Occurrence, Fate, Transport, and Impacts of Contaminants of Emerging Concern in Riverine Systems

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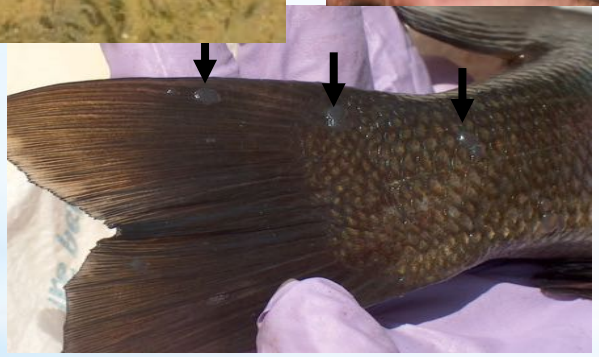
U. S. Geological Survey

Fish Kills and Skin Lesions

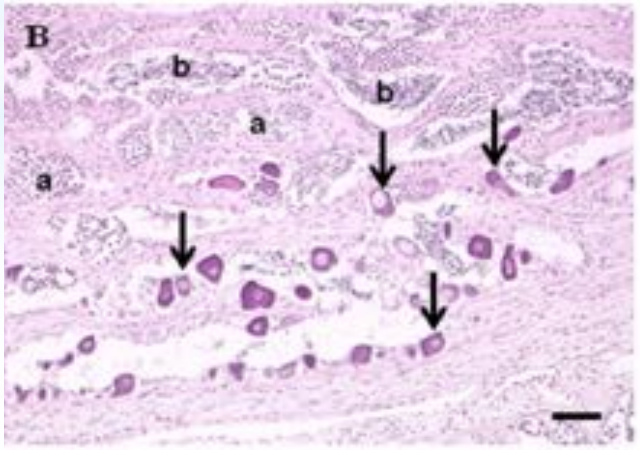
- Adult bass and other species in the spring around the spawning period
  - 2003 - South Branch Potomac River
  - 2004 - Shenandoah
  - 2009 - Monocacy
- Young of year smallmouth bass in the summer
  - 2005 - Susquehanna

Findings of Fish Kill Investigations Adults

- Multiple Co-infections – nothing consistent
- Bacterial, parasites, viral



- High prevalence of intersex,
- Vitellogenin in male fishes



Mortalities of YOY Smallmouth Bass

- Coinfections – fish only 2-3 months old

- *Aeromonas hydrophila* and other motile Aeromonads
- *Flavobacterium columnare*
- Largemouth Bass Virus
- Trematodes
- Cestodes
- Myxozoan parasites

Early Findings

- Co-occurrence
  - indicators of exposure to estrogenic compounds
  - Indication of immunomodulation/reduced disease resistance

- Suggested the same contaminants and/or environmental stressors responsible for both

Smallmouth Bass as Bioindicators

- Widespread – allows for geographical comparisons
- Top predator – bioaccumulation and biomagnification of some chemicals
- Important recreational species and so lesions raise concern of the public and resource managers
- Are a sensitive species, particularly to estrogenic chemicals

Adverse Effects Monitoring

- **Utilize wild fish species – often in response to observed fish health issues**
- **Responses incorporate the variety of stressors – chemical, environmental, infectious**
- **Not all fish are created equal – evaluating multiple species can provide additional insights**

Complexities of Chemicals of Emerging Concern in Wild Populations

- Many were produced to have a biological effect and so may affect nontarget organisms at very low levels
- Endocrine/Immune systems - chemical communication and feedback mechanisms
- Lack of classic dose response curve – hormesis
- Multiple contaminant exposure routes - water, sediment, food, maternal (yolk sac)
- Short term exposure at sensitive life stages can have long term effects
- Many chemicals – may have additive, synergistic

