP	131-17-9	Diallyl phthalate	DH	25724-58-7	Decylhexyl phthalate
DPrP	131-16-8	Dipropyl phthalate	DOP	117-84-0	Dioctyl phthalate
DIPrP	605-45-8	Diisopropyl phthalate	DIOP	27554-26-3	Diisooctyl phthalate
DBP	84-74-2	Dibutyl phthalate	DecOP	119-07-3	Decyloctyl phthalate
DIBP	84-69-5	Diisobutyl phthalate	DNP	84-76-4	Dinonyl phthalate
BCHP	84-64-0	Butylcyclohexyl phthalate	DINP	28553-12-0/ 68515-48-0	Diisononyl phthalate
CHIBP	5334-09-8	Cyclohexyl 2-methylpropyl phthalate	B2HP	53306-54-0	Di-2-propylheptyl phthalate
DPP	131-18-0	Dipentyl phthalate (Diamyl phthalate)	DDeC	84-77-5	Didecyl phthalate
DIPP	605-50-5	Diisopentylphthalate	NonU	65185-89-9	Nonylundecyl phthalate
BBP	85-68-7	Benzylbutyl phthalate (Butylbenzyl phthalate)	DIDP	26761-40-0/ 68515-49-1	Diisodecyl phthalate
DCHP	84-61-7	Dicyclohexyl phthalate	B84P	16883-83-3	Benzyl 3-isobutyryloxy-1-isopropyl-2,2-dimethylpropyl phthalate
DHxP	84-75-3	Dihexyl phthalate	DUP	3648-20-2	Diundecyl phthalate
DIHxP	71850-09-4	Diisohexyl phthalate	DIUP	85507-79-5/96507-86-7	Diisoundecyl phthalate
DBzP	523-31-9	Dibenzyl phthalate	DDoP	2432-90-8	Didodecyl phthalate
HOP	61827-62-1	Hexyloctyl phthalate	BIOP	27215-22-1	Benzyloctyl phthalate
DHpP	3648-21-3	Diheptyl phthalate	B79P (S261)	68515-40-2	Benzyl octyl phthalate
DIHpP	71888-89-6	Diisoheptyl phthalate	DTDP (Jayflex)	68515-47-9 AKA: 27253-26-5, 119-06-2	Undecyl dodecyl phthalate
DMCHP	27987-25-3/18249-11-1	Dimethylcyclohexyl phthalate			

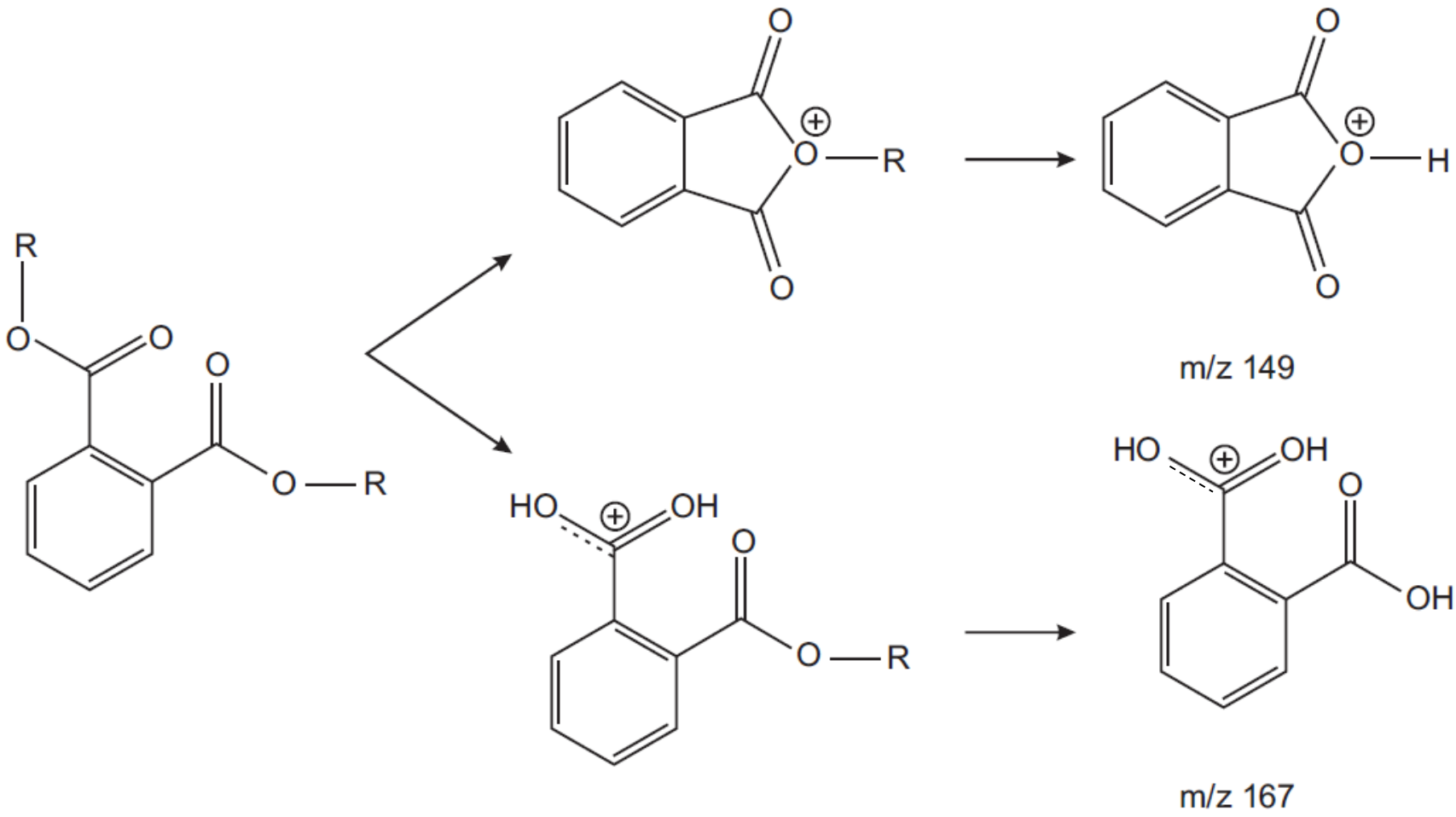
Summary of Phthalates:

- 39 different phthalates:
  - Single Compounds
  - Iso Phthalates
  - UVCB Phthalates

