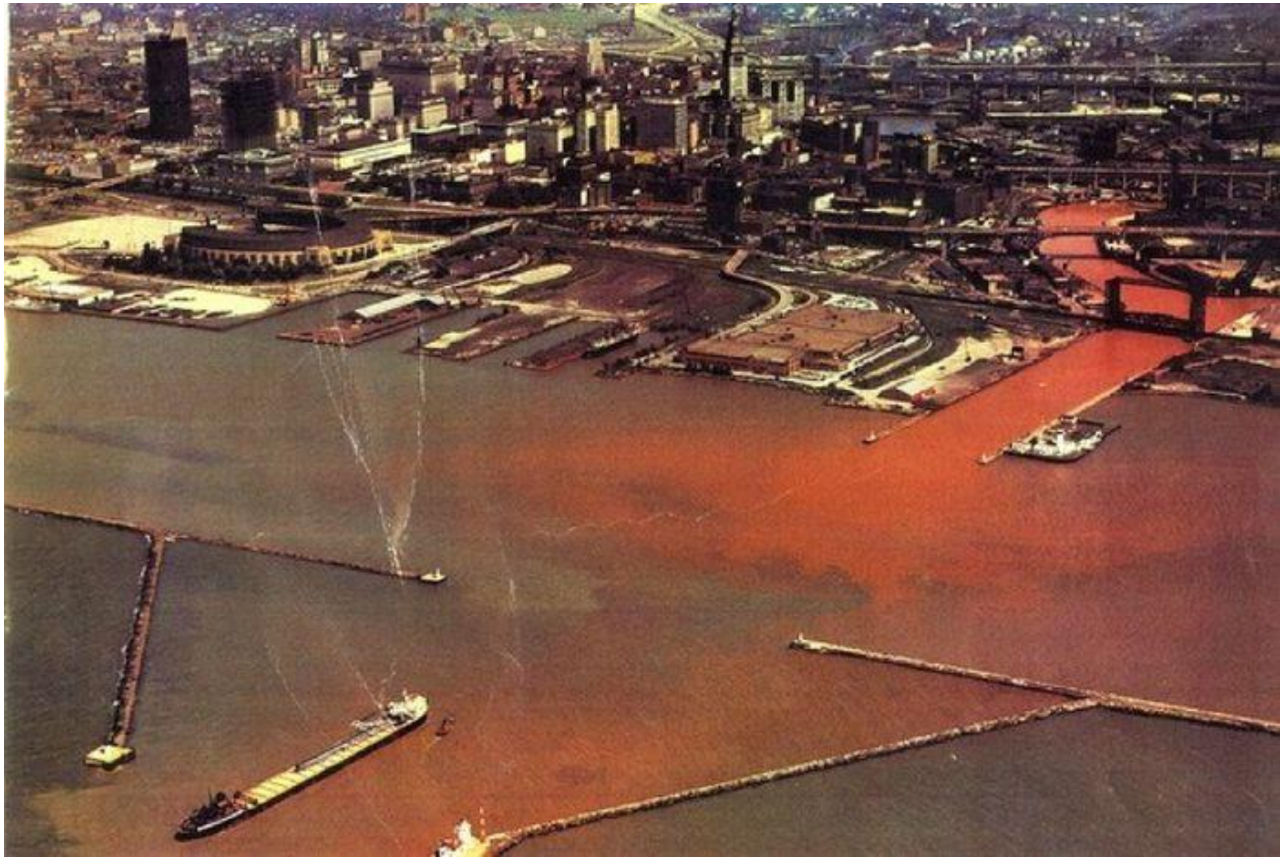
Chemical Contaminants

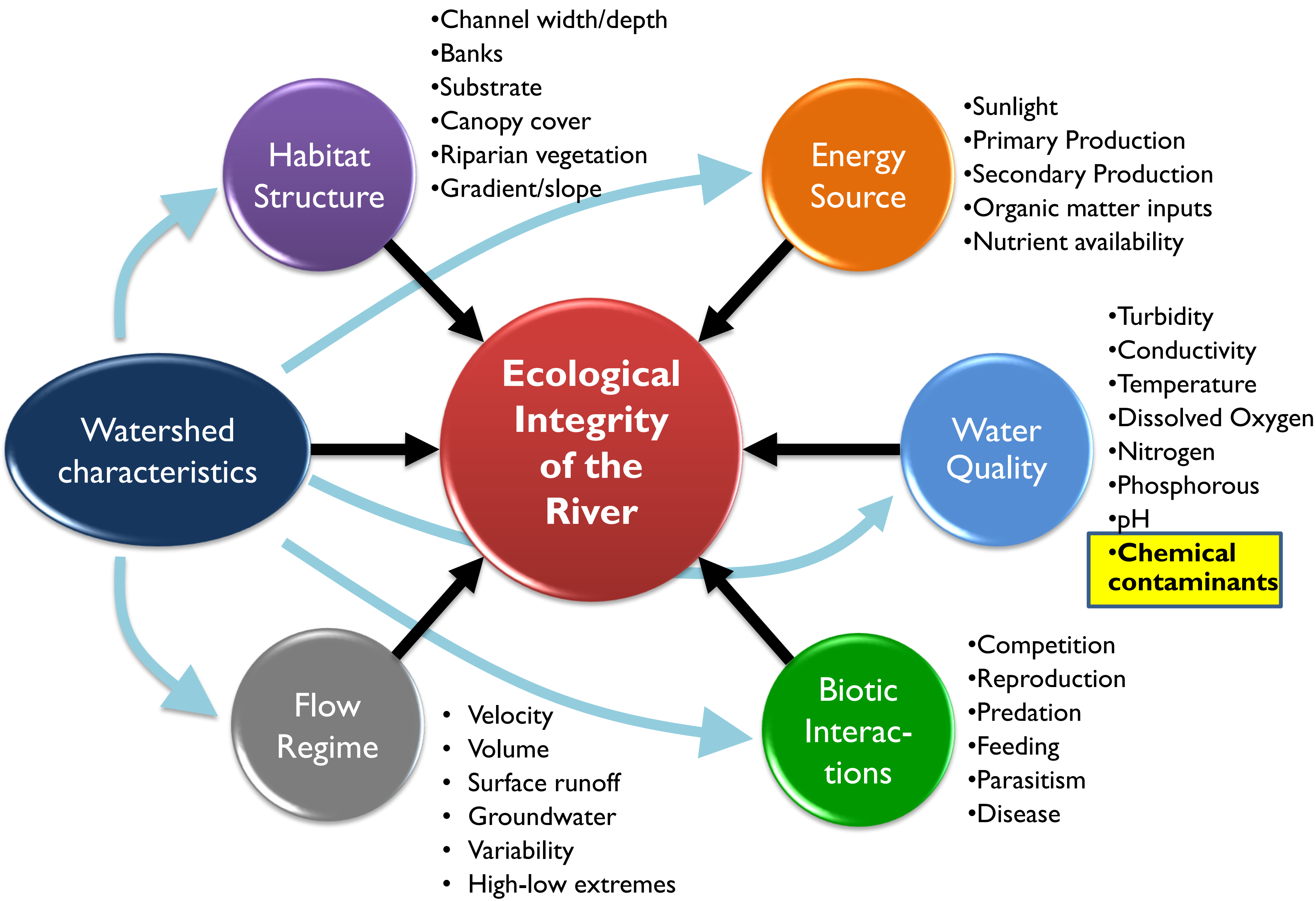


1967, Cuyahoga River emptying into Lake Erie.
www.ncseglobal.org

Watershed 102

Diana Oviedo-Vargas, PhD

Stroud Water Research Center



Habitat Structure
•Channel width/depth
•Banks
•Substrate
•Canopy cover
•Riparian vegetation
•Gradient/slope
Energy Source
•Sunlight
•Primary Production
•Secondary Production
•Organic matter inputs
•Nutrient availability
Watershed characteristics
Ecological Integrity of the River
Water Quality
•Turbidity
•Conductivity
•Temperature
•Dissolved Oxygen
•Nitrogen
•Phosphorous
•pH
•Chemical contaminants
Flow Regime
• Velocity
• Volume
• Surface runoff
• Groundwater
• Variability
• High-low extremes
Biotic Interac-tions
•Competition
•Reproduction
•Predation
•Feeding
•Parasitism
•Disease

Outline

- Definition of chemical contaminants
- Naturally occurring chemicals in increased concentrations
  - Heavy metals
  - Inorganic Acids
  - Salts
- Synthetic chemicals
  - Persistent Organic Pollutants
  - Pesticides
  - Contaminants of Emerging Concern

nature chemistry

ARTICLES
PUBLISHED ONLINE: 2014

A comprehensive overview of chemical-free consumer products

Alexander F. G. Goldberg[1] and CJ Chemjobber[2*]

Manufacturers of consumer products, in particular edibles and cosmetics, have broadly employed the term 'Chemical free' in marketing campaigns and on product labels. Such characterization is often incorrectly used to imply — and interpreted to mean — that the product in question is healthy, derived from natural sources, or otherwise free from synthetic components. We have examined and subjected to rudimentary analysis an exhaustive number of such products, including but not limited to lotions and cosmetics, herbal supplements, household cleaners, food items, and beverages. Herein are described all those consumer products, to our knowledge, that are appropriately labelled as 'Chemical free'.

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Everything on Earth is a chemical substance!

nature chemistry
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"…there are just two types of chemicals: Those which we understand. And those which we do not." – C.A. Palma.

What is a chemical contaminant?

- A chemical substance that is either present in an environment where it does not belong or is present at levels that might cause harmful effects to life.

What is a chemical contaminant?

- A chemical substance that is either **present in an environment where it does not belong** or is present at levels that might cause harmful effects to life.

Synthetic chemicals

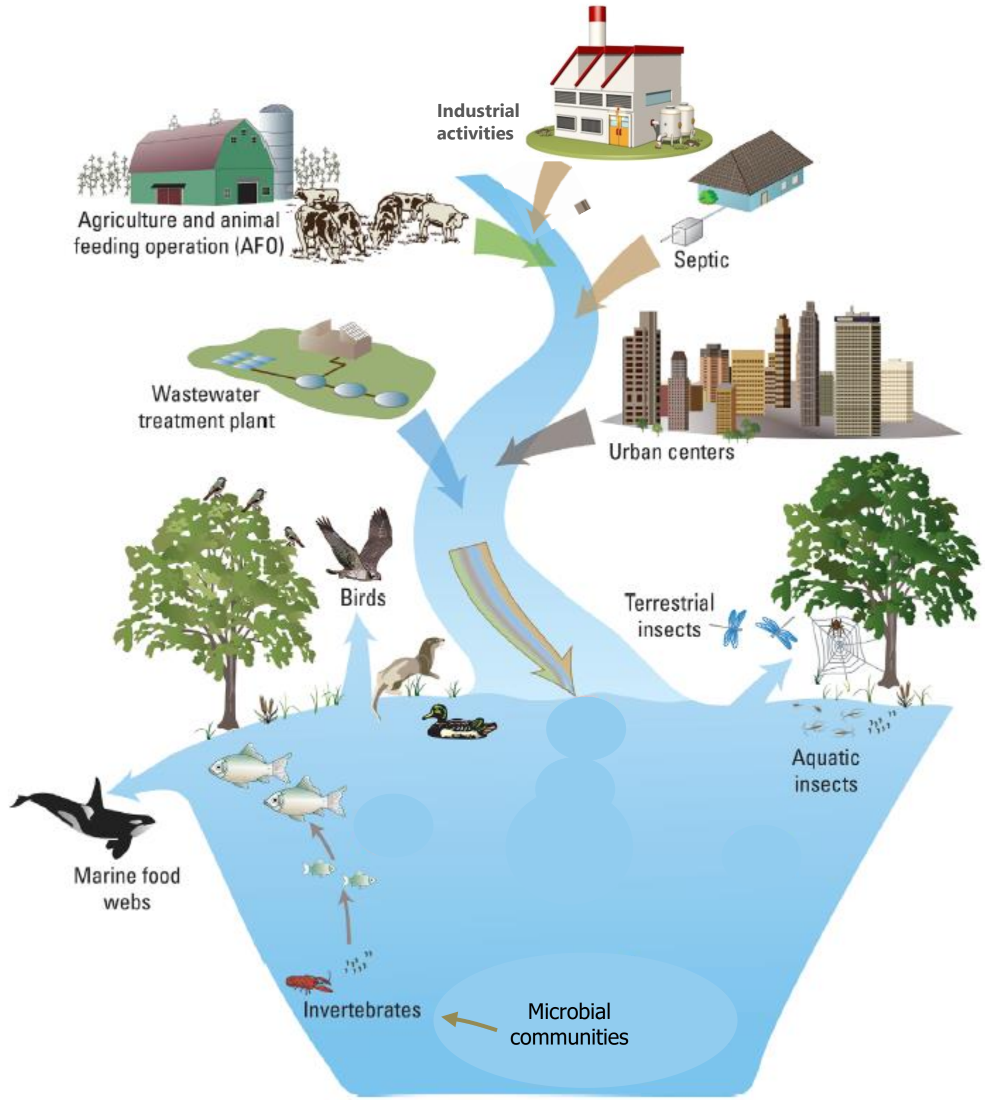
- From 25,000 to 84,000 chemicals in commerce
  Identifying and Reducing Environmental Health Risks of Chemicals in Our Society: Workshop Summary. Washington (DC): National Academies Press (US); 2014 Oct 2. https://www.ncbi.nlm.**nih**.gov/books/NBK200888/ doi: 10.17226/18710

- Chances are many of them are likely to have made it to our streams and rivers –**where they do not belong**.

- How much do we know and understand about them and their interaction with the natural environment?

Sources of synthetic contaminants

- Industrial activities
  - Industrial byproducts
- Agricultural activities
  - Insecticides
  - Fungicides
  - Herbicides
- Consumer activities
  - Pharmaceuticals
  - Personal-care products
  - Household-care products
- Breakdown or transformation products
  - Disinfection byproducts
  - ????

