Report to Scientific Guidance Panel

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Overview

- ❑ Staff changes
- ❑ Method updates
- ❑ Ongoing projects
- ❑ Recent publications
- ❑ Future work

Staff Changes

APHL Fellow:

- Dr. Rosario Amado-Sierra

New Hire:

- Dr. Shizhong Wang

Visiting Scholar:

- Li Fang

Vacancy:

- Sample Manager

Method Updates

- ❑ As speciation
- ❑ Semi-targeted analysis
- ❑ Development of master method

As Speciation

	As(III) (µg L^{-1})	As(V) (µg L^{-1})	MMA (µg L^{-1})	DMA (µg L^{-1})	AB (µg L^{-1})
2011 EHL MDL (10x dilution)	1.00	1.00	1.00	1.00	1.00
2016 EHL MDL (10x dilution)	**0.0239**	**0.0243**	**0.0291**	**0.0184**	**0.0166**
Improvement factor	40x	40x	30x	60x	50x

Semi-targeted Analysis

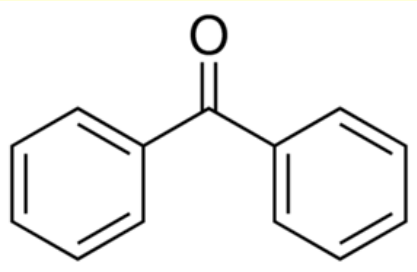
Detection of Structurally Related Compounds:

- Model chemical: Benzophenones in urine
- Consider all possible chemical formulas with different combinations of functional groups: hydroxy, methyl, methoxyl, Cl, and S
- Database of 72 compounds for *proof of concept*

Semi-targeted Analysis (cont.)

Benzophenone Structurally Related Analogs Database (partial list):

Compound Name	Common Name	Chemical Formula	Exact Mass
OH-2, Me-0, CL-0, S-0	BP-1	C13H10O3	213.0557
OH-2, Me-0, CL-0, S-1		C13H10O6S	293.0125
OH-2, Me-0, CL-1, S-0		C13H9O3CL	247.0168
OH-2, Me-0, CL-1, S-1		C13H9O6CL1S1	326.9736
OH-2, Me-1, CL-0, S-0	BP-3	C14H12O3	227.0714
OH-2, Me-1, CL-0, S-1	BP-4	C14H12O6S1	307.0282
OH-2, Me-1, CL-1, S-0		C14H11O3CL1	261.0324
OH-2, Me-1, CL-1, S-1		C14H11O6CL1S1	340.9892
OH-2, Me-2, CL-0, S-0	BP-10	C15H14O3	241.0870
OH-2, Me-2, CL-0, S-1		C15H14O6S1	321.0438
OH-2, Me-2, CL-1, S-0		C15H13O3CL1	275.0481
OH-2, Me-2, CL-1, S-1		C15H13O6CL1S1	355.0049
OH-2, Me-3, CL-0, S-0		C16H16O3	255.1027
OH-2, Me-3, CL-0, S-1		C16H16O6S1	335.0595
OH-2, Me-3, CL-1, S-0		C16H15O3CL1	289.0637
OH-2, Me-3, CL-1, S-1		C16H15O6CL1S1	369.0205



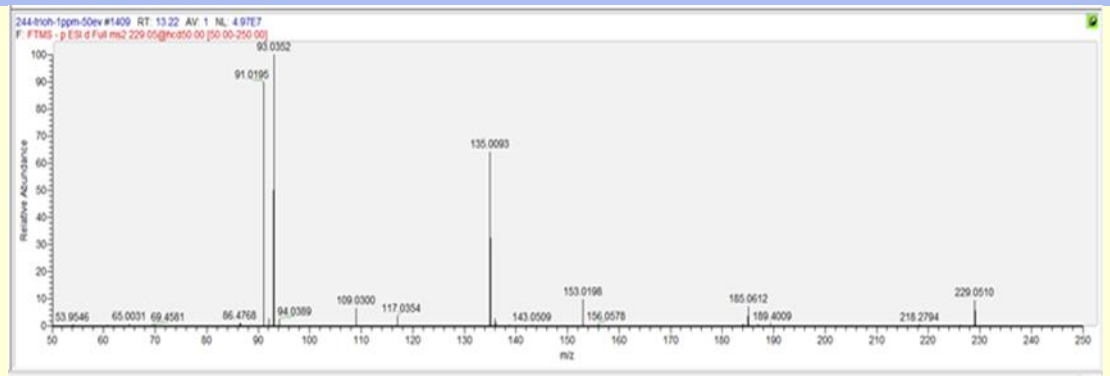
Semi-targeted Analysis (cont.)