Suite of Biological Indicators

- Morphometric and necropsy-based
  - Comparisons based on sex, age,
  - Identifies visible abnormalities,
  - Condition factor/relative weight, hepatosomatic/gonadosomatic indices
- Blood/Plasma
  - Hormones – estrogen, testosterone, thyroid
  - Vitellogenin
- Histopathological
  - Diagnose causes of gross observations, identify emerging pathogens, identify specific effects of contaminants, with image analyses quantify parasites, macrophage aggregates
- Molecular
  - mRNA for reproductively related genes (vitellogenin, estrogen receptors), immune system indicators (TGF-β, hepcidin), contaminant-related (CYP1A, oxidative stress), stress (glucocorticoid receptors)

What We Learned from the "Historic Summary"

- Bass are very sensitive to estrogenic endocrine disruptors in agricultural watersheds
- Did not see a relationship with disease or indicators of estrogenic exposure (intersex, vitellogenin) with wastewater treatment effluent
- See considerable spatial variation as well as temporal variation monthly and yearly in total estrogenicity as well as fish health indicators
- Hard to make any conclusions as to "cause" based on the chemical data available

Correlations with Landuse/Chemicals and Intersex

- Both the Susquehanna and Potomac – correlations with % agriculture upstream
- Potomac (7 site spring study) – correlations with % agriculture, animal feeding operations, animal density, poultry houses

- Susquehanna (low flow, summer) – estrone
- Potomac (spring, moderate flow) – atrazine, metolachlor (water), hormones/plant sterols (sediment)

Factors to Consider

- **Temporal nature of chemical exposures – climatic and other factors that influence exposure**
- **Exposure pathways during critical life stage**
- **High concentrations when the most vulnerable life stages are present may be important**

Biomarkers of Exposure Estrogenic Contaminants

- Intersex
  - most likely induced very early
  - exposure during sexual differentiation increases sensitivity later in life
- Vitellogenin in males
  - Plasma Vtg - indicative of recent exposure (days to months)
  - Vtg gene transcripts – hours to days

Induction of Testicular Oocytes Experimentally

- Estradiol
- Ethinyl estradiol – synthetic estrogen
- Nonylphenol
- 4-tert-pentylphenol and octylphenol
- DDT
- Bisphenol A
- Phytoestrogens/Isoflavones – equol, genistein
- Metformin – diabetic drug
- Atrazine - amphibians

Gene Expression – Great Lakes Sites

Parameter	Parameter	Spearman rho	p value
Male			
Bass (both species) testicular oocyte severity	Plasma vitellogenin	0.3397	0.0011
	Hepatic vitellogenin transcripts	0.2462	0.0193
	Estrogen receptor α	0.3866	0.0002
	Estrogen receptor β2	0.3416	0.0010
	Androgen receptor β	-0.3256	0.0017
	Phosphoenolpyruvate carboxykinase	-0.2370	0.0245

USGS Chesapeake Bay Endocrine Disruption Study Agricultural Integrator Sites

- 4 - 6 sites where monthly to biweekly water samples, plus storm events, are collected and analyzed for hormones, pesticides, phytoestrogens and total estrogenicity from Nov. 2014 to present
- Sediment samples in spring and fall
- Tissue samples for contaminant analyses
- Adult fish are collected in the spring prespawn (2013-2017) and at some sites in the summer and fall
- YOY (1-3 months of age) are collected in early summer (2013-2017)

