Chemicals of emerging concern in waters, sediments, and subsistence fish used by the Grand Portage Band of Chippewa

Seth Moore, Grand Portage Band of Lake Superior Chippewa

Tiffany Wolf, University of Minnesota

Mark Ferrey, Minnesota Pollution Control Agency

Mark Jankowski, U.S. Environmental Protection Agency

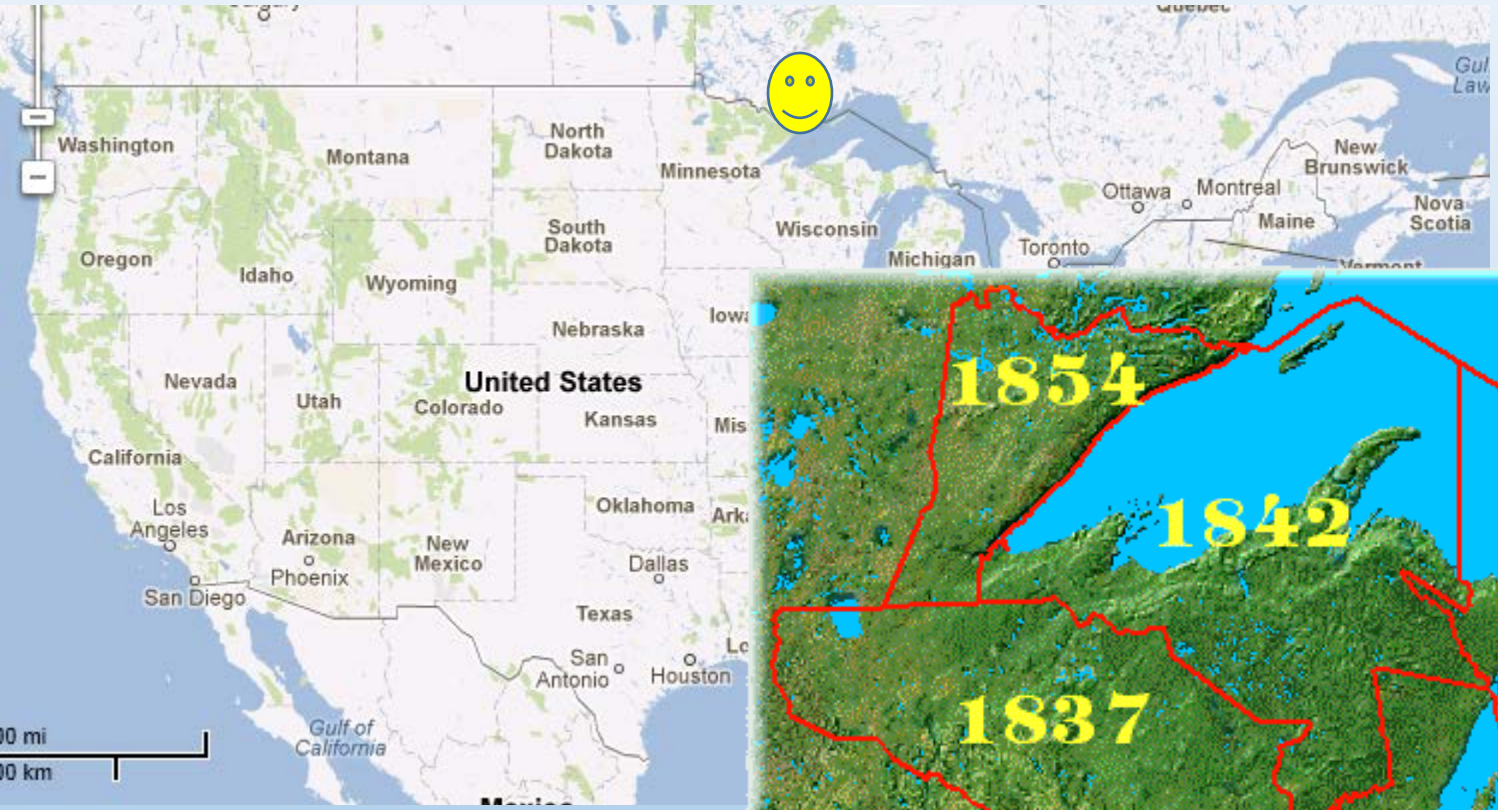
Jessica Deere, University of Minnesota

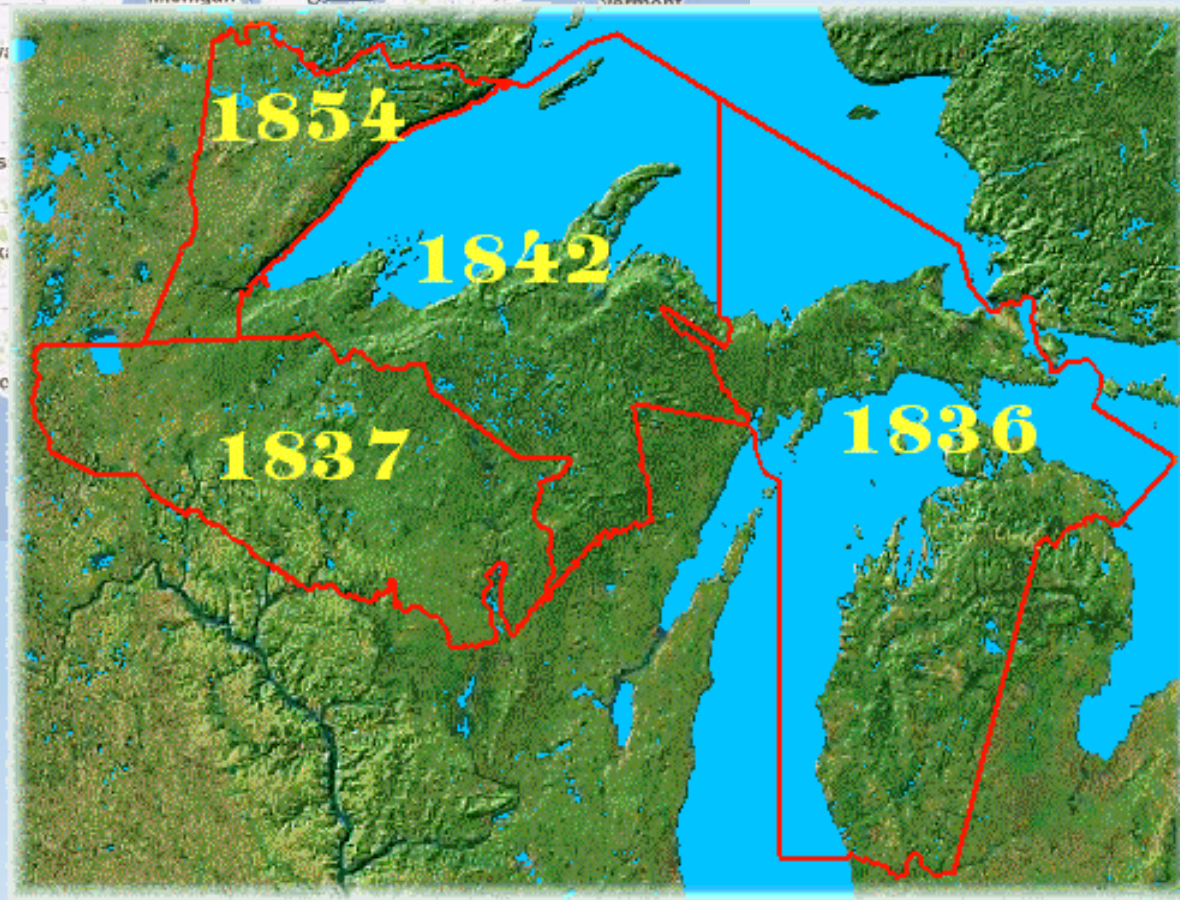
Mateo Convertino, University of Minnesota