Urine Sample Compound Hit List:

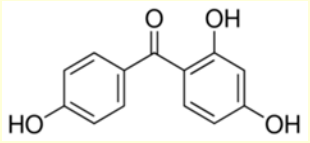
Compound Name	Detected in Replicates	Status
BP-3	6/6	Found; confirmed
BP-1	6/6	Found; confirmed
BP-4	6/6	Found; to be confirmed
BP-6	6/6	Found; to be confirmed
BP-8	6/6	Found; to be confirmed
TriOH-BP	6/6	Found; confirmed
BP-10	3/6	
BP-12	0	
BP-7	0	
BP-9	0	
OH-1, Me-1, CL-0, S-0	6/6	Unknown; to be confirmed
OH-1, Me-1, CL-0, S-1	6/6	Unknown; to be confirmed
OH-2, Me-0, CL-0, S-1	6/6	Unknown; to be confirmed
OH-3, Me-2, CL-0, S-1	6/6	Unknown; to be confirmed

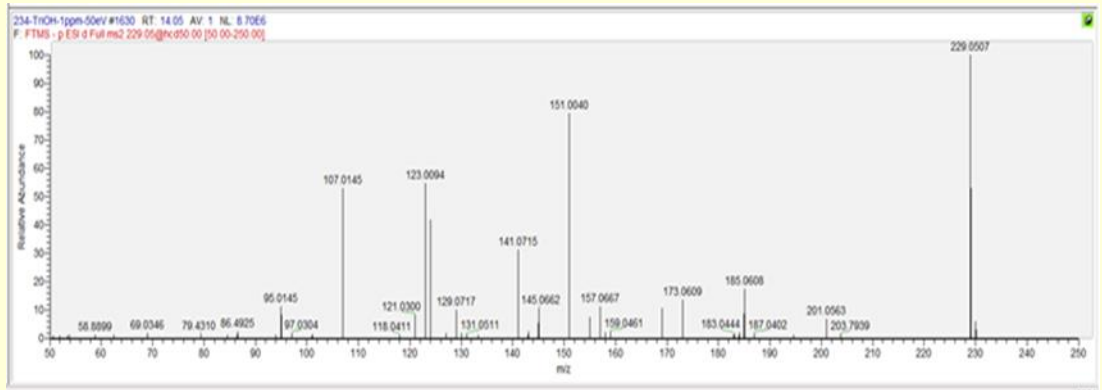
Plus more…

Semi-targeted Analysis (cont.)