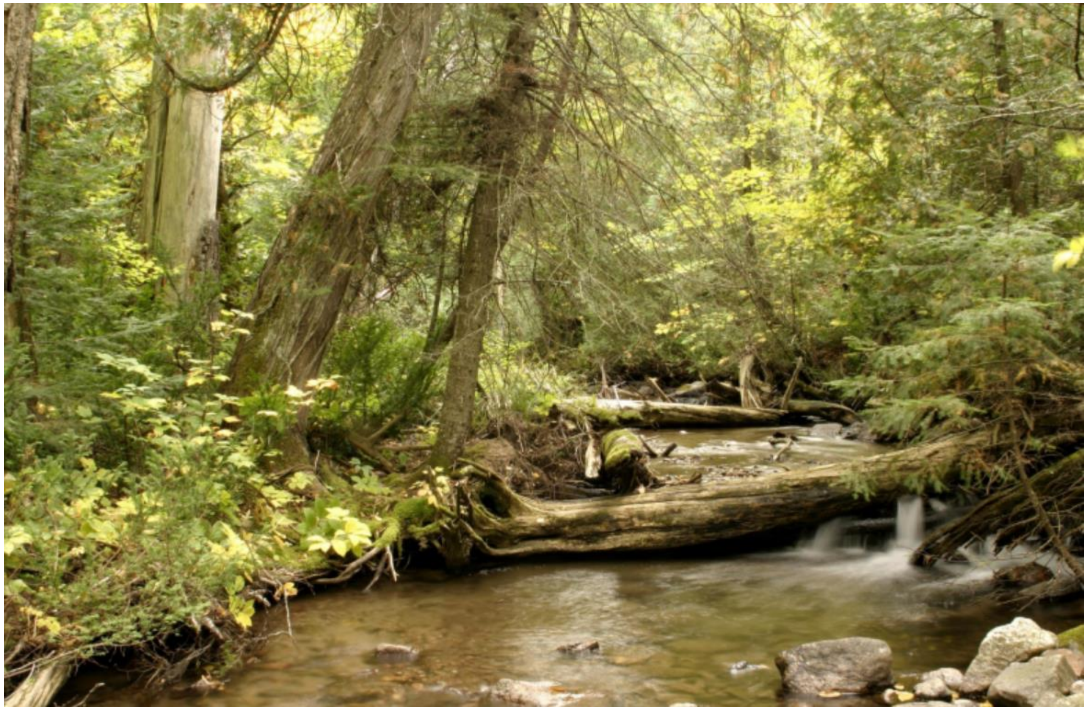


Environmental Toxicology and Chemistry, 2019;38:46–60—E. Nilsen et al.

Synthetic chemical contaminants

- Natural, reference river.

0



What is a chemical contaminant?

- A chemical substance that is either present in an environment where it does not belong or **is present at levels that might cause harmful effects to life**.
  - N and P – Marc covered,
  - Heavy metals
  - Inorganic acids
  - Salts

Solubility of chemical contaminants in water

- Will define where in the river ecosystem you will find them.

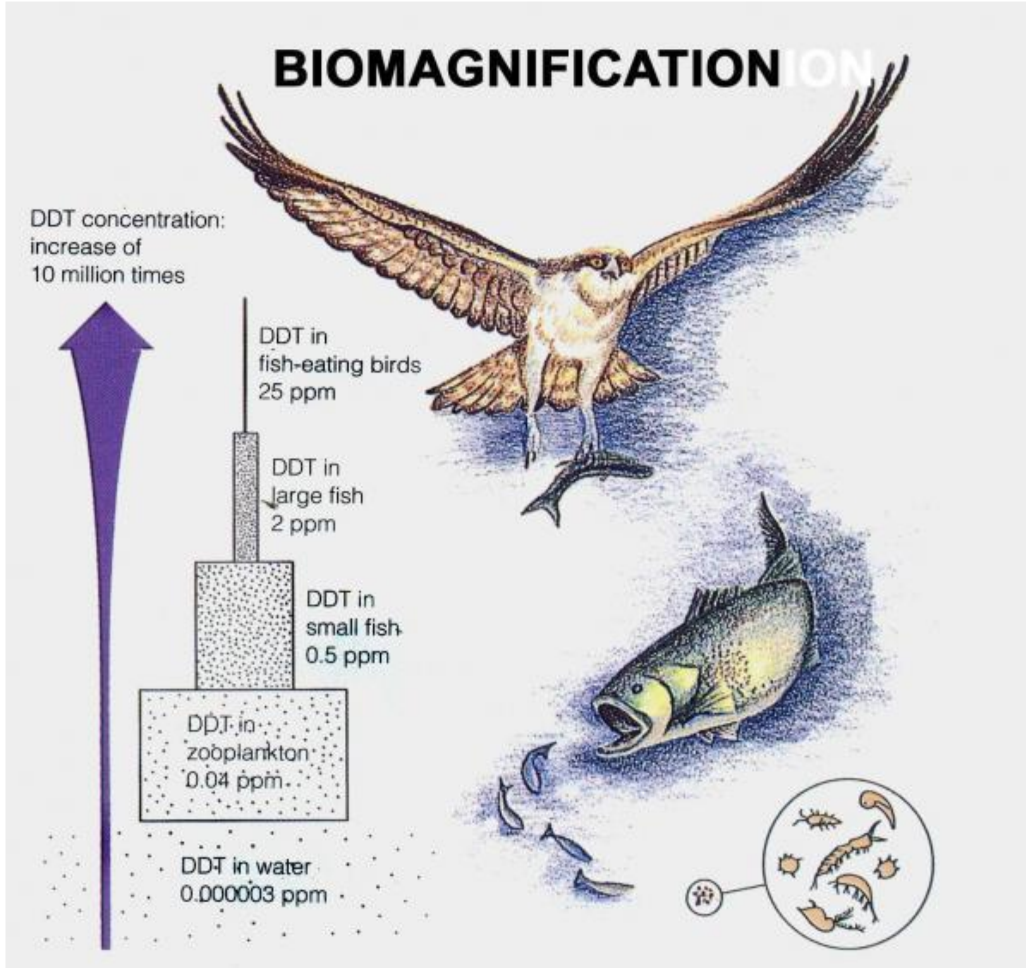
- **Hydrophobic**: does not mix with water
- **Hydrophilic:** soluble in water

- Where do they go?

Bioaccumulation and biomagnification

- **Bioaccumulation:** net result of more rapid uptake than release of rate of a persistent contaminant.

- **Biomagnification:** increased concentrations of a contaminant in successively higher levels of trophic structure.



Heavy metals

- Antimony, Arsenic, Beryllium, Cadmium, Chromium, Copper, Lead, Mercury, Nickel, Selenium, Silver, Thallium, Zinc (**Heavy metals, toxic pollutants under the Clean Water Act**)

- Sources
  - Coal combustion
  - Mining
  - Waste incineration
  - Cement manufacturers
  - Electronic waste

- Hydrophobic- sediments and fat tissues
- Bioaccumulate

HYDROLOGICAL PROCESSES
Hydrol. Process. **26**, 1090–1114 (2012)
Published online 8 February 2012 in Wiley Online Library
(wileyonlinelibrary.com) DOI: 10.1002/hyp.8437

Concentrations and annual fluxes of sediment-associated chemical constituents from conterminous US coastal rivers using bed sediment data†

Arthur J. Horowitz,[1]* Verlin C. Stephens,[2] Kent A. Elrick[1] and James J. Smith[1]
[1] *US Geological Survey, Peachtree Business Center, Suite 130, 3039 Amwiler Road, Atlanta, GA 30 360, USA*
[2] *US Geological Survey, Denver Federal Center, Building 53, MS 415 Lakewood, CO, 80 225, USA*

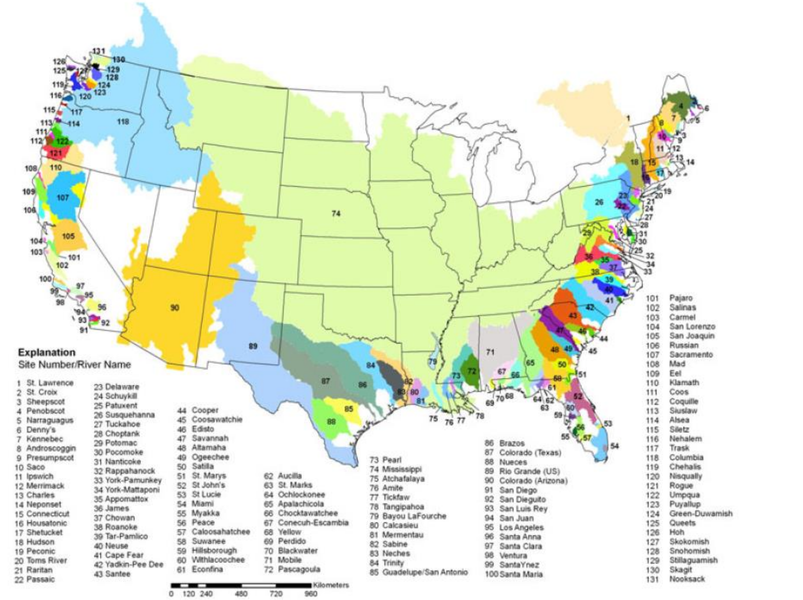
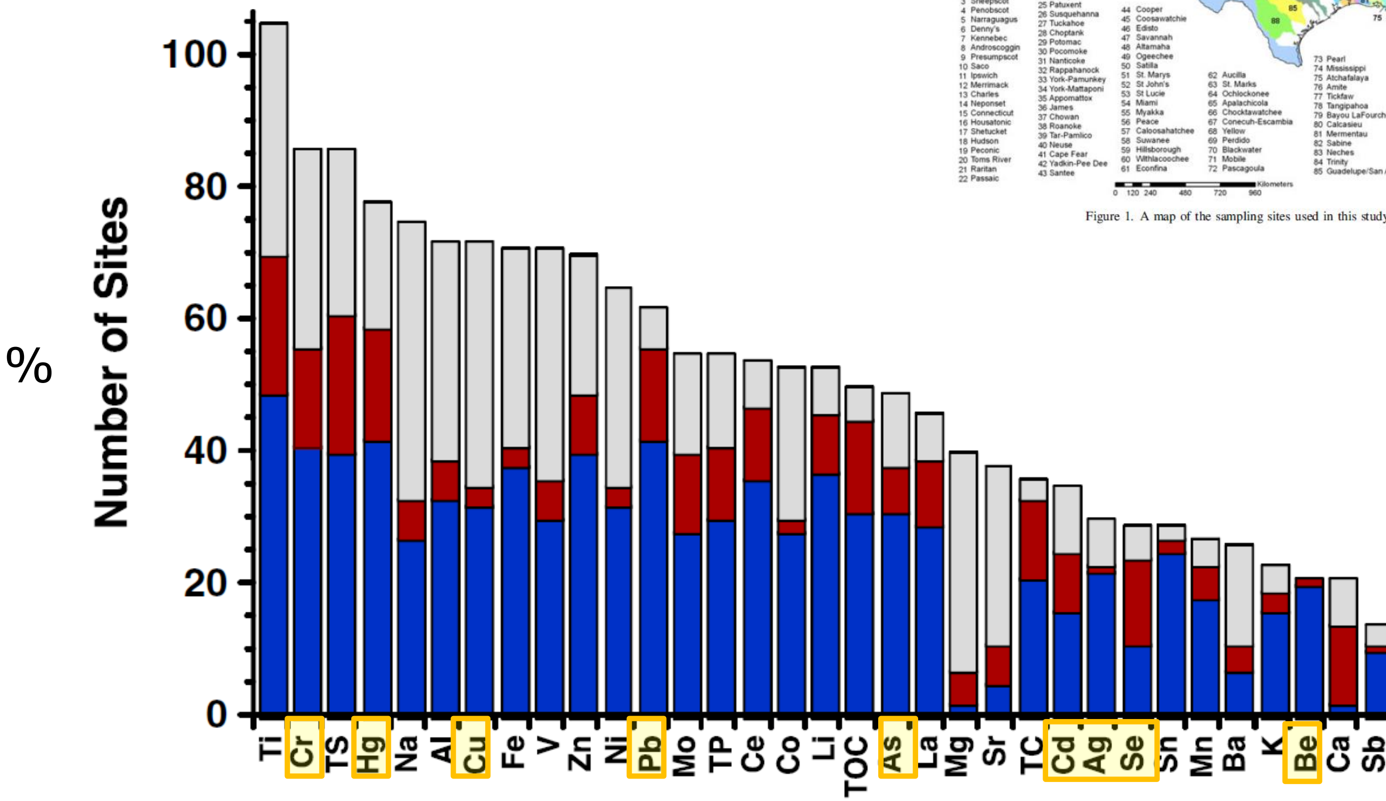


Figure 1. A map of the sampling sites used in this study and the basins they represent



- Study of 132 coastal watersheds in the US: Elevated heavy metals frequently occurred in association with present/former industrial areas and/or urban centers, particularly along the northeast Atlantic coast.

Pennsylvania Impaired Waters

Pennsylvania 2004 Causes of Impairment for 303(d) Listed Waters

Description of this table

NOTE: Click on a cause of impairment (e.g. pathogens) to see the specific state-reported causes that are grouped to make up this category. Click on the "Number of Causes of Impairment Reported" to see a list of waters with that cause of impairment.

