Biomonitoring Updates from New York

Division of Environmental Health Sciences
Wadsworth Center
NY State Department of Health

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APHL ANNUAL MEETING June 1-4, 2014 Little Rock, AR

Biomonitoring
The Next Five Years?

Where to focus efforts for the next five years?

- Review what has been accomplished during the last five+ years.
- New ideas for advancing the field of biomonitoring
- How to continue building a national biomonitoring network or system

Outline

- Current Projects
  - NYC Community Health and Nutrition Examination Survey (CHANES)
  - National Lead Industries – Depleted Uranium Exposure
    - Response to public concerns
  - Chinese Mercury Study –
    - Biomonitoring linked with an Environmental Investigation
  - Environmental Public Health Tracking (EPHT) and Biomonitoring – Great Lakes Studies
  - Emerging Environmental Contaminants – BPA analogues etc.
  - Newborn Screening

Biomonitoring History at Wadsworth

- 2001 Biomonitoring Planning Grant (2 years)
  25 states and state consortia funded by CDC
- 2003 Biomonitoring Implementation Award
  - 3 Awards (NH, Rocky Mt. Consortium, NY)
- 2003-2008 Biomonitoring Implementation Funding
  - Purchase of GC/HRMS + funded one analytical staff
  - NYS Tobacco Control Program – State Legislation
  - NYC HANES Study (Trace elements, cotinine, pesticides)
  - Pilot Projects (PFC, PBDE, OH-PAHs, trace element speciation, etc)
- 2009-2014 Expanding NY PHL Capability & Capacity
  - Method development and validation
  - Staff, Automation, Instrumentation

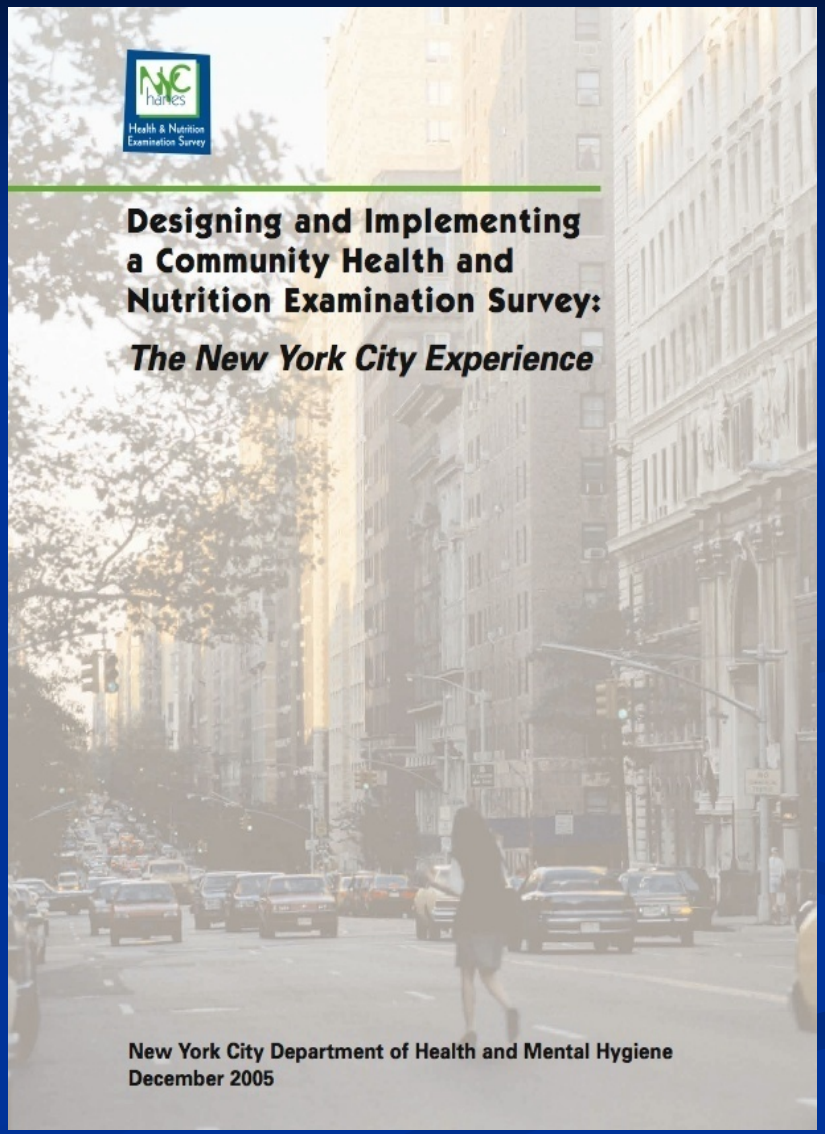
NYS Biomonitoring Program
(2003-2008)

- Major Projects:
  - Impact of NYS Legislation Banning Smoking in Public Places (7/2003)
    - Working with NYSDOH Center for Community Health Tobacco Program
    - Saliva Cotinine (1,800 self administered sample collection)
  - NYC Health and Nutrition Examination Survey (CHANES)
    - Analysis of 1,811 Whole Blood (Pb, Cd, and Hg)
    - Analysis of 1,820 Urine Hg
    - Analysis of 1,500 Serum Cotinine
  - Use of NBS Blood Spots
    - Tracking Perfluorinated Compound (PFCs) levels over last 10 years
  - These major projects plus others continued into the next funding cycle (2009-2014)

New York City Community Health and Nutrition Examination Survey - 2004 (CHANES)

New York City Community Health and Nutrition Examination Survey - 2013 (CHANES -II)

Trace elements, Cotinine, archive Blood and Urine.