Nicholas Phelps, University of Minnesota

Alexander Primus, University of Minnesota

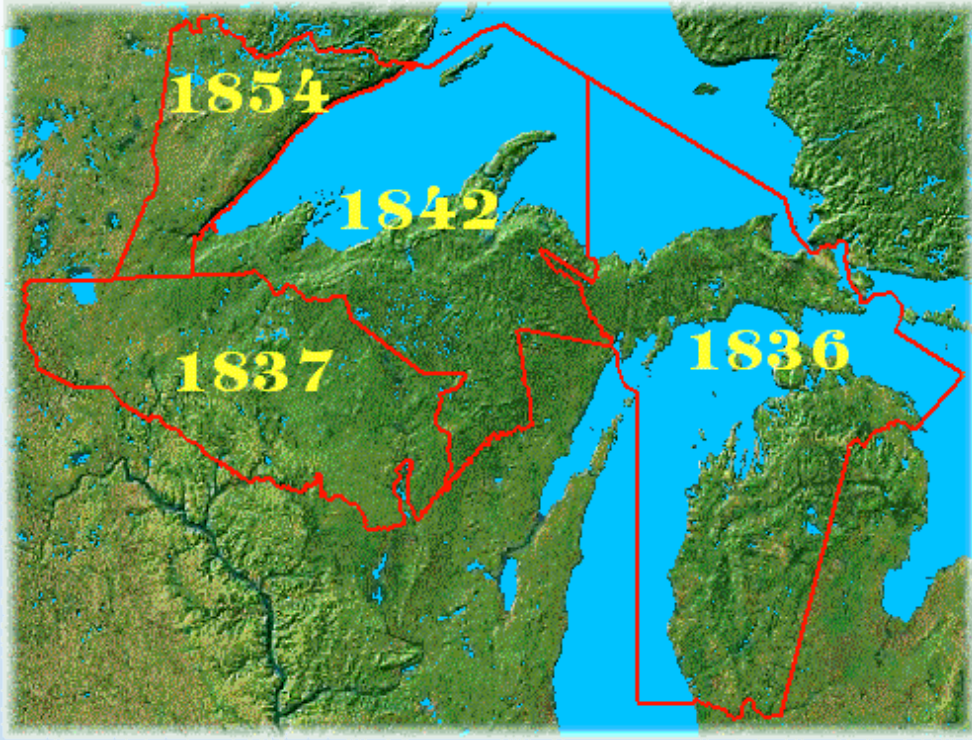
Where is Grand Portage?

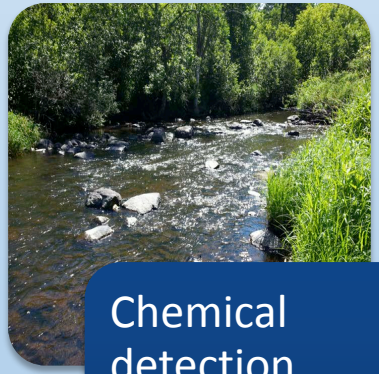




Concerns

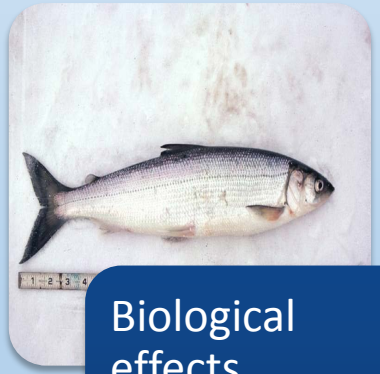
- Ecological effects
- Human health effects





Chemical detection

- Water
- Sediment
- fish



Biological effects

- Stress
- Parasites
- Fitness
- Reproductive state

Ecological effects

- Community structure

Human/Biological impacts

Diclofenac

Introduced to India for treatment of livestock in 1990s

Lethal to Gyps vultures

- Visceral gout in internal organs and acute renal tubular necrosis

The contamination of 1/760 livestock carcasses is sufficient to explain collapse in vulture population

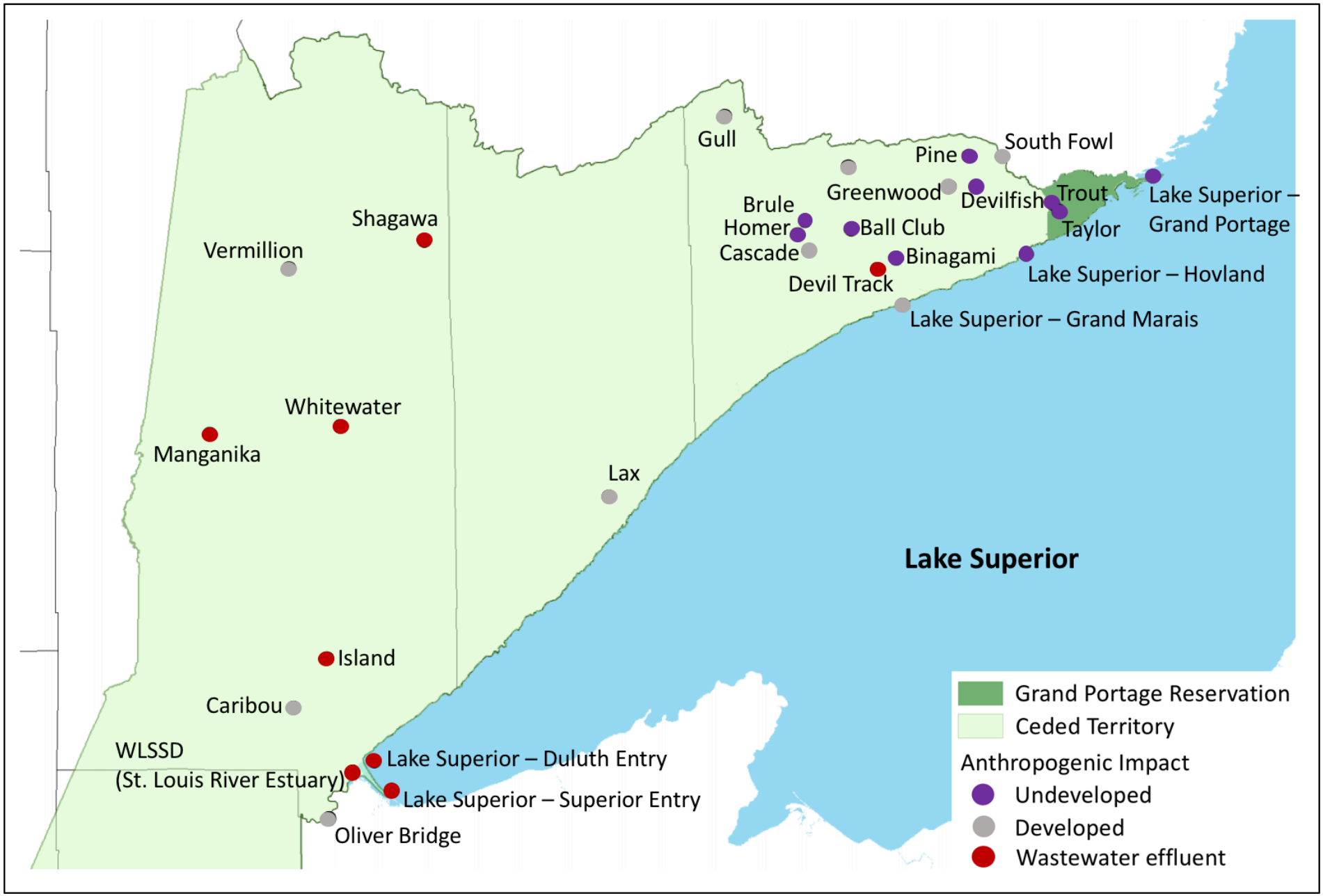
Led to rabies increase

Biological Effects

- ✓Dosing an experimental lake with 5 parts per trillion of the synthetic estrogen ethinylestradiol caused the minnow population to collapse.
- ✓30 parts per trillion fluvoxamine (an SSRI) in water triggers immediate spawning in mussels.
- ✓Fish behavior is altered after exposure to 1 part per trillion of estradiol.
- ✓Iopamidol + Chlorine = triiodomethanes (highly toxic compounds).