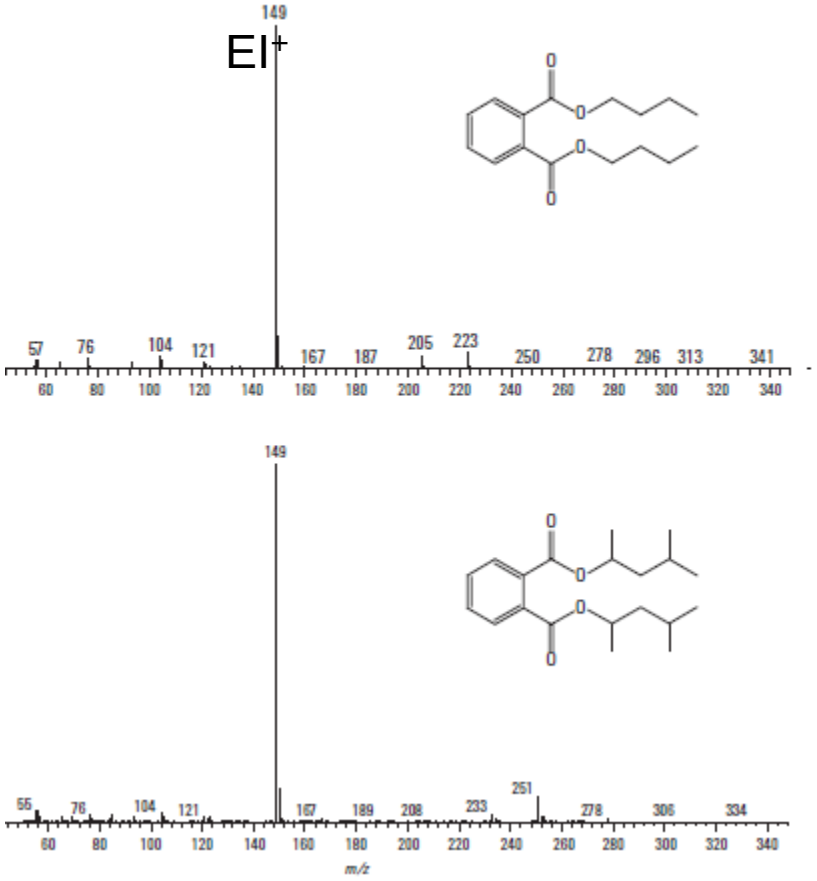




Analytical Challenge:



EI $^{+}$ Mass Spectra of Phthalates



From George and Prest, 2001

Challenges in Phthalate Analysis:

- Phthalates are ubiquitous and present everywhere including solvents, laboratory air and dust
- To prevent laboratory contamination:
  - High Purity solvents
  - Disposable glassware that is fired at 400^{o}C before use
  - Closed systems – sample is only really exposed for longer period of times during concentration
- Laboratory Reagent Blank (LRB) -- An aliquot of reagent water that is treated exactly as a sample including exposure to all glassware, equipment, solvents, reagents, internal standards, and surrogates that are used with other samples.
- To date we have **not found a satisfactory** source of water that can be used as a blank
- Using solvent blanks to assess any phthalate contributions form the extraction method

LC/MS/MS Conditions

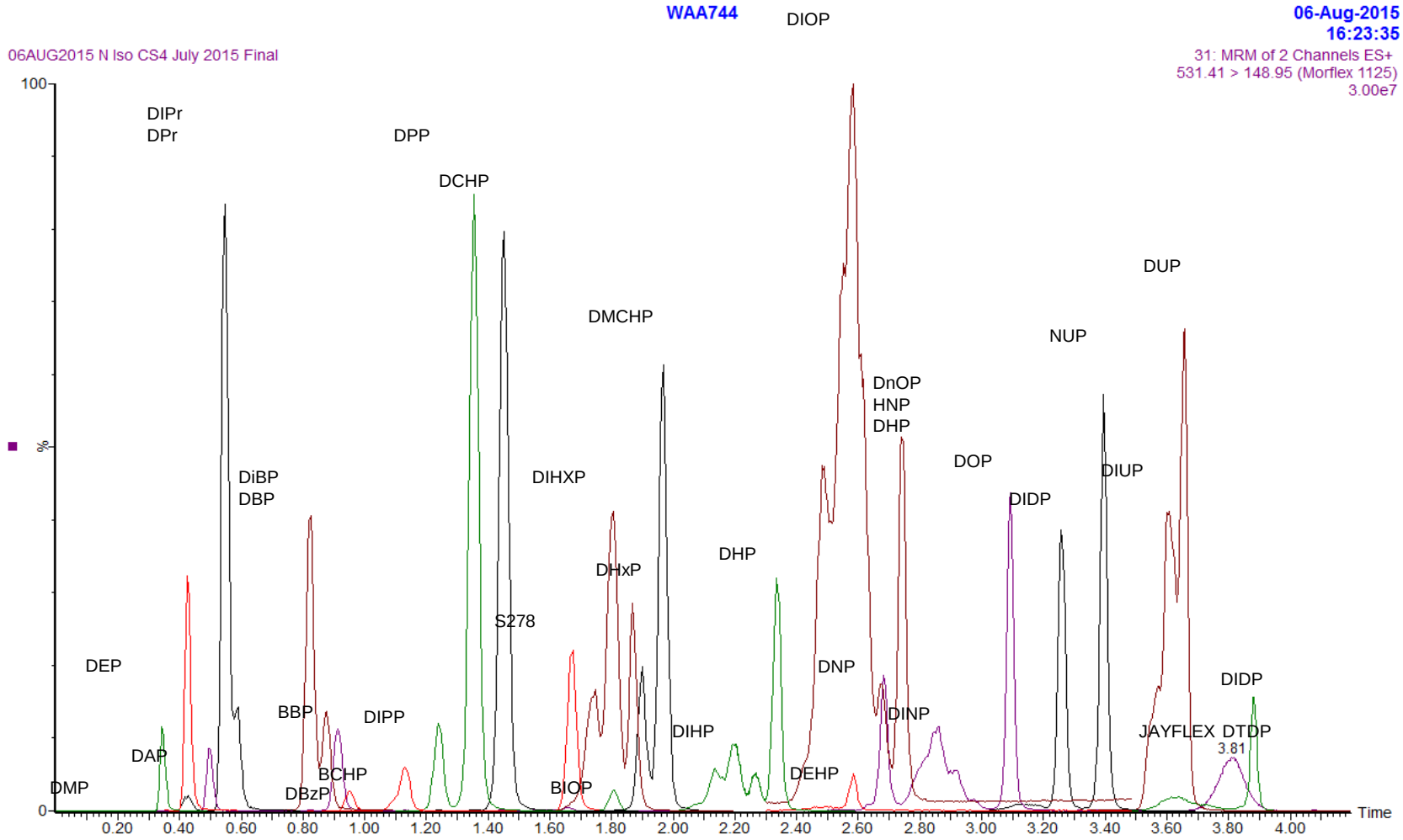
- Determination of phthalates were accomplished using a UHPLC coupled to a triple quadrupole mass spectrometer
- Analytical LC Column:
  - Phenyl Hexyl column HT 2.1x50mm 1.8µm
- In-line Mobile Phase Scrubber Column:
  - C_{18} 2.5µm, 2.1X50mm
- Triple quadrupole was operated in MRM and positive mode monitoring transition between (M+1)+ ions to m/z 149

