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

Jessica Deere, University of Minnesota

Mark Ferrey, Minnesota Pollution Control Agency

Mark Jankowski, U.S. Environmental Protection Agency

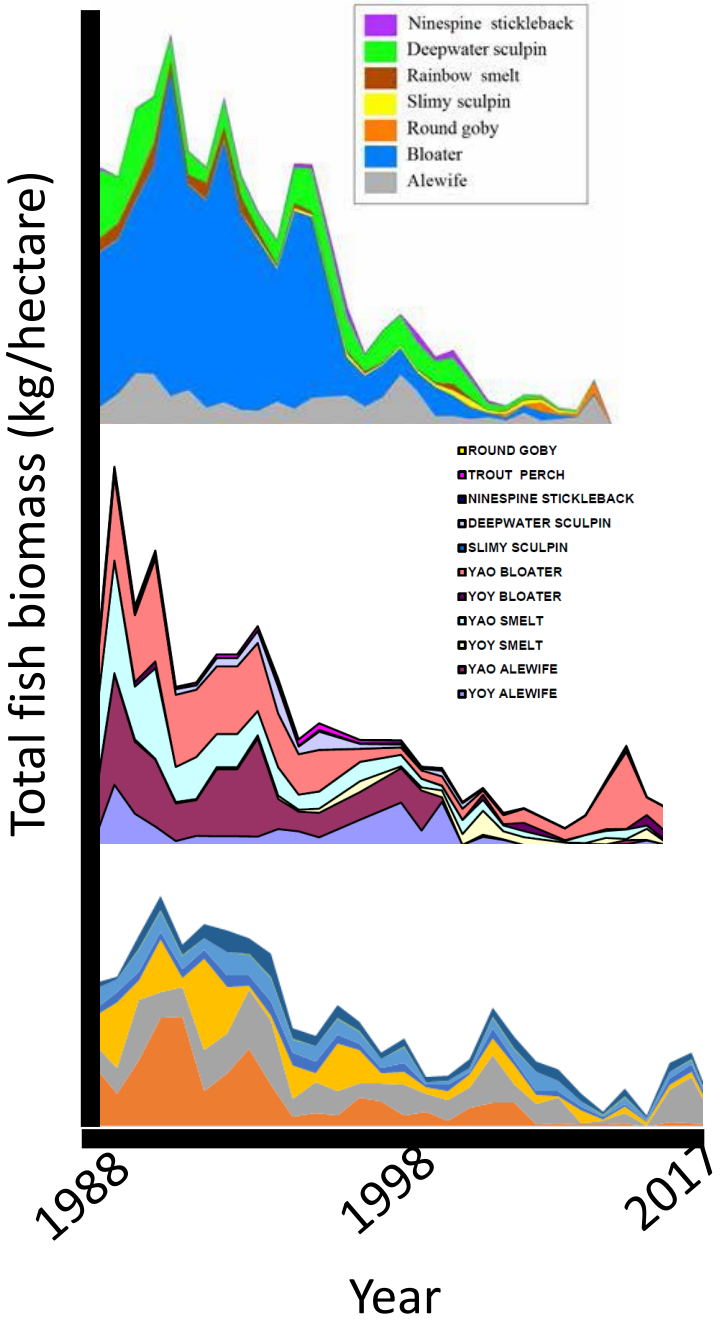
Mateo Convertino, University of Minnesota