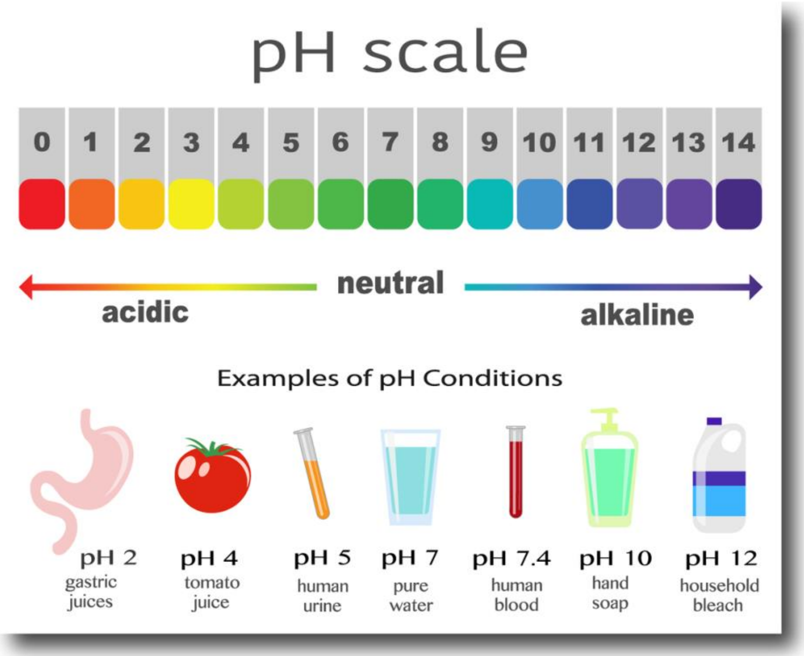
Cause of Impairment Group Name	Number of Causes of Impairment Reported
Sediment	3,585
Metals (other than Mercury)	2,361
pH/Acidity/Caustic Conditions	1,449
Nutrients	1,164
Organic Enrichment/Oxygen Depletion	746
Turbidity	386
Cause Unknown	367
Toxic Inorganics	136
Polychlorinated Biphenyls (PCBs)	132
Mercury	112
Pathogens	77
Salinity/Total Dissolved Solids/Chlorides/Sulfates	69
Pesticides	66
Temperature	32
Algal Growth	31
Oil and Grease	30
Toxic Organics	29
Total Toxics	25
Habitat Alterations	18
Chlorine	6
Ammonia	4
Taste, Color and Odor	4
Noxious Aquatic Plants	2
Dioxins	2
Other Cause	1

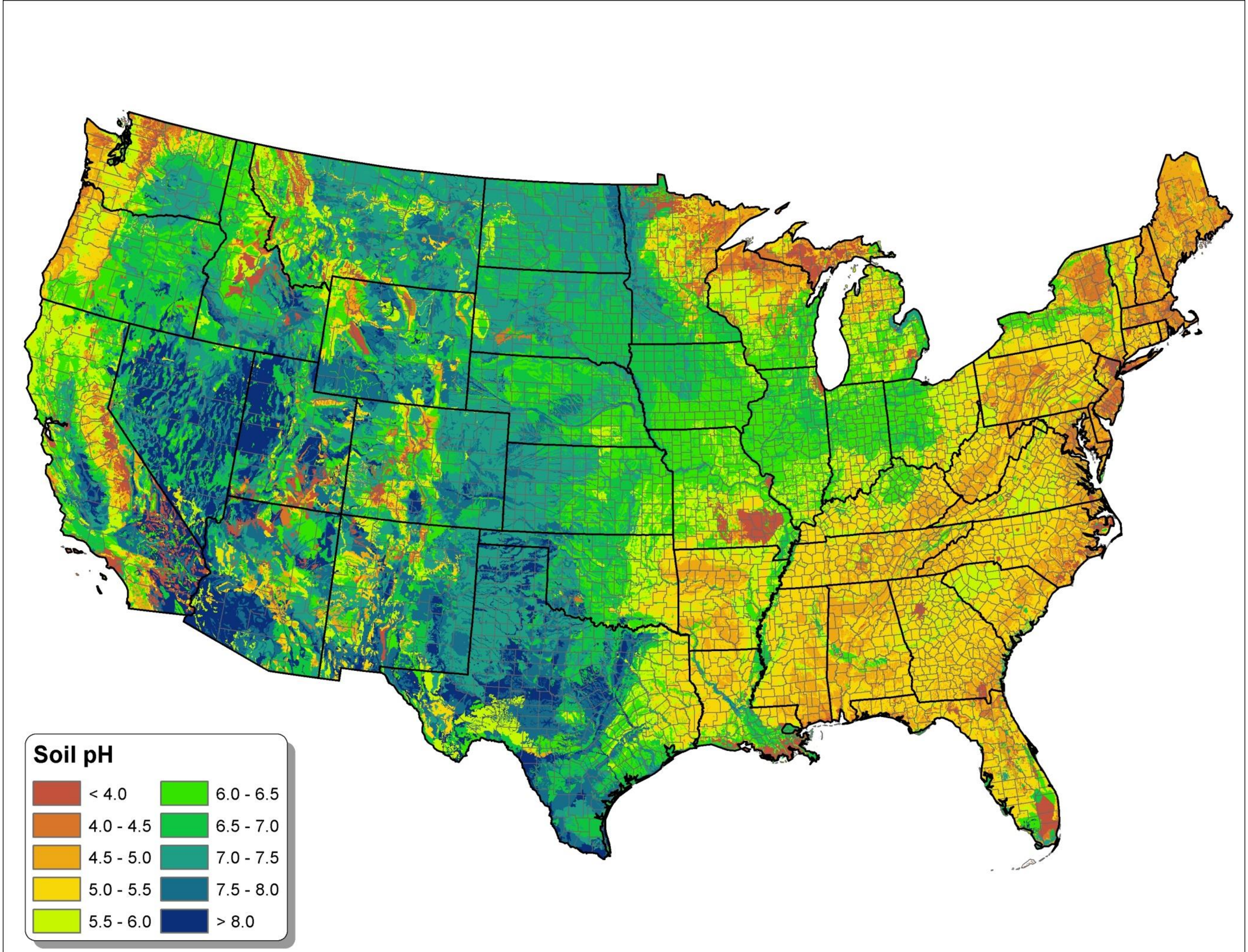
Inorganic Acids

- Nitric and sulfuric acid
- Hydrogen ions: H^+
- pH
- Sources
  - Acid Rain
  - Acid mine drainage
- Biota, sensitive
- River pH can naturally range from 4 to 9

$HNO_3 \rightarrow H^+ + NO_3$

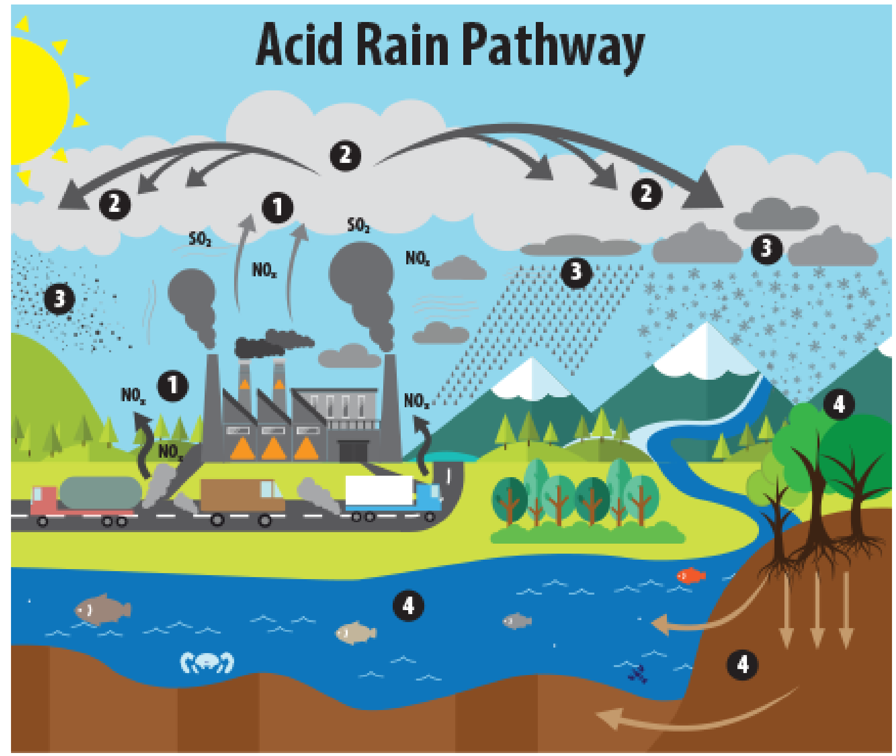
$H_2SO_4 \rightarrow H^+ + SO_4$




Soil pH
< 4.0
4.0 - 4.5
4.5 - 5.0
5.0 - 5.5
5.5 - 6.0
6.0 - 6.5
6.5 - 7.0
7.0 - 7.5
7.5 - 8.0
> 8.0

Acid deposition (rain)

- Fossil fuel burning produce SO_2 and NO_x gases.
- In the atmosphere react with water to produce sulfuric and nitric acid.
- Northeastern US.
- Acidification but also mobilization of other chemicals (Al).
- Decreased since the early 1990s.
  - Slow recovery in streams and rivers



This image illustrates the pathway for acid rain in our environment: (1) Emissions of SO_2 and NO_x are released into the air, where (2) the pollutants are transformed into acid particles that may be transported long distances. (3) These acid particles then fall to the earth as wet and dry deposition (dust, rain, snow, etc.) and (4) may cause harmful effects on soil, forests, streams and lakes.

Acid mine drainage (AMD)

- Metal mining
- Sulfidic minerals- most commonly mined
- In contact with water and oxygen produce sulfuric acid (H_2SO_4)
- Abandoned coal mines
- Thousands in PA
- https://www.srbc.net/minedrainageportal/Map

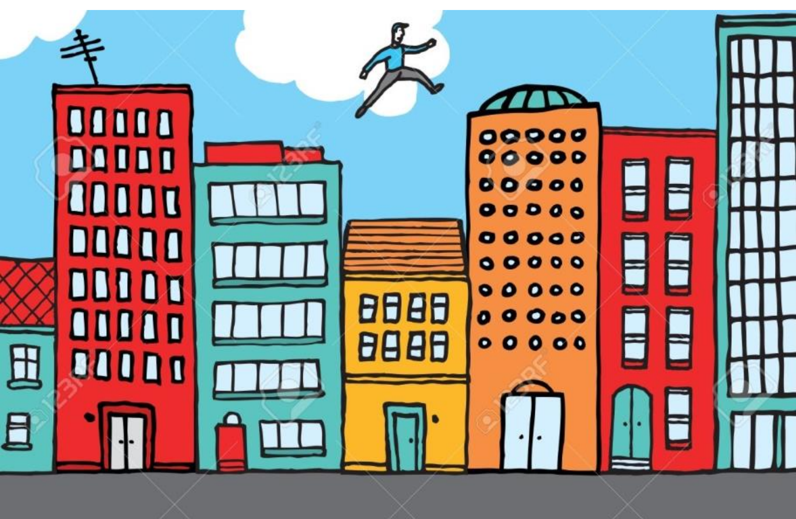
Shamokin Creek, PA

Salts: freshwater salinization syndrome

- Increasing concentration of salts.
- Has affected nearly 40% of the drainage area of the contiguous US in last 100 years.
- Most prominent in the densely populated eastern and midwestern US

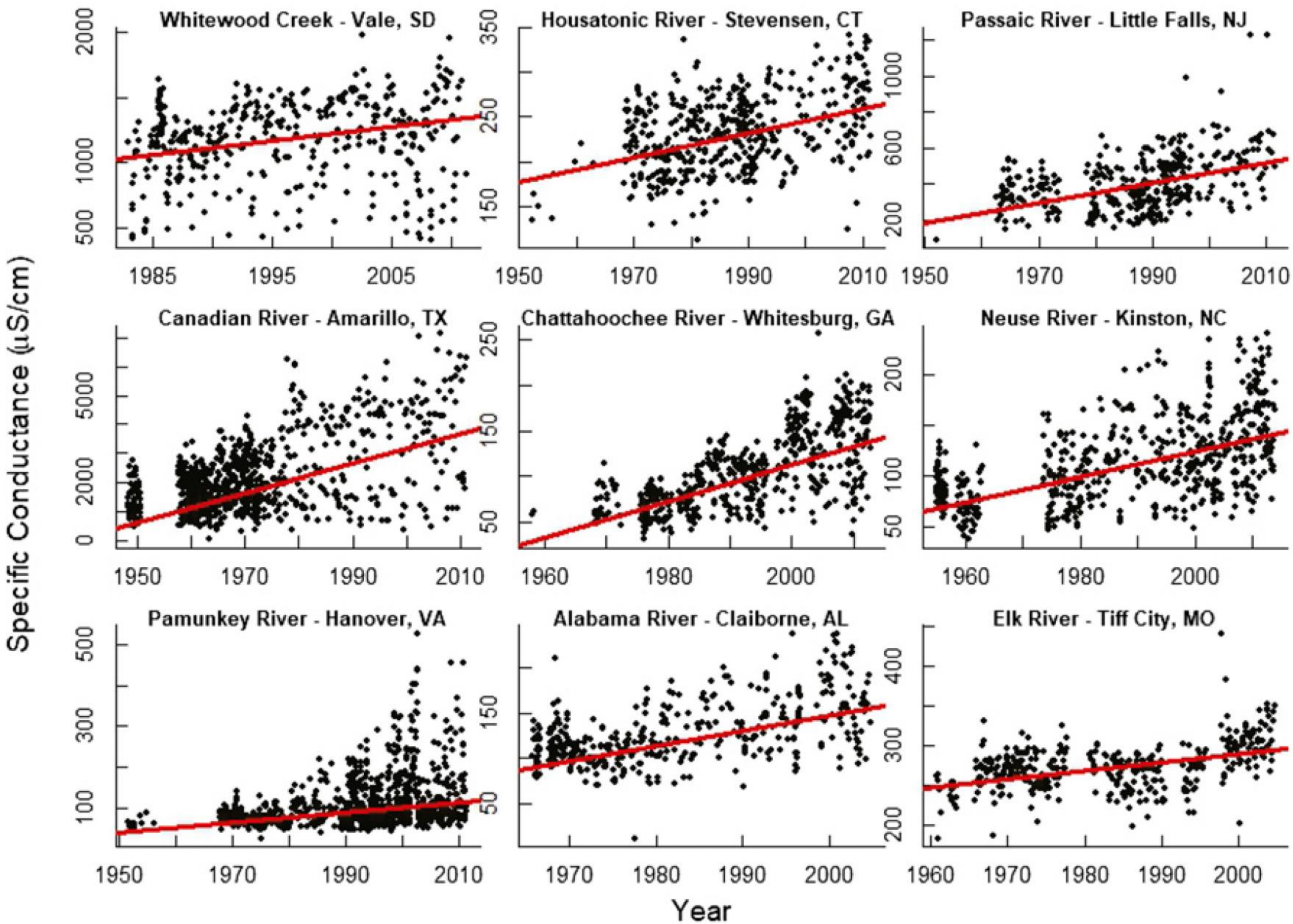
Salts: freshwater salinization syndrome

- Causes:
  - Salt pollution:
    - Road deicers, irrigation runoff, sewage.
  - Accelerated weathering of natural geologic materials by strong acids (e.g., acid rain, fertilizers, and acid mine drainage)
  - Easily weathered minerals used in agriculture (lime) and urbanization (concrete).