LC/MS/MS Conditions

Time (min)	Flow (ml/min)	%A (0.1% Acetic acid)	%B (0.1% Acetic acid in Acetonitrile)
Initial	0.5	40	60
0.5	0.5	40	60
4.00	0.5	1	99
7.5	0.5	1	99
9.0	0.5	40	60
15.0	0.5	40	60

- ESI Parameters:
  - Desolvation temperature 600 ^{o}C
  - Desolvation 1000L/hr
  - Cone 150 L/Hr
  - Nebulizer 7 Bar
  - Source temp 150 ^{o}C

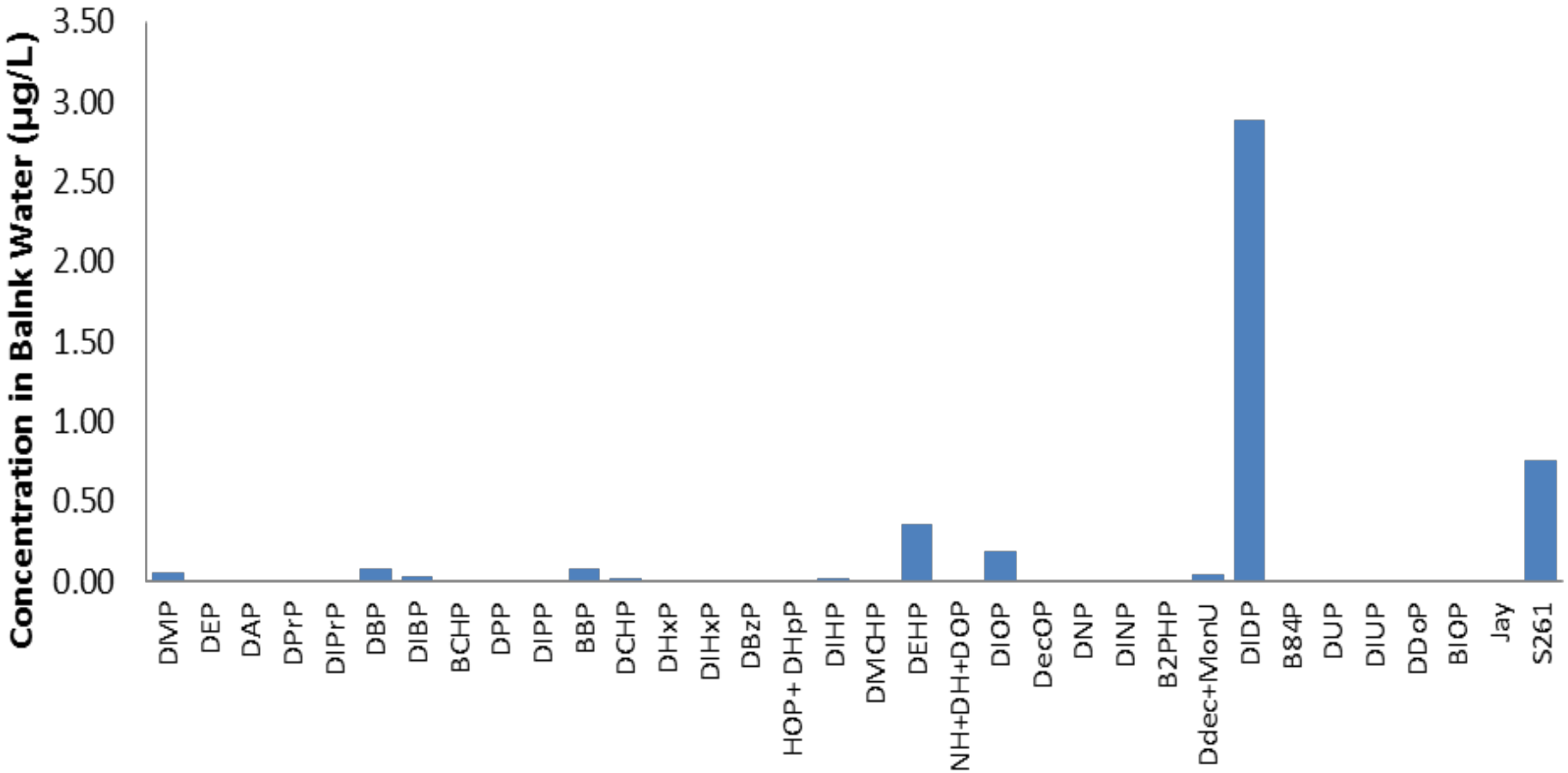
LC Separation of 39 Phthalate Compounds



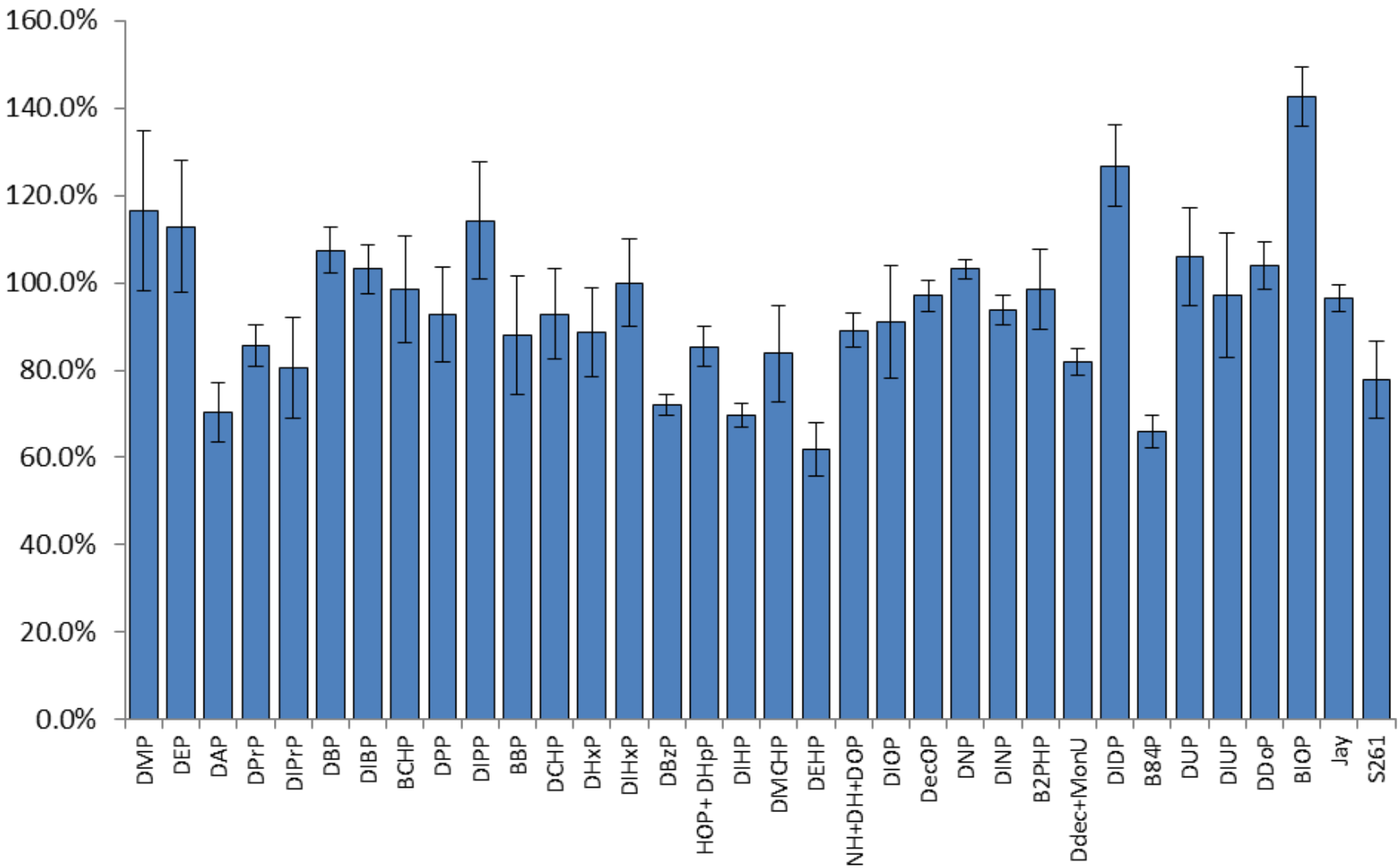
QuEChERS Extraction Method

- 10ml Sample or MQ Water added to 50mL glass centrifuge tube