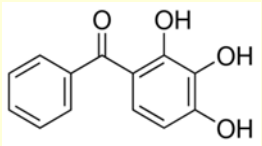


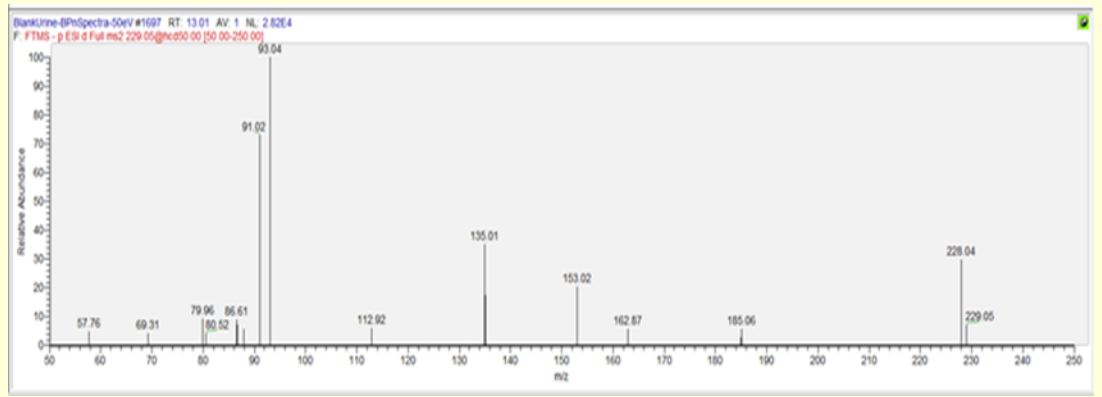
Spectrum of 2,4,4'-trihydroxy-benzopenone standard



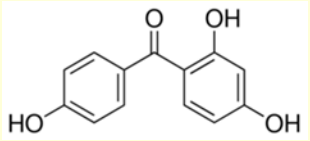


Spectrum of 2,3,4-trihydroxy-benzopenone standard





Spectrum of compound in urine sample on the Hit List



Master Method

Compounds	LOD*
(mCPP)mono-3-carboxypropyl phthalate	0.5
(mEP)mono-ethyl phthalate	0.2
(miBP)mono- isobutyl phthalate	0.2
(mBP)mono-n-butyl phthalate	0.2
(mECPP)mono-(2-ethyl-5-carboxypentyl) phthalate	0.2
(MP)methyl paraben	0.2
(mBzP)mono-benzyl phthalate	0.2
(mEOHP)mono-(2-ethyl-5-oxohexyl) phthalate	0.2
(mCHP)mono-cyclohexyl phthalate	0.2
(mEHHP)mono-(2-ethyl-5-hydroxyhexyl)phthalate	0.2
(EP)ethyl paraben	0.2
(BP2)2,2',4,4'-tetrahydroxybenzophenone	0.2
(2,4-DCP)2,4-dichlorophenol	1
(2,5-DCP)2,5-dichlorophenol	1
(2,3,4-TriOH) 2,3,4-Trihydroxybenzophenone	0.2
(2,4,4'-TriOH)2,4,4'-Trihydroxybenzophenone	0.2
(PP)propyl paraben	0.2
(mEHP)mono-2-ethylhexyl phthalate	0.2
(2,4,5-TCP)2,4,5-trichlorophenol	1
(2,4,6-TCP)2,4,6-trichlorophenol	1
(BPA)bisphenol A	0.2
(BP)butyl paraben	0.2
(OPP)ortho-phenylphenol	0.2
(BP1)2,4-dihydroxybenzophenone	0.2
(BP3)oxybenzone	0.2
(BP8)dioxybenzone	0.2
(BP6)2,2'-dihydroxy-4,4'-dimethoxybenzophenone	<0.2
(BP7)5-chloro-2-hydroxybenzophenone	0.5
(BP10)mexenone, 2-hydroxy-4-methoxy-4'-methyl-benzophenone	0.5
(BP12)octabenzone	0.5

Master Method (cont.)

Phthalates in current master method:

Phthalates	RT (min)	Expected m/z	Measured m/z	LOD*	Range	R^2
(mCPP)mono-3-carboxypropyl phthalate	2.37	251.0561	251.0561	0.5	1.0-200	0.9887
(mEP)mono-ethyl phthalate	3.46	193.0506	193.0508	0.2	1.0-200	0.9892
(miBP)mono- isobutyl phthalate	11.36	221.0819	221.0822	0.2	1.0-200	0.9830
(mBP)mono-n-butyl phthalate	11.70	221.0819	221.0822	0.2	1.0-200	0.9827
(mECPP)mono-(2-ethyl-5-carboxypentyl) phthalate	15.78	307.1187	307.1187	0.2	1.0-50	0.9807
(mBzP)mono-benzyl phthalate	14.66	255.0663	255.0663	0.2	1.0-200	0.9964
(mEOHP)mono-(2-ethyl-5-oxohexyl) phthalate	14.87	291.1238	291.1238	0.2	1.0-200	0.9951
(mCHP)mono-cyclohexyl phthalate	15.78	247.0976	247.0977	0.2	1.0-200	0.9964
(mEHHP)mono-(2-ethyl-5-hydroxyhexyl) phthalate	15.15	293.1395	293.1395	0.2	1.0-200	0.9930
(mEHP)mono-2-ethylhexyl phthalate	18.89	277.1445	277.1444	0.2	1.0-200	0.9962