Salts: freshwater salinization syndrome

- Not only table salt (NaCl)
- Also other anions and cations
  - Magnesium
  - Sulfate
  - Carbonate
  - Potassium
- Electric conductivity
  - Measurement of the concentration of chemicals that can transfer electric current
  - Salts
  - Naturally ranges 10-500 μS/cm



Freshwater salinization syndrome on a continental scale. Kaushal et al. 2018, PNAS

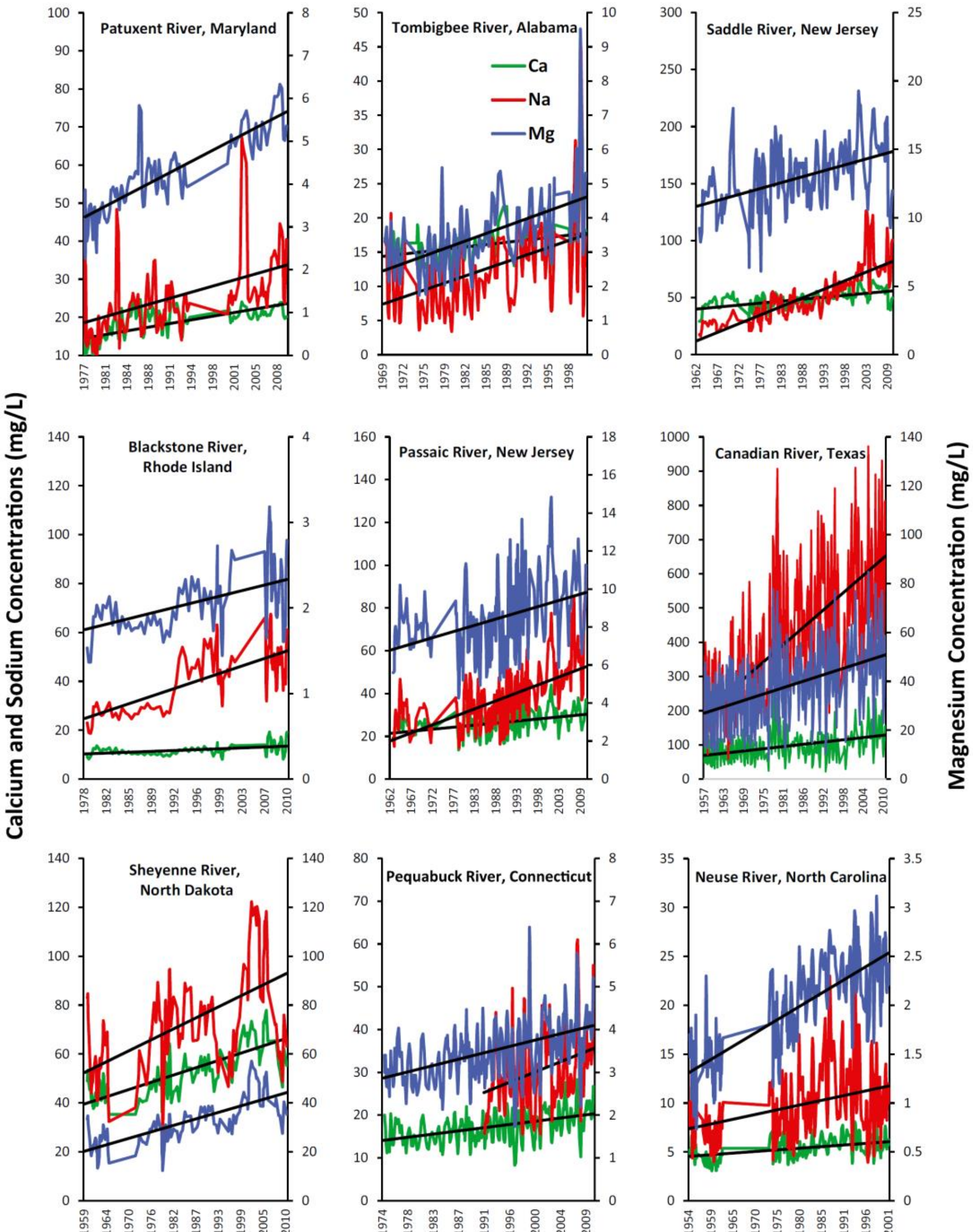
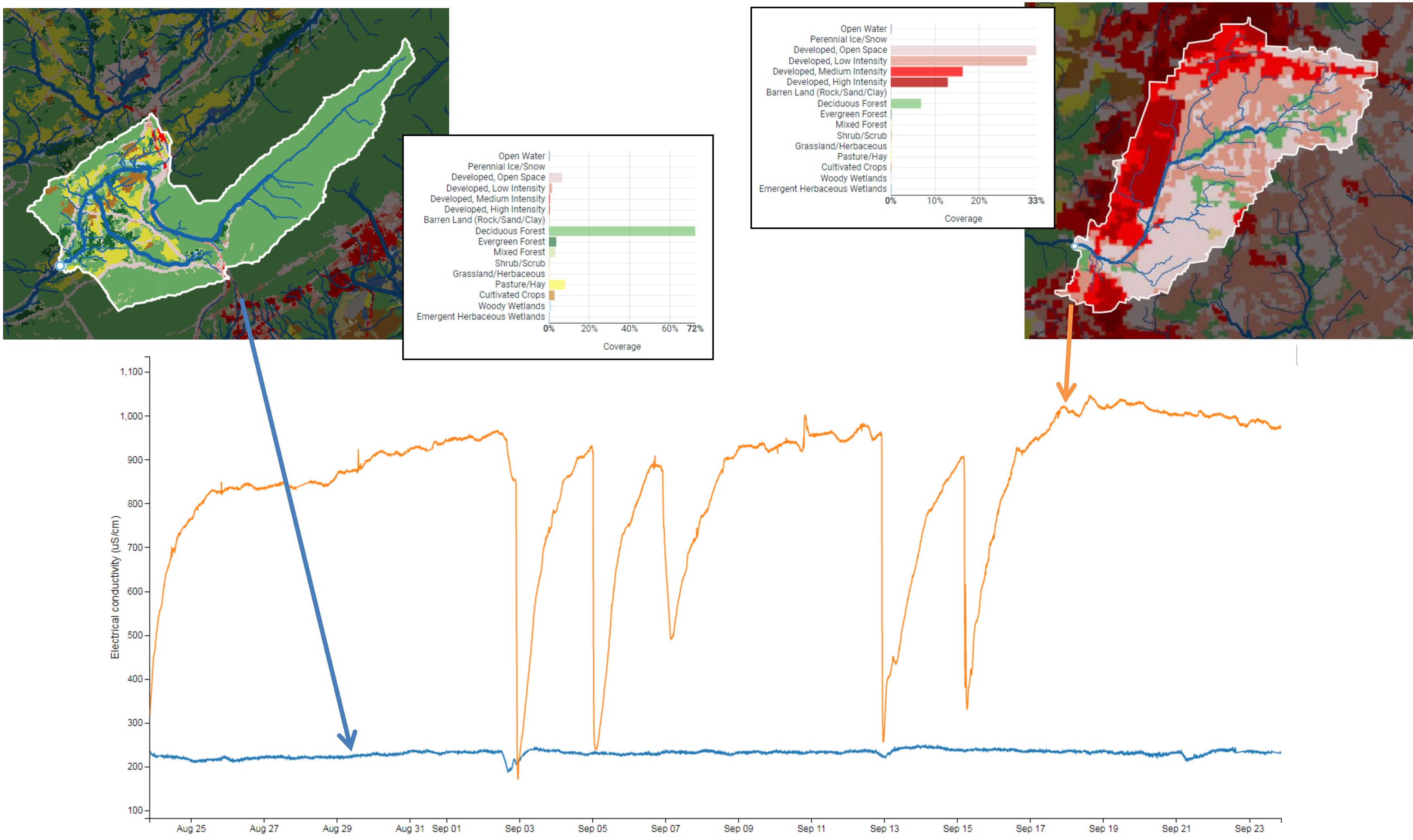


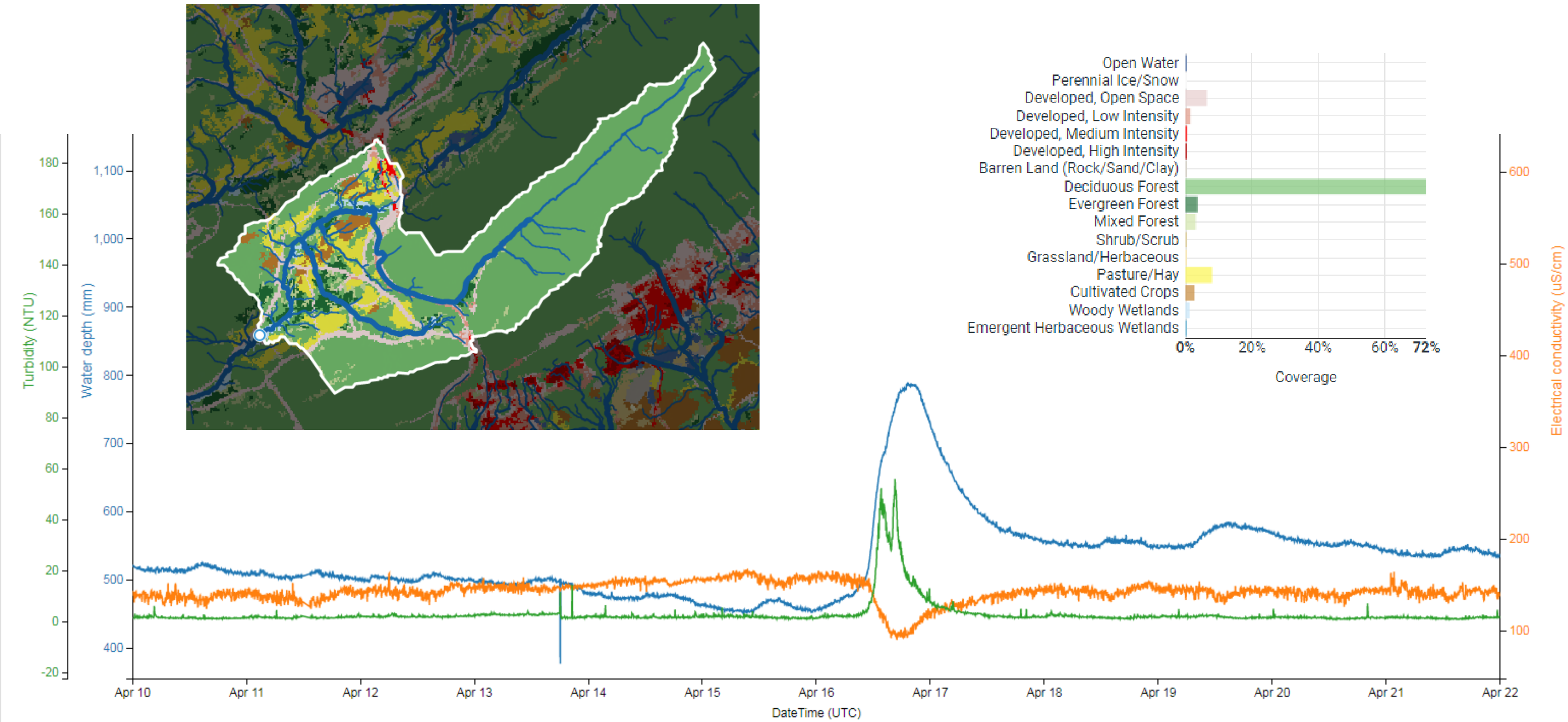
Fig. 5. Examples of increasing trends in base cations (sodium, calcium, and magnesium) in stream water throughout the continental United States. Time series were smoothed as moving averages over every three data points/observations. Please note that vertical axes differ.