Nicholas Phelps, University of Minnesota

Alexander Primus, University of Minnesota

Dominic Travis, University of Minnesota

Great Lakes fish biomass



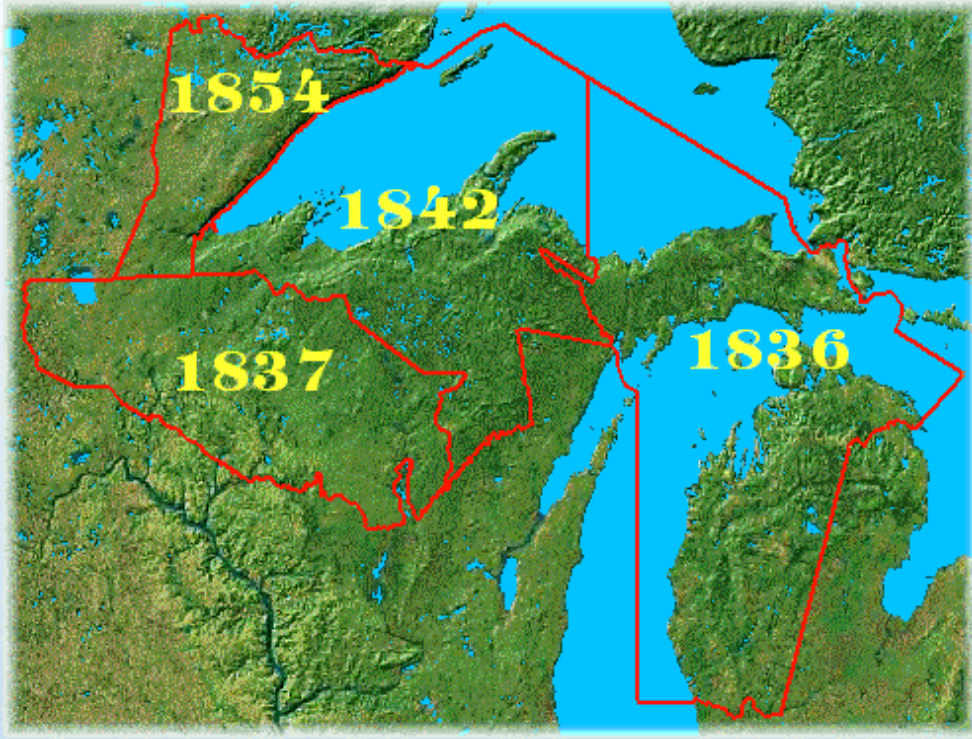
Lake Michigan
89% decline

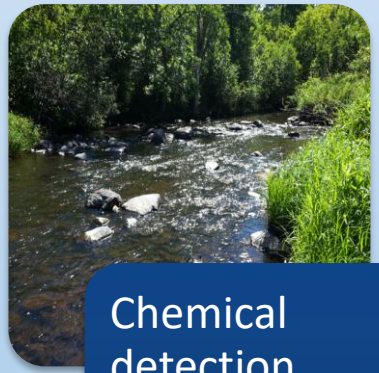
Lake Huron
87% decline

Lake Superior
80% decline

Concerns

- Ecological 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

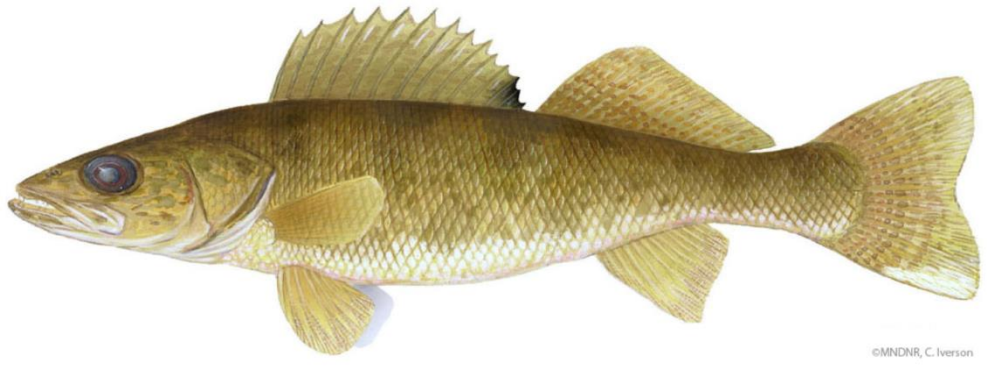
- ✓Dosing an experimental lake with 5 parts per trillion of the synthetic estrogen ethinylestradiol caused the minnow population to collapse.
- ✓30 parts per trillion fluvoxamine (an SSRI) in water triggers immediate spawning in mussels.
- ✓Fish behavior is altered after exposure to 1 part per trillion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

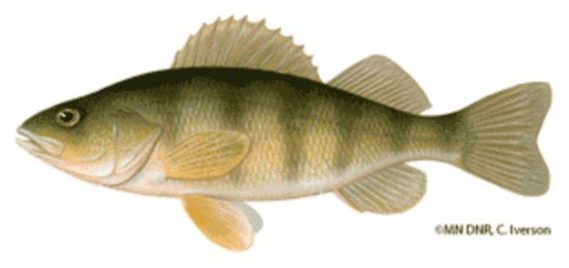
Experimental Design

Anthropogenic Impact	Sample Size
Heavily Impacted/Wastewater Treatment Effluent	N=8
Developed	N= 10
Undeveloped/Wilderness	N= 9
Lake Superior	N=6

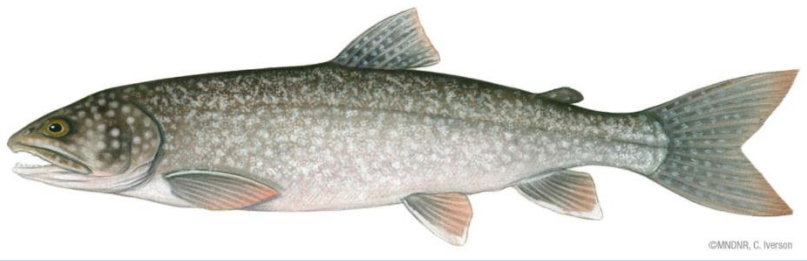
Sample collection

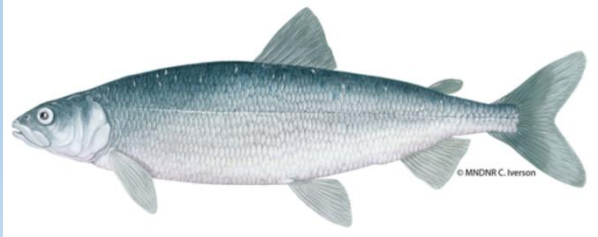
Walleye and Yellow Perch from 13 inland sites