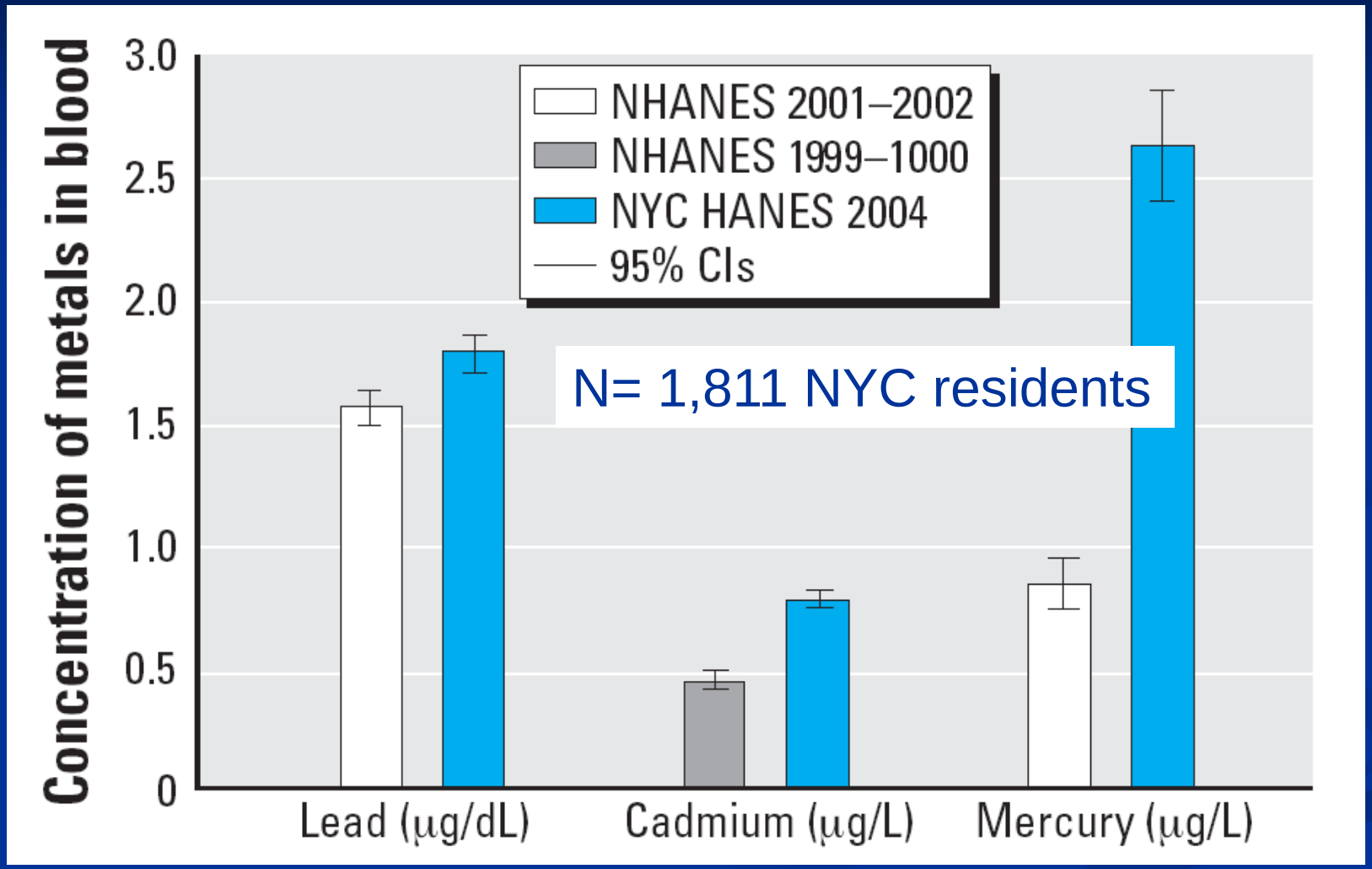
NYC CHANES 2004

- Whole Blood
  - Heavy Metals – Lead , Cadmium , Mercury (1,811)
  - Mercury Speciation (438)
  - Manganese & Selenium (method validation, analysis)
- Serum
  - Cotinine (1,800)
  - PCBs, DDT, DDE, PBDEs (1,052)
- Urine
  - 21 Trace Elements (1,876)
  - Mercury (1,876)
  - Dialkylphosphates (886)
  - Hydroxy PAHs (~1,000)

Biomarkers of mercury exposure

- Urine Hg (<10-20 μg/L)
  - Urine Hg levels are a good indicator of exposure to iHg and Hg^0, but it is unreliable for MeHg which is eliminated mostly in feces.
- Blood Hg (<5 μg/L)
  - $t_{½}$ ~44 days so Blood Hg levels reflect acute exposure. Blood Hg contains both iHg and MeHg. So some kind of separation can be helpful.
- Hair Hg (<1.0 μg/g)
  - Hair has high -SH groups that bind Hg. But lack of standardized protocols, and environmental contamination raise questions about reliability. It is thought that Hg is excreted in hair mostly as MeHg.

CHANES 2004 – Mercury in Blood



McKelvey et al., Environmental Health Perspectives, 115, (2007), 10, pp. 1435-1441.

Blood Hg in NY City Adults by Fish Consumption

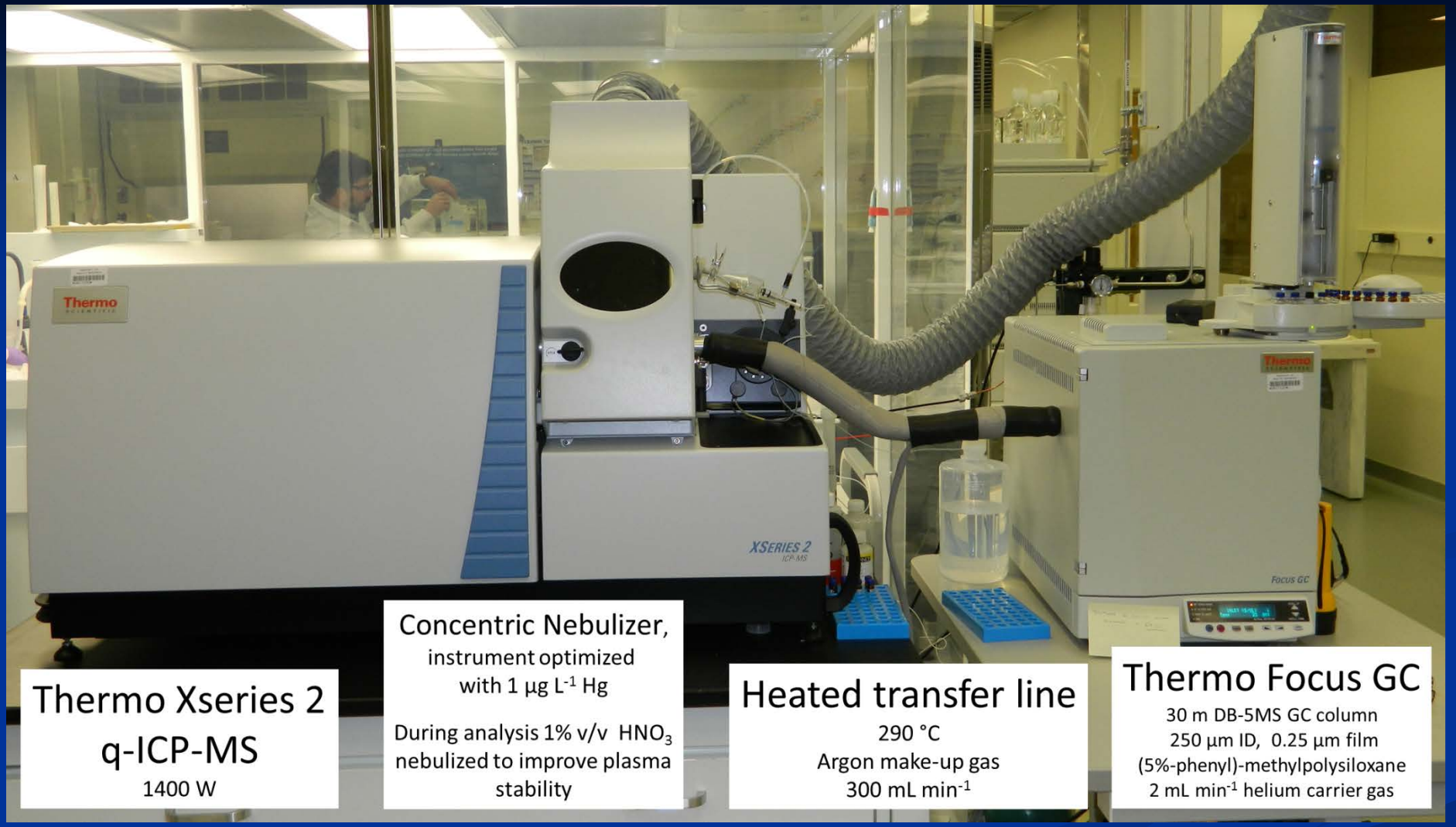
Variable	No. of participants in study	Geometric mean BHg, µg/L (95% CI)	95th percentile BHg µg/L (95% CI)	% BHg ≥5 µg/L (95% CI)
Fish or shellfish consumption (last 30 days)				
Never	**209**	**1.31** (1.14-1.50)	**5.39** (4.40-7.16)	**7.3%** (4.0-13.0)
Up to 9 times	**1,216**	**2.60** (2.46-2.74)	**9.34** (7.96-10.27)	**20.5%** (17.8-23.4)
10-19 times	**255**	**4.25** (3.79-4.76)	**19.19** (12.03-23.45)	**44.1%** (37.0-51.4)
20 times or more	**114**	**5.65** (4.80-6.65)	**18.13** (14.70-21.65)	**56.2%** (45.4-66.5)