- Freshwater salinization syndrome on a continental scale. Kaushal et al. 2018, PNAS

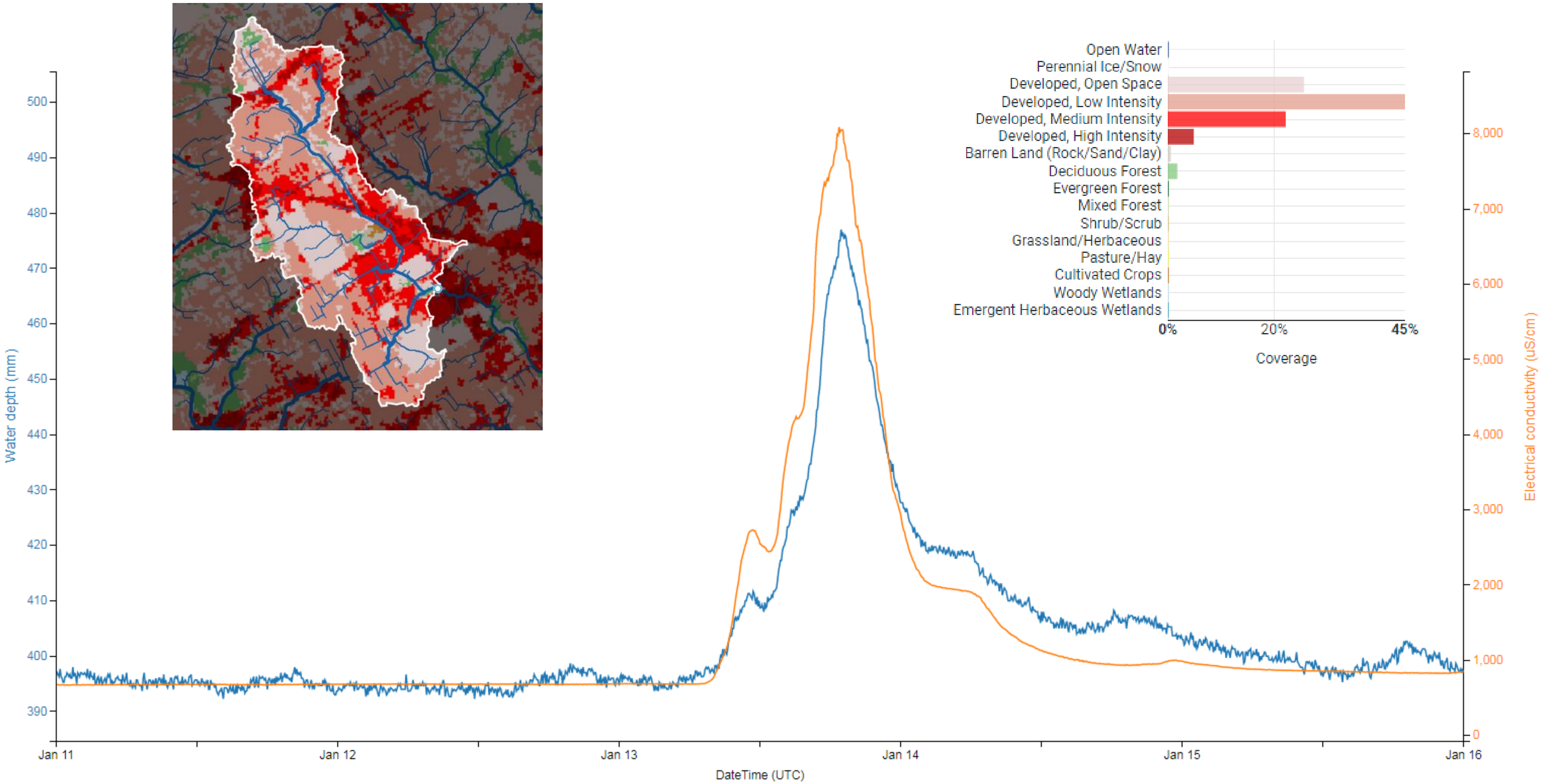
Natural versus Urban – Electric conductivity



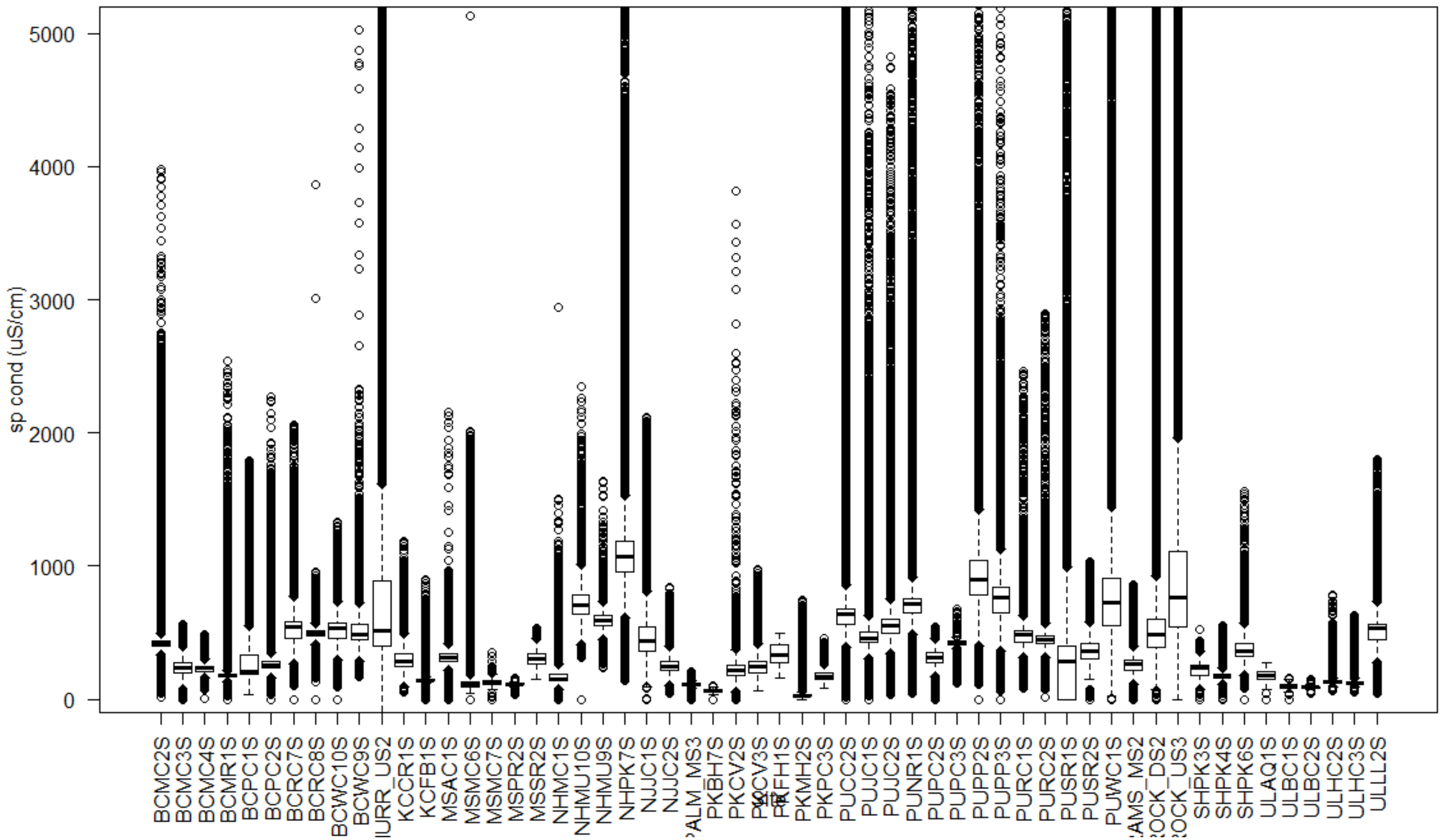
Mostly Forested Watershed



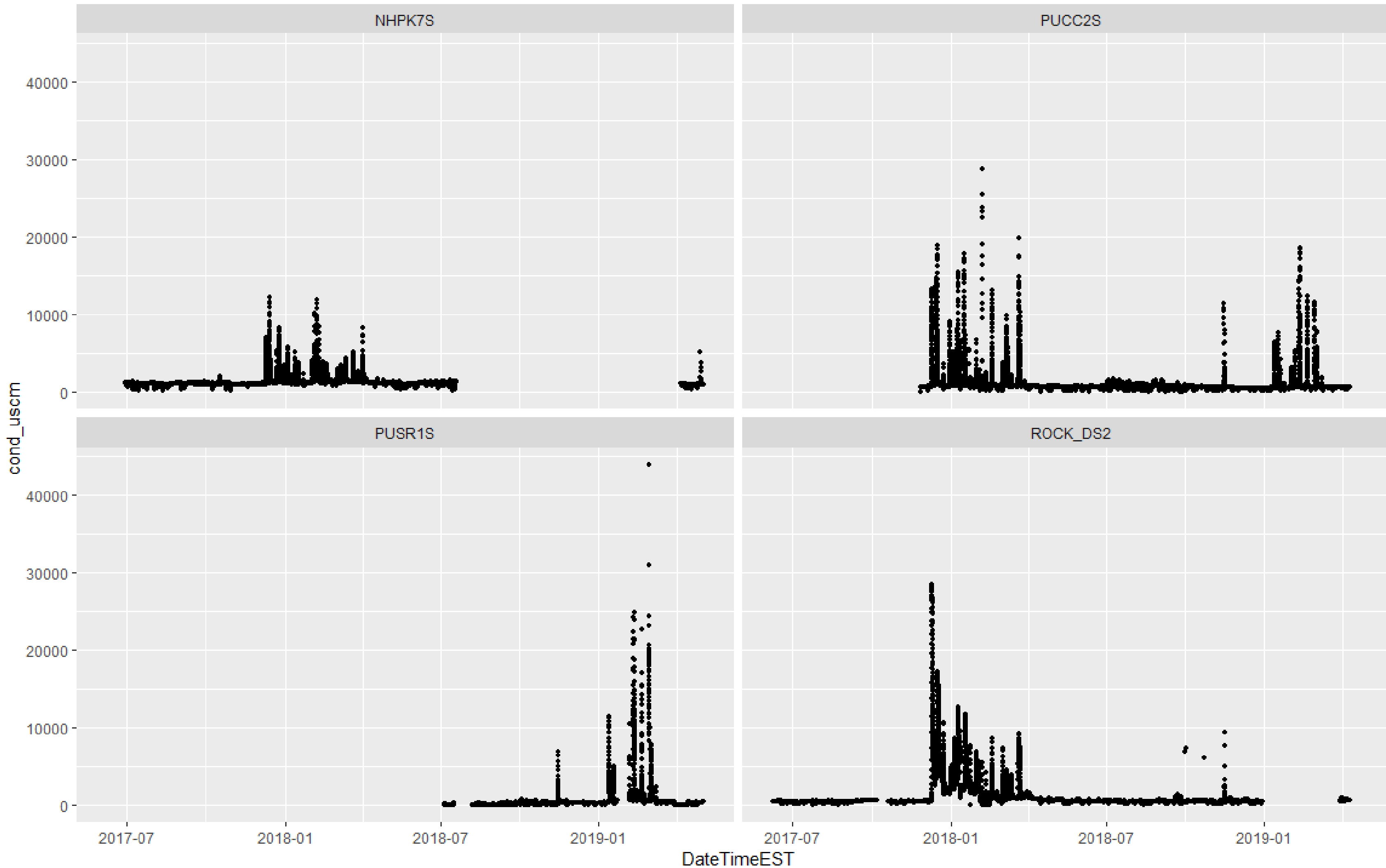
Mostly urban: impervious surfaces



DRWI sites, electric conductivity



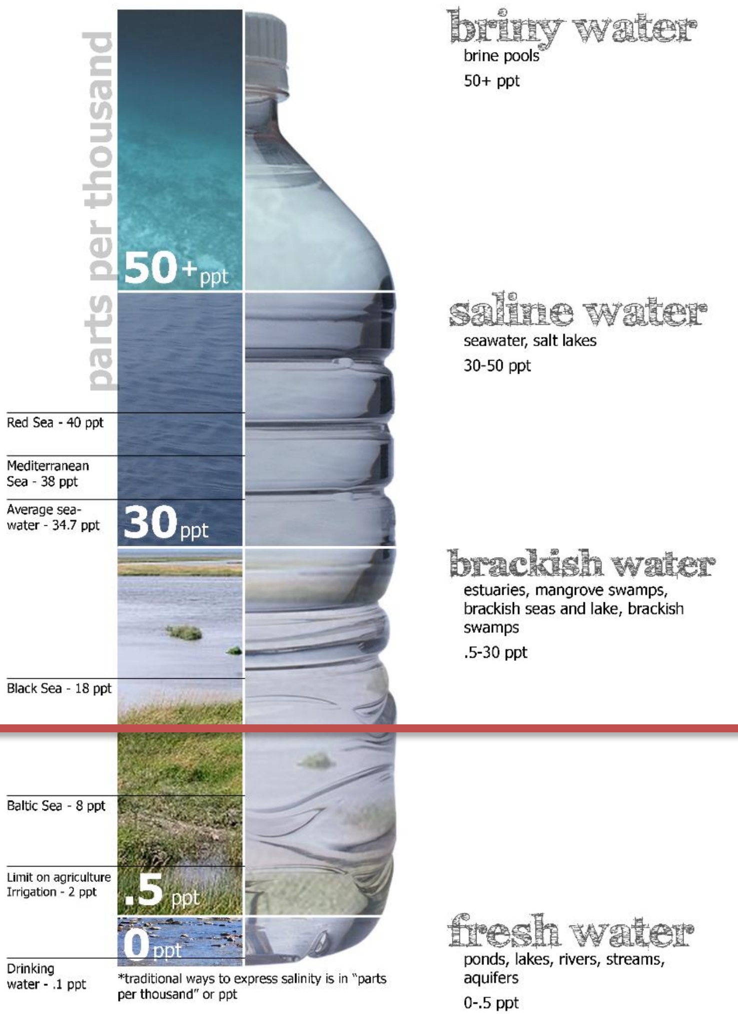
DRWI sites, electric conductivity



Electric conductivity to salinity

- 30 000 µS/cm
- Assuming it is mostly NaCl (likely)
- = 15 000 mg/L ~ 15 ppt

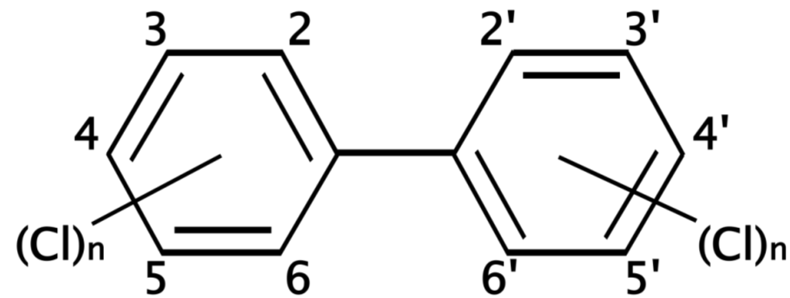
15 ppt

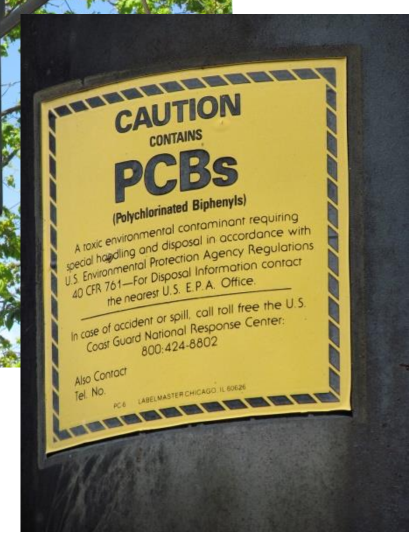


Synthetic chemical contaminants

Persistent organic pollutants (POPs)

- Polychlorinated biphenyls (PCBs)
  - 209 different forms
  - Dielectric and coolant fluids (transformers, capacitors), lubricants, plasticizers
  - Use is banned in the US.
  - 1930s -1970s, the total global production ~1.3 million tonnes.
  - ~65% in landfills or still within electrical equipment,
  - with the other 35% residing in sediments and open oceans
  - Hydrophobic and biomagnify.