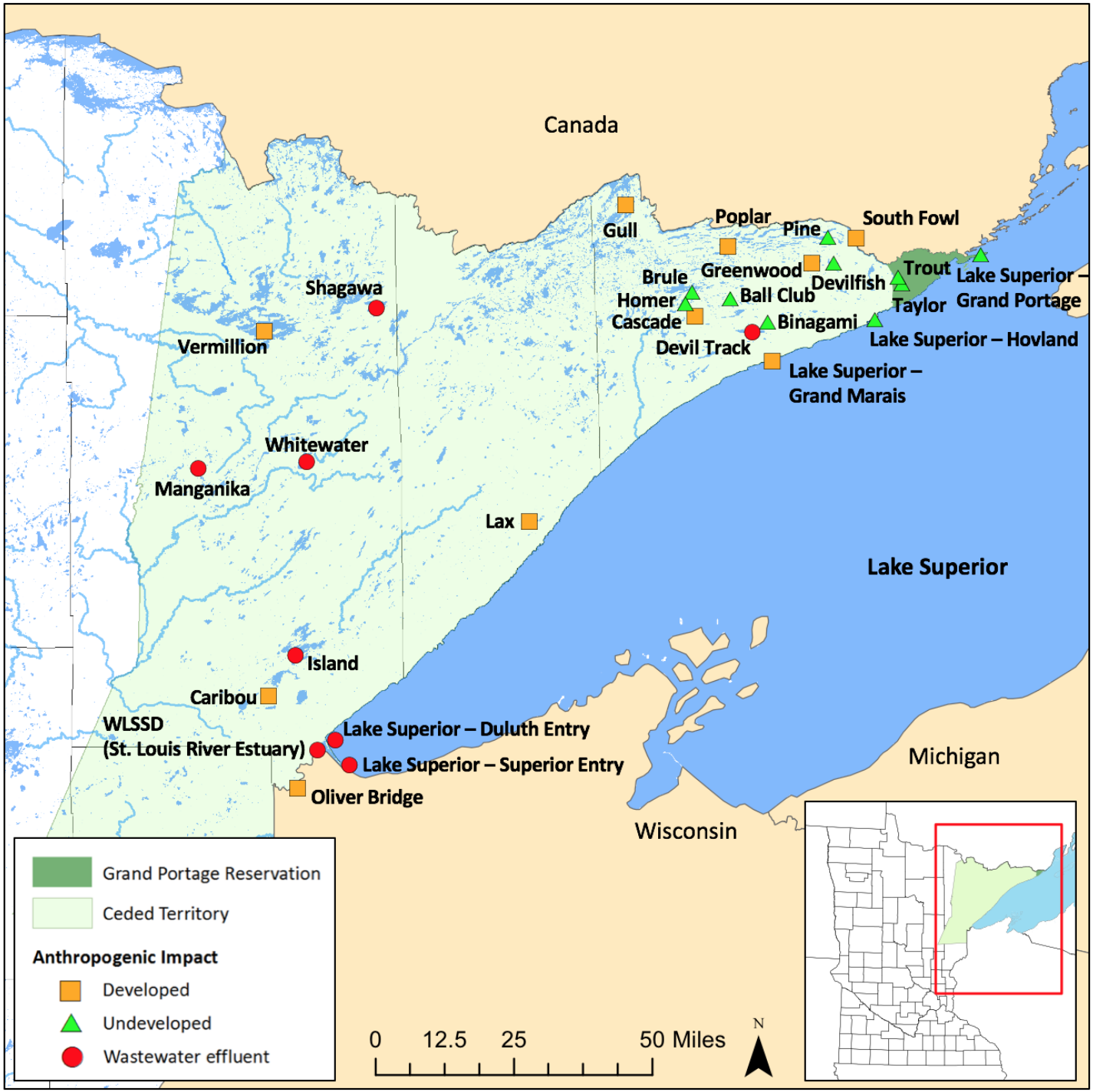




Lake Trout and Cisco (Lake Herring) from 6 Lake Superior sites






Canada
Gull
Poplar
Pine
South Fowl
Trout
Lake Superior – Grand Portage
Brule
Greenwood
Devilfish
Taylor
Homer
Ball Club
Cascade
Binagami
Lake Superior – Hovland
Devil Track
Lake Superior – Grand Marais
Shagawa
Vermillion
Whitewater
Manganika
Lax
Lake Superior
Island
Caribou
WLSSD (St. Louis River Estuary)
Lake Superior – Duluth Entry
Lake Superior – Superior Entry
Oliver Bridge
Michigan
Wisconsin
Grand Portage Reservation
Ceded Territory
Anthropogenic Impact
Developed
Undeveloped
Wastewater effluent
0 12.5 25 50 Miles
N