Blood Hg in NYC adults by population subgroups

Variable	No. of participants in study	Geometric mean BHg, µg/L (95% CI)	95th percentile BHg µg/L (95% CI)	% BHg ≥5 µg/L (95% CI)
Race/ethnicity				
White, non-hispanic	529	2.83 (2.62-3.07)	10.85 (9.36-14.21)	25.5% (21.5-29.9)
Black, non-hispanic	390	2.61 (2.36-2.88)	9.26 (7.77-12.26)	23.3% (18.6-28.9)
Asian, non-hispanic	231	4.11 (3.24-5.21)	19.19 (14.03-23.95)	46.2% (36.6-56.1)
Hispanic	630	2.27 (2.11-2.43)	8.46 (7.03-9.93)	16.7% (13.5-20.5)

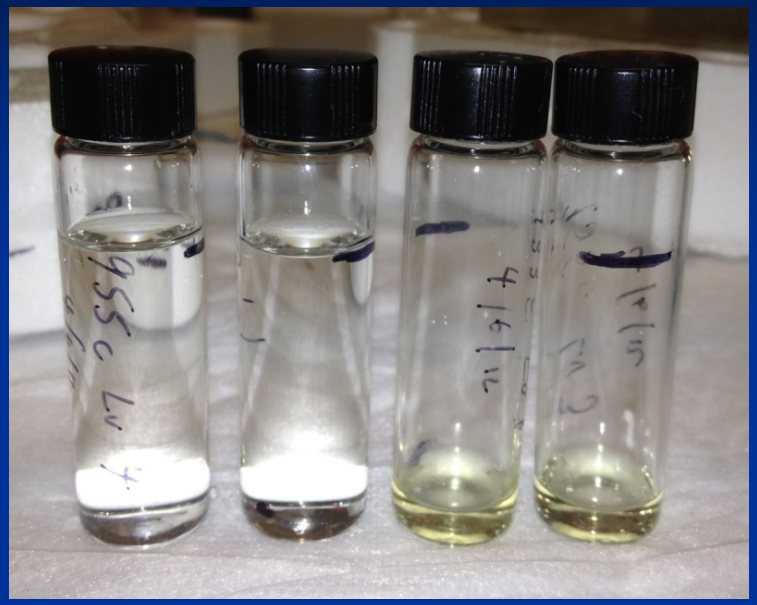
NYC CHANES BHg – Speciation Goals
numbers of specimens

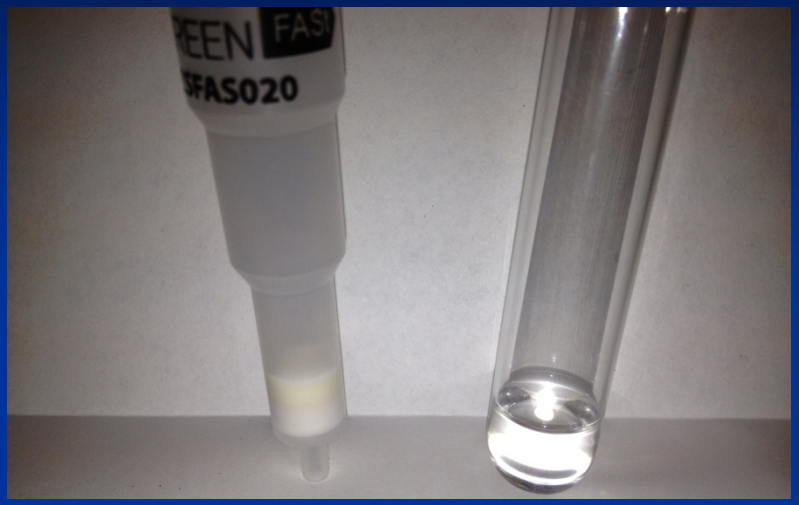
Found Blood Hg, µg/L	No. of NYC HANES 2004 specimens with corresponding conc.
≥ 2.0	1141
≥ 5.0	438
≥ 8.0	178
≥ 10.0	117
≥ 15.0	54
≥ 20.0	25

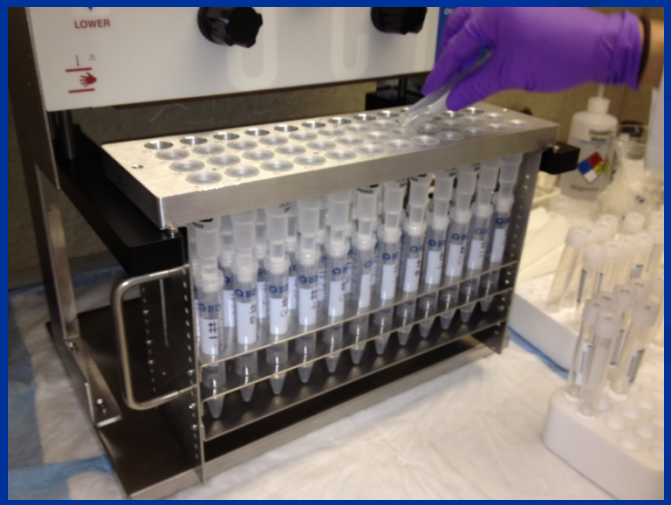


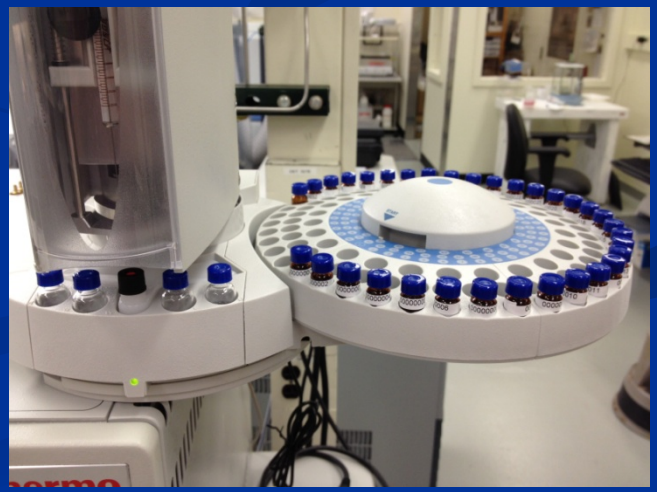
Thermo XSeries2 ICP-MS with Thermo Focus GC and heated transfer line
Install date – June 2011