Experimental Design

Anthropogenic Impact	Sample Size	Examples
Heavily Impacted/Wastewater Treatment Effluent	N=8	Wastewater effluent/developed lakes
Developed	N= 10	Greenwood lake/Island Lake
Undeveloped/Wilderness	N= 9	North/South Fowl Lakes
Longitudinal	N=4	Up/Downstream St. Louis River
Discretionary	N=6	Moose/deer/rice/spring water


Gull
South Fowl
Pine
Greenwood
Devilfish
Trout
Lake Superior –
Grand Portage
Brule
Homer
Cascade
Ball Club
Taylor
Shagawa
Vermillion
Binagami
Devil Track
Lake Superior – Hovland
Lake Superior – Grand Marais
Whitewater
Manganika
Lax
Lake Superior
Island
Caribou
WLSSD
(St. Louis River Estuary)
Lake Superior – Duluth Entry
Lake Superior – Superior Entry
Oliver Bridge
Grand Portage Reservation
Ceded Territory
Anthropogenic Impact
Undeveloped
Developed
Wastewater effluent

2016 and 2017 combined

- 28 sites

2016

- Water, sediment, and fish
  - Samples from 14 different sites

2017

- Water, sediment, and fish
  - Samples from 17 different sites

Water samples

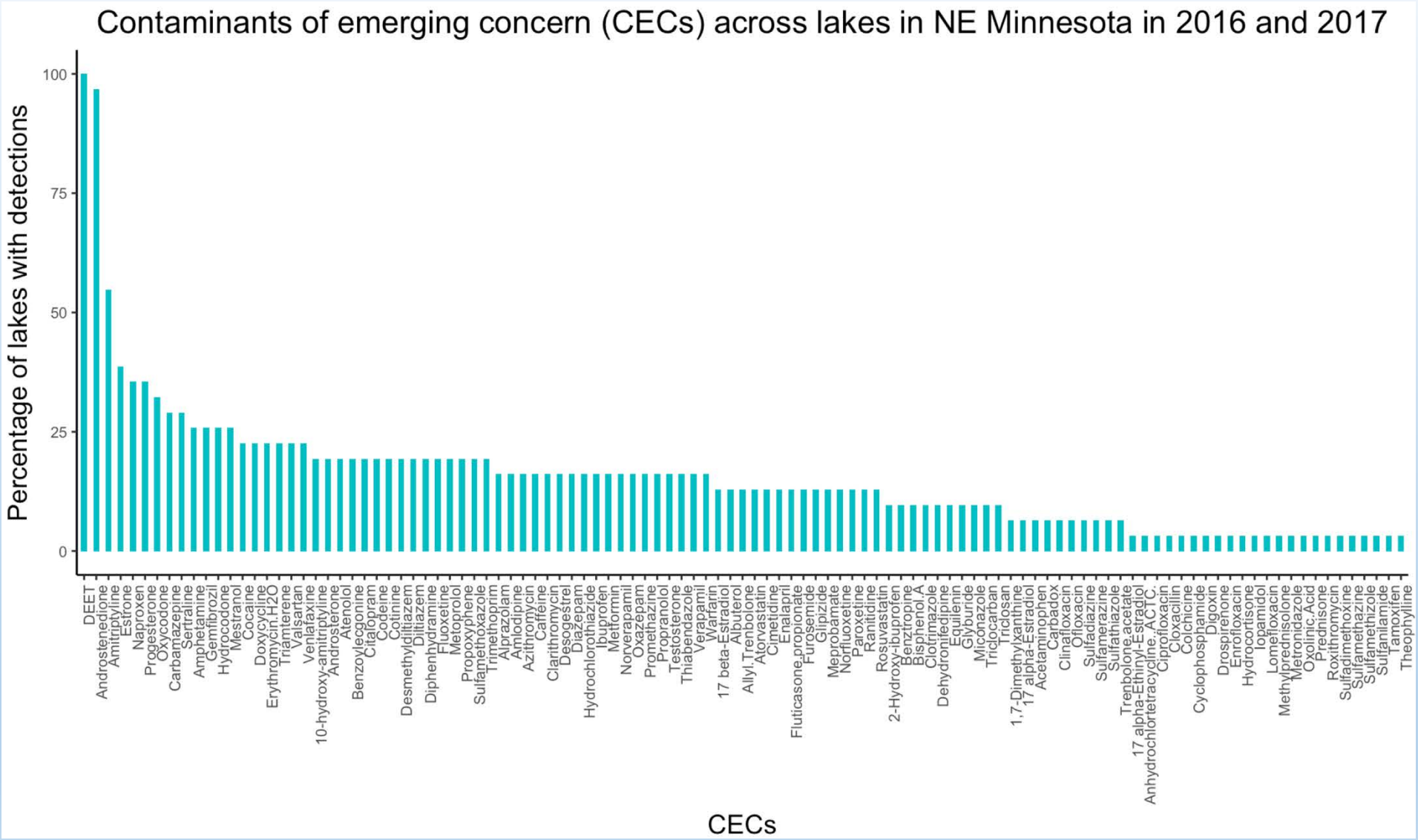
- 17 sites
- Screened 141 CECs (lists 1-6)
  - 93 CECs found in water samples (66% of those tested for)
- 1 – 77 detects in water samples per site
  - Undeveloped: 3 – 7 detects
  - Developed: 4 – 10 detects
  - Wastewater effluent: 49 – 84 detects
- Screened 16 hormones