Water samples

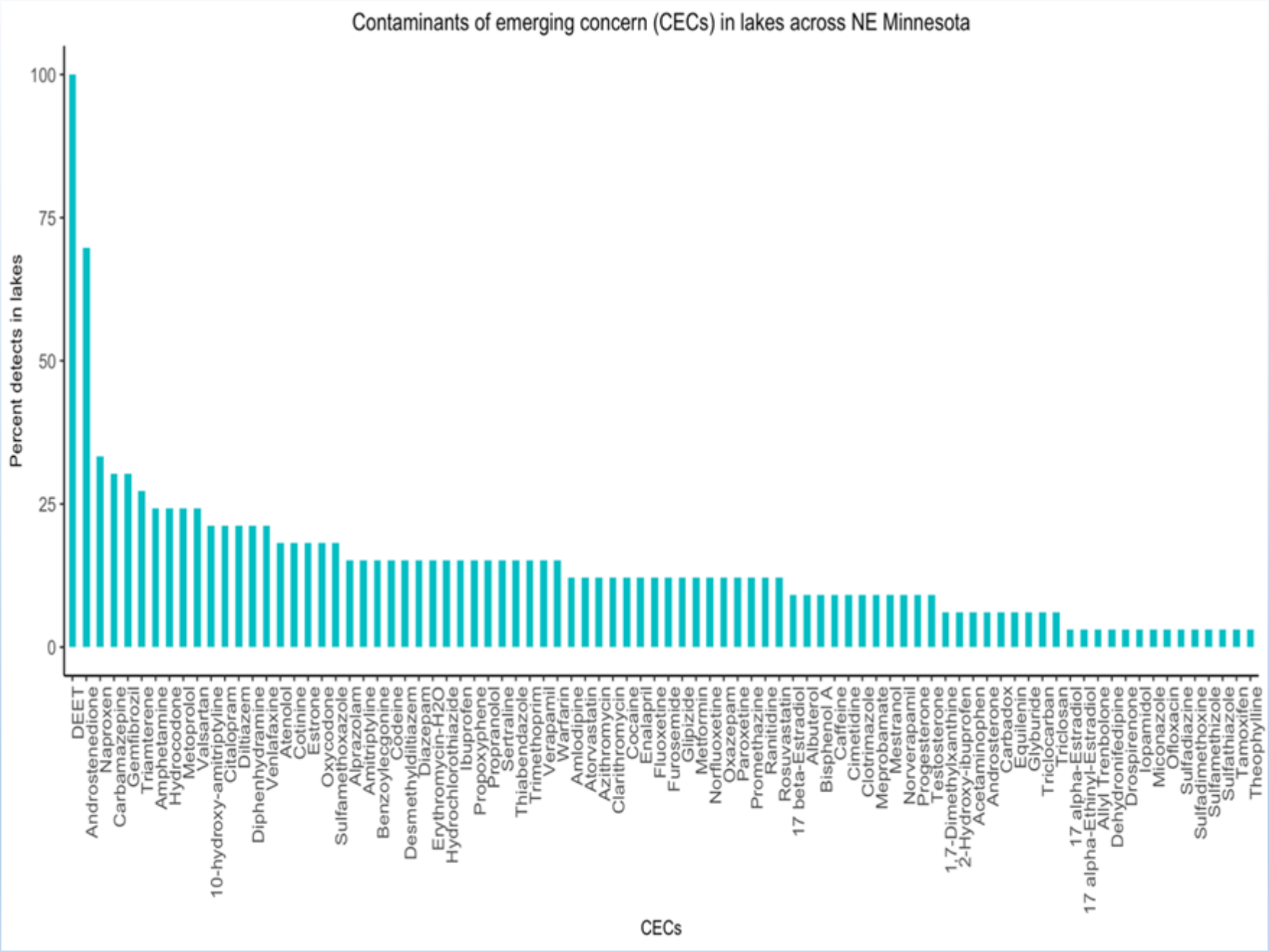
- 28 sites
- Screened 141 CECs (lists 1-6)
  - 93 CECs found in water samples (66% of those tested for)
- 1 – 77 detects in water samples per site
  - Undeveloped: 3 – 7 detects
  - Developed: 4 – 10 detects
  - Wastewater effluent: 49 – 84 detects
- Screened 16 hormones

Sediment samples

- 28 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
Subsistence species used:

- 28 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

Minnesota's Aquatic Toxicity Profiles (ATP)

- Developed to characterize the potential for contaminants detected in Minnesota's environment to cause adverse effects on aquatic life
  - ATPs: weight-of-evidence to determine potential impacts of specific contaminants in aquatic environments
  - Goal: to determine the contaminants of highest concern, when compared to other contaminants
  - Include: physicochemical properties, occurrence, toxicity, and production/importation volume

High priority contaminants are:

Water

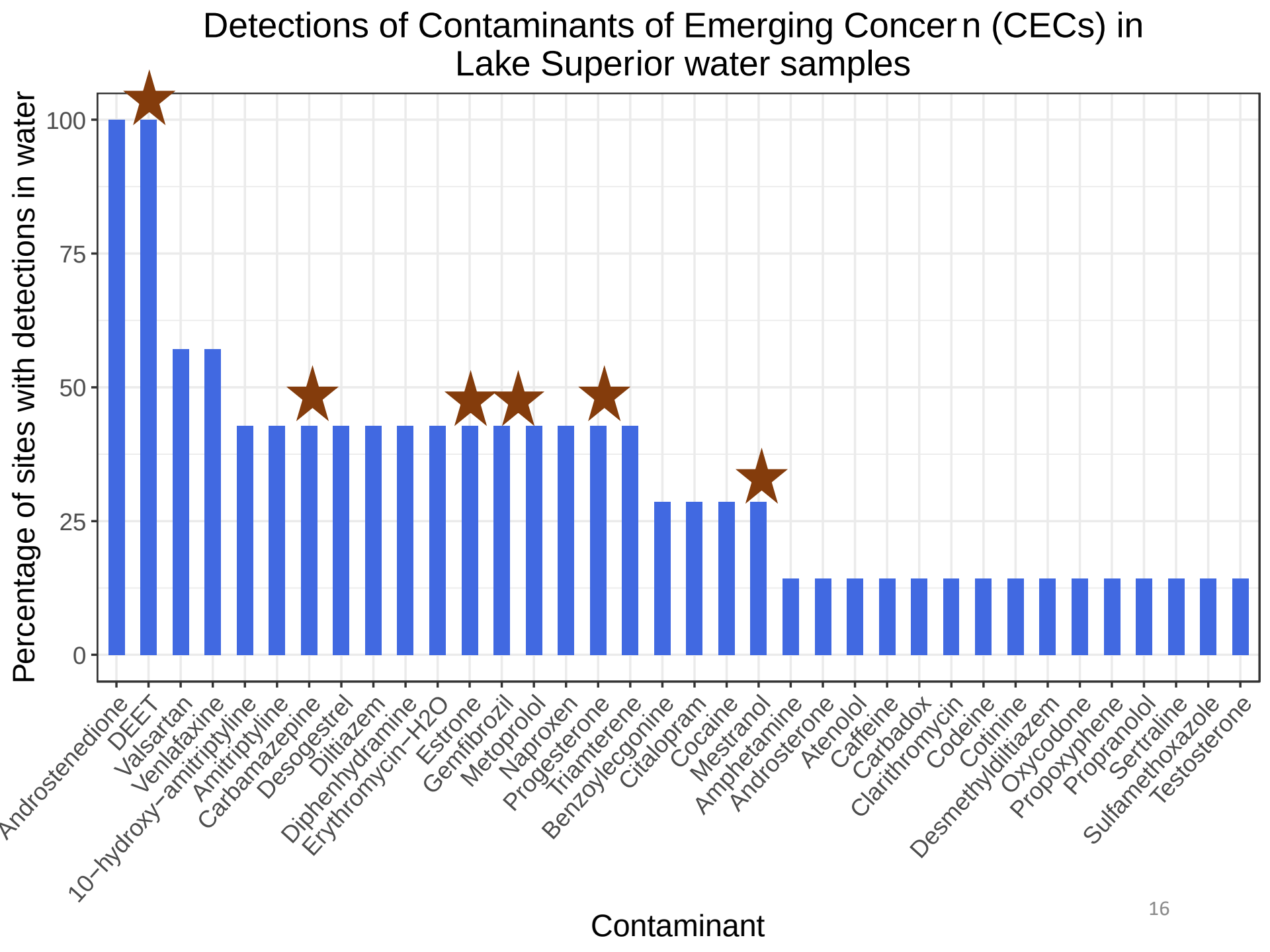
- Estrone
- Progesterone
- Carbamazepine
- Gemfibrozil
- Mestranol
- DEET