Clean-up of hexane extracts





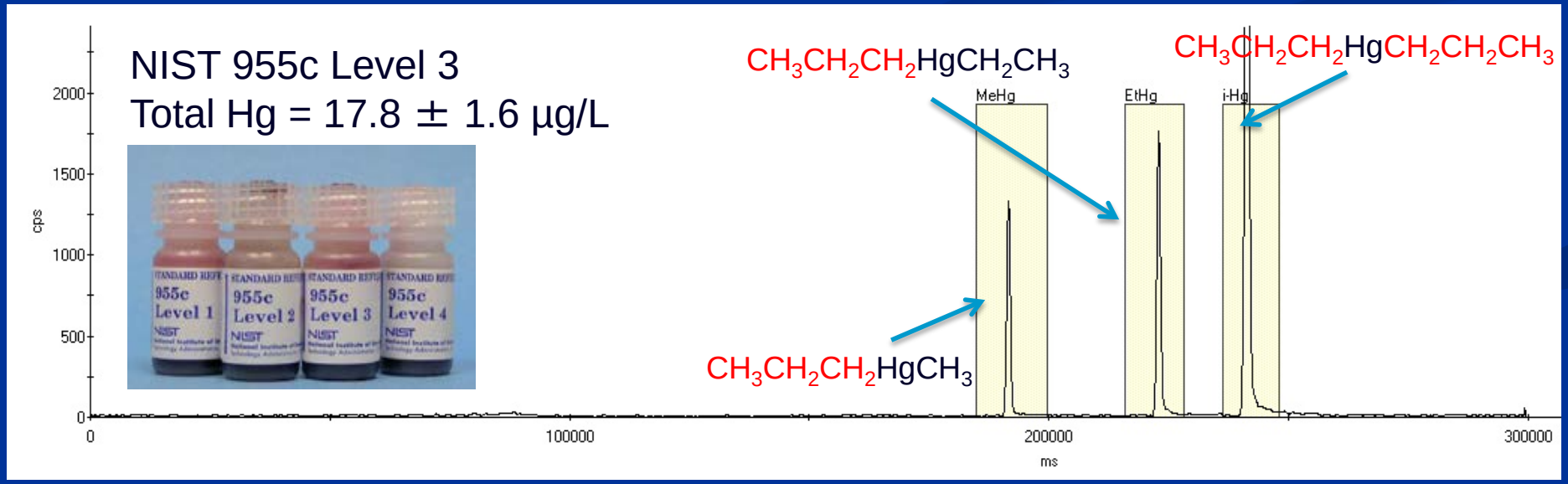




Blood Mercury Speciation

- Blood speciation method – Inorganic, methyl and ethyl mercury following dissolution with tetramethyl ammonium hydroxide and derivatization with sodium tetra (n-propyl) borate. Hexane extraction, SPE clean-up and GC-ICP-MS with triple isotope spike.

- Although we have chosen a back-extraction of Hg derivatives into hexane, and the CDC has chosen a solid-phase microextraction (SPME) approach, we will use the IRAT branch's Isotope Pattern Deconvolution spreadsheets to maintain a degree of cross-comparability between our two labs.



Method Detection Limits

ICP-MS Biomonitoring Method
Mercury in Blood

LOD = 0.24 µg/L

GC-ID-ICP-MS Speciation Method LODs

MeHg = 0.15 µg/L
EtHg = 0.10 µg/L
iHg = 0.01 µg/L

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- Current Projects
  - NYC Community Health and Nutrition Examination Survey (CHANES) Mercury speciation applied to elevated bHg.
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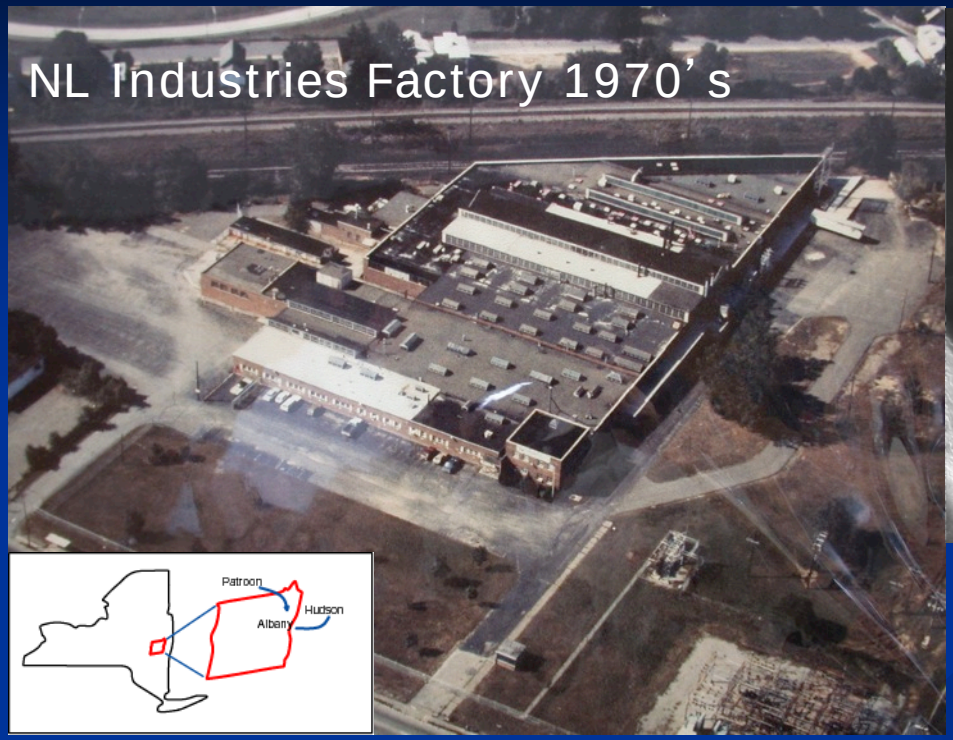
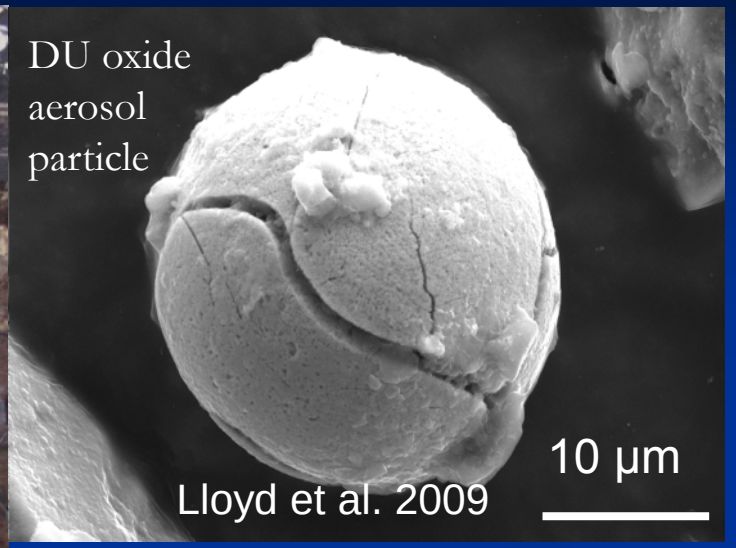
Depleted Uranium (DU)

- By-product of uranium enrichment
- Depleted in the fissile isotope ^{235}U (<0.72 %)
- May contain ^{236}U from reprocessed fuel
- Primary exposure through inhalation of fine particles or embedded shrapnel
- Animal experiments link DU to cancer, kidney disease, and cell damage.

