Prioritizing organic waste chemicals and locations of ecological concern in sediment from Great Lakes tributaries

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United States Environmental Protection Agency

Great Lakes Restoration

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A fundamental challenge with assessment of environmental chemistry results

Thousands of potential contaminants

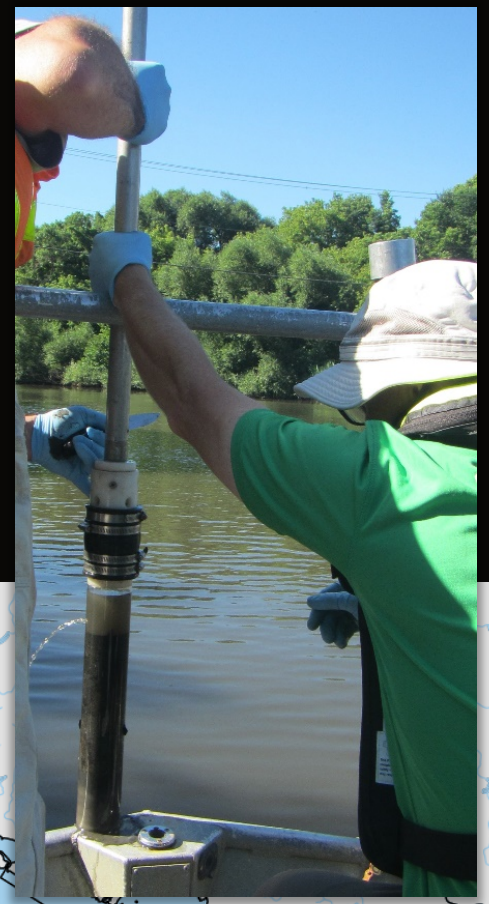
- Improved analytical techniques
  → Detection of tens or hundreds of chemicals/site
- Difficult to identify the chemicals of greatest concern

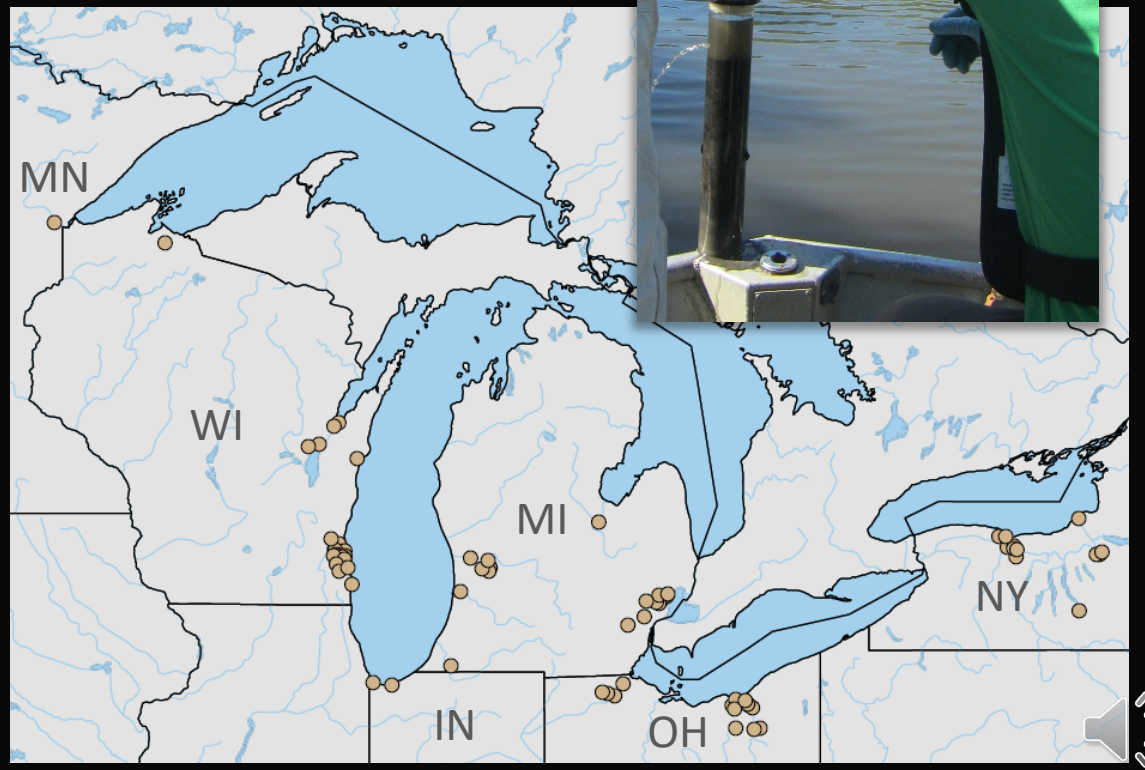
Prioritization methods are needed

- Chemical prioritization
  - Which detected chemicals are biologically relevant?
- Site prioritization
  - At which sites are the biologically relevant chemicals present?
  - At which sites could risk be increased by co-occurrence (mixtures)?

Sediment sampling in Great Lakes tributaries

- 71 locations (26 watersheds), wide range of
  - drainage areas (3.5 - 16,300 km^2)
  - land uses (0.7 - 100% urban; 0 to 90% agricultural)
  - population densities (2.8 - 2,260 people/km^2)
  - wastewater contributions (0 - 48% of streamflow)
- Cores 6” deep, composited
- Targeted fine sediments
- Analyzed for 87 organic waste chemicals (OWCs)
  - antimicrobial disinfectants, antioxidants, detergent metabolites, dyes, fire retardants, flavors/fragrances, fuels, herbicides, insecticides, PAHs, plasticizers, solvents, sterols