- Spiked with 5 ng of Deuterated Phthalate Mix
- 10ml Acetonitrile added
- Shaken for 1 min by hand
- 3g of NaCl added
- Shaken for 1 min by hand
- 5000ul aliquot of MeCN blown down to 500ul
- Performance standard was added and the sample was analyzed by LCMSMS

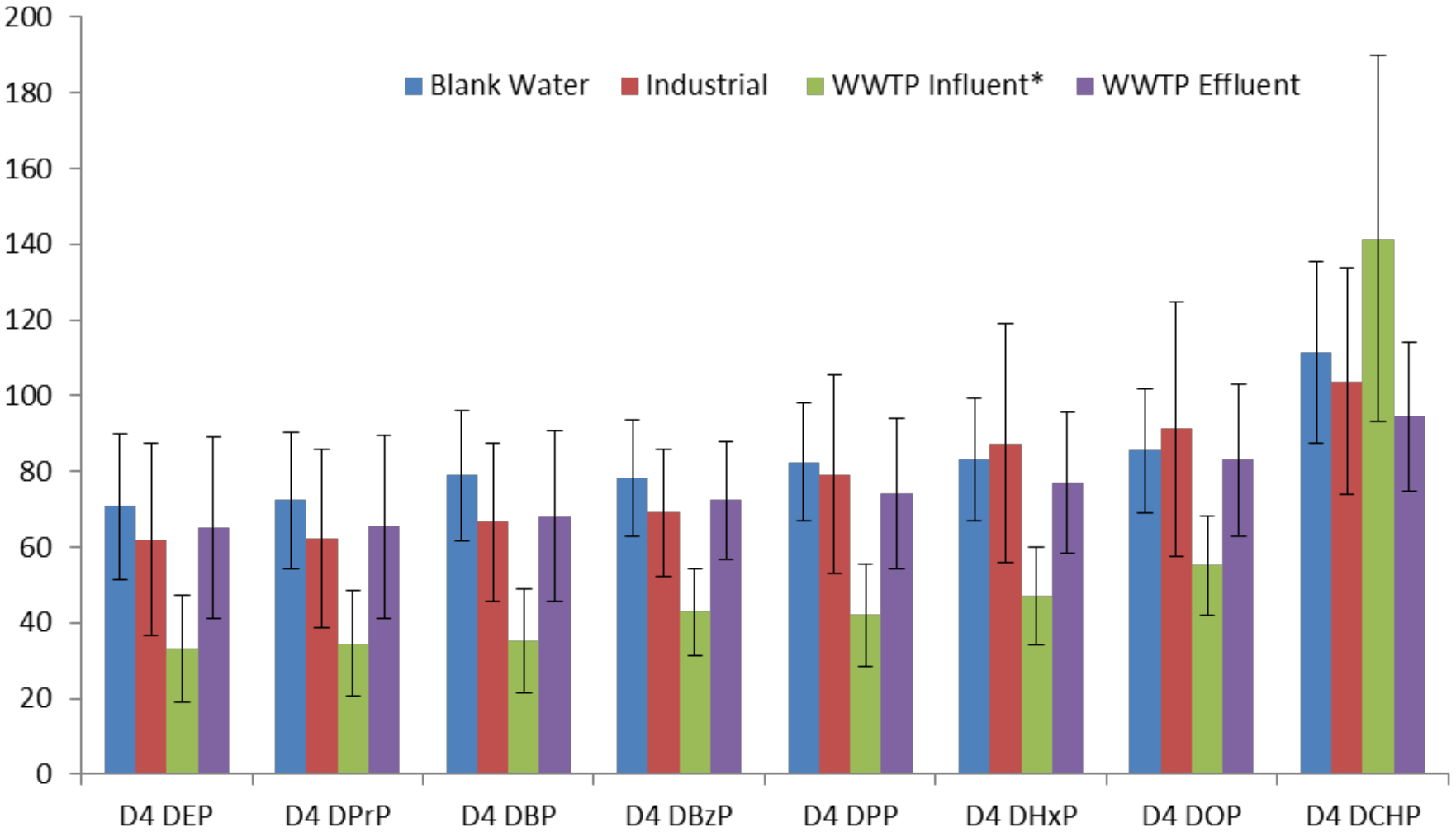
Concentration of phthalates in blank water (HPLC grade water) (n=5)



Percent recovery for phthalates in water using QuEChRES method (n=9)



Average percent recovery for internal standards used during the course of this study.