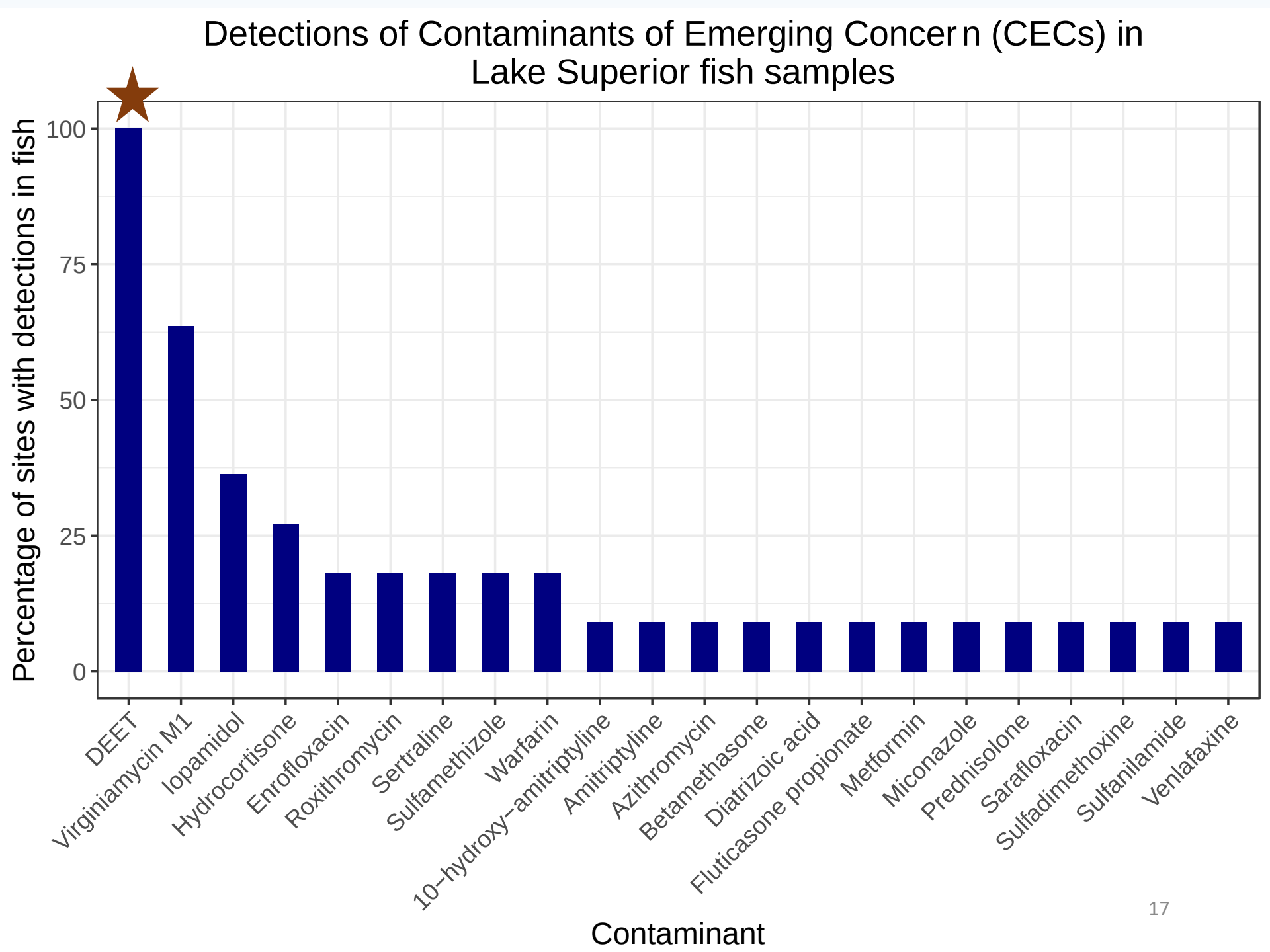
Fish

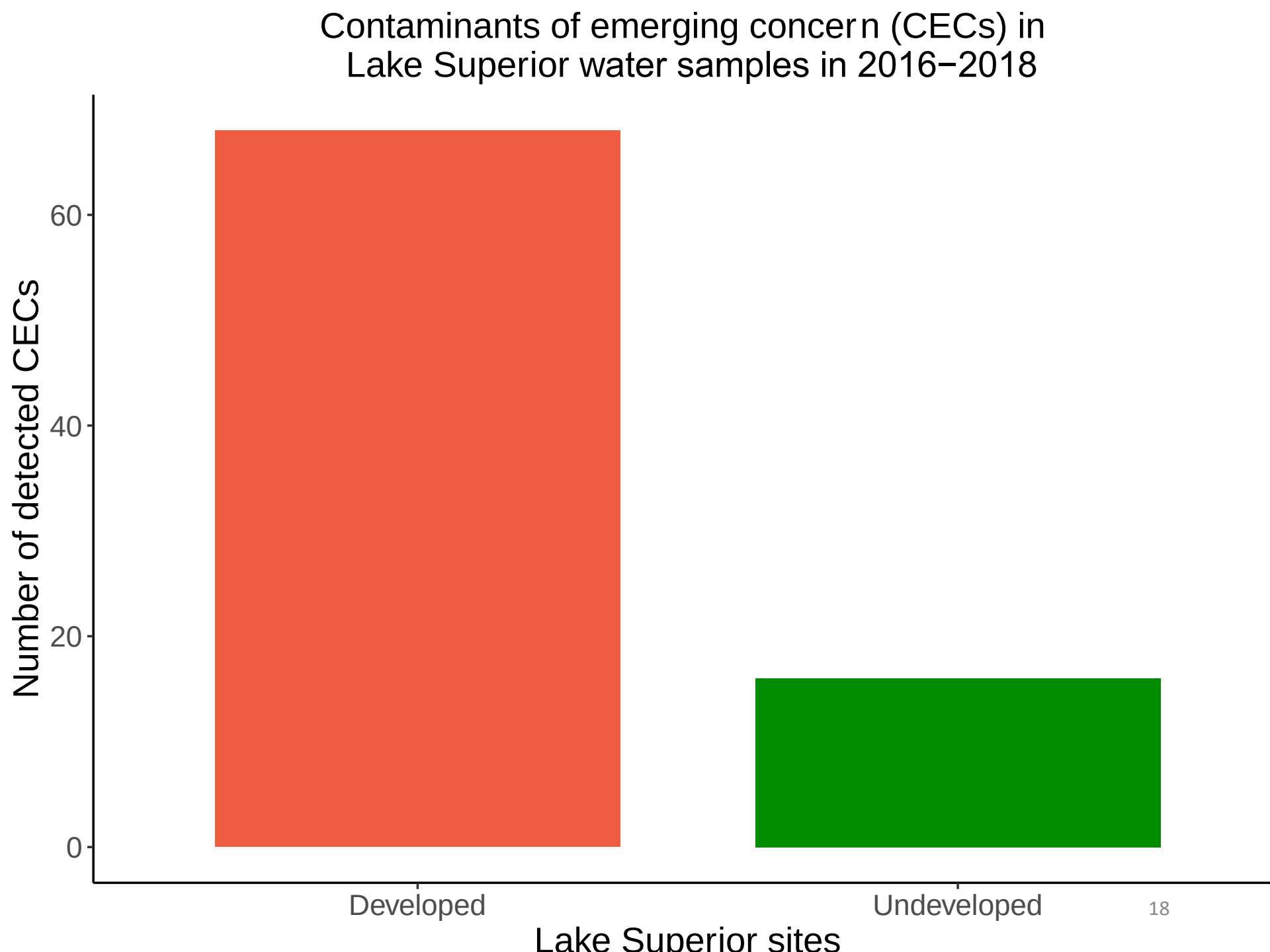