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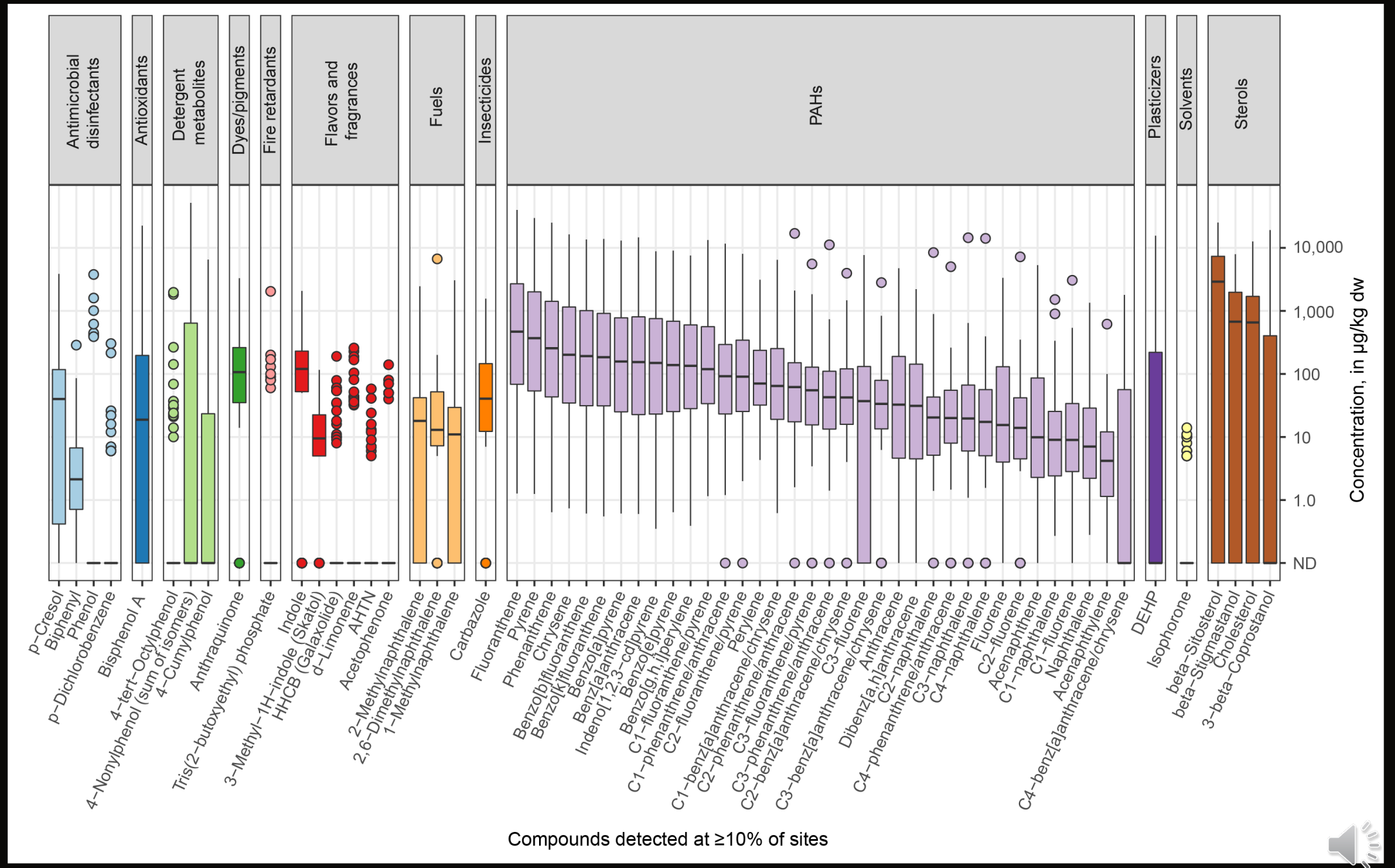
Chemical concentrations in sediment

Which chemicals are of greatest concern biologically?



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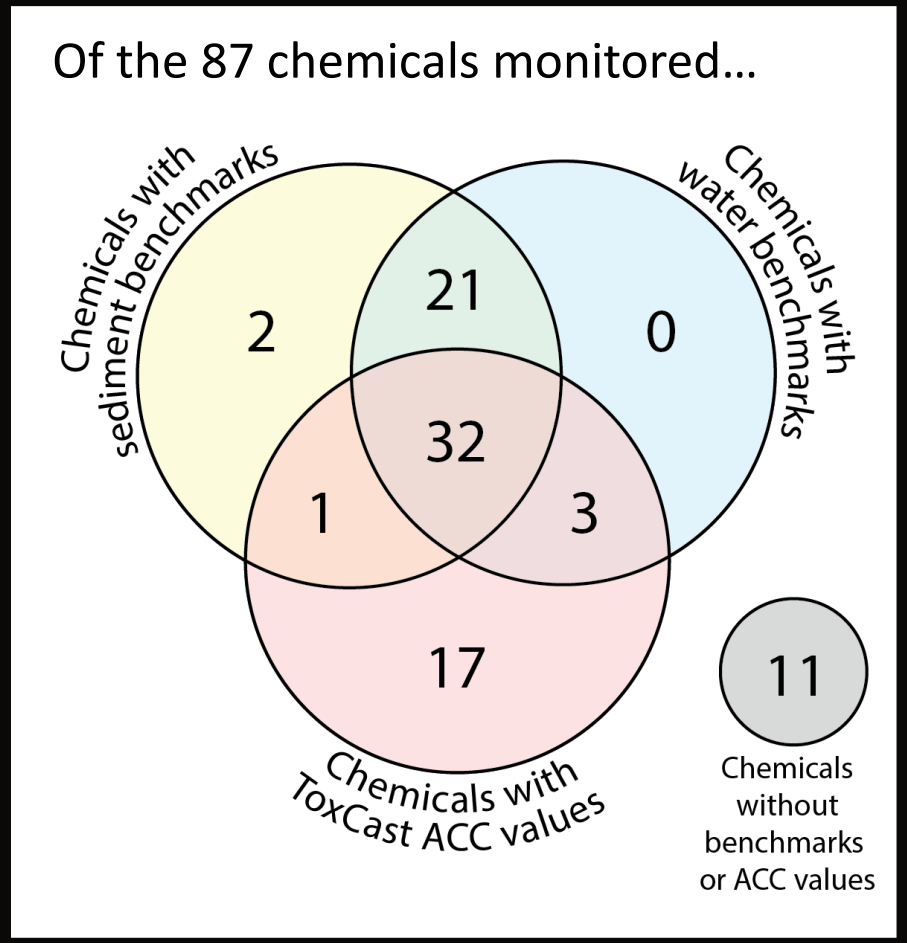
Chemical prioritization

Multiple risk-based approaches:

- Sediment quality benchmarks
- Water quality benchmarks
- ToxCast benchmarks (“ACC values”)

Benefits:

- Maximize the number of chemicals screened
- Strengthen common conclusions



Chemical prioritization

- Sediment and Water Quality Benchmarks
  - Established benchmarks from USEPA, Canadian Council of Ministers of the Environment, etc
  - Porewater concentrations estimated from sediment concentrations, partitioning coefficients, and the fraction of organic carbon

- $Toxicity\ Quotient\ (TQ) = \frac{Measured\ concentration}{Benchmark\ concentration}$

Chemical prioritization

- ToxCast benchmarks ("ACC values")
  - EPA high-throughput screening database
  - Over 9,000 chemicals in more than 700 assay endpoints covering a broad range of cellular responses (estrogen/androgen receptors, enzyme activity, etc)
  - Biological pathways influenced
    - Link to Adverse Outcomes
    - Additive effects of chemical mixtures

- ***ToxEval*** **R Package:**
  - http://usgs-r.github.io/toxEval/index.html
- ***ToxMixtures*** **R Package:**
  - For release in 2021