*signal enhancement was observed in two WWTP influent samples

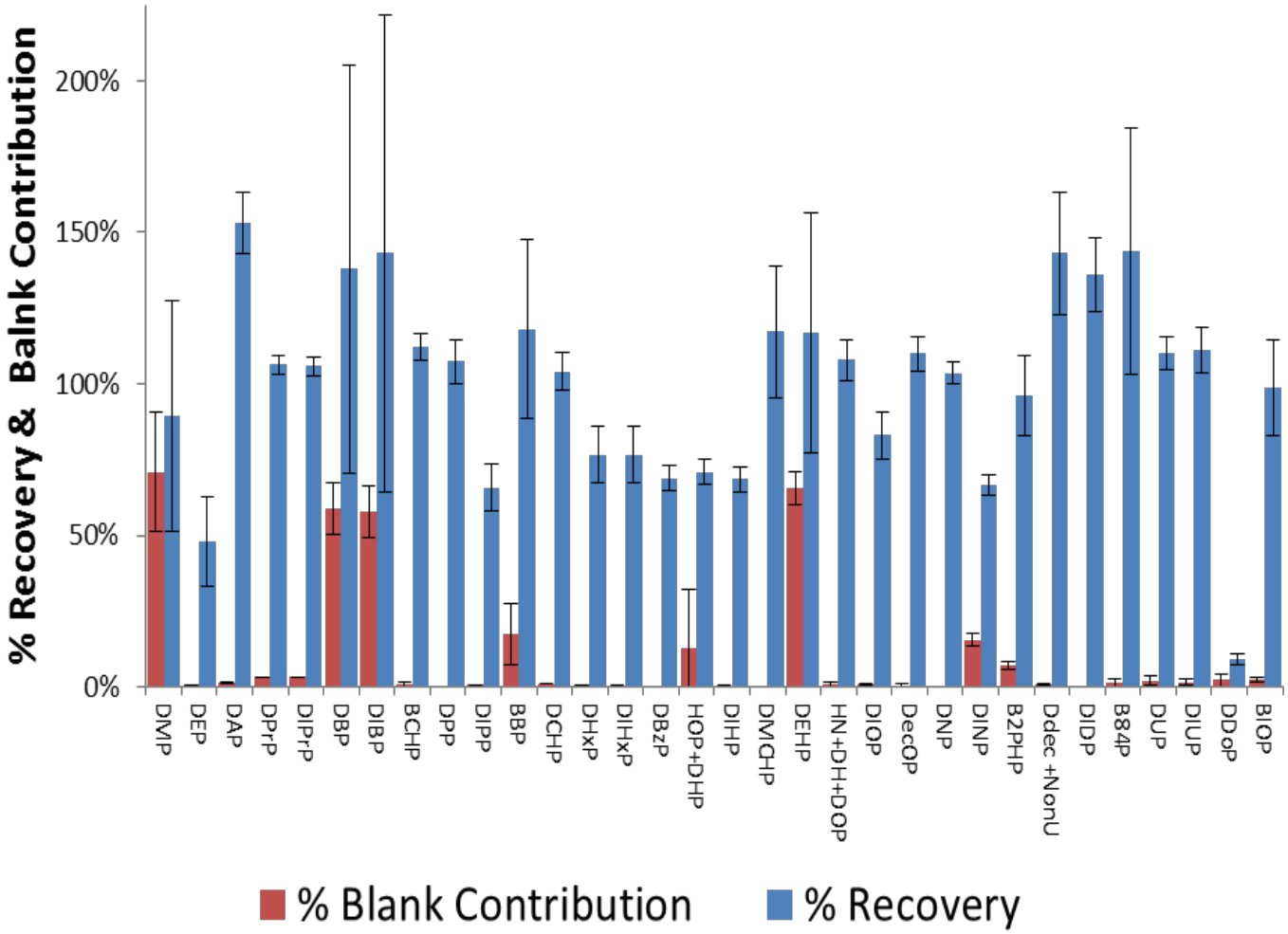
Method for determination of Phthalates in Sediment & Biosolid

- A modified QuEChERS method was used for extraction of phthalates from sediments and biosolids.
- One gram sediment samples and 0.1g biosolid samples were placed into a 50 mL centrifuge tube and spiked with deuterated (D4) phthalate internal standard.
- 10 mL of HPLC grade water was added to the sample and vortexed for 30 sec.
- Subsequently 10 mL of acetonitrile was added to centrifuge tubes and sonicated for an hour.
- QuEChERS extraction salts containing 4g $MgSO_4$ and 1g or NaCl were added to each centrifuge tube and vortexed for 30 seconds. The tubes are then placed in a centrifuge and centrifuged at 3500rpm for 10 minutes.

Method for determination of Phthalates in Sediment & Biosolid

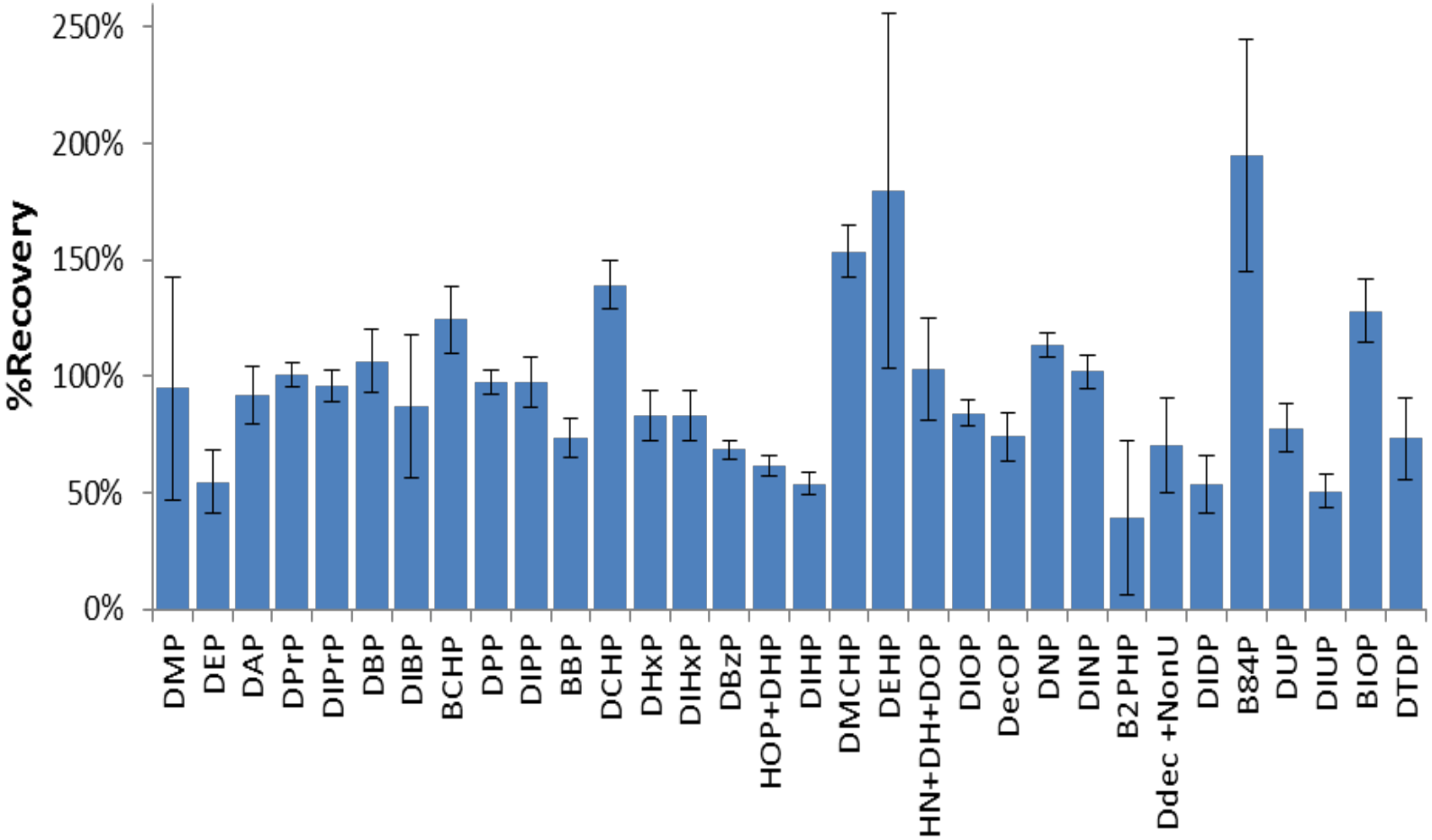
- Disperse solid phase extraction (dSPE) was used to remove interferences from the sediment and biosolid samples.
- 5 mL of the resulting extracts were transferred to a 15mL QuEChERS centrifuge tube containing 900mg $MgSO_4$ and 150mg PSA.
- Interferences adhered to PSA after vortexing for 30 seconds.
- Samples were then centrifuged at 3500rpm for 10 minutes.
- Two mL of the supernatant was removed and reduced to 200µL under a gentle stream of nitrogen.
- One hundred µL of sample was transferred to an LC vial, deuterated DCHP performance standard was added prior to injection.