- Colchicine
- DEET

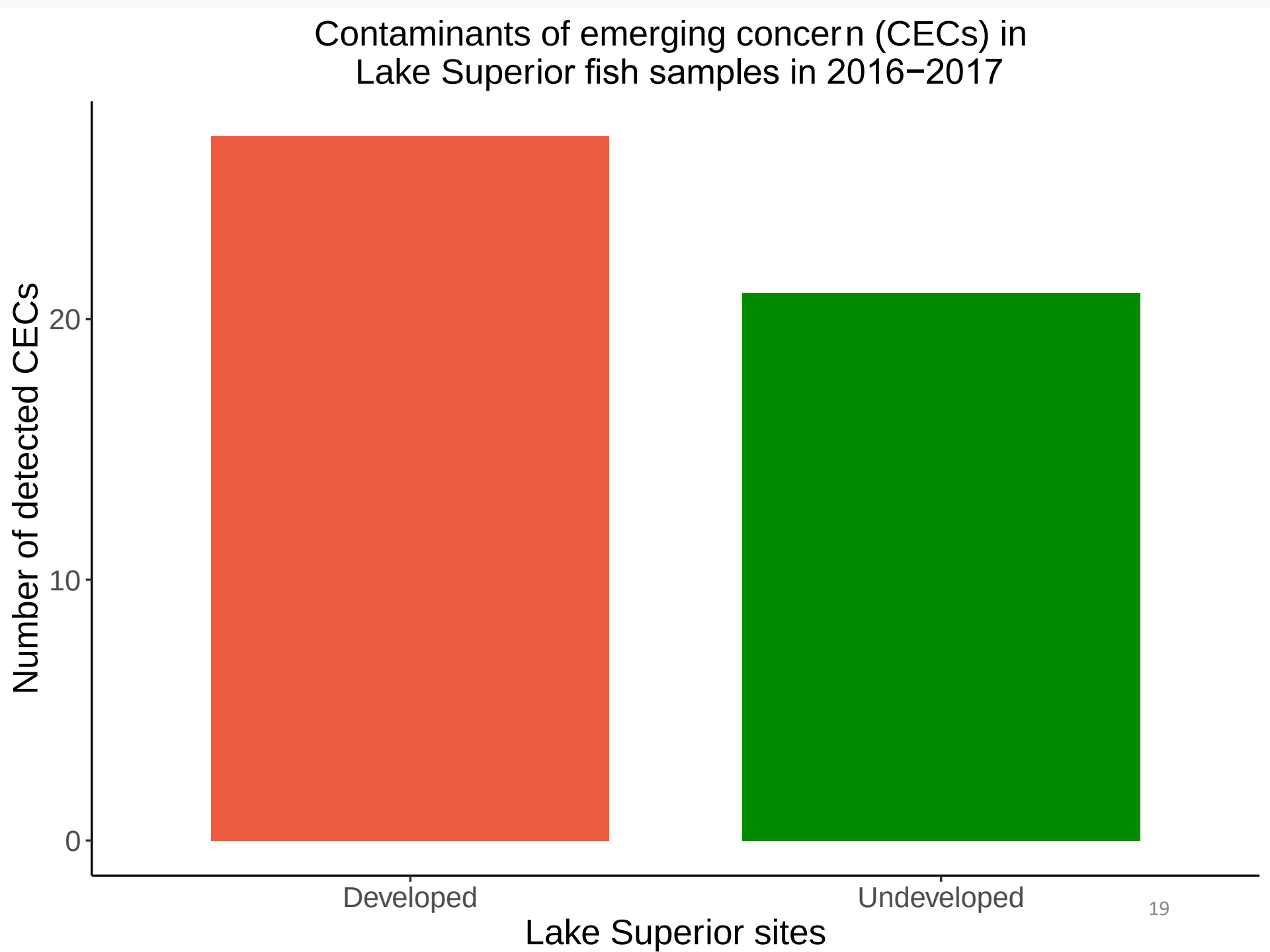
Sediment

