



BIOLOGICAL RESPONSE INDICATOR DEVICES FOR GAUGING ENVIRONMENTAL STRESSORS	
BRIDGES	
Ecological Risk: New Tools and Approaches Litilized by Superfund Research Program	•
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WHY BIOAVAILABLE ?

• Estimating exposure concentration

• Predicting environmental fate

• Understanding Environmental Factors on Diseases...

• MUST develop new bio-analytical tools to measure exposure • L.S. Birnbaum, EHP, 2010







BEYOND CHEMICAL ANALYSIS...

• Exposure dose (exposure concentration)

- Chemical **mixtures**
- Predicting environmental fate
- Advantage not to "lump" bioavailable processes
 - Insight will depend on *isolating* processes
 - For example $\ensuremath{\mathrm{FIRST}}$ step in aquatic food chain
- o Integration of space-time into health risk framework
 - Ambient rough estimate
 - Bio-monitoring transient estimate
- o Multi-media



PASSIVE SAMPLING DEVICES FOR EXAMPLE: LIPID FREE TUBE (LFT)

- Bioavailability processes include chemical (cell membrane lipophilic ٠
 - character) and physical (pore size ~9.5A) control of contaminant uptake.
- Passive sampling devices (such as LFT) mimic both chemical and physical processes
 - lipophilic membrane character, and
 - pore size ~10A •

- Other types of membranes: ο Polymer film or tubes
 - low density polyethylene 0
 - o silicone or silastic 0
 - polypropylene
- Södergren, 1987 dialysis bag filled with 0 hexane
- o Huckins et al, 1992 developed semipermeable membrane device (SPMD) tube filled with a triolein
- Reviewed in: Namiesnik, J.; o Zabiegalal, B.; Kot-Wasik, A.; Partyka, M.; Wasik, A., Passive sampling and/or extraction techniques in environmental analysis: a review. Anal. Bioanal. Chem. 2005, 381, 279-301



PASSIVE SAMPLING DEVICES DEPLOYED AT SUPERFUND SITES

• **PSD theory:** our LFTs are constructed of sealed polyethylene lay flat tubes which represent an organic lipid membrane. Like a membrane, LFTs discriminate against particulate bound material. As *in situ* time integrative passive samplers, LFTs may be deployed for extended periods of time to sequester contaminants. This overcomes potential issues such as detection limits, bioavailable fraction collection and fluctuating contaminant concentrations.





















SOURCES OF PAHS IN THE ENVIRONMENT • Biogenic (minor)

• Petrogenic

- Generated by geological processes
 - NATURAL- seeps, coal outcrops
 - ${\sf o}$ ANTHROPOGENIC –fossil fuel release $~(0.2\mathchar`{O} PAHs)$

• Pyrogenic

Generated by high temperature combustion of organic matter
NATURAL –forest fires, piare fires

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• ANTHROPOGENIC- wood stoves, car exhaust, coal tar



EXAMPLES: PASSIVE SAMPLING DEVICES IN GULF OF MEXICO PRE-, POST-IMPACT DEEPWATER HORIZON BLOWOUT

- 4 sites FL, AL, MS, LA
- o Early, May, Early June
- *Paired* Air and Water
- o Paired Chem- and Bio-
- ${\bf o}$ Grande Isle hit by oil



BEYOND, NEXT CHEMISTRY

• Expanded PAHs

- 302 isomers
- alkylated

o Oxygenated PAHs

- facilitated by dispersant
- more bioavailable
- as toxic as PAHs
- Screening method imperative for mixture assessment
 - 1,200+ analytes



PAHS	Flair	ALair	MSair	LAair	FLwater	ALwater	MS water	LA water
Vapntnalene	x	X	x	X	X	x	x	x
Vaprinalene-Zmeinyi	v	x	X	X	X	X	X	X
Napininalene-mileinyi Filoranthene	× ×	~	×	×	×	X	×	×
Renzolalanthracene	Ŷ	×	nd	nd	x	×	×	×
Benzolalovrene	nd	nd	nd	nd	nd	nd	×	nd
		3	•			R		







SITE-SPECIFIC HAZARD QUOTIENT PROFILES

• Divide the concentration by the chronic toxicity value

- (Neff et al, Integr. Environ. Assess. Manage., 2005)
- Normalizes the concentrations by relative toxicity
- Provides a more realistic estimate of the relative contribution of each chemical to the observed biological responses





INTEGRATED ENVIRONMENT AND HEALTH

 embryonic zebrafish exposed to environmental contaminant mixtures obtained from passive samplers deployed in a model river system show site-specific biological responses that can be associated with differences in the chemical profiles of the sites





CHEMISTRY + BIOLOGY INTEGRATED ENVIRONMENTAL AND HUMAN HEALTH

- Adding passive sampler concentrations to health risk models increases spatial and temporal precision, improves risk estimates, reduces animal collection, and reduces costs.
- Passive samplers can supplement fish/shellfish data in health assessments to provide specific spatial and temporal contaminant information and thereby help public health and remediation professionals more precisely evaluate and relate exposure and risk