Average percent recovery and % blank contribution for phthalates in Ottawa sand (n=7)

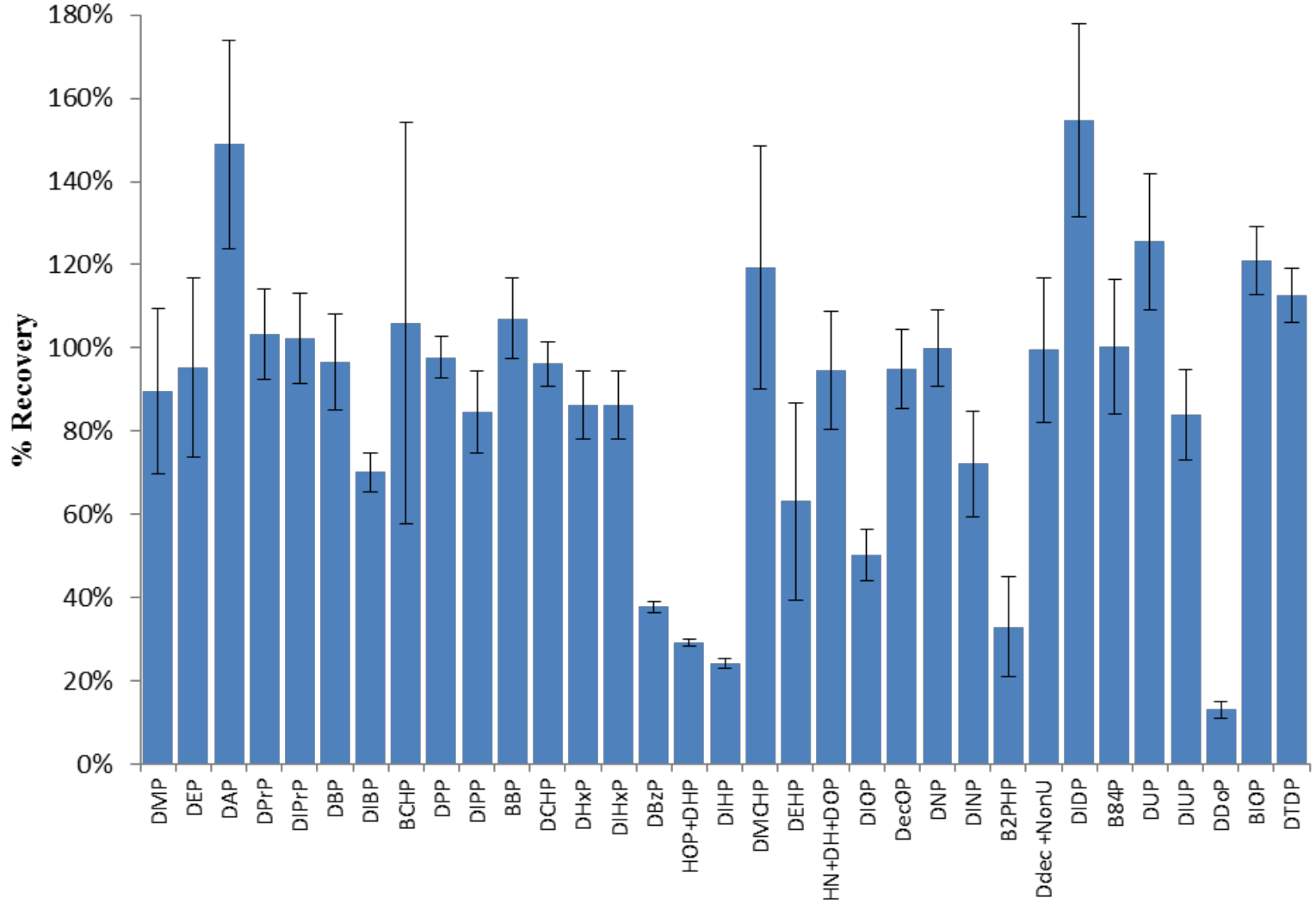


Average Percent recovery for phthalates in a sediment sample from Lake Erie

(n=7)