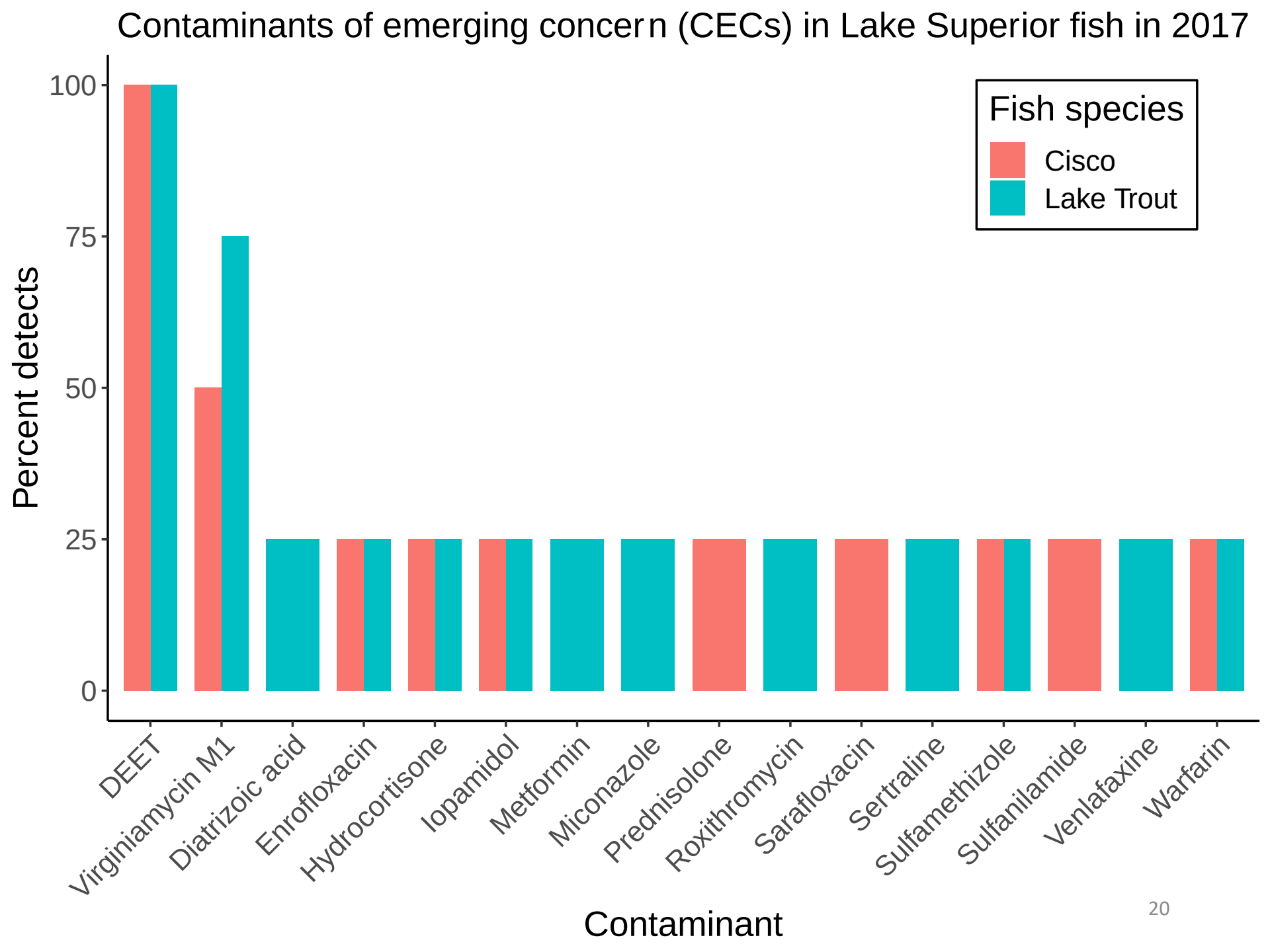
- Mestranol
- Clotrimazole
- Triclocarban
- DEET