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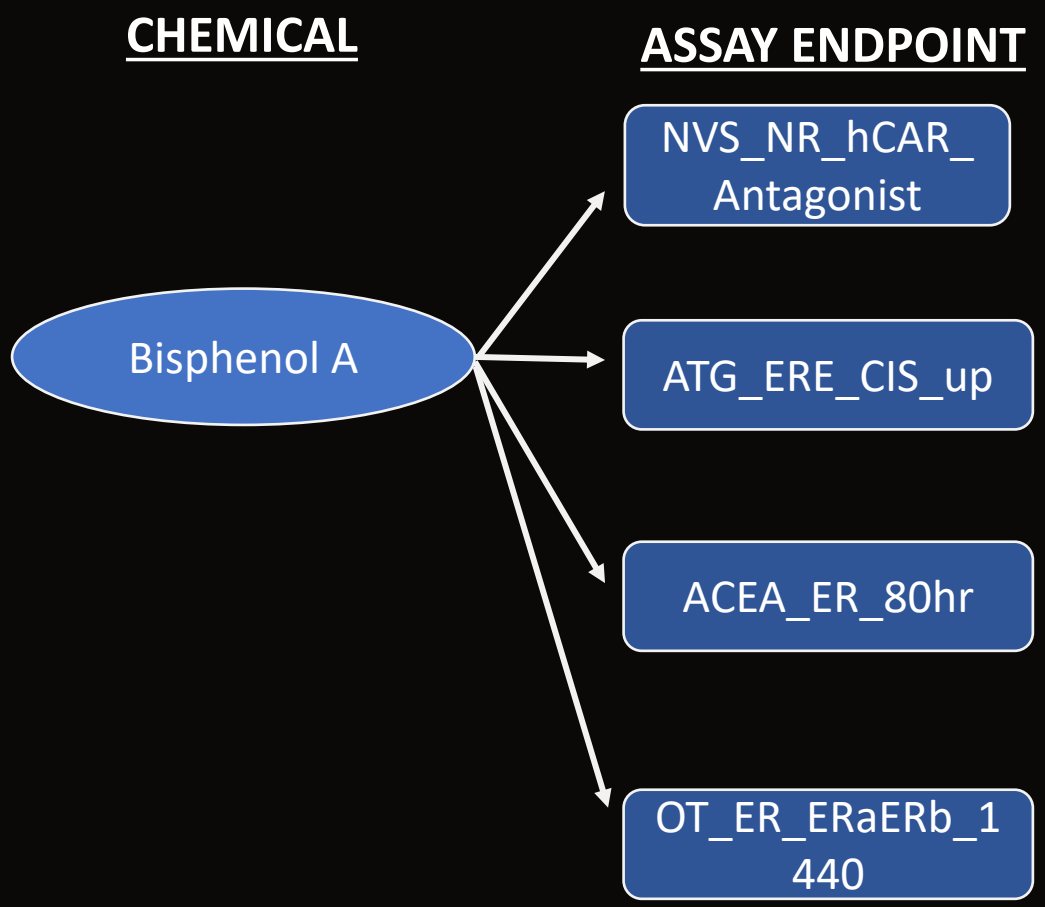
Chemical prioritization

Example of ToxCast data



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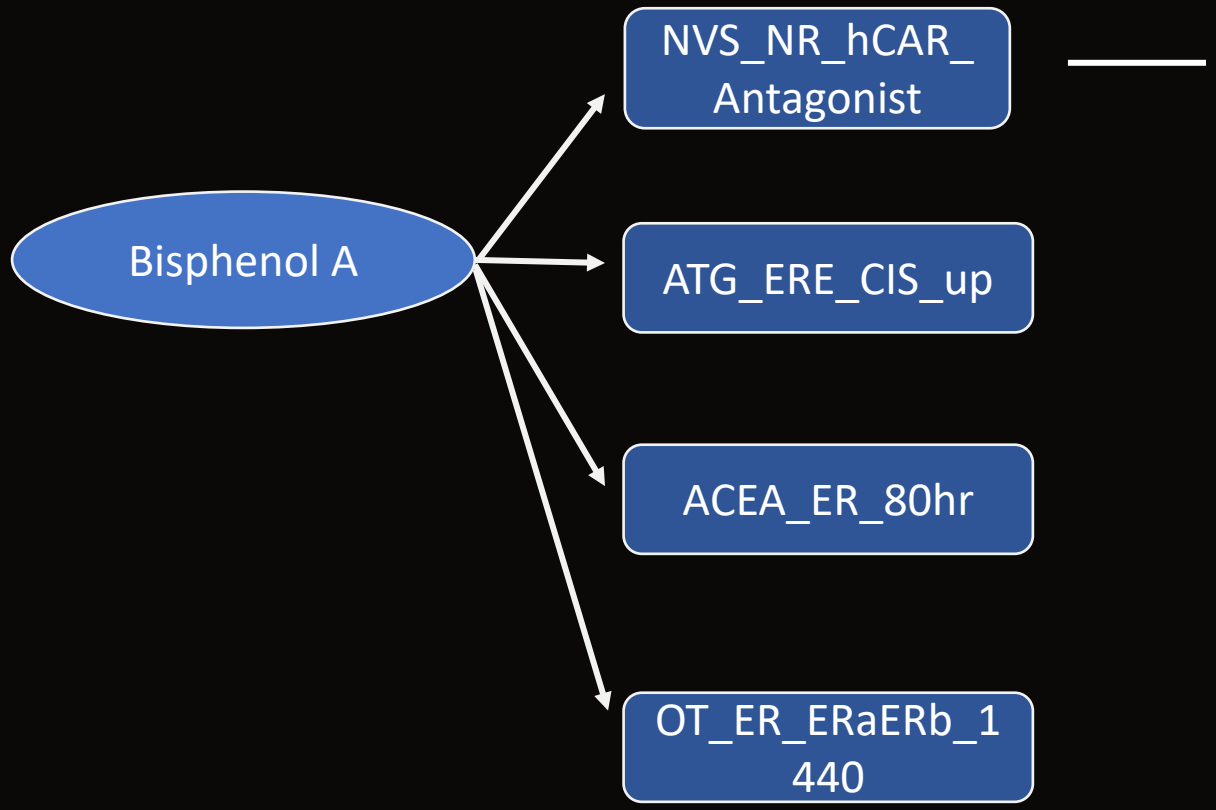
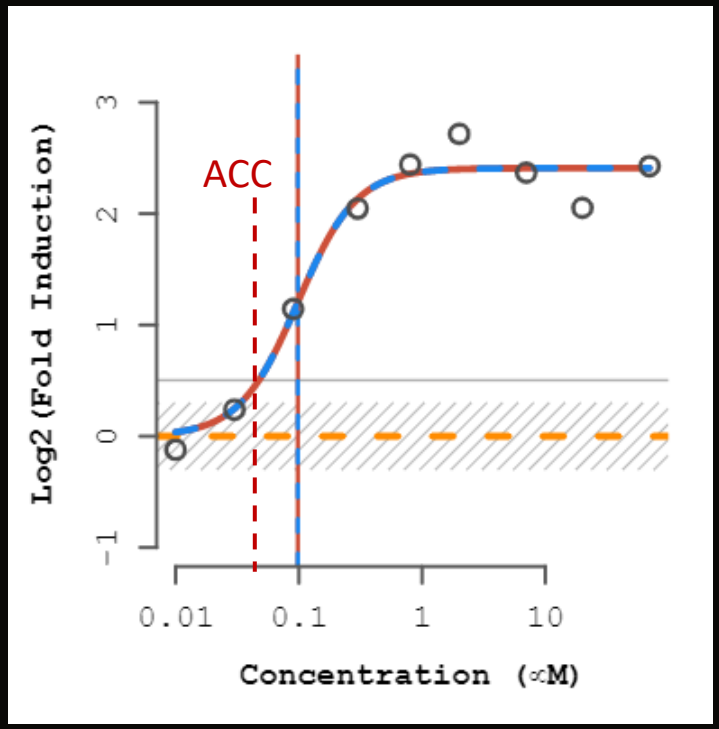
Chemical prioritization

Example of ToxCast data

CHEMICAL

ASSAY ENDPOINT





Assay dose-response curve
-> Activity concentration at cutoff (ACC)