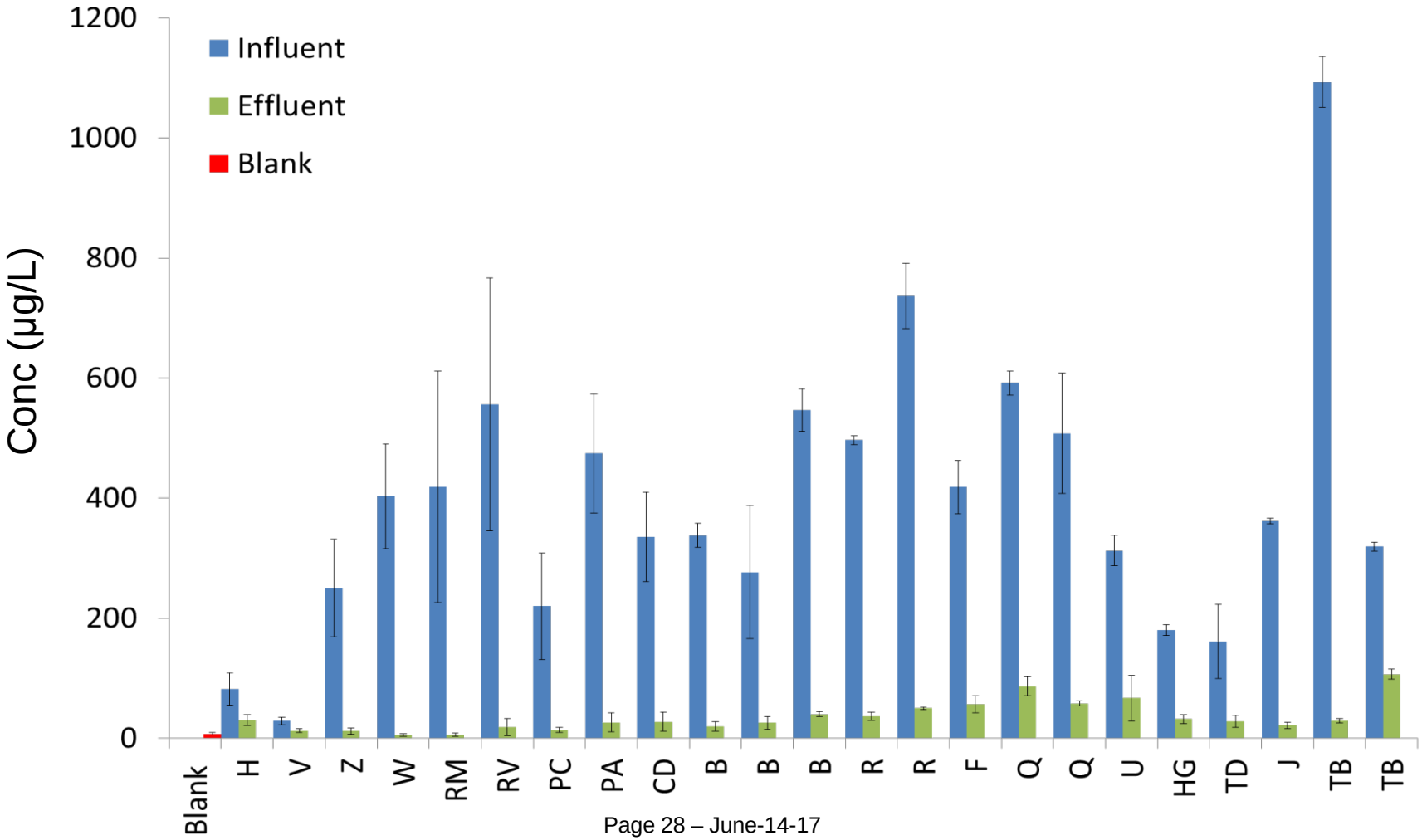
Average percent recovery for phthalates in biosolid samples from a secondary WWTP (n=7)



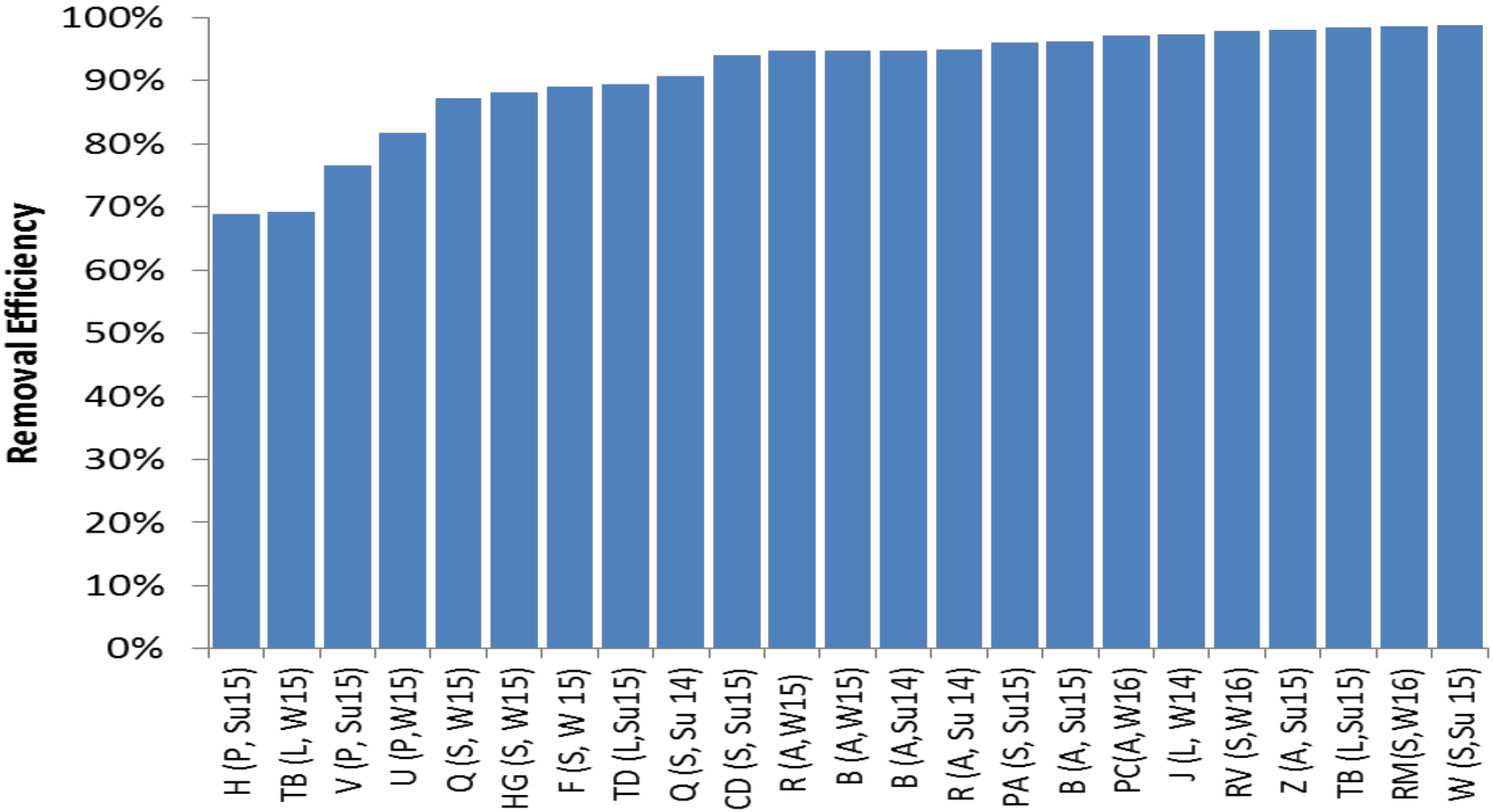
Composite Samplers

- 400ml samples were collected every 30 minutes to generate a 24hr composite using HACH Sigma 900 refrigerated autosamplers
- All samples were transferred into pre-cleaned 1L amber glass bottles with Teflon lined lids and stored in ice packed coolers until they were transported back to the lab
- Samples were refrigerated at 4^{O}C until analysis upon arrival to the lab