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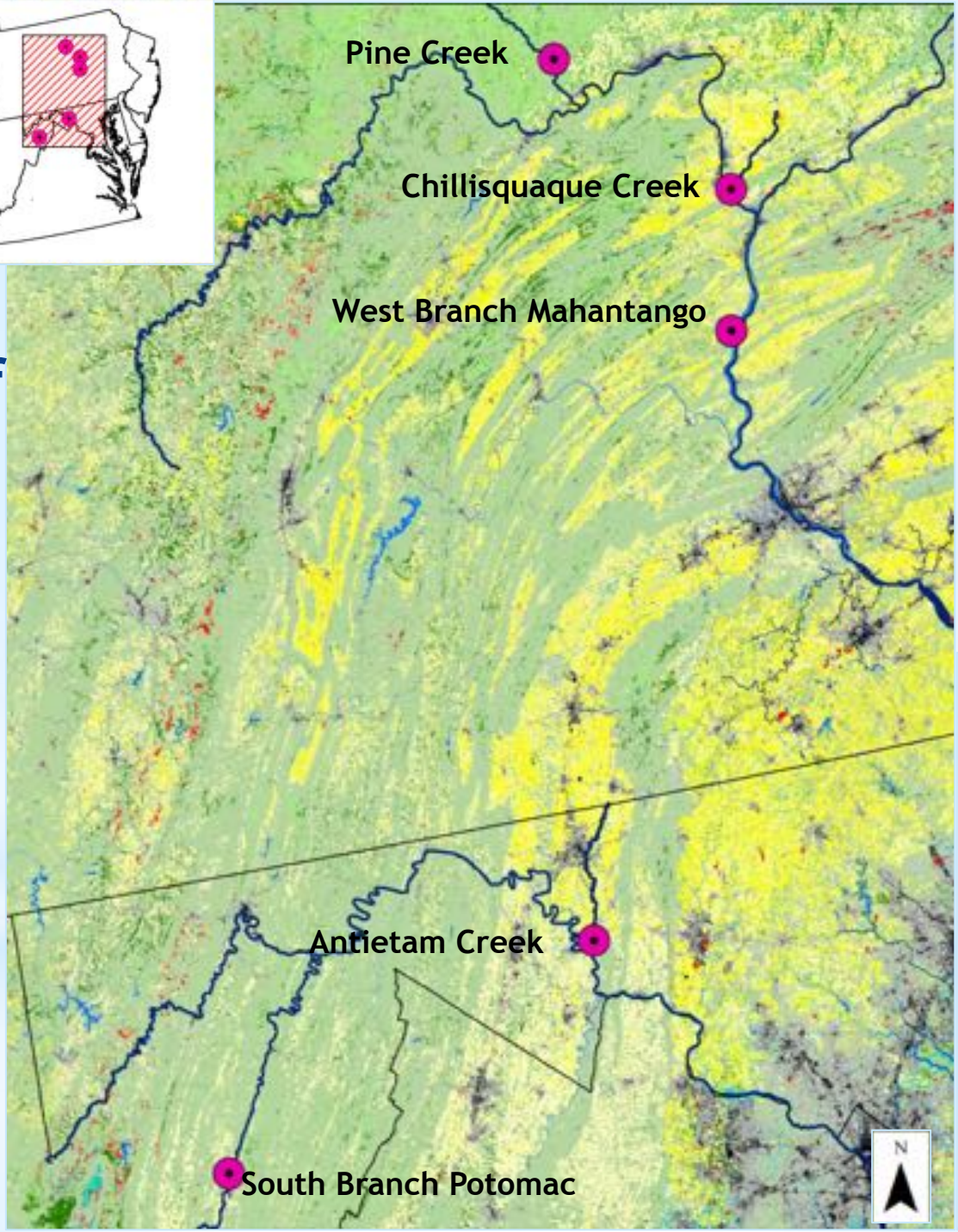
Location of Integrator Sites



Integrator Site Water Samples

- Analyzed for hormones, phytoestrogens and pesticides

- Analyzed for 130 pesticides or degradates (GC)
- Detected 30 at least once
- Most only occasionally detected
- Atrazine, simazine, metolachlor – most common; fipronil, metalaxyl next most common