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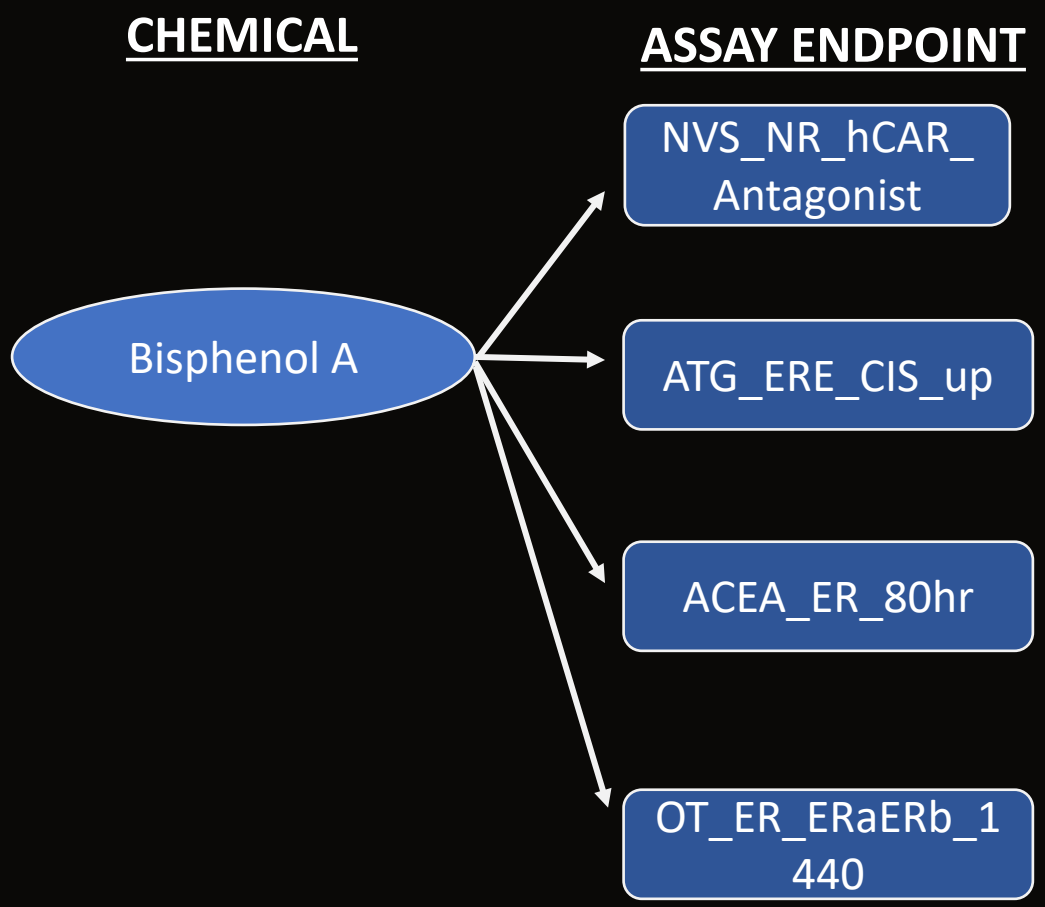
Chemical prioritization

Example of ToxCast data



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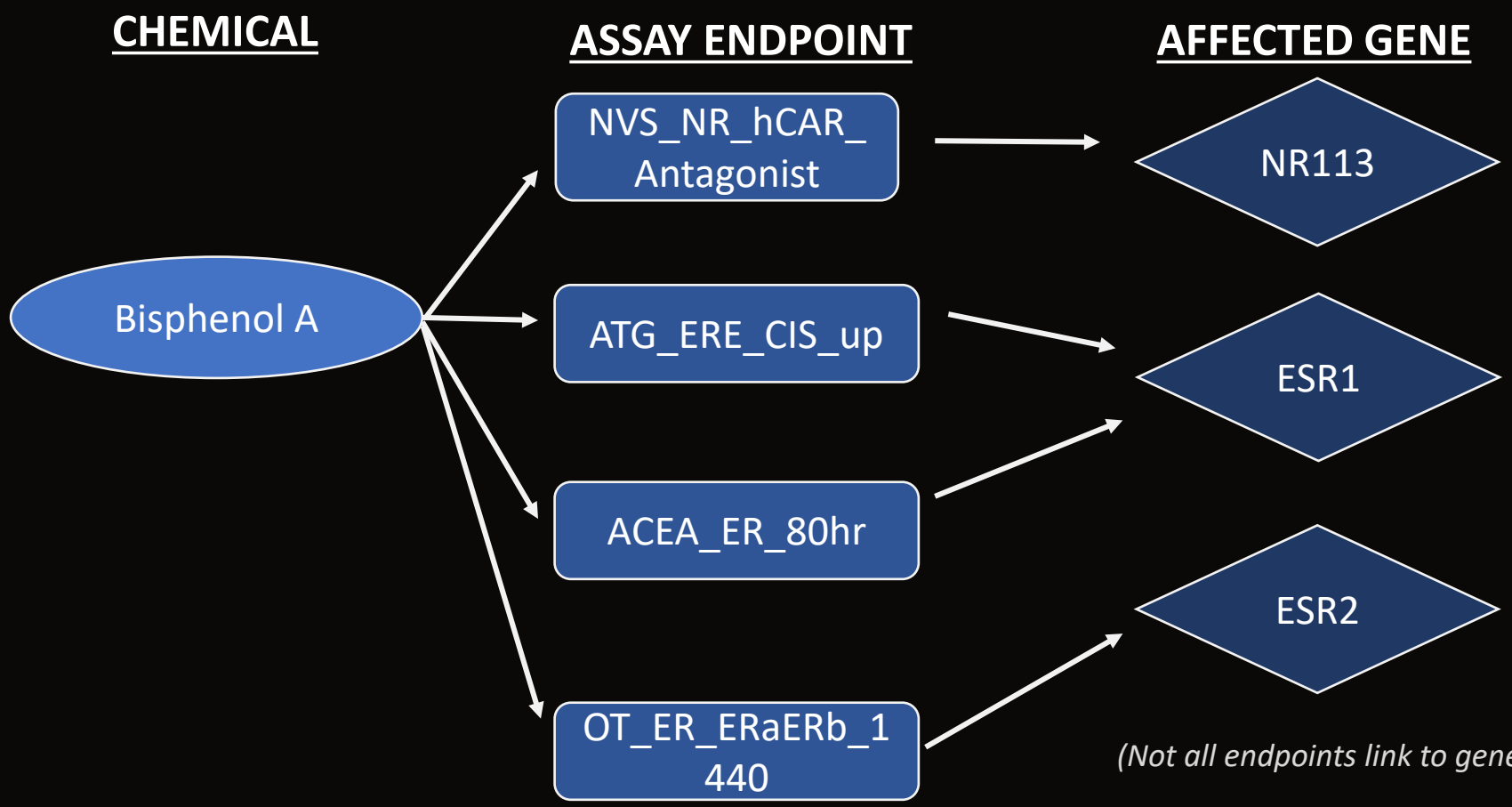
Chemical prioritization

Example of ToxCast data



(Not all endpoints link to genes)