Former NL Industries Site

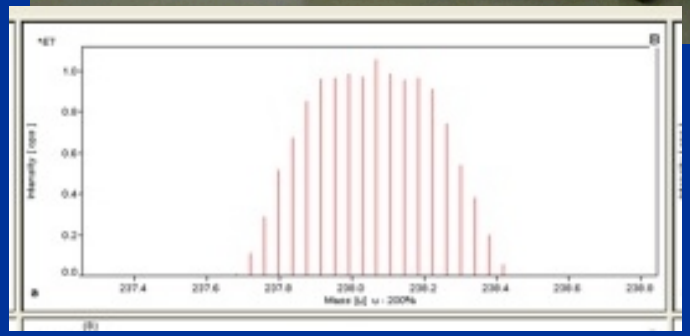




- 1958 - 1984: Processing of DU and small amounts of enriched uranium (EU)
- Uranium waste incinerated and converted to DU oxide aerosol
- Estimated 4.8 metric tons DU deposited in surrounding soils
- 750 workers employed during this time period
- Factory located in residential/commercial district

Study Objectives

1. Measure [U] urine levels in a large cohort of workers and residents using urine specimens collected under controlled conditions
2. Develop and validate a relatively rapid and cost effective method for measuring $^{235}U/^{238}U$ and $^{236}U/^{238}U$ in urine specimens with [U] as low as 1 ng/L using existing instrumentation (SF-ICP-MS)
3. Measure uranium isotope ratios in a smaller cohort of workers and residents who were most likely exposed to DU/EU
4. Urine sample collection started and 200+ residents and former employees contacted.



Instrumentation

- Thermo Element 2 ICP-SF-MS
- Cetac Aridus™ II desolvation nebulizer system with self-aspirating 100 uL/min nebulizer (all teflon)
- ICP-MS run in low resolution mode for highest sensitivity & flat-topped peaks
- Natural uranium (IRMM 3184) used to correct for instrumental mass bias

Certified Isotopic Reference Materials

- Critical for isotope ratio accuracy
- 2 sources:
  - IRMM (Geel, Belgium)
  - New Brunswick Labs, DOE (Chicago, USA)
- Natural, depleted, and enriched U available
- ^{233}U (NBL CRM 112) used as internal standard for ICP-MS

Summary

- Random (spot) urine specimens are preferred to reduce contamination and permit large number specimens to be collected and stored.
- Method can accurately measure $^{235}U/^{238}U$ and $^{236}U/^{238}U$ at occupational exposure levels ([U]=50 ng L^{-1}) with RSD's of < 1% and < 5%, respectively.
- Method can accurately measure $^{235}U/^{238}U$ at biomonitoring levels ([U]= 1- 5 ng L^{-1}) with RSD of < 1% and can reliably distinguish urine containing as little as 3% DU from natural uranium.

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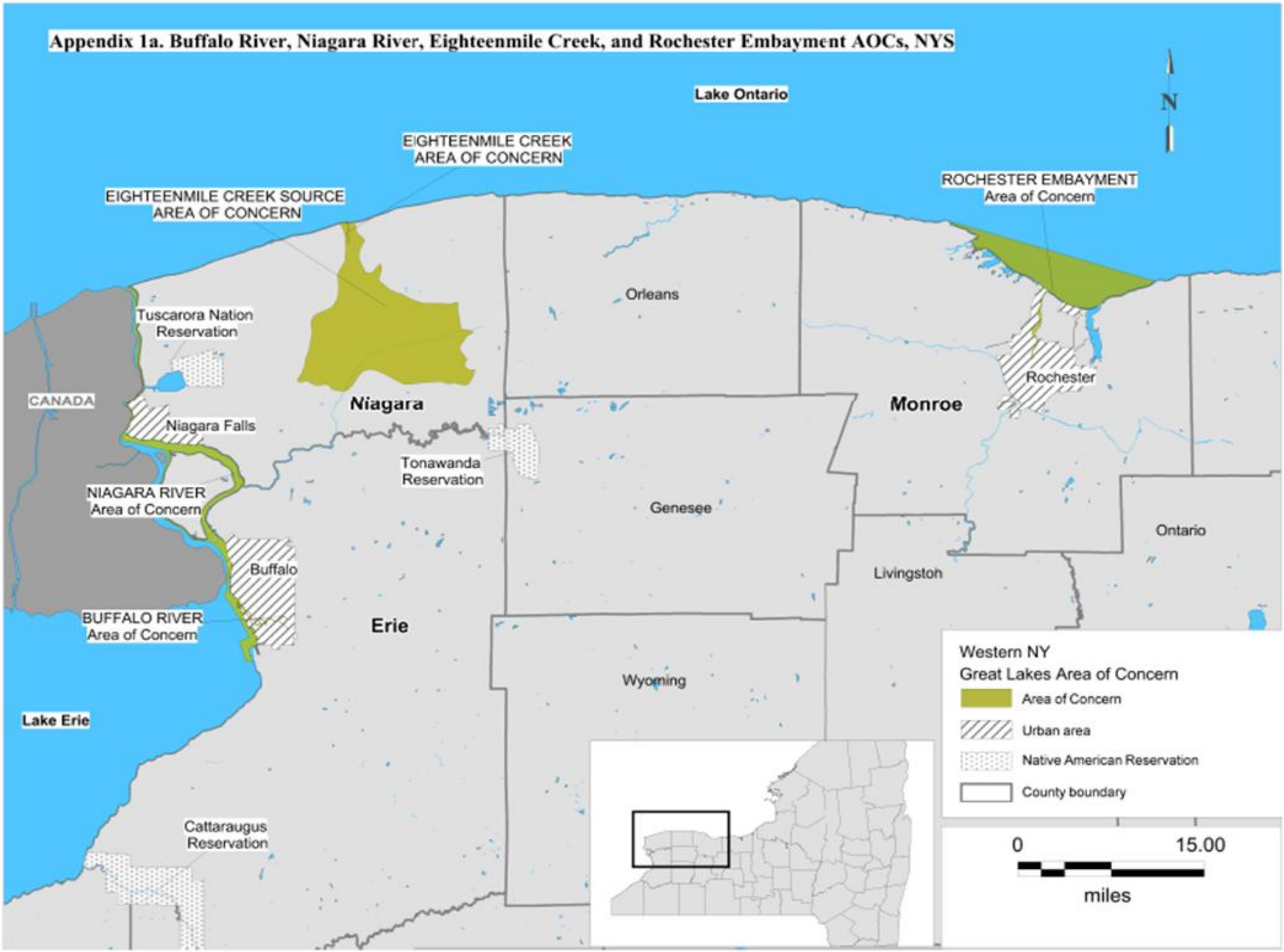
Biomonitoring and Great Lakes

- ATSDR Funded study with NYSDOH EPHT and Wadsworth.
- Areas of Concern (AOC) related to lake contamination with "legacy" chemicals (PCBs, PAHs, Mirex, Declorane)
- Vulnerable populations (sport and subsistence fishermen (ethnic communities - Burmese refugees)
- Study planning completed, participants identified and clinics set up and collected samples of whole blood, serum and urine
- Laboratory assisted EPHT staff with sample collection
- Laboratory analysis is underway for trace element, legacy persistent organic pollutants.