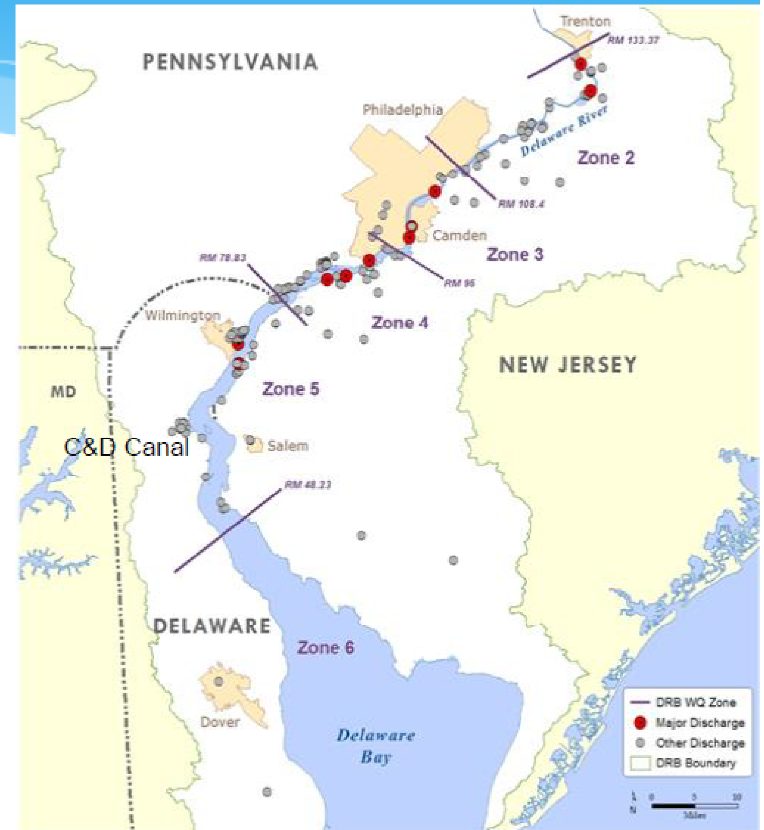


PCB TMDL Implementation

PMP required through >90 NPDES permits or Commission regulations beginning in 2005
Goal is to reduce PCB Loadings

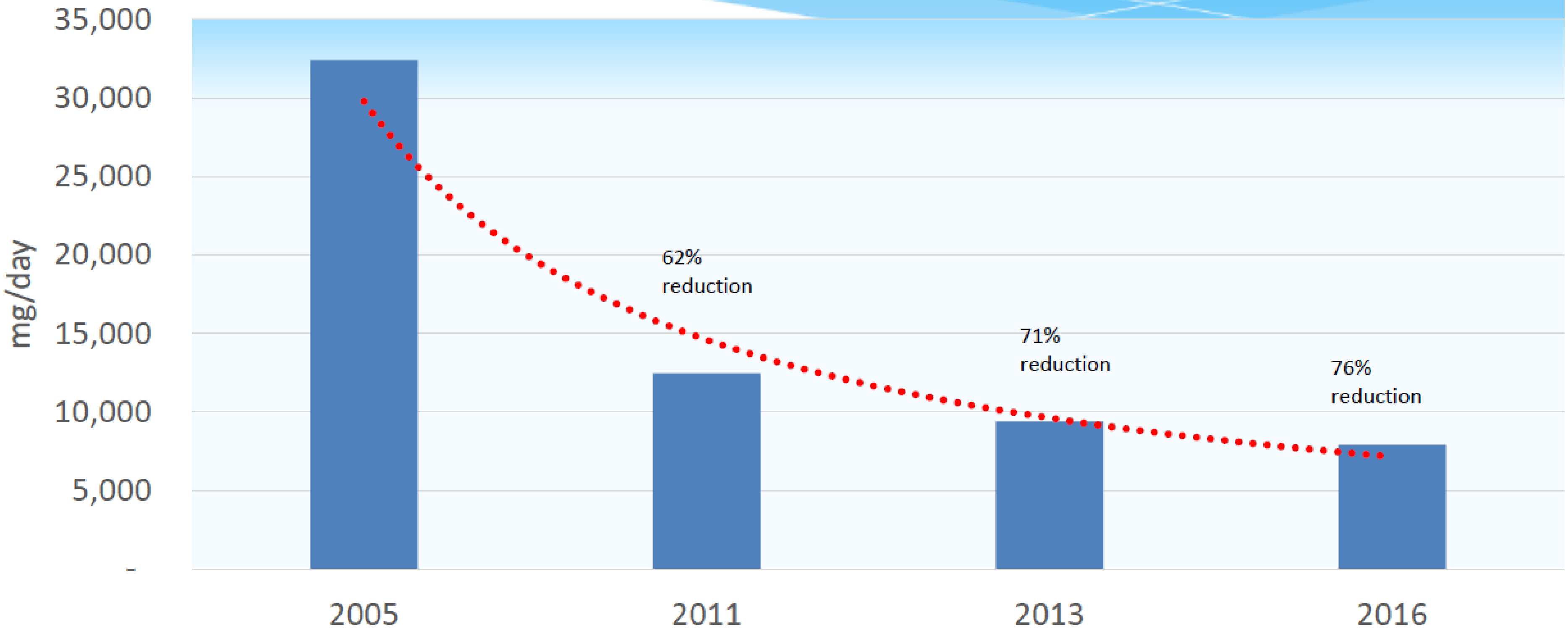
Key Elements
Source identification and reduction
Monitoring and progress reports
Measuring effectiveness of initiatives

Approaches
Remove PCB transformers and capacitors
Trackdown studies to identify and remove sources
Sediment control and removal

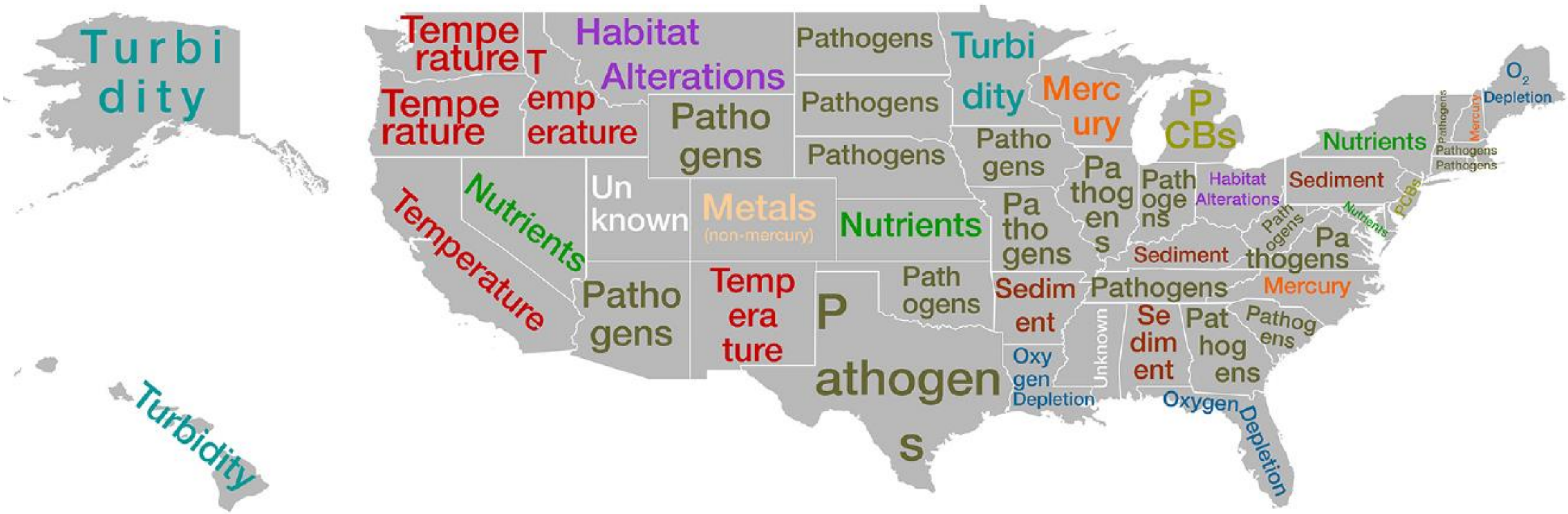


- Waters of the Lower Delaware River and Estuary at concentrations up to 1,000 times higher than the water quality criteria

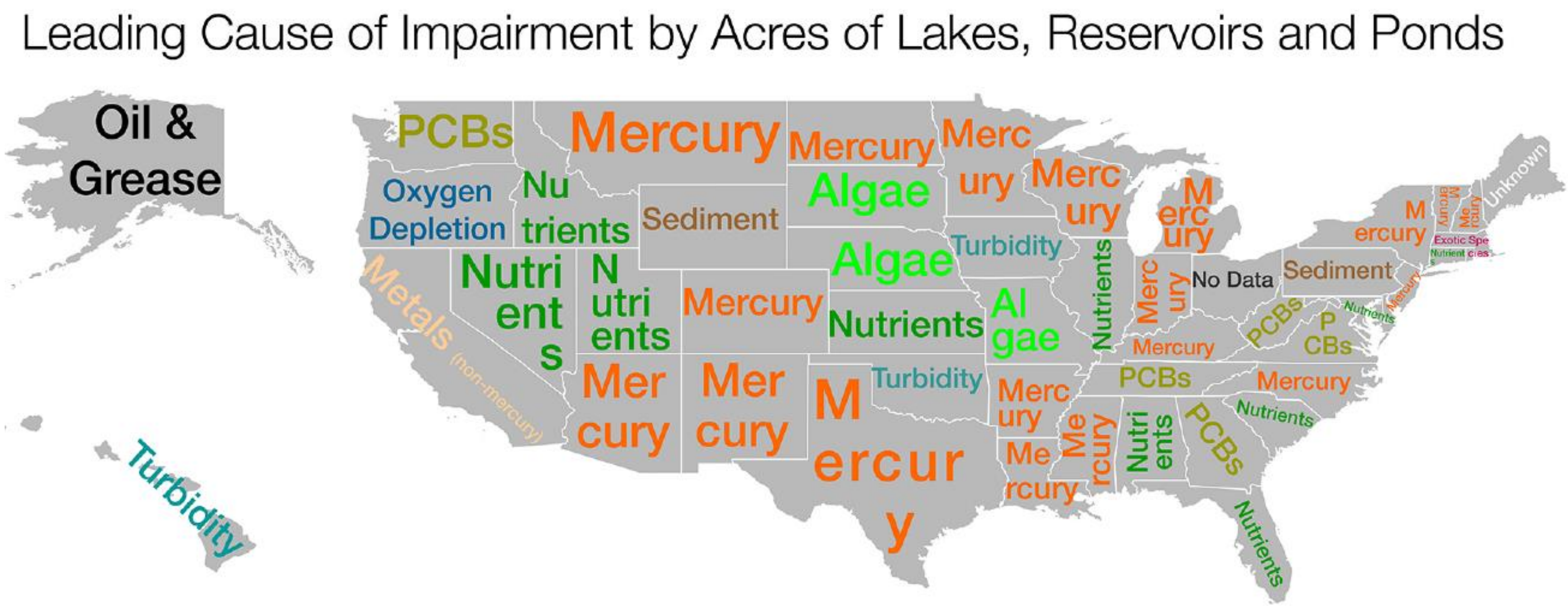
PCB Loadings Top Ten Point Source Dischargers mg/day



Leading Cause of Impairment by Miles of Rivers and Streams



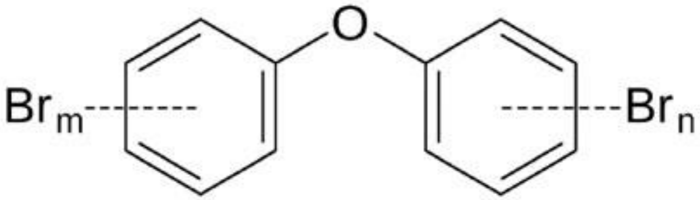
- Infographic from ewg.org, data from USEPA



- Infographic from ewg.org, data from USEPA

Persistent organic pollutants (POPs)

- Polybrominated diphenyl ethers (PBDEs)
  - Flame retardants
    - building materials, electronics, furnishings, motor vehicles, airplanes, plastics, polyurethane foams, and textiles
  - Banned in the US
  - 209 congeners, only a few were commercialized (mixtures)
  - Hydrophobic and biomagnify.



nature ecology & evolution

BRIEF COMMUNICATION

PUBLISHED: 13 FEBRUARY 2017 | VOLUME: 1 | ARTICLE NUMBER: 0051

Bioaccumulation of persistent organic pollutants in the deepest ocean fauna

Alan J. Jamieson[1*†], Tamas Malkocs[2], Stuart B. Piertney[2], Toyonobu Fujii[1] and Zulin Zhang[3]

The legacy and reach of anthropogenic influence is most clearly evidenced by its impact on the most remote and inaccessible habitats on Earth. Here we identify extraordinary levels of persistent organic pollutants in the endemic amphipod fauna from two of the deepest ocean trenches (>10,000 metres). Contaminant levels were considerably higher than documented for nearby regions of heavy industrialization, indicating bioaccumulation of anthropogenic contamination and inferring that these pollutants are pervasive across the world's oceans and to full ocean depth.

organisms have reported higher concentrations than in nearby surface-water species[11,12]. However, although these studies are described as 'deep sea', they rarely extend beyond the continental shelf (<2,000 m), so contamination at greater distances from shore and at extreme depths is hitherto unknown.