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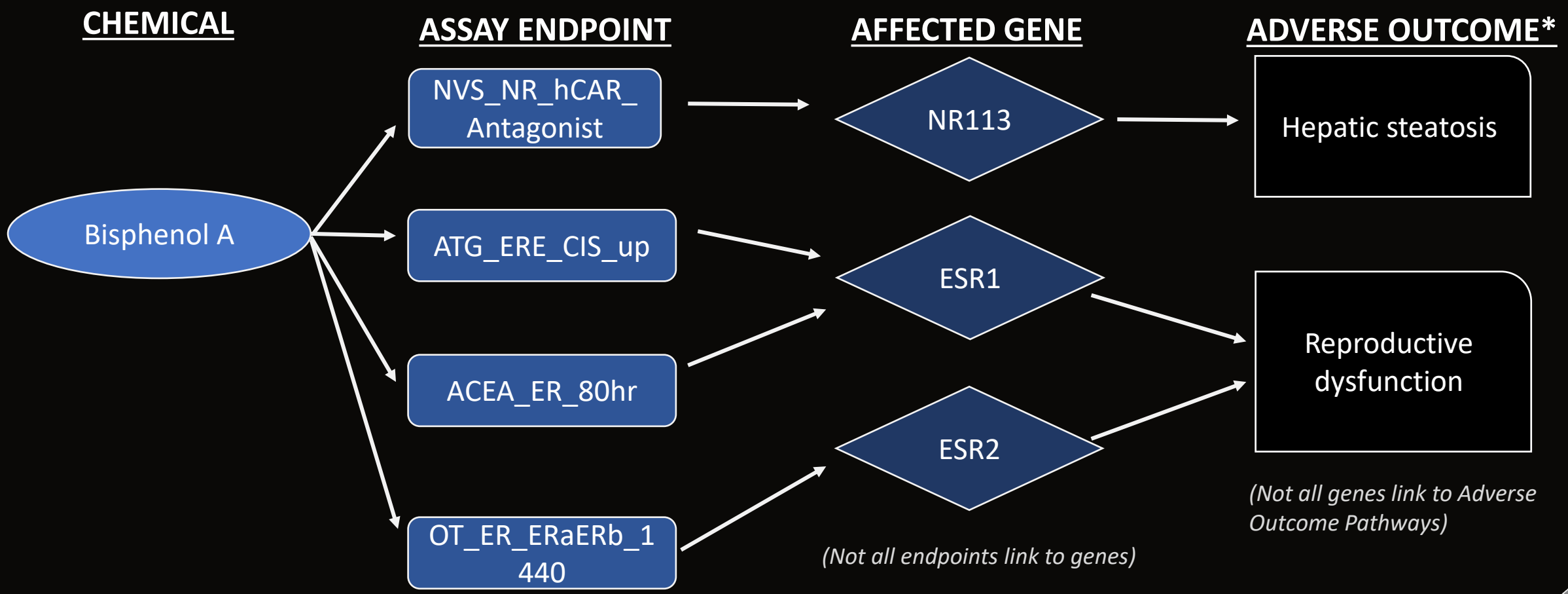
Chemical prioritization

Example of ToxCast data



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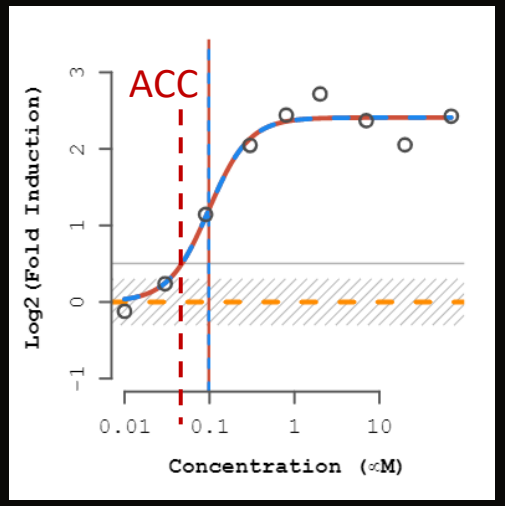
*https://aopwiki.org

Chemical prioritization

- ToxCast benchmarks



ToxCast dose-response curve.
Assay: ATG_ERE_CIS_up
Chemical: Bisphenol-A

$$Exposure\ Activity\ Ratio\ (EAR) = \frac{Measured\ concentration}{ACC}$$

- EAR > 1.0:
  - Measured concentration > ACC
- EAR > 0.001:
  - Shown to be a level of potential concern based on comparison to established water quality benchmarks

Chemical prioritization

Priority level 3

$TQ_{Max} > 0.1$ or $EAR_{Max} > 0.001$ at >20% of sites

Priority level 2

$TQ_{Max} > 1.0$ or $EAR_{Max} > 0.01$ at >20% of sites

Priority level 1 (highest)

$TQ_{Max} > 10$ or $EAR_{Max} > 0.1$ at >20% of sites

Low Priority

No $TQ_{Max} > 0.1$ or $EAR_{Max} > 0.001$ at any site, or not detected

Chemical class abbreviations: *A*, antioxidant; *AD*, antimicrobial disinfectant; *DM*, detergent metabolite; *DP*, dye/pigment; *FF*, flavors and fragrances; *FR*, fire retardant; *H*, herbicide; *I*, insecticide; *ND*, nonprescription drug; *P*, plasticizer; *PAH*, polycyclic aromatic hydrocarbon

Chemical prioritization

Priority level 3

$TQ_{Max} > 0.1$ or $EAR_{Max} > 0.001$ at >20% of sites

Priority level 2

$TQ_{Max} > 1.0$ or $EAR_{Max} > 0.01$ at >20% of sites

Priority level 1 (highest)

$TQ_{Max} > 10$ or $EAR_{Max} > 0.1$ at >20% of sites

bisphenol-A *(A)*
4-nonylphenol *(DM)*
indole *(FF)*
carbazole *(I)*
anthracene *(PAH)*
benz[a]anthracene *(PAH)*
benzo[a]pyrene *(PAH)*
benzo[k]fluoranthene *(PAH)*
fluoranthene *(PAH)*
indeno[1,2,3-cd]pyrene *(PAH)*
naphthalene *(PAH)*
phenanthrene *(PAH)*
pyrene *(PAH)*
C3-fluorene *(PAH)*

Low Priority

No $TQ_{Max} > 0.1$ or $EAR_{Max} > 0.001$ at any site, or not detected

Chemical class abbreviations: *A*, antioxidant; *AD*, antimicrobial disinfectant; *DM*, detergent metabolite; *DP*, dye/pigment; *FF*, flavors and fragrances; *FR*, fire retardant; *H*, herbicide; *I*, insecticide; *ND*, nonprescription drug; *P*, plasticizer; *PAH*, polycyclic aromatic hydrocarbon

Chemical prioritization

Priority level 3

TQ_{Max} > 0.1 or EAR_{Max} > 0.001 at >20% of sites

1-methylnaphthalene *(fuel)*
2-methylnaphthalene *(fuel)*
acenaphthylene *(PAH)*
benzo[e]pyrene *(PAH)*
benzo[g,h,i]perylene *(PAH)*
fluorene *(PAH)*
C1,C2,C3-benz[a]anthracene/chrysene *(PAH)*
C1-fluoranthene/pyrene *(PAH)*
C1,C2,C3,C4-phenanthrene/anthracene *(PAH)*
C3,C4-naphthalene *(PAH)*
bis(2-ethylhexyl) phthalate *(P)*