INTEREST IN PASSIVE SAMPLING DEVICES PSD PROVIDED TO SBR RESEARCHERS UPON REQUEST o Using PSDs for Risk

Passive Sampling Devices Attributes:

- sequesters specific fraction (dissolved, bioavailable)
- comparative data rapidly developing •
- iterative (captures episodic events) •
- . composite without mechanical equipment or on-site power requirements
- no seasonal issues with PSD compared w/ $% \left({{{\rm{PSD}}}} \right)$ • organisms
- very low detection limits possible with relative . analytical ease
- minimizes decomposition or chemical change transport/storage
- does not lump biological processes
- Less expensive .
- Easier to replicate spatially ٠
- Greener technology
- adequately mimics biological
- ٠ not as many negatives as organisms with more positives than grabs...
- . in-situ assessment of environmental contaminants that are most biologically relevant
- have ability to use in bio-assays •
- easily able to do exposure concentration dependent bio-assays

Assessment

o Advantages

- Inexpensive
- · Easy to analyze
- Site specific
- Bio-available fraction ٠
- No metabolic activity
- Nondestructive ٠




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Ecological Factors Controlling Mercury Bioaccumulation in Aquatic Food Webs

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Toxicity of MeHg

In Humans: >95% retained from diet

Main organs affected: •Brain •Kidney •Fetal CNS

Effects: Impairs hearing, speech, vision, gait

Most damage thought to be irreversible.



Mad Hatter's Syndrome 1800's

Minimata Disease 1956

Chemical Forms of Hg

- Elemental Hg⁰
 Mostly atmospheric
 Long residence time 0.5-2 yrs
- Oxidized Hg²⁺
 Dominant form in atmosphere and water
 Reactive gaseous Hg (RGM)
 Particulate Hg (PHg)
- •CH₃Hg⁺ monomethylmercury (MeHg)
 - •Toxic form
 - •Bioavailable form













Lake Characteristics						
	Variable	Range				
AND AND	Lake area	5.5 – 902 hectares				
	Watershed Area	0.9 – 799 hectares				
	Maximum Depth	2.0 – 20.9 meters				
	рН	6.0 - 9.3				
		54				

Field Sampling and Sample Analysis



- Trace metal clean technique
- Plankton metal and taxonomy samples (45-202 and >202 µm)
- pH, TN, TP, DO, Cond., DOC, Chlorophyll
- Calculated variables (BMF, Food web structure) 55

Metal Analysis: Dartmouth Trace Element Analysis Core

- Acid digestions
- High resolution ICP-MS (Trace Metal Lab Facility)
- Hg analysis via cold/vapor ICP-MS









Variable Category	Variables	NIEHS	REMAP VT- NH	EMAP	ME REMAP
Physical	Lake area Watershed area Depth (max.) Elevation	X X X	x x x x	X X (WLR) X X	x x x
Chemical	pH Alkalinity DOC SO4 Conductivity Total P Total N N:P	x x x x x x x x	X X (Epi ANC) X (Epi DOC) X (Epi SO4) X X	X X (ANC) X X X X X X X	x x x
_anduse	Population Disturbed Residential Hay/Perm. Past, Comm/Ind/Transp. Forest Wetland Road density	x x x	X (911 count) X X X (Forest/Wetl.)	X X (AG) X (URB) X X X X	X
Ecological	Linkages Max. chain length Chorophyll Algal biomass Zoop. abundance Zoop. Biomass	× × × × × × ×	X X X	x x	x x
Hg conc.	Aqueous Zooplankton	XX	X (Epi THg) X		

Common Variables Spearman Rank Correlation, P<0.05					
Variable Category	Common Variables	Relationship to Hg in Fish			
Physical	Lake area (3/4) Watershed area (2/3)	(+)			
Chemical	pH (3/4) ANC (alkalinity) (3/4) Conductivity (2/4) SO4 (2/2) Nutrients (2/3)	(-)			
Land Use	Residential, Agricultural, Commercial Industrial, Roads, Disturbed (3/3)	(-)			
Ecological	Zooplankton abundance (3/4)	(-)			
61 Bonferroni Adjustment Chen et al. 200					

2. Experimental Approach in Mesocosms to Investigate Biomass Dilution and Trophic Transfer











3. A Field Approach in Coastal Marsh Ecosystems to Investigate Feeding Pathways of Trophic Transfer









Sampling in the Field





Biotic Samples:

Primary consumers: Snails, Mussels Secondary consumers: Killifish, Green Crabs

Metal Analysis

-whole organisms freeze dried & homogenized

-Hg speciation by isotope dilution purge and trap GC-ICPMS at Dartmouth

Isotope Analysis

-separate set of samples collected in field simultaneously -whole organisms freeze dried and homogenized $\delta^{13}C,\,\delta^{15}N$






















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