Great Lakes Target Analytes

Analyte	Samples received	Specimen type	Samples Extracted	Samples Analyzed
Organic chemicals				
PCBs (8 required congeners 28, 52, 101, 105, 118, 138, 153, and 180)	606	Blood/Serum	606	
PBDEs (predominant congeners)	606	Blood/Serum	606	In progress
Perfluorinated compounds (PFOS, PFOA)	606	Blood/Serum	606	
DDT/DDE	606	Blood/Serum	606	
Mirex	606	Blood/Serum	606	
Hexachlorobenzene (HCB)	606	Blood/Serum	606	
Toxaphene (Parlar 26, 50)	606	Blood/Serum	606	
Chlordane	606	Blood/Serum	606	
Oxychlordane and trans-nonachlor	606	Blood/Serum	606	
Dieldrin*	606	Blood/Serum		
Dechlorane Plus*	606	Blood/Serum		
Metals				
Mercury (total)	615	Blood		350
Lead	615	Blood		603
Cadmium	615	Blood		603
Mercury (total inorganic)	615	Urine		603
Adjustment measurements				
Cholesterol/triglycerides	615	Blood		
Creatinine	615	Urine		214


Great Lakes Areas of Concern
Great Lakes Basin Boundary
Nipigon Bay
Jackfish Bay
Thunder Bay
Peninsula Harbour
St. Louis River and Bay
LAKE SUPERIOR
Torch Lake
Deer Lake
MICHIGAN
ONTARIO
St. Marys River
Spanish River Mouth
Manistique River
St. Lawrence River
Menominee River
Severn Sound
WISCONSIN
Fox River/ Southern Green Bay
Sheboygan River
LAKE HURON
Bay of Quinte
Collingwood Harbour
Port Hope
MINNESOTA
MICHIGAN
LAKE ONTARIO
Metro Toronto
Oswego River
Hamilton Harbour
Rochester Embayment
White Lake
Saginaw River and Bay
Niagara River
Eighteenmile Creek
Muskegon Lake
St. Clair River
NEW YORK
Milwaukee Estuary
Wheatley Harbour
Buffalo River
Kalamazoo River
Clinton River
Detroit River
Waukegan Harbor
Rouge River
Presque Isle Bay
Grand Calumet River
River Raisin
Ashtabula River
LAKE ERIE
Maumee River
Black River
PENNSYLVANIA
ILLINOIS
INDIANA
Cuyahoga River
OHIO
Legend
U.S. AOCs
Binational AOCs
Canadian AOCs
Areas in Recovery
Delisted Canadian AOCs
Delisted U. S. AOCs
June 16, 2010


Appendix 1a. Buffalo River, Niagara River, Eighteenmile Creek, and Rochester Embayment AOCs, NYS
Lake Ontario
N
EIGHTEENMILE CREEK
AREA OF CONCERN
EIGHTEENMILE CREEK SOURCE
AREA OF CONCERN
ROCHESTER EMBAYMENT
Area of Concern
Orleans
Tuscarora Nation
Reservation
CANADA
Niagara
Monroe
Rochester
Niagara Falls
Tonawanda
Reservation
NIAGARA RIVER
Area of Concern
Genesee
Ontario
Buffalo
Livingston
BUFFALO RIVER
Area of Concern
Erie
Wyoming
Lake Erie
Cattaraugus
Reservation
Western NY
Great Lakes Area of Concern
Area of Concern
Urban area
Native American Reservation
County boundary
0
15.00
miles

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Expanding Capability for Emerging Contaminants

- **Method development for emerging contaminants**
  - Free and conjugated BPA and its substituted forms
  - Different forms of bisphenols (BPS, BPF, BPAF,etc)
  - Bisphenol A diglycidyl ether (BADGE) analysis in urine
  - Benzophenone analysis in urine
  - Benzothiazole and benzotriazole analysis in urine
  - Paraben analysis in urine
  - OH-PAH analysis in urine
- **Participation in inter-laboratory comparison studies**
  - CDC, NIEHS, AMAP
- **Application to other biomonitoring projects and pilot studies**

Biomonitoring Specimen Collection

Blood and Urine Collection

Breath Sampling

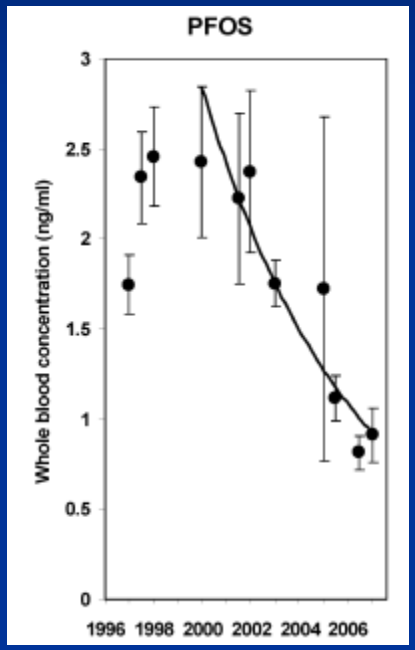
Saliva Collection

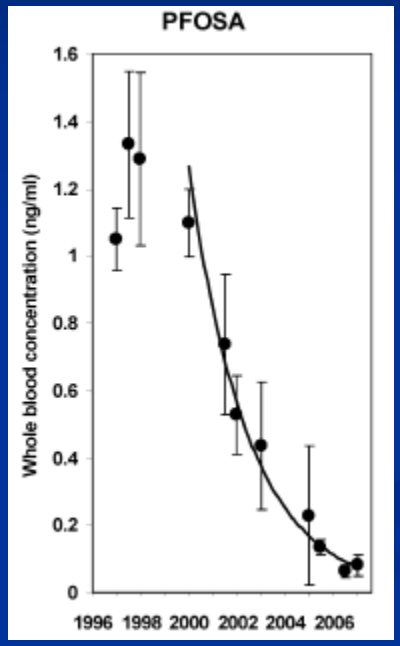
Dried Blood Spots

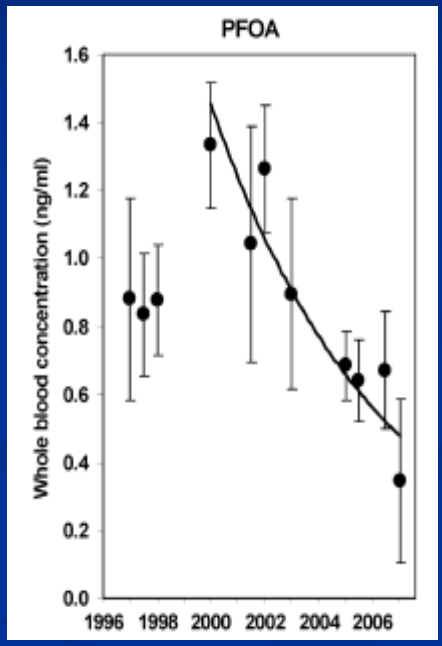
Newborn Screening Blood Samples

- Archived samples provide resource for tracking changing exposure over time of newborn infants
- Methods being developed for several persistent organic compounds and biomarkers
- Possible to automate sample preparation
- Simple sample collection and transport
- Care to reduce contamination of sample during sampling and storage
- Small sample volume available
- Application to other screening studies

Use of Blood Spots in detecting declining levels of PFCs in New York State Infants (1997 – 2007)







Production of these PFCs was phased out 2000 - 2002

Samples composite of 24 spots, 10 samples each date

Spliethoff, H.M., Tao, L., Shaver, S., Aldous, K.M., Pass, K., Kannan, K. and Eadon, G. (2008). Use of Newborn Screening Program Blood Spots for Exposure Assessment: Declining Levels of Perfluorinated Compounds in New York State Infants. Environmental Science and Technology, 42, 5361-5367.