We measured the concentrations of key PCBs and PBDEs in multiple endemic and ecologically equivalent Lysianassoid amphipod Crustacea from across two of the deepest hadal trenches — the oligotrophic Mariana Trench in the North Pacific, and the more eutrophic Kermadec in the South Pacific. Two endemic amphi-

- PCBs and PBDEs detected in amphipod fauna living >10 000 m deep in the ocean.

Pesticides

https://water.usgs.gov/nawqa/pnsp/usage/maps/compound_listing.php?year=2016&hilo=H

Science of the Total Environment 538 (2015) 431–444

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Trends in pesticide concentrations and use for major rivers of the United States

Karen R. Ryberg [a,*], Robert J. Gilliom [b]

[a] U.S. Geological Survey (USGS), 821 E Interstate Avenue, Bismarck, ND 58503, USA
[b] USGS, 6000 J Street, Placer Hall, Sacramento, CA 95819, USA

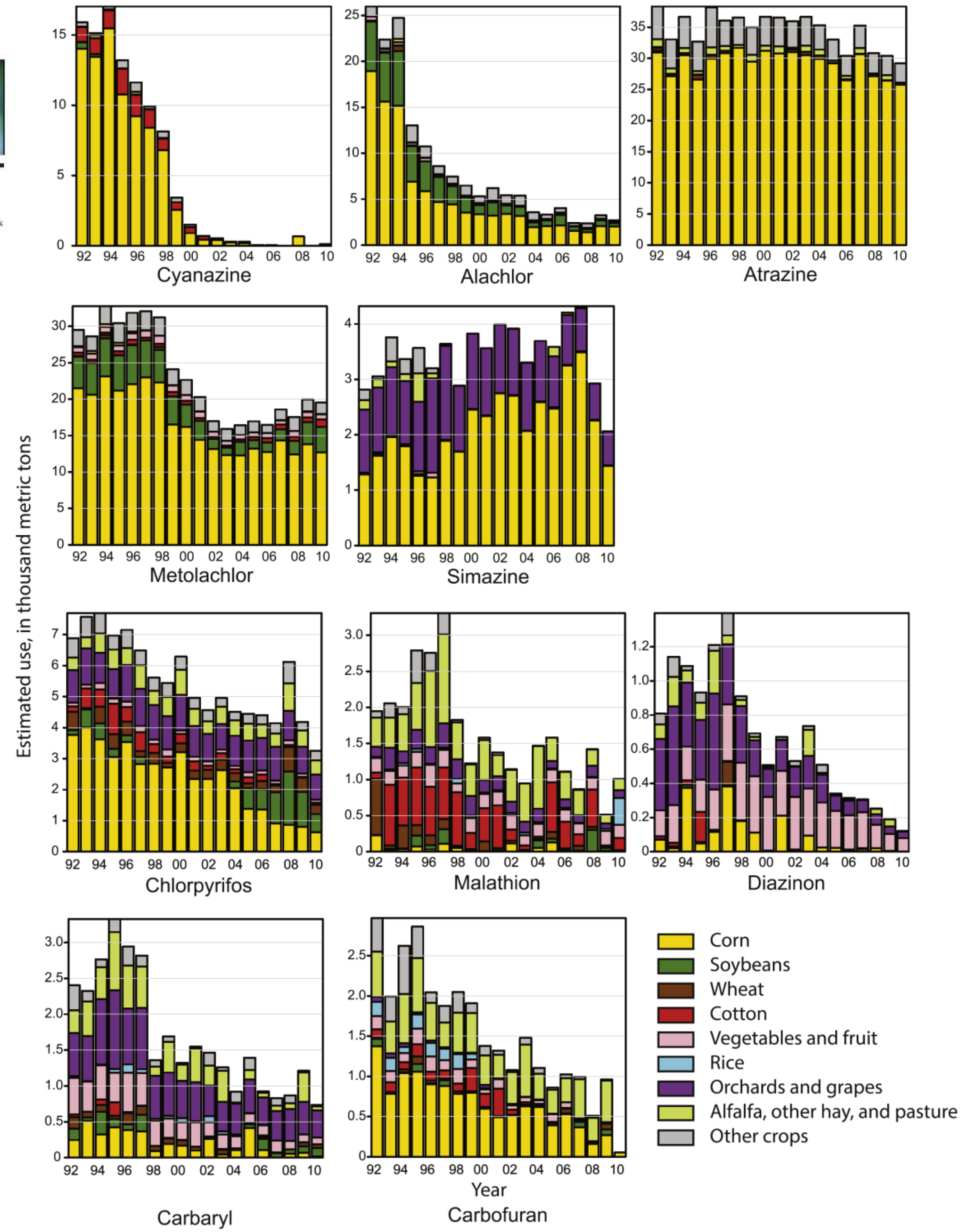
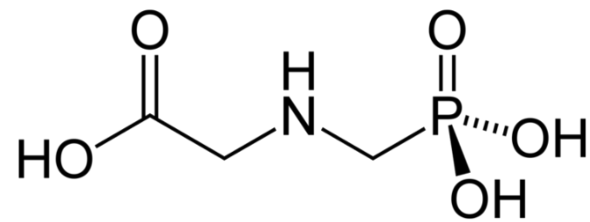
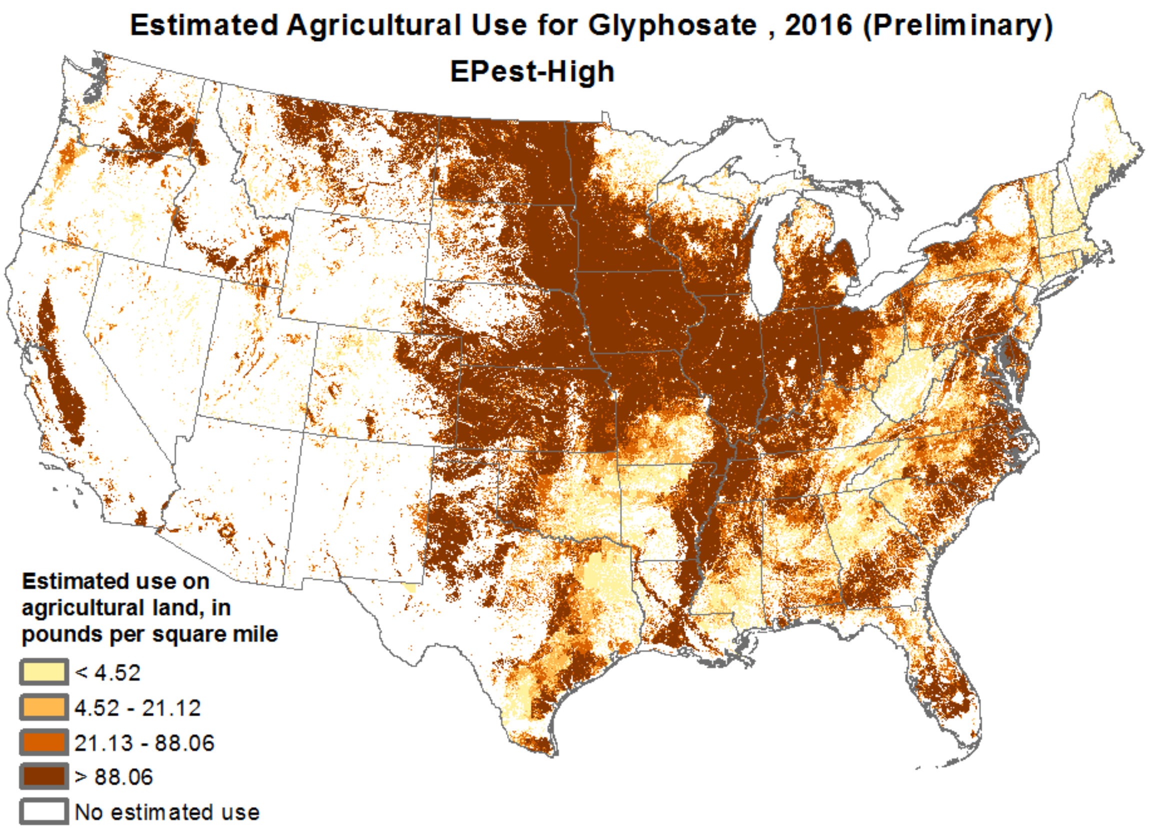


Fig. 2. National estimates of annual agricultural use during 1992–2010 for 10 pesticides for which concentration and use trends were assessed.

Glyphosate

- Wide spectrum herbicide
- Most commonly used in the US
- (Roundup-Monsanto)





Glyphosate

Ecological Applications, 15(4), 2005, pp. 1118–1124

THE LETHAL IMPACT OF ROUNDUP ON AQUATIC AND TERRESTRIAL AMPHIBIANS

RICK A. RELYEA[1]

Department of Biological Sciences, University of Pittsburgh, Pittsburgh, Pennsylvania 15260 USA

Toxicology 392 (2017) 32–39

Contents lists available at ScienceDirect

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TOXICOLOGY

journal homepage: www.elsevier.com/locate/toxicol

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Full length article

Glyphosate and Roundup® alter morphology and behavior in zebrafish

CrossMark

Daiane Bridi[a], Stefani Altenhofen[b], Jonas Brum Gonzalez[b], Gustavo Kellermann Reolon[b], Carla Denise Bonan[a,b,*]

[a] *Laboratório de Neuroquímica e Psicofarmacologia, Departamento de Biologia Celular e Molecular, Programa de Pós-Graduação em Biotecnologia Farmacêutica, Faculdade de Biociências, Pontifícia Universidade Católica do Rio Grande do Sul, Porto Alegre, RS, Brazil*
[b] *Laboratório de Neuroquímica e Psicofarmacologia, Departamento de Biologia Celular e Molecular, Programa de Pós-Graduação em Biologia Celular e Molecular, Faculdade de Biociências, Pontifícia Universidade Católica do Rio Grande do Sul, Porto Alegre, RS, Brazil*

Aquatic Toxicology 193 (2017) 210–216

ontents lists available at ScienceDirect

Aquatic Toxicology

AQUATIC TOXICOLOGY

journal homepage: www.elsevier.com/locate/aqtox

ELSEVIER

Research Paper

Stronger effects of Roundup than its active ingredient glyphosate in damselfly larvae

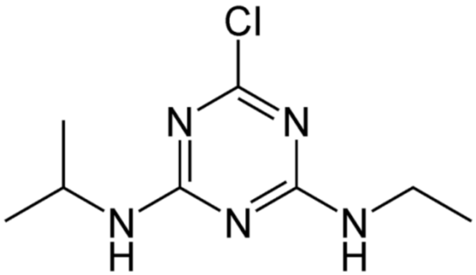
CrossMark

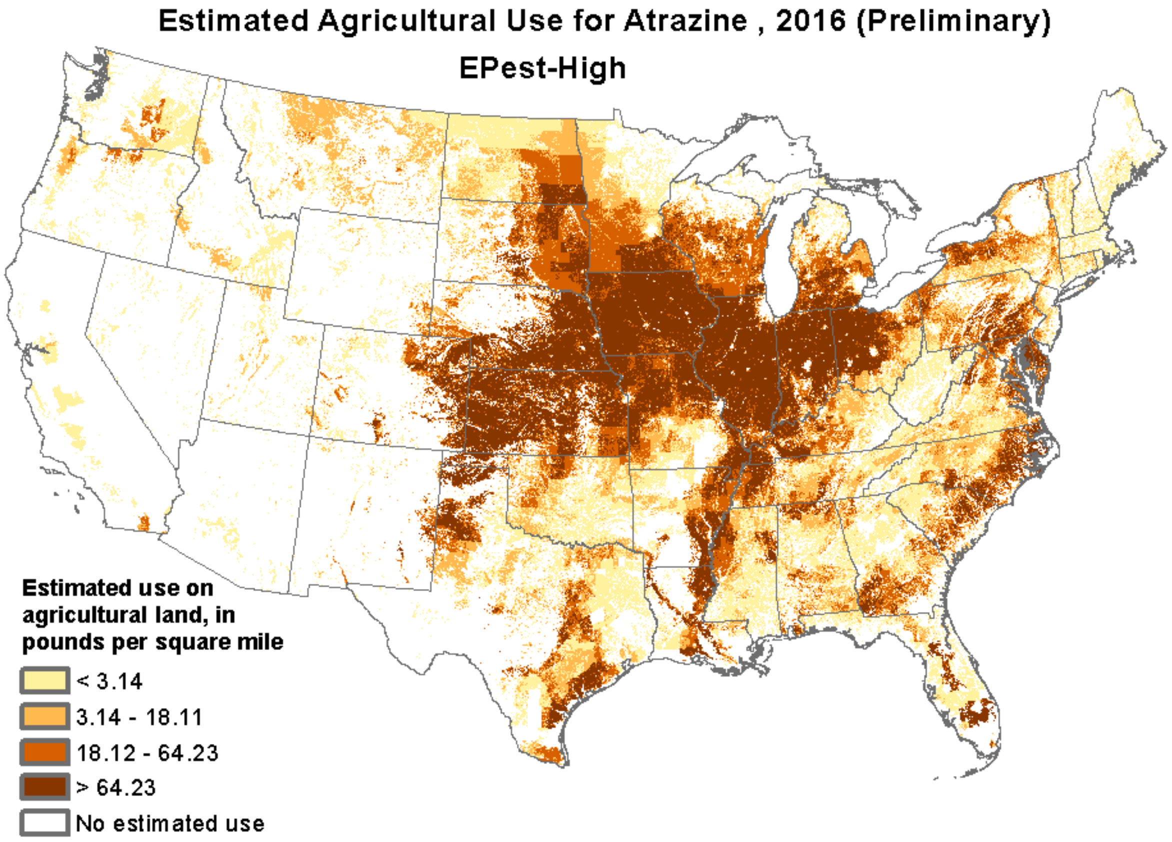
Lizanne Janssens[*], Robby Stoks

Evolutionary Stress Ecology and Ecotoxicology, University of Leuven, Deberiotstraat 32, B-3000 Leuven, Belgium

Atrazine

- Broad-leaf herbicide
- Banned in European Union
- Most commonly used in the US





Atrazine

Hermaphroditic, demasculinized frogs after exposure to the herbicide atrazine at low ecologically relevant doses

Tyrone B. Hayes*, Atif Collins, Melissa Lee, Magdelena Mendoza, Nigel Noriega, A. Ali Stuart, and Aaron Vonk

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Communicated by David B. Wake, University of California, Berkeley, CA, March 1, 2002 (received for review December 20, 2001)

This release can be found in the USGS Newsroom at: http://www.usgs.gov/newsroom/article.asp?ID=2467.