Sediment samples

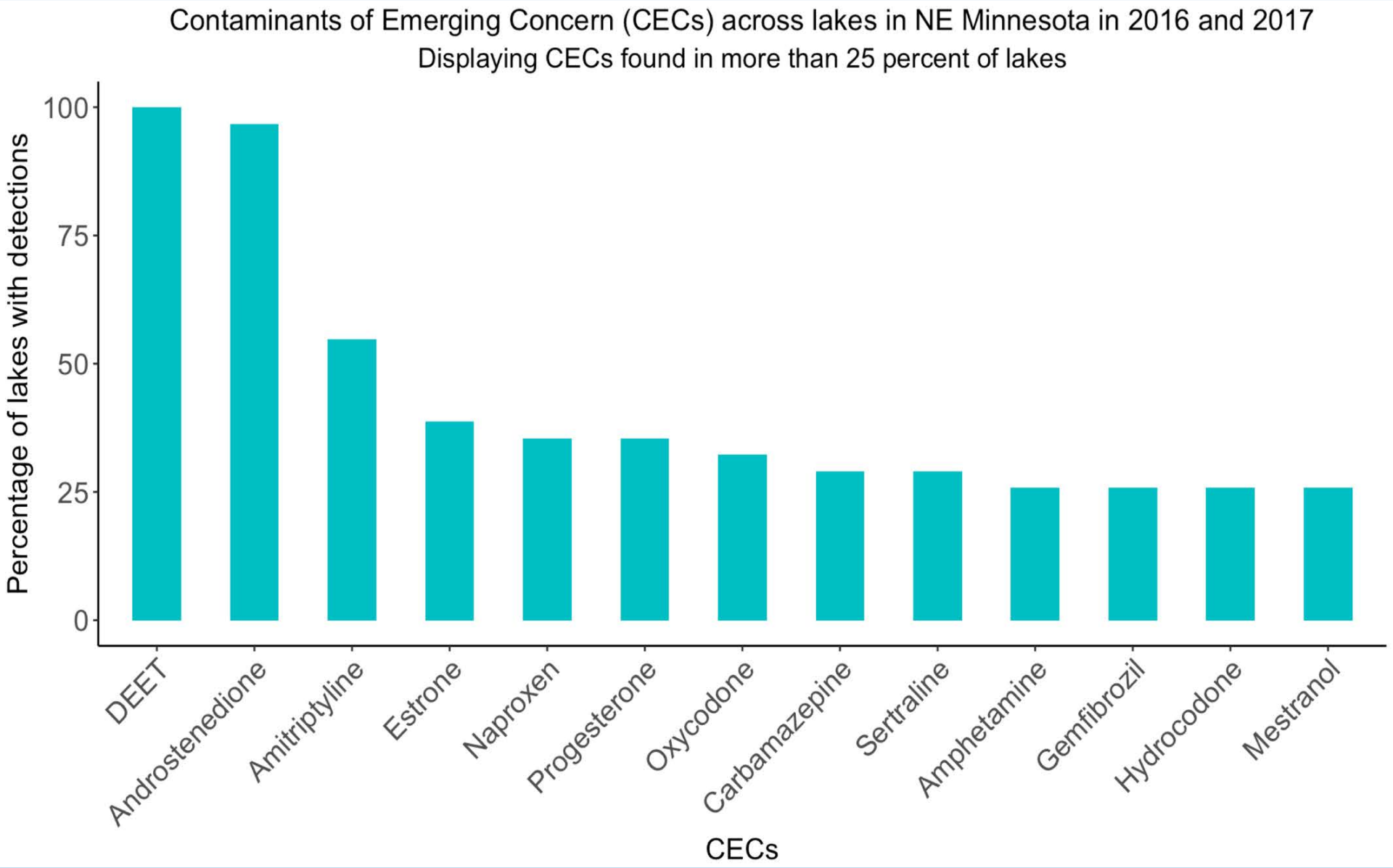
- 19 sites
- Screened 141 CECs (lists 1-6)
  - 57 CECs found in sediment samples (40% of those tested for)
- 2 – 59 detects in sediment samples per site
  - Undeveloped: 2 – 6 detects
  - Developed: 1 – 3 detects
  - Wastewater effluent: 3 – 59 detects

