Screening of biological tissues for chemicals of emerging concern

John Kucklick

National Institute of Standards and Technology (NIST)

Susan Klosterhaus

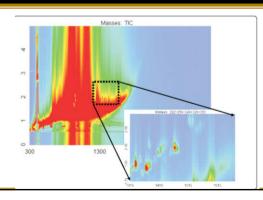
San Francisco Estuary Institute (SFEI)

Nathan Dodder, Keith Maruya Southern California Coastal Water Research Project (SCCWRP)

Euhna Hoh

San Diego State University (SDSU)







Background

- Vast majority of biological monitoring efforts only measure pollutants from a set list
- Recent studies provide evidence for pollutants that likely bioaccumulate but are not monitored
- Rarely do studies incorporate screening of "unknowns" into their design

Objective

- Use two-dimensional gas chromatography mass time-offlight spectrometry (GC X GC TOF) to screen estuarine & marine tissue samples for emerging pollutants
 - Allows for resolution of complex mixtures
 - Growing mass spectral libraries will assist with unknown ID
- Major questions
 - A: Which chemicals have the potential to impact humans and aquatic life and should be monitored?
 - B: What potential for impacts on humans and aquatic life exists due to contaminants in estuarine and marine ecosystems?

Approach

- Year 1
 - Harbor seal sample collection by the Marine Mammal Center (Sausalito, CA)
 - Archived bottlenose dolphin samples provided by NOAA Southwest Fisheries Center (La Jolla, CA)
 - Plan and conduct mussel deployment in SF Bay
 - Method refinement using California Sea lion blubber and serum control materials
 - Apply method to harbor seal and bottlenose dolphin samples (blubber and liver)

Progress to date

- Collaborating with NOAA Fisheries & The Marine Mammal Center to obtain
 - SF Bay harbor seal samples
 - Bottlenose dolphin (inshore SoCal Bight) samples
- Coordinated GC x GC TOF work
 - NIST/Gaithersburg (E. McGaw): human serum screening
 - SCCWRP/SDSU (Dodder/Hoh): sea lion blubber screening
- Shared method development initiated March 2010
 - "Front end" (sample) processing (NIST/SCCWRP/SDSU)
 - "Back end" mass spectral data processing (SCCWRP/SDSU)

Future plans

- Spring/summer: continue method development
 - construct broadscan library
- Fall/winter:
 - apply method to marine mammal samples
 - append library with newly discovered compounds
 - begin method development for mussel tissue
- **2011**
 - Initiate mussel and complete marine mammal analysis
 - append library with new compounds
 - explore use of LC-QTOF
 - First manuscript

Proposed approach: blubber

- Homogenate V: Sea lion blubber from 2001 round robin
- Pressurized fluid extraction
- Minimal cleanup
- Size exclusion chromatography (SEC)

cleanup

- GC × GC TOF compare spectra to NIST library
- Analyze SEC extract pre and post MTBSTFA derivatization

analysis

Proposed approach: Serum or liver

MMCMI: sea lion serum used in 2007 round robin

Microwave extraction method for lipophilics

Normal cleanup for lipophilics (acidified silica, alumina)

 Raw serum, crash protein, remove supernatant, take to dryness and derivatize

cleanup

GC x GC TOF of lipophilic extract pre and post derivatization

GC x GC TOF of derivatized, protein free serum

Compare spectra to NIST library

anaľysis