*: Instrument LOD

Master Method (cont.)

Environmental phenols in current master method:

Environmental Phenols	RT (min)	Expected m/z	Measured m/z	LOD*	Range	R^2
(MP)methyl paraben	9.10	151.0401	151.0404	0.2	1.0-200	0.9949
(EP)ethyl paraben	16.57	165.0557	165.0560	0.2	1.0-200	0.9905
(2,4-DCP)2,4-dichlorophenol	10.10	160.9566	160.9573	1.0	2.0-200	0.9973
(2,5-DCP)2,5-dichlorophenol	10.10	160.9566	160.9573	1.0	2.0-200	0.9973
(PP)propyl paraben	18.20	179.0714	179.0718	0.2	1.0-200	0.9858
(2,4,5-TCP)2,4,5-trichlorophenol	17.94	194.9167	194.9169	1.0	1.0-200	0.9956
(2,4,6-TCP)2,4,6-trichlorophenol	17.94	194.9167	194.9169	1.0	1.0-200	0.9956
(BPA)bisphenol A	19.12	227.1078	227.1081	0.2	1.0-200	0.9956
(BP)butyl paraben	19.36	193.0870	193.0873	0.2	0.5-200	0.9812
(OPP)ortho-phenylphenol	19.42	169.0659	169.0662	0.2	1.0-200	0.9926
(BP3)oxybenzone	20.24	227.0714	227.0717	0.2	0.5-200	0.9770

*: Instrument LOD

Master Method (cont.)

Benzophenones in current master method:

Benzophenones	RT (min)	Expected m/z	Measured m/z	LOD*	Range	R^2
(BP1)2,4-dihydroxybenzophenone	19.61	213.0557	213.0561	0.2	0.5-200	0.9714
(BP2)2,2',4,4'-tetrahydroxybenzophenone	16.99	245.0456	245.0452	0.2	1.0-200	0.9889
(BP3)oxybenzone	20.24	227.0714	227.0717	0.2	0.5-200	0.9770
(BP6)2,2'-dihydroxy-4,4'-dimethoxybenzophenone	21.22	273.0769	273.0768	0.2	0.2-200	0.9946
(BP7)5-chloro-2-hydroxybenzophenone	21.24	231.0218	231.0223	0.5	1.0-200	0.9930
(BP8)dioxybenzone	20.31	243.0663	243.0662	0.2	1.0-200	0.9954
(BP10)mexenone, 2-hydroxy-4-methoxy-4'-methyl-benzophenone	14.89	241.0870	241.0870	0.5	1.0-200	0.9676
(BP12)octabenzone	24.02	325.1804	325.1809	0.5	1.0-200	0.9803
(2,3,4-TriOH)2,3,4-Trihydroxybenzophenone	13.62	229.0506	229.0506	0.2	1.0-200	0.9872

*: Instrument LOD

Project Updates

- Previous Biomonitoring projects: Firefighter Occupational Exposures (FOX) Project & Expanded Biomonitoring Exposures Study (EBEST)
- Pregnancy, Environment, and Lifestyle Study (PETALS)
- Asian/Pacific Islander Community Exposures (ACE) Project