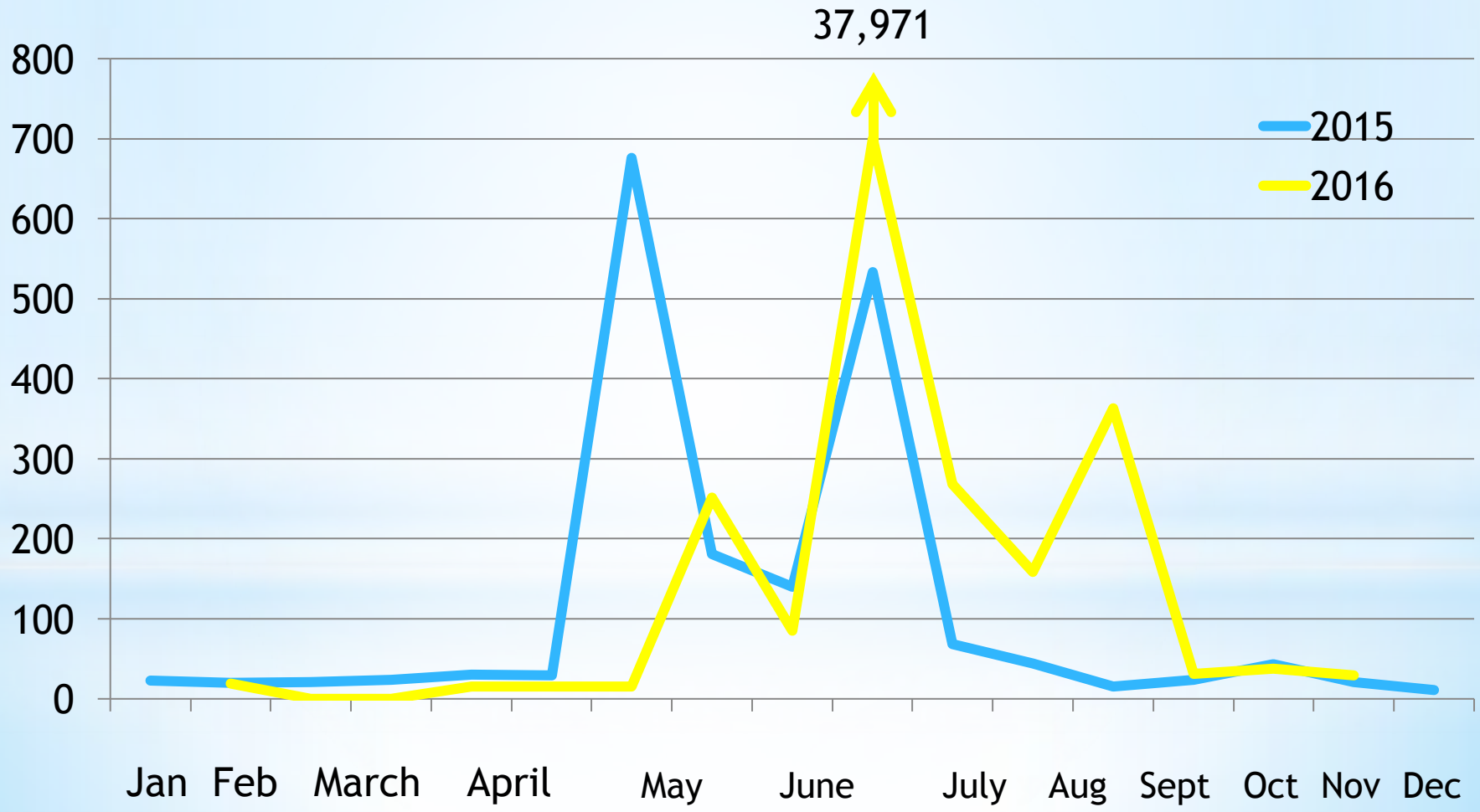
Pesticides Detected

← Herbicides → Insecticide Fungicide

Site	Total Samples	Atrazine	Simazine	Metolachlor	Fipronil	Metalaxyl
Pine	43[a]	19[b] (1[c])	1 (0)	12 (1)	0 (0)	1 (0)
WB Mahantango	47	41 (17)	12 (1)	34 (9)	2 (0)	2 (0)
Chillisquaque	36	34 (9)	14 (3)	32 (9)	0 (0)	7 (0)
Antietam	42	41 (17)	36 (3)	39 (5)	11 (0)	0 (0)
SB Potomac	41	18 (0)	3 (0)	10 (1)	0 (0)	1 (0)