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News Release

May 19, 2010 Catherine Puckett 352-264-3532 cpuckett@usgs.gov
Don Tillitt 573-876-1886 dtillitt@usgs.gov

Commonly Used Atrazine Herbicide Adversely Affects Fish Reproduction

Chemosphere 193 (2018) 24–31

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Chemosphere

journal homepage: www.elsevier.com/locate/chemosphere

ELSEVIER

Habitat fragmentation caused by contaminants: Atrazine as a chemical barrier isolating fish populations

CrossMark

Cristiano V.M. Araújo [a, *], Daniel C.V.R. Silva [b, c], Luiz E.T. Gomes [c, d], Raphael D. Acayaba [d], Cassiana C. Montagner [d], Matilde Moreira-Santos [e], Rui Ribeiro [e], Marcelo L.M. Pompêo [b]

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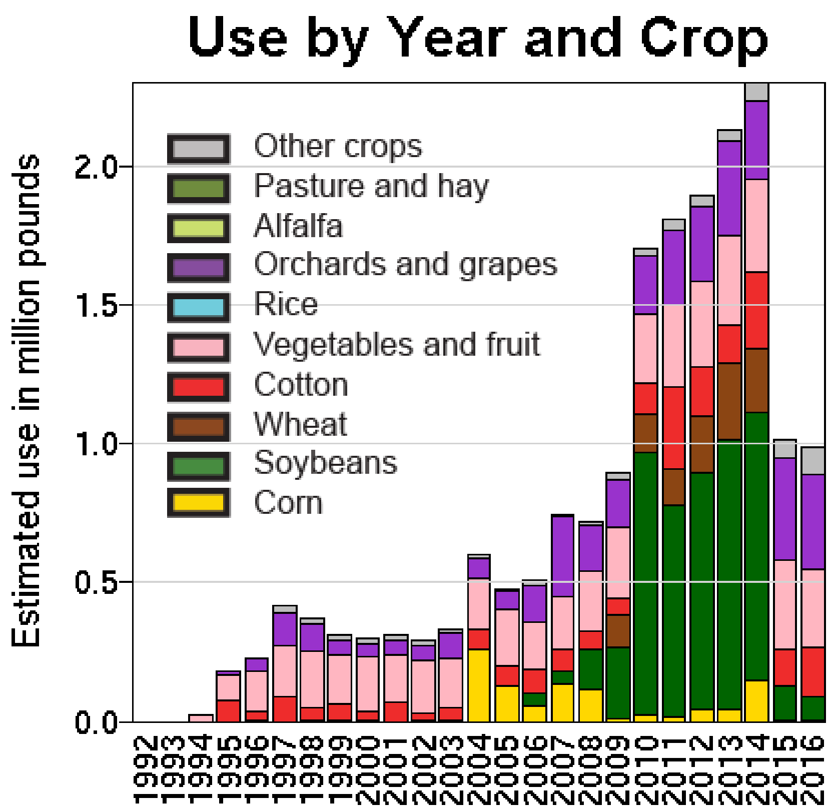
Neonicotinoids

- Neuro-active insecticides
- Clothianidin, Imidacloprid and Thiametoxam
- Banned by EU in 2018
- Affect pollinators
- Hydrophilic



Imidacloprid

Neonicotinoids

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http://dx.doi.org/10.1071/EN15061

First national-scale reconnaissance of neonicotinoid insecticides in streams across the USA

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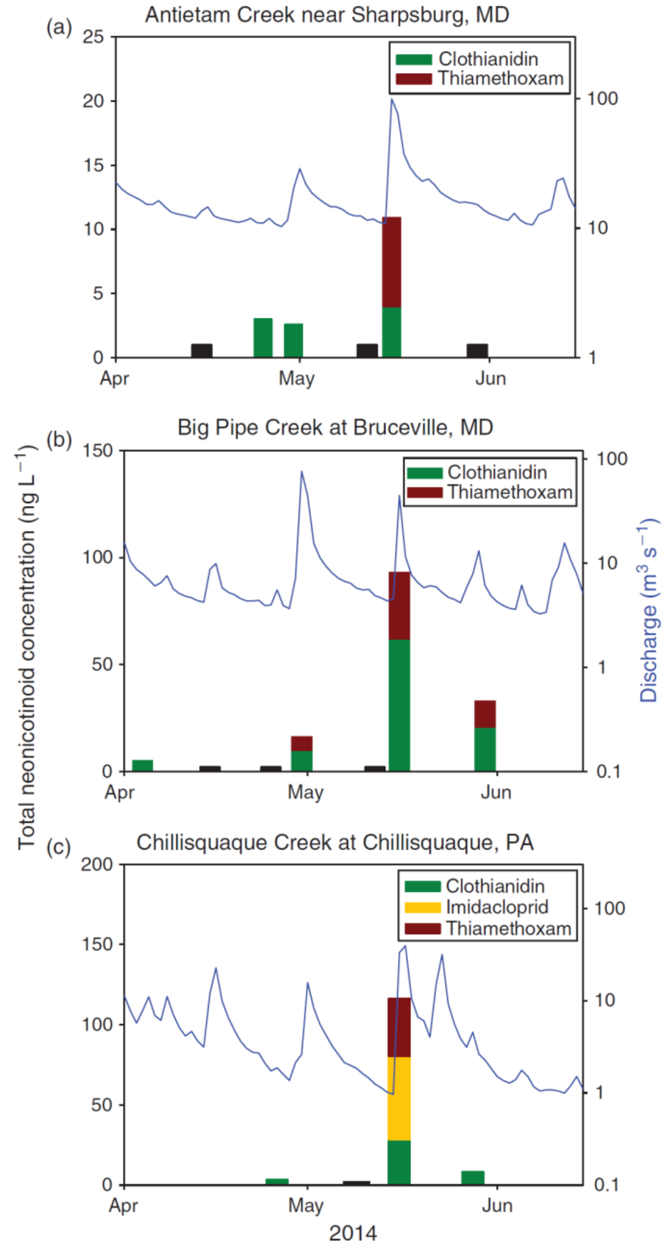


Fig. 6. Concentrations of clothianidin, imidacloprid and thiamethoxam and the corresponding stream discharge at three sites in the Chesapeake Bay area sampled in 2014. Black bars represent samples where no neonicotinoids were detected.

Contaminants of emerging concern (CECs)

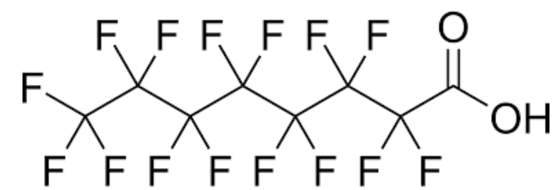
- *Scarcity of information in the scientific literature or there are poorly documented issues about the associated potential problems they could cause*
- Very low concentrations in streams and rivers
  - Difficult to quantify
  - Difficult to legislate
- Endocrine disruptors (compounds that alter the normal functions of hormones)
- Low acute toxicity
- **Remain in wastewater and beyond because treatment plants weren't designed to remove them**

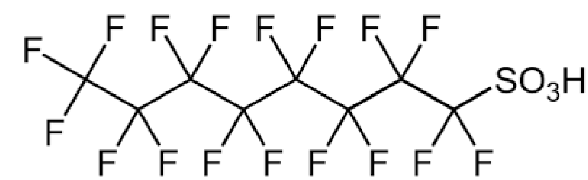
Contaminants of emerging concern (CECs)

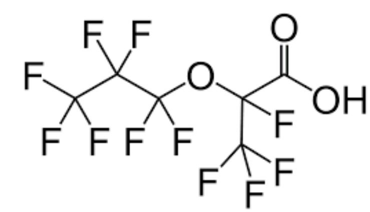
- We use in our everyday life:
  - prescription and non-prescription drugs
  - Personal care products
  - Hygiene products
  - Additives (preservatives)
  - Nanoparticles
  - Plasticizers
  - PFAS
  - Traditional contaminants with emerging issues

Per- and poly-fluoroalkyl substances (PFAS)

- Produced since 1940
- Highly resistant to degradation (strong C-F)
- Highly hydrophilic
- More than 5000 compounds
- Only about 30 have been quantified
- Most commonly studied (not produced any more)
  - Perfluorooctanoic acid (PFOA)
  - Perfluorooctane sulfonic acid (PFOS)
- Replaced by GenX technology







GenX

Per- and poly-fluoroalkyl substances (PFAS)

- Present in:
  - Food packaging
  - Stain- and water-repellent fabrics
  - Nonstick products (e.g., Teflon)
  - Polishes, waxes, paints, cleaning products
  - Fire-fighting foams

- Sources to river contamination
  - Landfills
  - Waste Water Treatment Plants
  - Airports and military bases where firefighting training occurs

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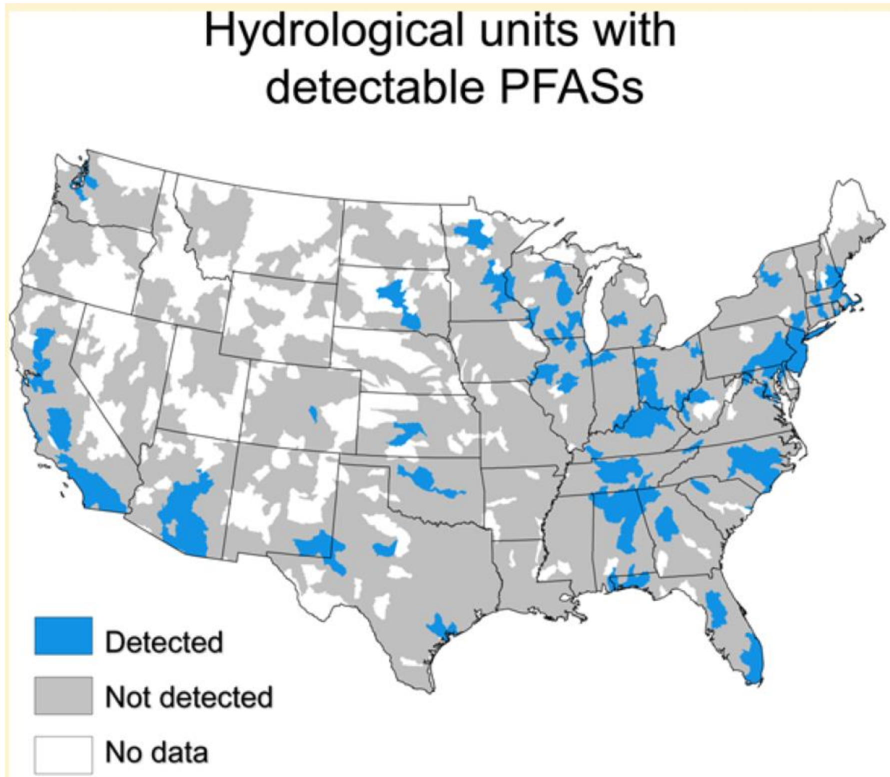
Detection of Poly- and Perfluoroalkyl Substances (PFASs) in U.S. Drinking Water Linked to Industrial Sites, Military Fire Training Areas, and Wastewater Treatment Plants

Xindi C. Hu,[*,†,‡] David Q. Andrews,[§] Andrew B. Lindstrom,[∥] Thomas A. Bruton,[⊥] Laurel A. Schaider,[#] Philippe Grandjean,[†] Rainer Lohmann,[@] Courtney C. Carignan,[†] Arlene Blum,[⊥,∇] Simona A. Balan,[●] Christopher P. Higgins,[○] and Elsie M. Sunderland[†,‡]



Stream and River Restoration

Stream and River Restoration

- Potentially same techniques used for nutrients and sediments.
  - Level lip spreaders
  - Retention ponds
  - Riparian buffers
  - Constructed wetlands
- POPs and metals: clean ups of contaminated soils (bioremediation), working with point-source polluters.
- Acid deposition, declining.
- AMD: chemical treatments (limestone additions), constructed wetlands.
- For the rest, toxicology towards aquatic non-target organisms largely unknown
  - Chemical cocktails
  - N, P and Sediments are not the true causes of impairment
  - WWTPs