ENVIRONMENTAL Science & Technology

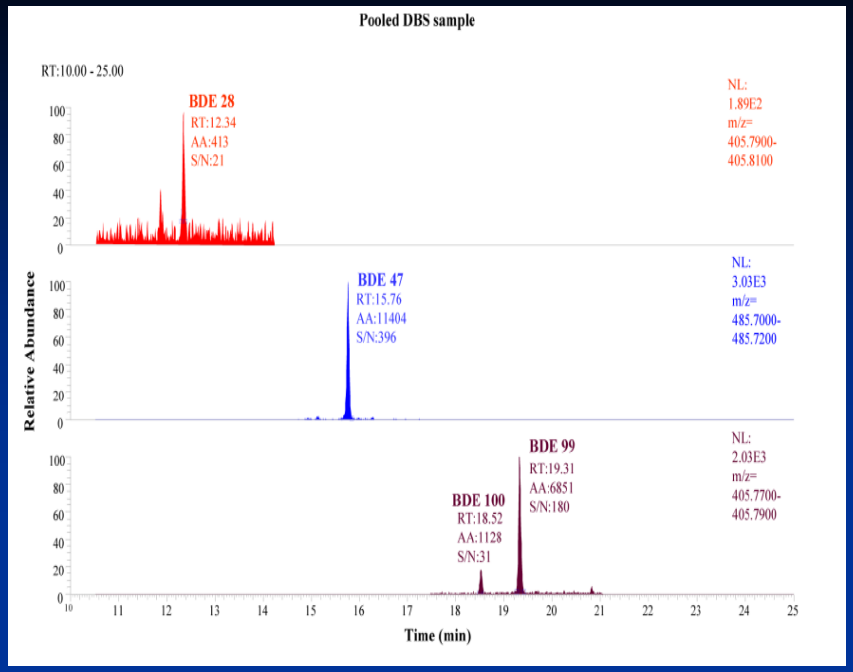
Article

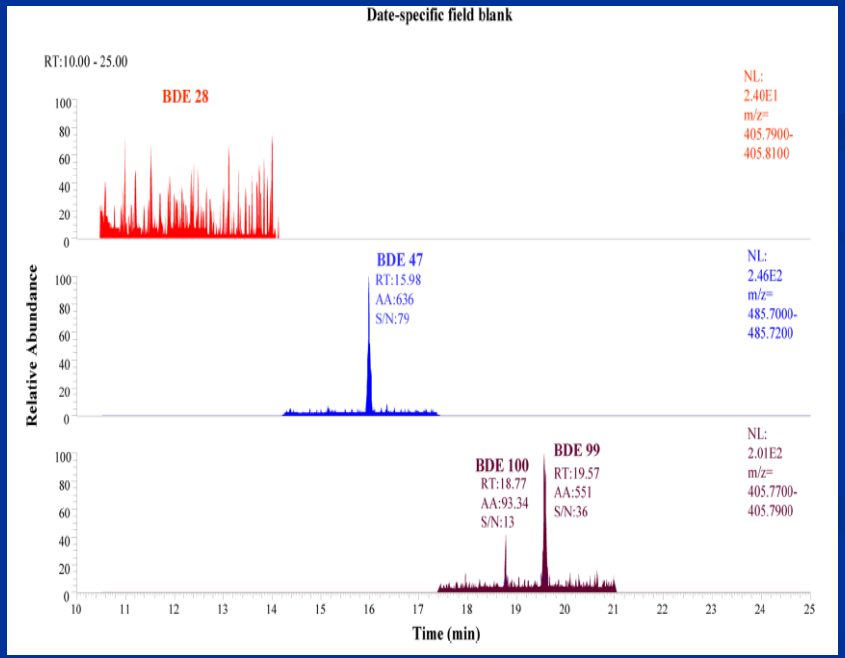
pubs.acs.org/est

Temporal Trends of Polybrominated Diphenyl Ethers (PBDEs) in the Blood of Newborns from New York State during 1997 through 2011: Analysis of Dried Blood Spots from the Newborn Screening Program

Wan-Li Ma,[†,‡] Sehun Yun,[†] Erin M. Bell,[§] Charlotte M. Druschel,[∥] Michele Caggana,[†] Kenneth M. Aldous,[†] Germaine M. Buck Louis,[⊥] and Kurunthachalam Kannan[†,‡,*]