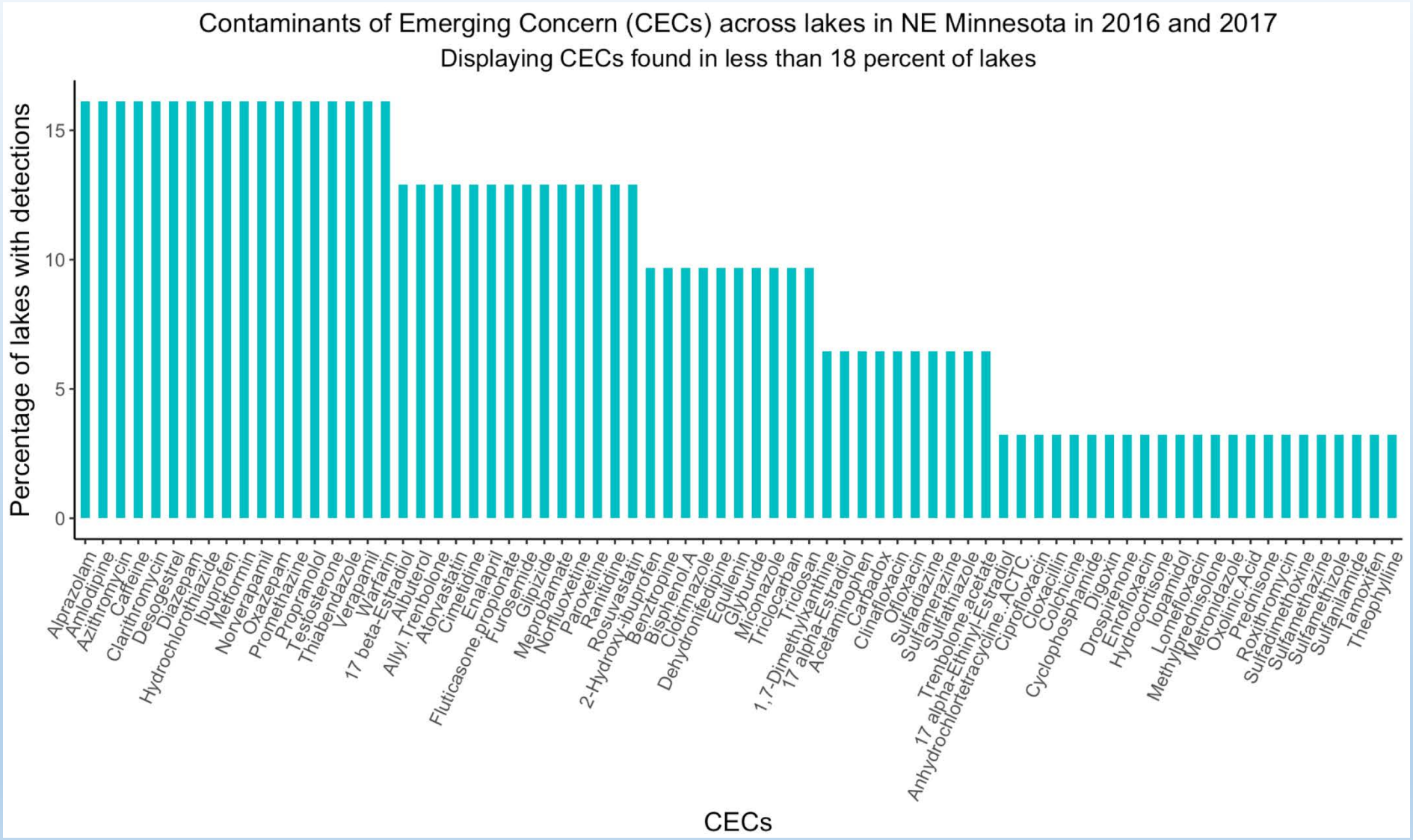
Fish samples

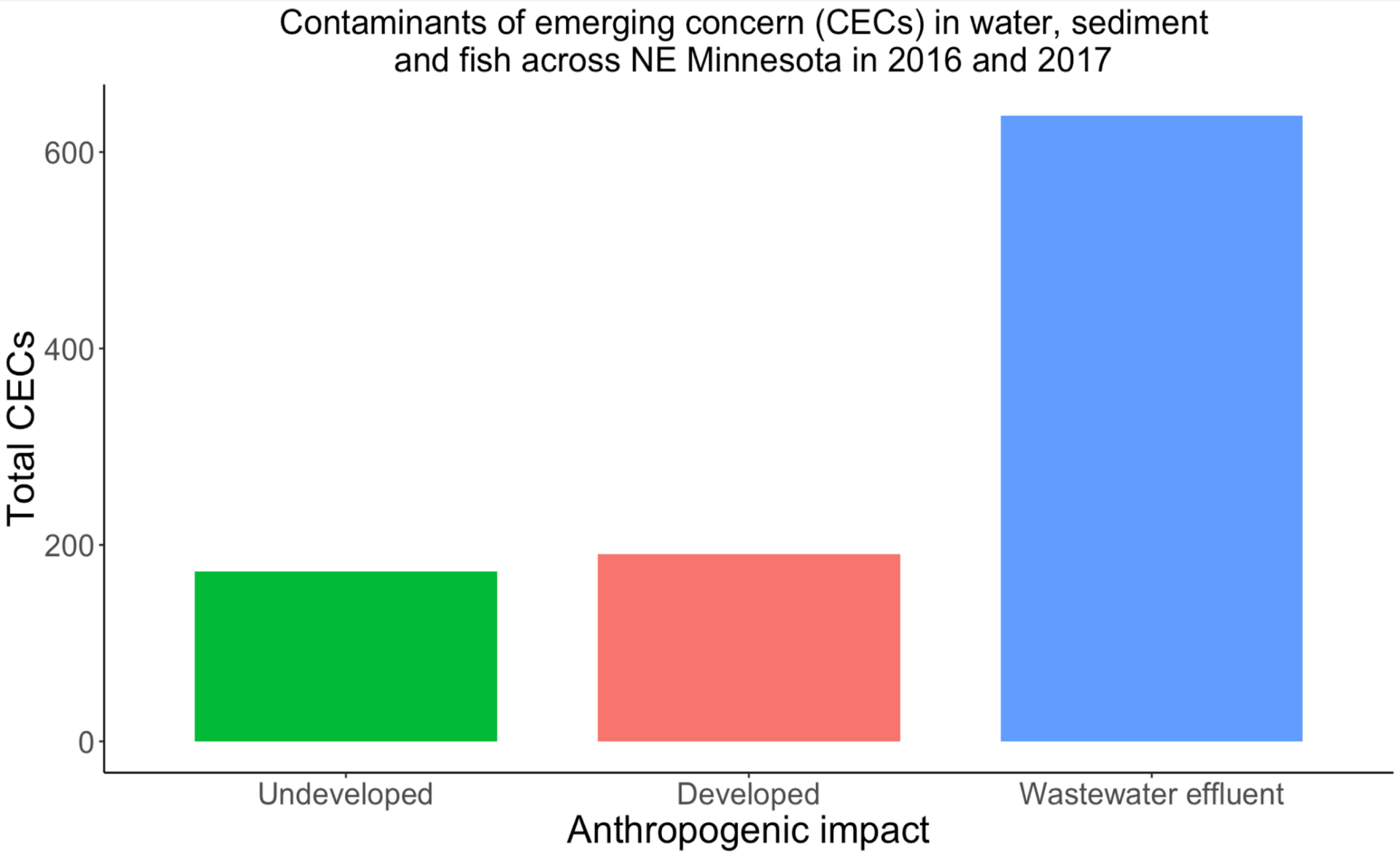
- 19 sites
- Screened 141 CECs (lists 1-6)
  - 26 CECs found in fish samples (18% of those tested for)
- 1 – 7 detects in fish samples per site
  - Undeveloped: 1 – 5 detects
  - Developed: 1 – 7 detects
  - Wastewater effluent: 2 – 7 detects