Priority level 2

TQ_{Max} > 1.0 or EAR_{Max} > 0.01 at >20% of sites

p-cresol *(AD)*
4-cumylphenol *(DM)*
anthraquinone *(DP)*
acenaphthene *(PAH)*
benzo[b]fluoranthene *(PAH)*
chrysene *(PAH)*
dibenz[a,h]anthracene *(PAH)*

Priority level 1 (highest)

TQ_{Max} > 10 or EAR_{Max} > 0.1 at >20% of sites

bisphenol-A *(A)*
4-nonylphenol *(DM)*
indole *(FF)*
carbazole *(I)*
anthracene *(PAH)*
benz[a]anthracene *(PAH)*
benzo[a]pyrene *(PAH)*
benzo[k]fluoranthene *(PAH)*
fluoranthene *(PAH)*
indeno[1,2,3-cd]pyrene *(PAH)*
naphthalene *(PAH)*
phenanthrene *(PAH)*
pyrene *(PAH)*
C3-fluorene *(PAH)*

Low Priority

No TQ_{Max} > 0.1 or EAR_{Max} > 0.001 at any site, or not detected

4-t-octylphenol monoethoxylate *(DM)*
4-n-octylphenol *(DM)*
4-nonylphenol diethoxylate *(DM)*
4-nonylphenol monoethoxylate *(DM)*
4-t-octylphenol diethoxylate *(DM)*
2,2',4,4'-tetrabromodiphenylether *(FR)*
benzophenone *(FF)*
HHCB (Galaxolide) *(FF)*
isoborneol *(FF)*
isoquinoline *(FF)*
bromacil *(H)*
prometon *(H)*
chlorpyrifos *(I)*
diazinon *(I)*
DEET *(I)*
menthol *(ND)*
tris(2-chloroethyl) phosphate *(P)*

Chemical class abbreviations: *A*, antioxidant; *AD*, antimicrobial disinfectant; *DM*, detergent metabolite; *DP*, dye/pigment; *FF*, flavors and fragrances; *FR*, fire retardant; *H*, herbicide; *I*, insecticide; *ND*, nonprescription drug; *P*, plasticizer; *PAH*, polycyclic aromatic hydrocarbon

Chemical prioritization

PAHs represented 41% of the chemicals analyzed but 69% of the chemicals prioritized

Priority level 3

TQ_{Max} > 0.1 or EAR_{Max} > 0.001 at >20% of sites

1-methylnaphthalene *(fuel)*
2-methylnaphthalene *(fuel)*
acenaphthylene *(PAH)* ☆
benzo[e]pyrene *(PAH)* ☆
benzo[g,h,i]perylene *(PAH)* ☆
fluorene *(PAH)* ☆
C1,C2,C3-benz[a]anthracene/chrysene *(PAH)* ☆
C1-fluoranthene/pyrene *(PAH)* ☆
C1,C2,C3,C4-phenanthrene/anthracene *(PAH)* ☆
C3,C4-naphthalene *(PAH)* ☆
bis(2-ethylhexyl) phthalate *(P)*

Priority level 2

TQ_{Max} > 1.0 or EAR_{Max} > 0.01 at >20% of sites

p-cresol *(AD)*
4-cumylphenol *(DM)*
anthraquinone *(DP)*
acenaphthene *(PAH)* ☆
benzo[b]fluoranthene *(PAH)* ☆
chrysene *(PAH)* ☆
dibenz[a,h]anthracene *(PAH)* ☆

Priority level 1 (highest)

TQ_{Max} > 10 or EAR_{Max} > 0.1 at >20% of sites

bisphenol-A *(A)*
4-nonylphenol *(DM)*
indole *(FF)*
carbazole *(I)*
anthracene *(PAH)* ☆
benz[a]anthracene *(PAH)* ☆
benzo[a]pyrene *(PAH)* ☆
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fluoranthene *(PAH)* ☆
indeno[1,2,3-cd]pyrene *(PAH)* ☆
naphthalene *(PAH)* ☆
phenanthrene *(PAH)* ☆
pyrene *(PAH)* ☆
C3-fluorene *(PAH)* ☆

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4-t-octylphenol monoethoxylate *(DM)*
4-n-octylphenol *(DM)*
4-nonylphenol diethoxylate *(DM)*
4-nonylphenol monoethoxylate *(DM)*
4-t-octylphenol diethoxylate *(DM)*
2,2',4,4'-tetrabromodiphenylether *(FR)*
benzophenone *(FF)*
HHCB (Galaxolide) *(FF)*
isoborneol *(FF)*
isoquinoline *(FF)*
bromacil *(H)*
prometon *(H)*
chlorpyrifos *(I)*
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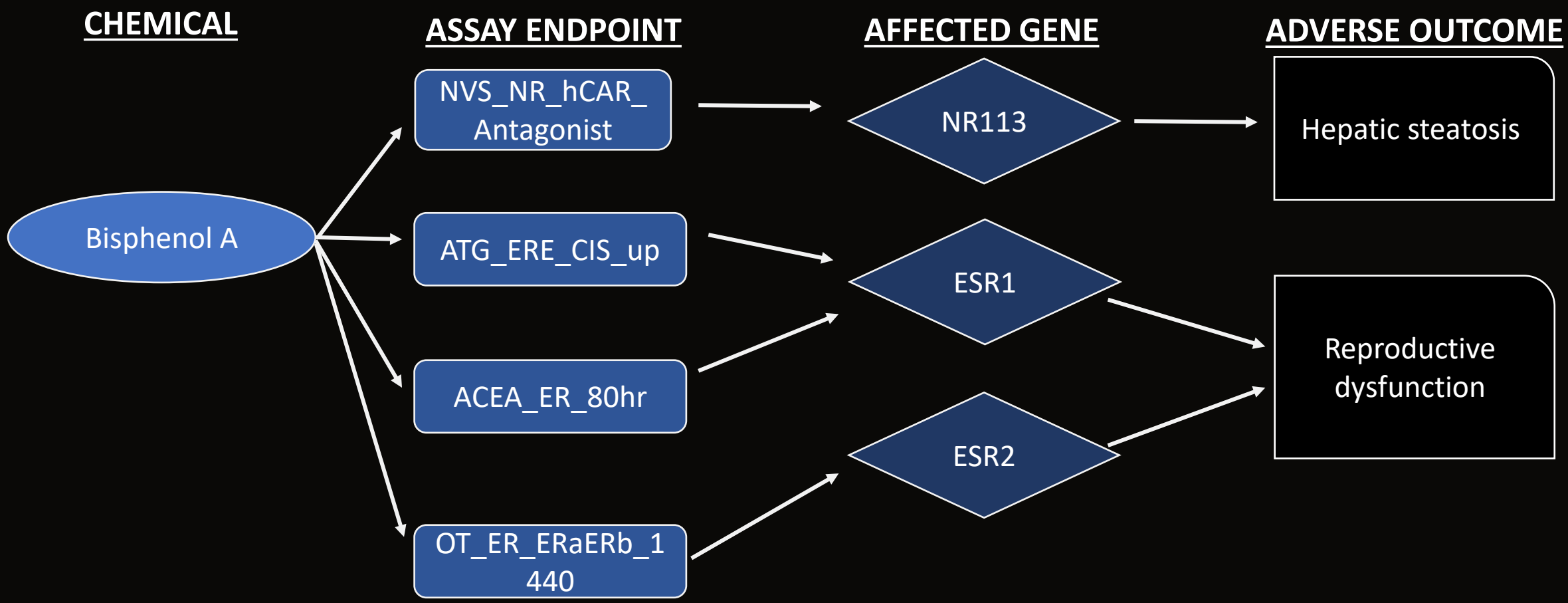
Chemical mixture prioritization