[a]Total number of water samples from 11/2014 through 7/2017
[b]Total detects
[c]Detects above the 100 ng/L

Chillisquaque Atrazine Concentrations (ng/L)



Key Exposure Periods

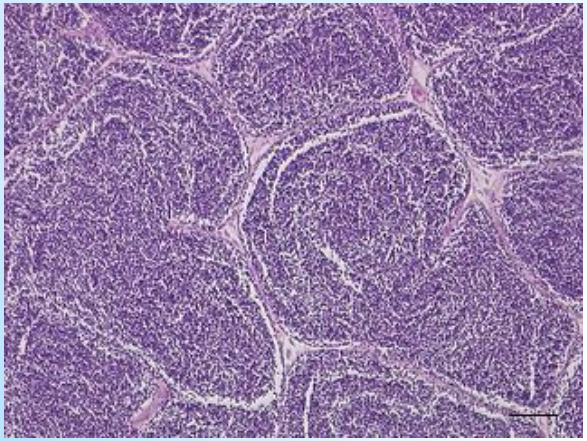
Nest/eggs – sediment/water

Water, maternal, sediment

Water food, sediment

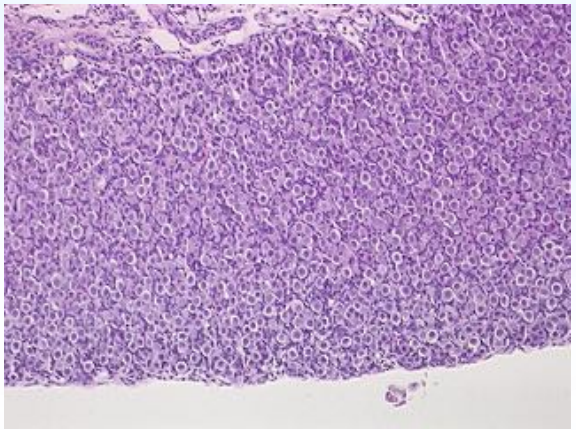
Final maturation, sperm quality

April – May



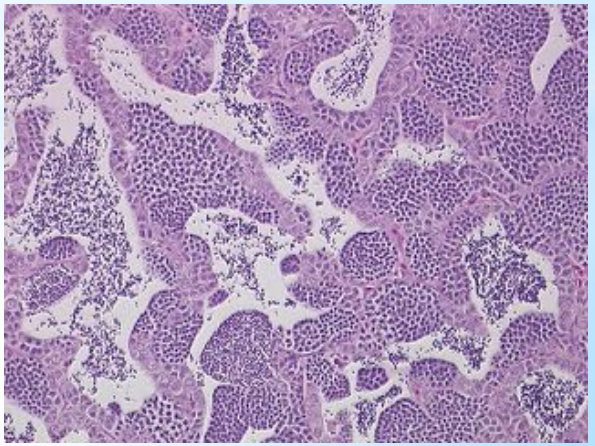
YOY – sexual differentiation and organ development

June – July



Adults - recrudescence

August – Dec - March



Water Versus YOY Tissue

- Bifenthrin (4) and pendimethalin (6) only occasionally detected in water samples from all sites

- Bifenthrin (insecticide) detected only once in the water at Chilli
- Pendimethalin (herbicide) not detected at all in water samples in 2015

YOY Whole Body Pesticides(ng/g; ppb) Chillisquaque

Fish	Bifenthrin	Metolachlor	p,p'DDD	p,p'-DDE	Pendimethalin
1				6.3	7.3
2	0.7		1.0	3.4	11.6
3	0.3	0.5	1.0	2.4	4.4
4	0.5	0.6	1.1	2.4	5.2
5	0.9			3.7	9.4
6					20.1
7	0.6	1.0		3.5	7.6
8					14.5
9	1.6	1.4	1.5	3.4	14.1