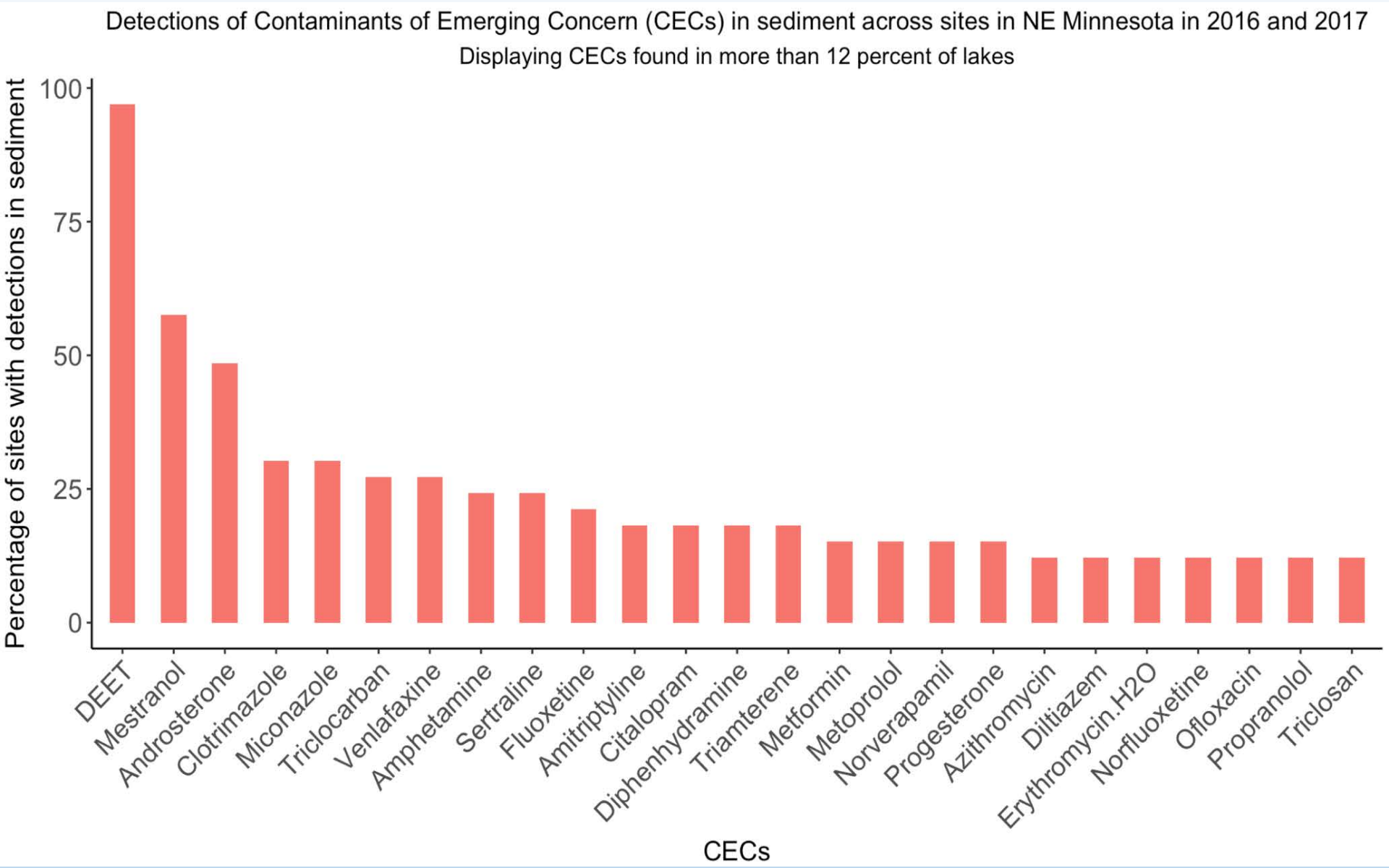


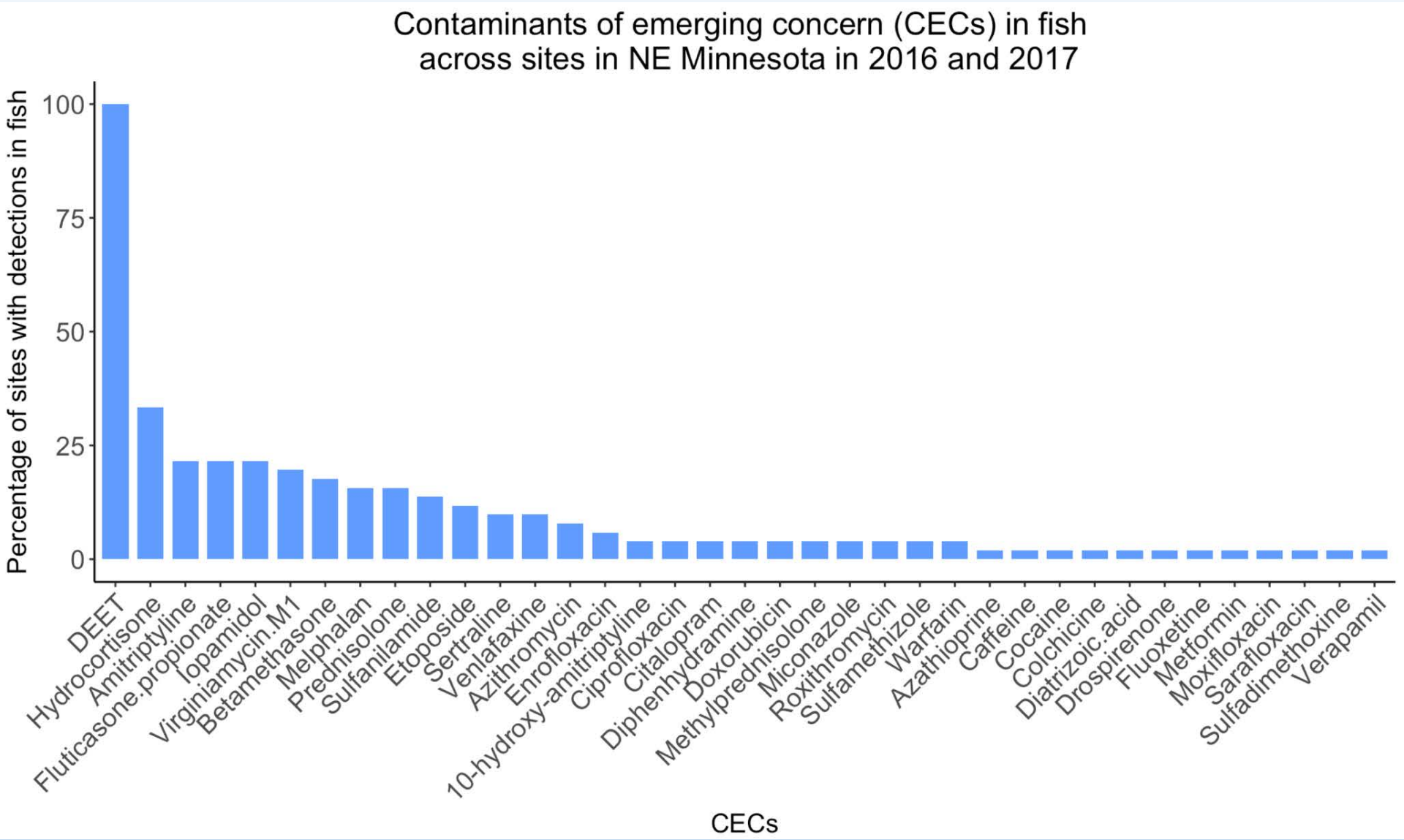
109 of 141 tested (77%) detected in samples across media and locations

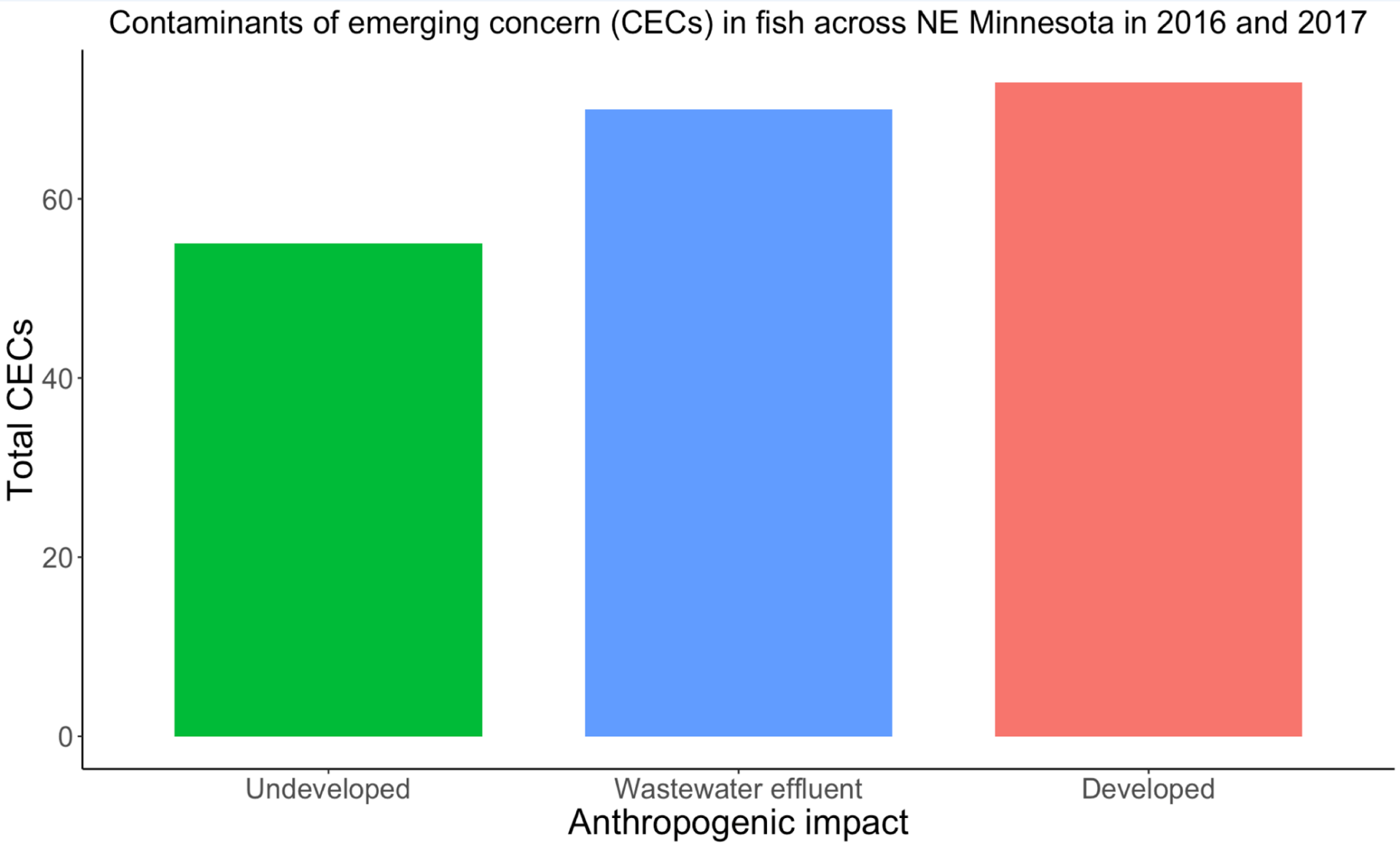

Contaminants of Emerging Concern (CECs) across lakes in NE Minnesota in 2016 and 2017
Displaying CECs found in more than 25 percent of lakes
Percentage of lakes with detections
100
75
50
25
0
DEET
Androstenedione
Amitriptyline
Estrone
Naproxen
Progesterone
Oxycodone
Carbamazepine
Sertraline
Amphetamine
Gemfibrozil
Hydrocodone
Mestranol
CECs


Contaminants of Emerging Concern (CECs) across lakes in NE Minnesota in 2016 and 2017
Displaying CECs found in less than 18 percent of lakes
Percentage of lakes with detections
0
5
10
15
CECs
Alprazolam
Amlodipine
Azithromycin
Caffeine
Clarithromycin
Desogestrel
Diazepam
Hydrochlorothiazide
Ibuprofen
Metformin
Norverapamil
Oxazepam
Promethazine
Propranolol
Testosterone
Thiabendazole
Verapamil
Warfarin
17 beta-Estradiol
Albuterol
Allyl.Trenbolone
Atorvastatin
Cimetidine
Enalapril
Fluticasone.propionate
Furosemide
Glipizide
Meprobamate
Norfluoxetine
Paroxetine
Ranitidine
Rosuvastatin
2-Hydroxy-ibuprofen
Benztropine
Bisphenol.A
Clotrimazole
Dehydronifedipine
Equilenin
Glyburide
Miconazole
Triclocarban
Triclosan
1,7-Dimethylxanthine
17 alpha-Estradiol
Acetaminophen
Carbadox
Clinafloxacin
Ofloxacin
Sulfadiazine
Sulfamerazine
Sulfathiazole
Trenbolone.acetate
17 alpha-Ethinyl-Estradiol
Anhydrochlortetracycline..ACTC.
Ciprofloxacin
Cloxacillin
Colchicine
Cyclophosphamide
Digoxin
Drospirenone
Enrofloxacin
Hydrocortisone
Iopamidol
Lomefloxacin
Methylprednisolone
Metronidazole
Oxolinic.Acid
Prednisone
Roxithromycin
Sulfadimethoxine
Sulfamethazine
Sulfamethizole
Sulfanilamide
Tamoxifen
Theophylline