Concentration of t-Phthalates in influent and effluent samples of WWTP from across Canada

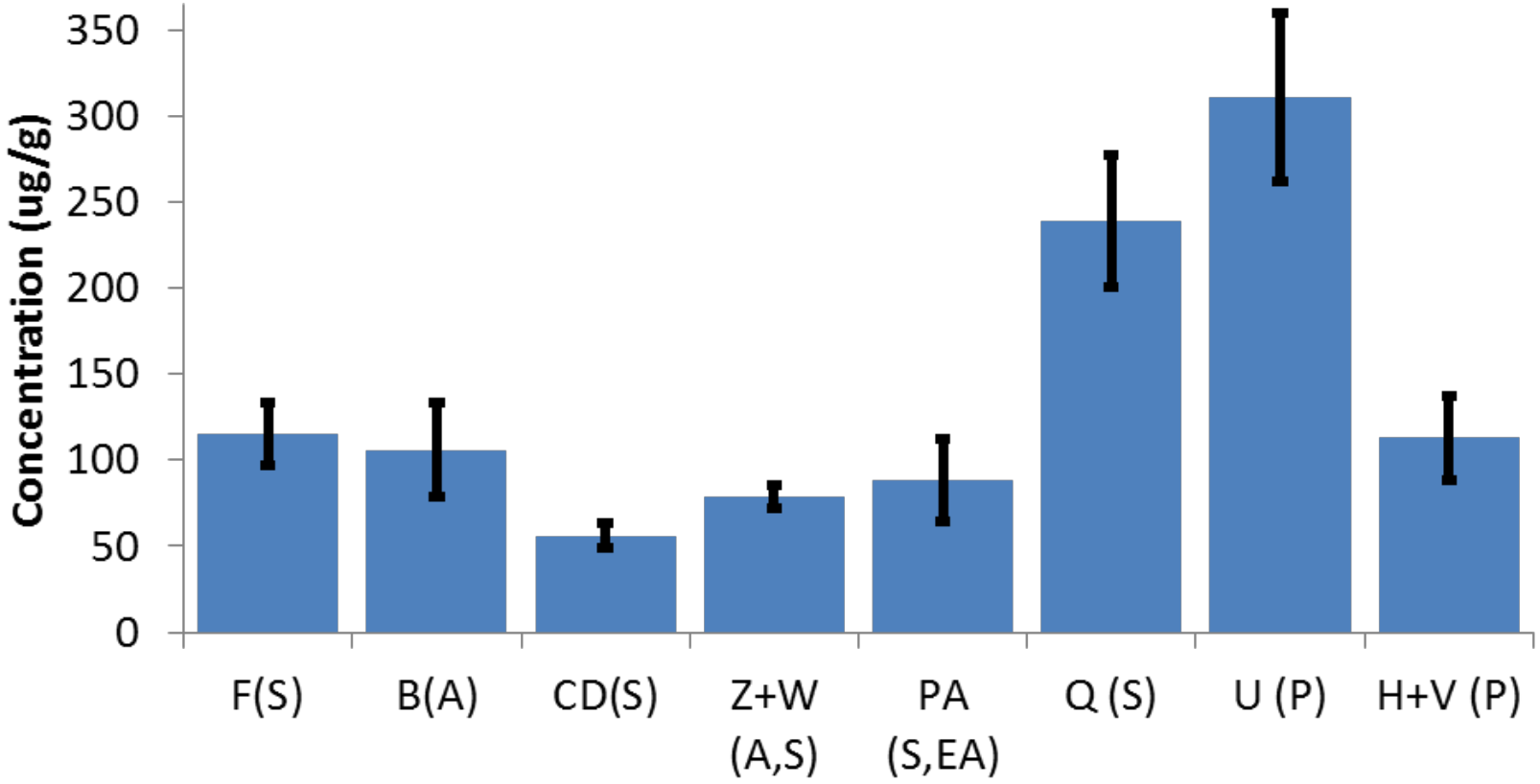


Removal efficiency for t-phthalates in selected WWTP across Canada



$$\text{Removal Efficiency} = \frac{[\text{influent}] - [\text{effluent}]}{[\text{influent}] - [\text{blank}]} \text{ X } 100$$

Concentration of t-phthalates in biosolids from selected WWTP in Canada



Analytical Method Summary:

- An LC/MSMS system was dedicated to this investigation. This instrument was equipped with a scrubbing column before the injection port removing all phthalate residues from the mobile phase.
- Less is more! Since all solvents contain phthalates, using less solvent results in less background interferences.
- The use of sealed centrifuge tubes in the QuEChERS method provides an ideal technique for extraction of phthalates from water, wastewater, sediment and biosolids minimizing contamination from laboratory air.
- Additional cleanup for sediment and biosolids were accomplished using dispersive solid phase extraction, once again, in a sealed centrifuge tube avoiding additional contamination from laboratory air.
- Use of an ultra-clean laboratory, this facility to lower method detection limit (MDL)

Environmental Fate Summary:

- A method for determination of phthalate monoesters in water and wastewater was also developed and validated.
- More than 350 wastewater samples from municipal and industrial treatment plants were analyzed and reported for risk assessment.
- Results from this investigation indicate high removal efficiency from both municipal and industrial WWTP.
- Levels of phthalate monoesters were lower than phthalate diesters and were removed efficiently from most WWTP. Formation of phthalate monoesters in WWTP is not significant and is not likely a removal mechanism for phthalate diesters.
- Binding to biosolids is the likely removal mechanism for phthalates from WWTP particularly for higher molecular weight phthalates.

Acknowledgements:

- Shirley Anne Smyth, Steven Teslic, Amber Adams and Eraj Gillani for collection of municipal wastewater samples
- WWTP operators for access to their facilities
- Funding for this study was provided by Chemicals Management Plan

Thank you!