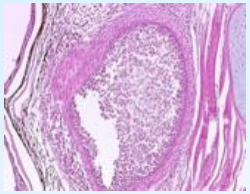
Current Work

- Compiling all the data at these sites – 2013-2017
  - Chemical – water, sediment, tissue
  - Biological – adults and YOY

- Geospatial information – Dan Jones
  - Landuse
  - Hydrology/climatic factors
  - Point and nonpoint source information
  - Pesticide usage etc.

Integrative Research
Megan Schall/Ty Wagner PSU

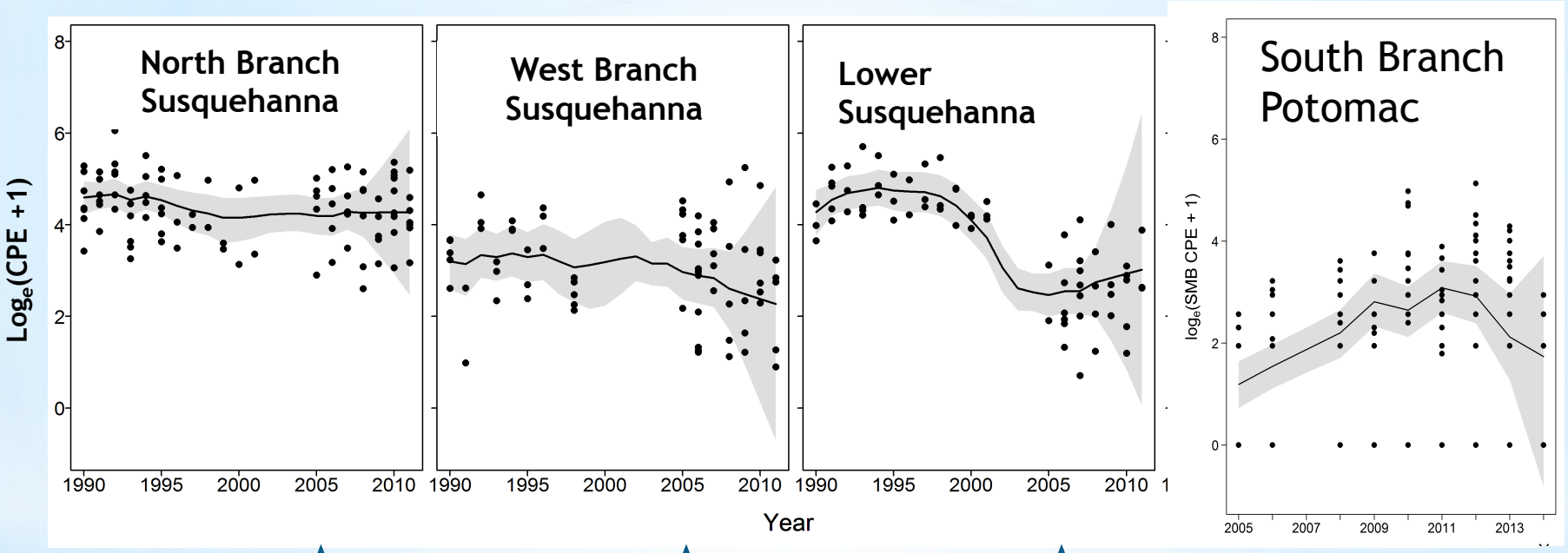
* Fish Health
  * Histology (tissues)
  * Pathogens and Parasites
  * Contaminants
  * Molecular



* Fish Ecology
  * Abundance
  * Population structure
  * Spatial movement ecology/life history

- Environment
  - Land use
  - Water quality
  - Contaminants

Population Trend Analyses



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