Additive effects of chemical mixtures based on common biological pathways



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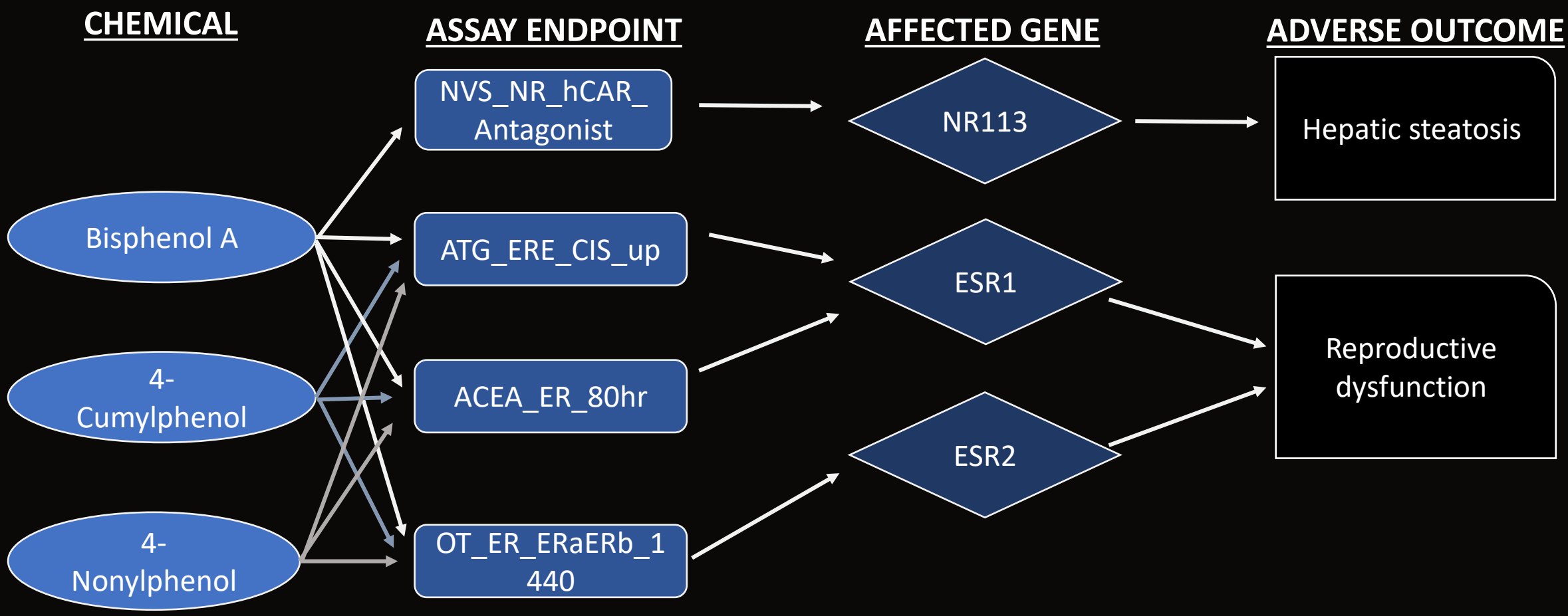
Chemical mixture prioritization

Additive effects of chemical mixtures based on common biological pathways



Common mixtures and their potential bioeffects

$EAR_{Mixture}$ > 0.1 at ≥ 20% of sites

https://aopwiki.org

Chemical mixture

Bisphenol-A

4-Cumylphenol

4-Nonylphenol

Affected genes

Estrogen Receptors 1 & 2 (ESR1 & ESR2):

Estrogen receptors (ER) essential for sexual development and reproductive function

Adverse Outcomes

Reproductive dysfunction, skewed sex ratios, breast cancer, and reduced survival

Common mixtures and their potential bioeffects

$EAR_{Mixture}$ > 0.1 at ≥ 20% of sites

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Chemical mixture	Bisphenol-A 4-Cumylphenol 4-Nonylphenol	Affected genes	*Estrogen Receptors 1 & 2 (ESR1 & ESR2):* Estrogen receptors (ER) essential for sexual development and reproductive function
Adverse Outcomes	Reproductive dysfunction, skewed sex ratios, breast cancer, and reduced survival		
Chemical mixture	Bisphenol-A Indole	Affected genes	*Thyroperoxidase (TPO):* Enzyme important in production of thyroid hormone
Adverse Outcomes	Neurodevelopmental outcomes in mammals, altered amphibian metamorphosis, impaired fertility in fish		