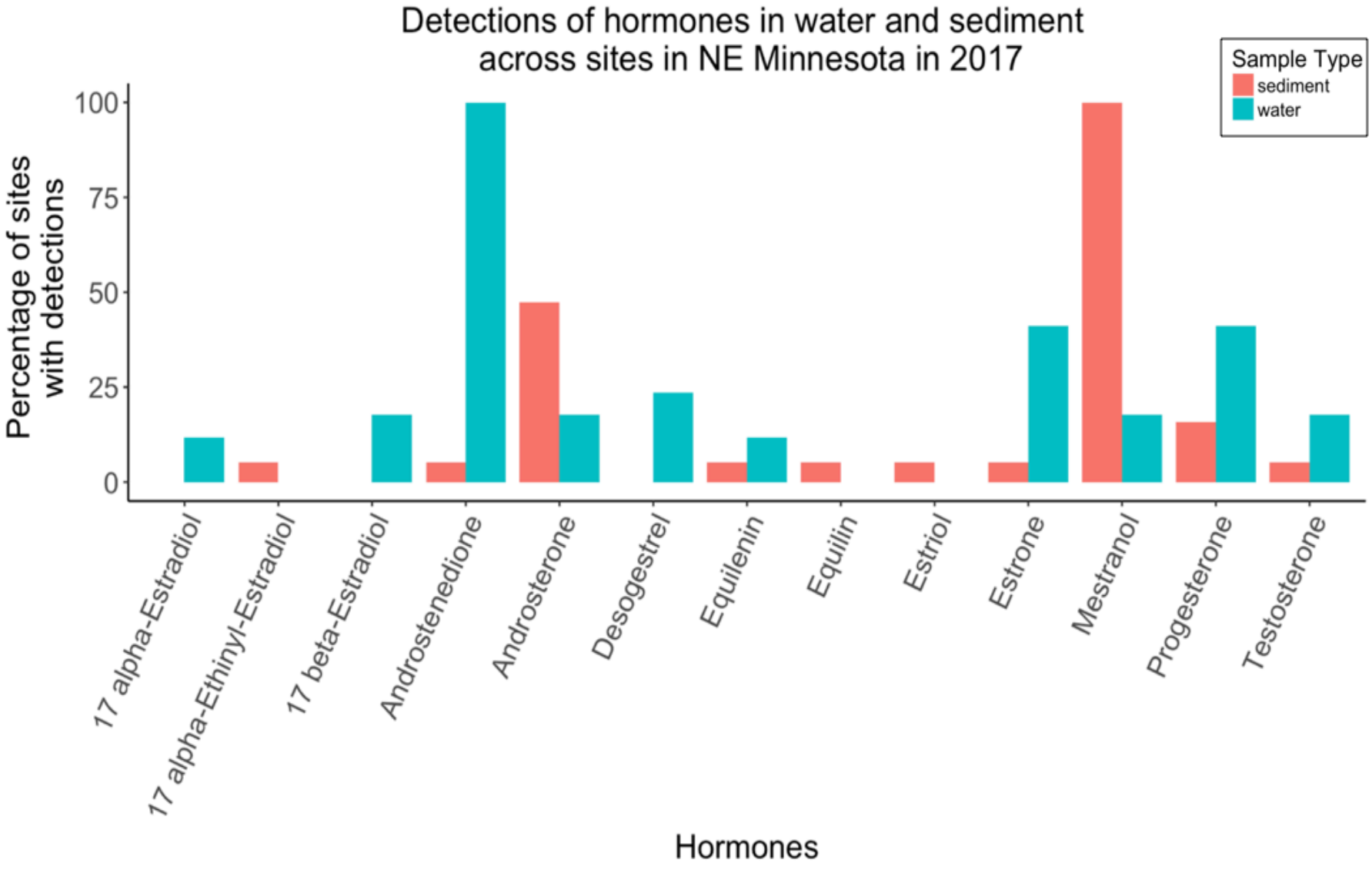

Contaminants of emerging concern (CECs) in water, sediment and fish across NE Minnesota in 2016 and 2017
Total CECs
600
400
200
0
Undeveloped
Developed
Wastewater effluent
Anthropogenic impact


Detections of Contaminants of Emerging Concern (CECs) in sediment across sites in NE Minnesota in 2016 and 2017
Displaying CECs found in more than 12 percent of lakes
Percentage of sites with detections in sediment
100
75
50
25
0
DEET
Mestranol
Androsterone
Clotrimazole
Miconazole
Triclocarban
Venlafaxine
Amphetamine
Sertraline
Fluoxetine
Amitriptyline
Citalopram
Diphenhydramine
Triamterene
Metformin
Metoprolol
Norverapamil
Progesterone
Azithromycin
Diltiazem
Erythromycin.H2O
Norfluoxetine
Ofloxacin
Propranolol
Triclosan
CECs