New Analyses: FOX & EBEST

STUDY	COLLABORATORS	ANALYSES/ SAMPLE #	STATUS
Firefighter Occupational Exposures (**FOX**) Project	University of California Irvine's Center for Occupational and Environmental Health (UCI COEH)	OP Flame Retardants (BCEP, BDCPP & DPP) in urine n=83	▪ All analyses completed ▪ Review pending
Expanded Biomonitoring Exposures Study (**EBEST**)	Kaiser Division of Research (DOR), Research Program on Genes, Environment, and Health (RPGEH) of Kaiser Permanente Northern California (KPNC)	Perchlorate in urine n=218	▪ Analyses pending

PETALS

STUDY	COLLABORATORS	ANALYSES/ SAMPLE #	STATUS
Pregnancy Environment & Lifestyle Study (**PETALS**)	Kaiser Permanente Northern California *(Assiamira Ferrara, MD, PhD)*	BPA, BP-3, triclosan & creatinine in urine n=600/yr (3 yrs) starting Dec. 2014	▪ 498 samples received to date ▪ All analyses completed ▪ All data reported

ACE

STUDY	COLLABORATORS	ANALYSES/ SAMPLE #	STATUS
Asian/Pacific Islander Community Exposures (**ACE**) Project	Asian Perinatal Advocates Family Support Services (APA)	Pb, Cd & Hg in blood n=100	▪ 84 samples received to date ▪ 56 samples analyzed ▪ 56 results reported
		As, Cd & Hg in urine Creatinine in urine n=100	▪ 86 urines received to date ▪ 69 urines analyzed ▪ Review pending
		As species in urine n=TBD	▪ 37 participants of the 69 samples analyzed to date will require As speciation analyses

Publications for 2016

- She et al. **Levels, Trends, and Health Effects of Dioxins and Related Compounds.** *Aquatic Biota, The Handbook of Environmental Chemistry* 49, Alaee (editor), pp 153-202, Springer.
- Choe &Gajek. **Determination of trace elements in human urine by ICP-MS using sodium chloride as a matrix-matching component in calibration.** *Anal. Methods*.
  http://dx.doi.org/10.1039/c6ay01877g
- Feng et al. **Effects of Acute Low-Dose Exposure to the Chlorinated Flame Retardant Dechlorane 602 and Th1 and Th2 Immune Responses in Adult Male Mice**, *Environ Health Perspect*,
  http://dx.doi.org/10.1289/ehp.1510314.
- Harley et al. **Reducing Phthalate, Paraben, and Phenol Exposure from Personal Care Products in Adolescent Girls: Findings from the HERMOSA Intervention Study.** *Environ Health Perspect*,
  http://dx.doi.org/10.1289/ehp.1510514
- Lin et al. **A validated method for rapid determination of dibenzo-p-dioxins/furans (PCDD/Fs), polybrominated diphenyl ethers (PBDEs) and polychlorinated biphenyls (PCBs) in human milk: focus on utility of tandem solid phase extraction (SPE) cleanup**. *Anal Bioanal Chem*,
  http://dx.doi.org/10.1007/s00216-016-9576-y
- Lu et al. **Identification of flurochloridone metabolites in rat urine using liquidchromatography/high resolution mass spectrometry.** *J Chromatography A*,
  http://dx.doi.org/10.1016/j.chroma.2016.03.080
- Waldman et al. **Exposures to environmental phenols in a cohort of California firefighters and findings of elevated urinary benzophenone-3 levels.** *Environ. Intern*.
  https://www.ncbi.nlm.nih.gov/pubmed/26821331.

Future Work

- Re-tests of total As and As speciation for EBEST samples
- PETALS study analyses continuing
- Development of a cotinine method

Future Work

Development of a cotinine method

- In the human body, nicotine is rapidly broken down:
  $T_{1/2}$ ~½ - 3 h.
- The primary metabolites of nicotine are cotinine (COT) and trans-3'-hydroxycotinine (HC):

  $T_{1/2}$ of COT ~ 15 - 20 h
  $T_{1/2}$ of HC ~ 5 - 6 h.
- We will evaluate nicotine exposures with measurements of its metabolites, COT and HC, in blood.