Common mixtures and their potential bioeffects

$EAR_{Mixture}$ > 0.1 at ≥ 20% of sites

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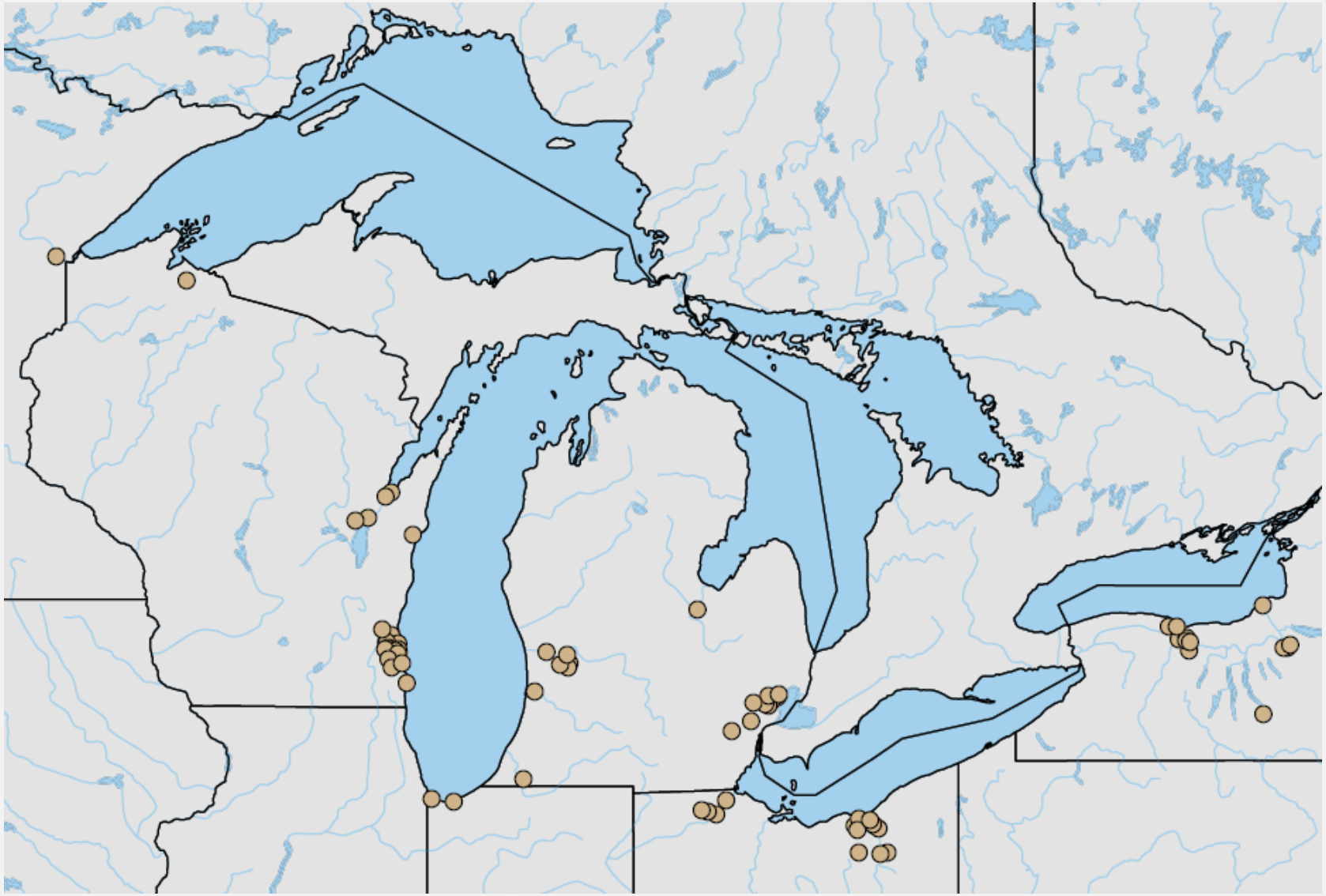
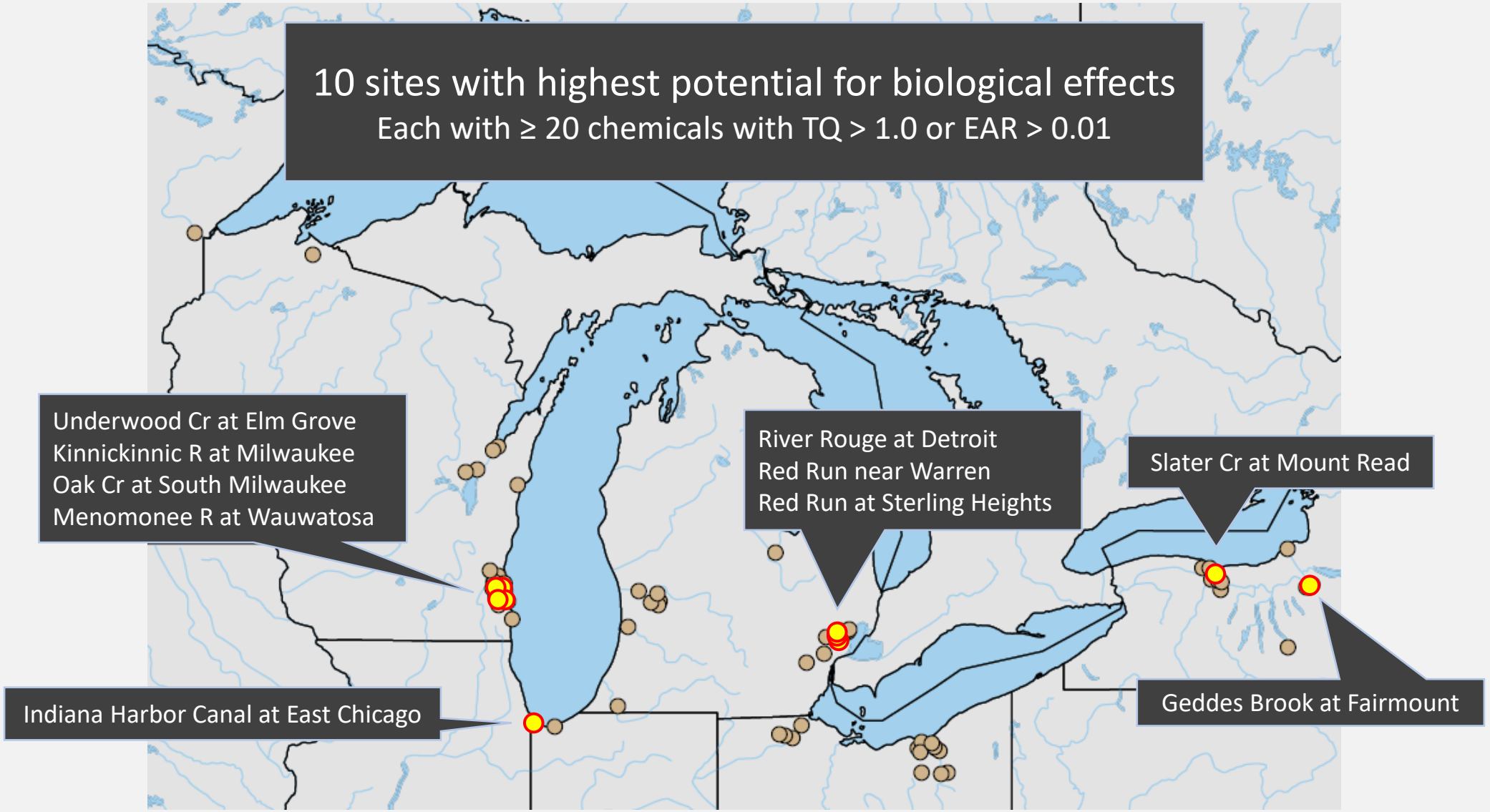
Chemical mixture	Bisphenol-A 4-Cumylphenol 4-Nonylphenol	Affected genes	*Estrogen Receptors 1 & 2 (ESR1 & ESR2):* Estrogen receptors (ER) essential for sexual development and reproductive function
Adverse Outcomes	Reproductive dysfunction, skewed sex ratios, breast cancer, and reduced survival		
Chemical mixture	Bisphenol-A Indole	Affected genes	*Thyroperoxidase (TPO):* Enzyme important in production of thyroid hormone
Adverse Outcomes	Neurodevelopmental outcomes in mammals, altered amphibian metamorphosis, impaired fertility in fish		
Chemical mixture	Indole Carbazole Benz(a)anthracene Indeno(1,2,3-cd)pyrene Benzo(b)fluoranthene Benzo(k)fluoranthene	Affected genes	Aryl hydrocarbon receptor (AHR): Regulates biological responses to planar aromatic hydrocarbons
Adverse Outcomes	Early life stage mortality in fish and birds, hepatic steatosis, rodent liver tumors; AHR mediated epigenetic reproductive failure		

Site prioritization



Site prioritization



Summary

Multiple risk-based approaches were used to prioritize chemicals, mixtures, and locations of ecological concern

Limitations

- Some detected chemicals lack benchmarks and ToxCast ACC values
- Adverse Outcomes (AOPs) are under development: not all ToxCast assays are represented by AOPs
- Porewater concentrations are estimates, not measured
- Screening-level approach – validation is needed to verify effects at the stream level

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