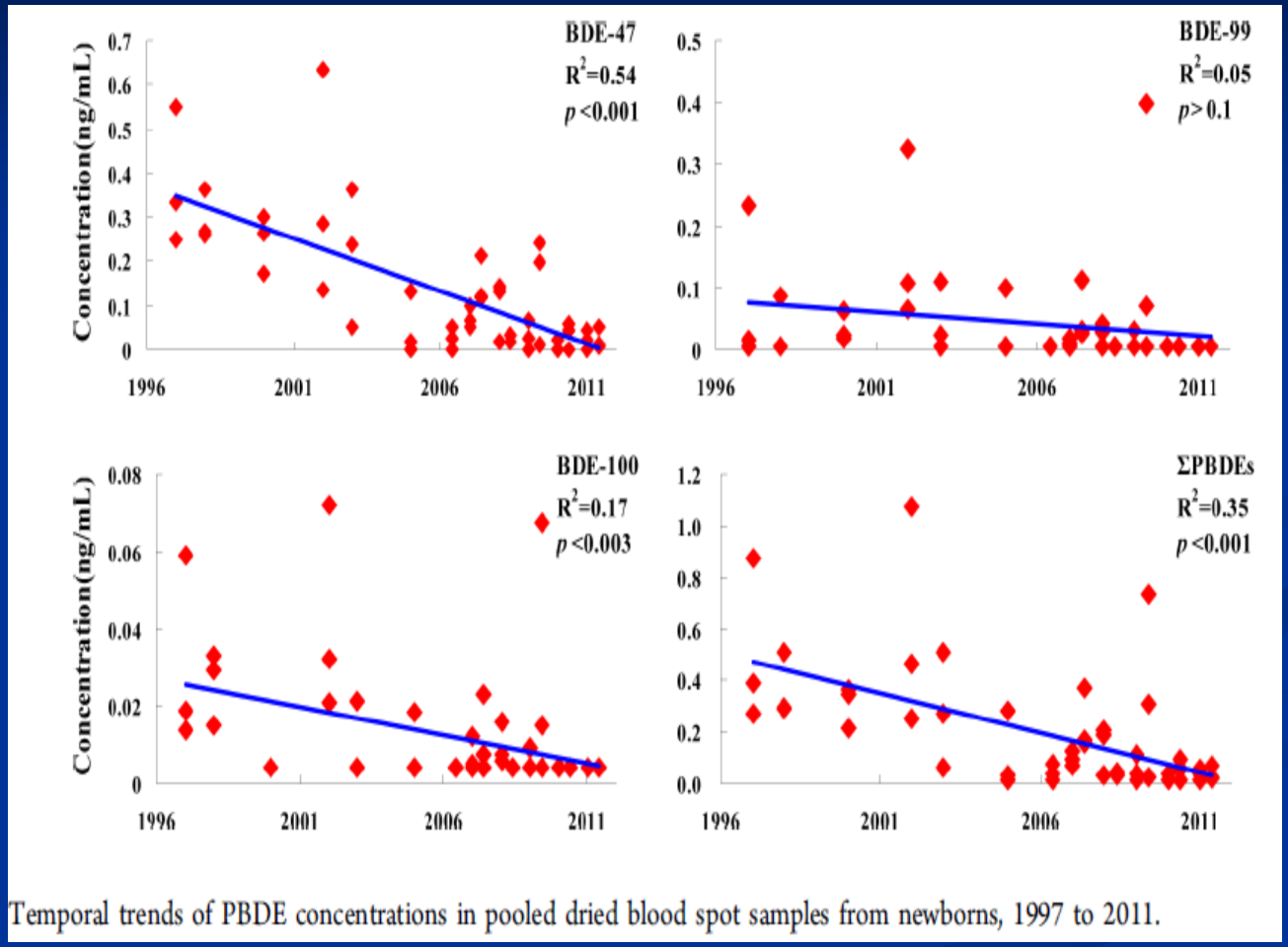
ES&T, 2013,
47, 8015-8021





Extracted ion chromatograms of PBDE congeners found in a pooled dried blood spot sample and a date-specific field blank (Concentrations determined in the DBS sample are: BDE-47, 1.71 ng/mL; BDE-99, 1.03 ng/mL; BDE-100, 0.21 ng/mL; BDE-28, 0.11 ng/mL; other congeners, not detected).

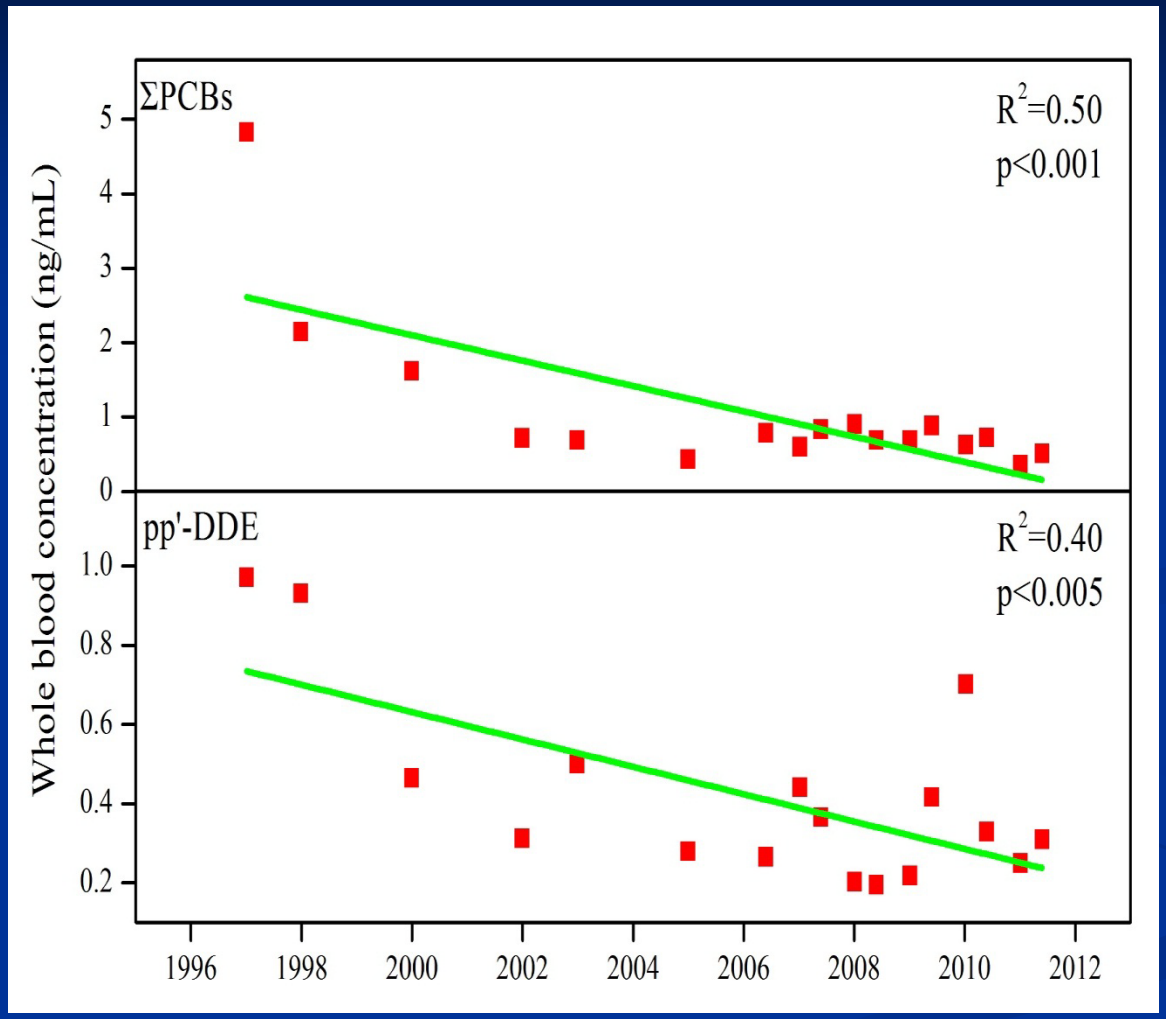
Trends of PBDEs in the blood of newborns in the US



Temporal trends of PBDE concentrations in pooled dried blood spot samples from newborns, 1997 to 2011.

ES&T, 2013, 47, 8015-8021

Trends of PCBs and DDE in the blood of newborns in the US



Other Biomonitoring Activities

- Upstate Kids – blood spot / method for PFCs and BPA is being applied to 3,800 samples. (NICHD)
- Hosted California organics biomonitoring group for 3 days and provided some training on PFCs, phthalates and bisphenol A analyses
- Papers published on biomonitoring projects funded in part through the CDC cooperative agreement. (69 paper s 2009-2014)
- Development of reference materials for trace elements (blood, urine)
- Provided training to several international visiting scientists

Moving Forward - Biomonitoring

- Strengthen the National Biomonitoring Network
- APHL develop a new 5 year plan for Biomonitoring
- Standardization of methods and data reporting formats
- Develop reference materials for method development and validation
- Develop collaborative studies with other states
- Many State PHL have capability to develop biomonitoring studies using LRN-C instrumentation
- Set up more collaborations and joint projects with EPHT/ EPI
- Evaluate other sample collection methods

Next Five Years

- Maintain investment in existing equipment and trained staff
- Continue to monitor background levels of legacy chemicals and those being introduced into current use.
- Continue building a national biomonitoring network or system
- Introduce new technologies

Acknowledgements

- NYS DOH Wadsworth Center
  - Kurunthachalam Kannan
  - Patrick Parsons
- NYS DOH Center for Environmental Health
  - Syni-An Hwang
- NYC DOHMH
  - Wendy McKelvey
  - Daniel Kass
- CDC Cooperative agreement funding
- APHL