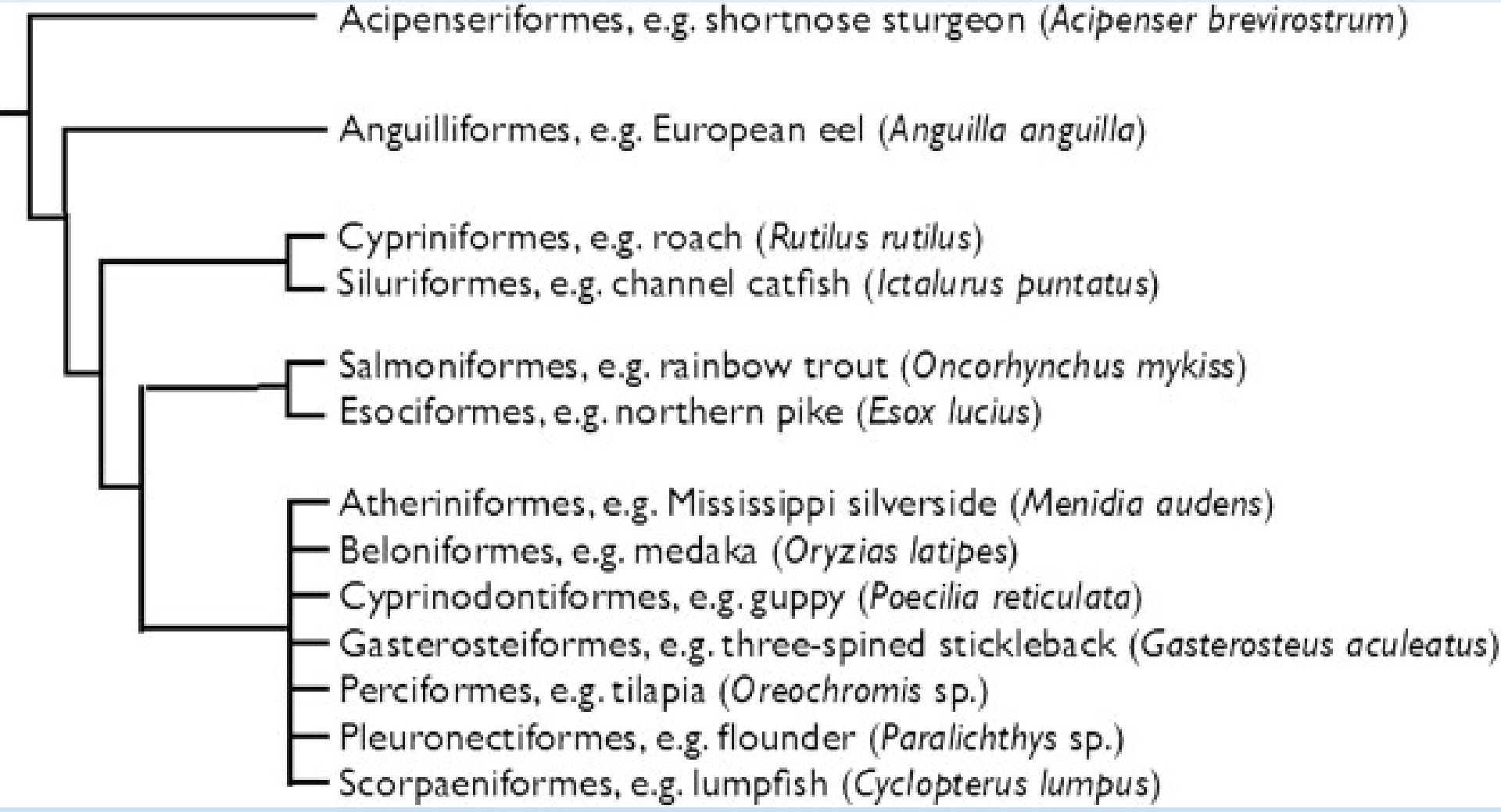

Contaminants of emerging concern (CECs) in fish across sites in NE Minnesota in 2016 and 2017
Percentage of sites with detections in fish
100
75
50
25
0
DEET
Hydrocortisone
Amitriptyline
Fluticasone.propionate
Iopamidol
Virginiamycin.M1
Betamethasone
Melphalan
Prednisolone
Sulfanilamide
Etoposide
Sertraline
Venlafaxine
Azithromycin
Enrofloxacin
10-hydroxy-amitriptyline
Ciprofloxacin
Citalopram
Diphenhydramine
Doxorubicin
Methylprednisolone
Miconazole
Roxithromycin
Sulfamethizole
Warfarin
Azathioprine
Caffeine
Cocaine
Colchicine
Diatrizoic.acid
Drospirenone
Fluoxetine
Metformin
Moxifloxacin
Sarafloxacin
Sulfadimethoxine
Verapamil
CECs

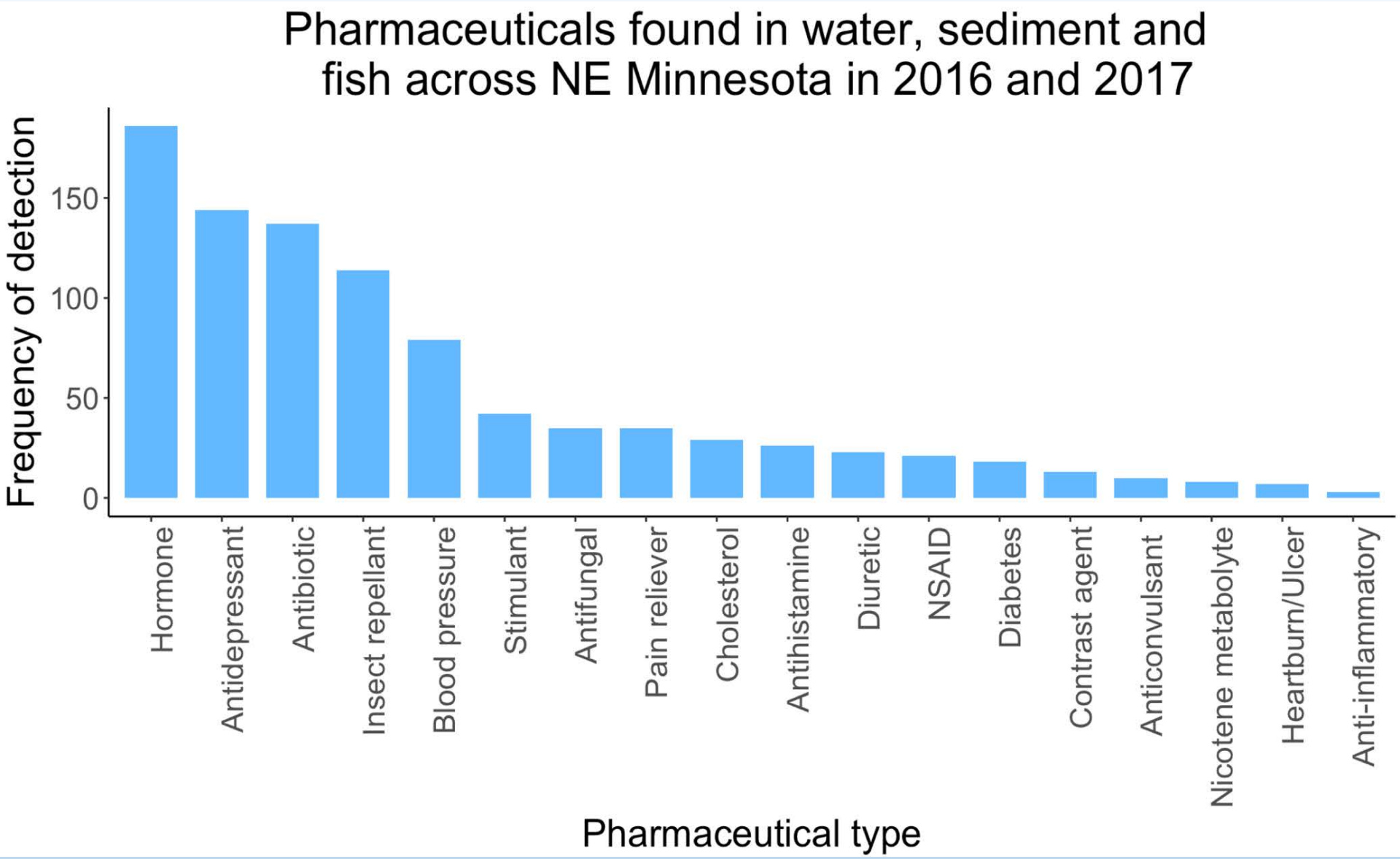

Contaminants of emerging concern (CECs) in fish across NE Minnesota in 2016 and 2017
Total CECs
0
20
40
60
Undeveloped
Wastewater effluent
Developed
Anthropogenic impact

Hormones


Detections of hormones in water and sediment across sites in NE Minnesota in 2017
Sample Type
sediment
water
Percentage of sites with detections
100
75
50
25
0
17 alpha-Estradiol
17 alpha-Ethinyl-Estradiol
17 beta-Estradiol
Androstenedione
Androsterone
Desogestrel
Equilenin
Equilin
Estriol
Estrone
Mestranol
Progesterone
Testosterone
Hormones

Ray-finned fish in which exposure to hormones or hormone-active substances have been shown to cause sex reversal or severe aberrations in gonadal development




Pharmaceuticals found in water, sediment and fish across NE Minnesota in 2016 and 2017
Frequency of detection
0
50
100
150
Hormone
Antidepressant
Antibiotic
Insect repellant
Blood pressure
Stimulant
Antifungal
Pain reliever
Cholesterol
Antihistamine
Diuretic
NSAID
Diabetes
Contrast agent
Anticonvulsant
Nicotene metabolyte
Heartburn/Ulcer
Anti-inflammatory
Pharmaceutical type

Concerns

- Hormones and Antidepressants most commonly found
- Desogestrel was found in ~16% of lakes
- Mestranol detected in 58% of sediment samples
- Anticancer drugs (antineoplastics) detections.
- Ubiquitous fish tissue detections of pharmaceuticals
- A widespread detection of contaminants in surface water and sediment – at undeveloped locations.

Management Implications

- What can we do?
- Prioritize CEC research (LSWG-LaMP/CLC GLFC)
- Alter how prescrips are delivered
- Water Quality standards
- Wastewater treatment improvements
- Wastewater reuse

Next Steps

- Hospitals?
- Terrestrial subsistence species
- Spatial and hydrological trends
- Adverse outcomes
- Human health