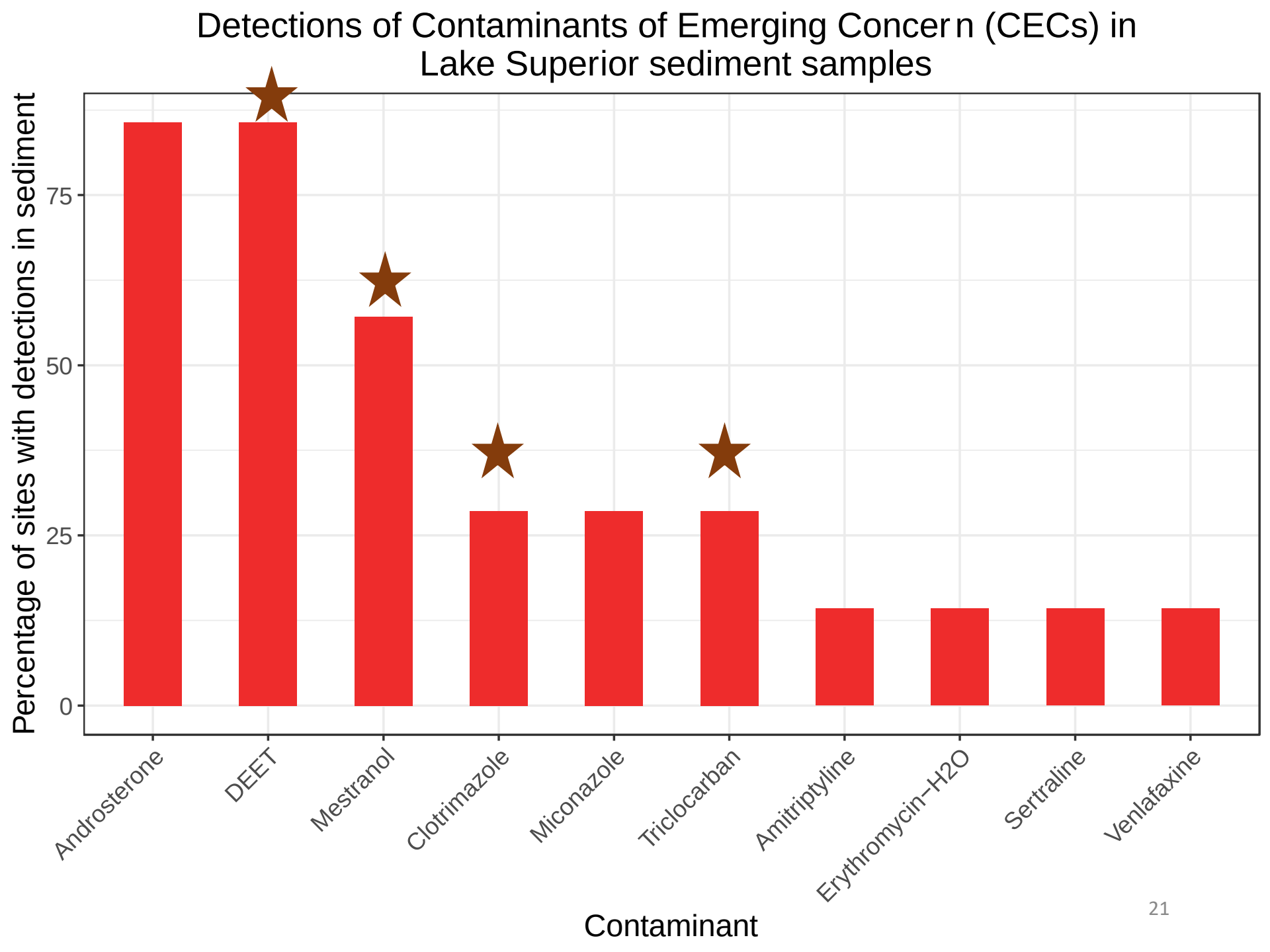

Detections of Contaminants of Emerging Concern (CECs) in Lake Superior water samples
Percentage of sites with detections in water
100
75
50
25
0
Androstenedione
DEET
Valsartan
Venlafaxine
10−hydroxy−amitriptyline
Amitriptyline
Carbamazepine
Desogestrel
Diltiazem
Diphenhydramine
Erythromycin−H2O
Estrone
Gemfibrozil
Metoprolol
Naproxen
Progesterone
Triamterene
Benzoylecgonine
Citalopram
Cocaine
Mestranol
Amphetamine
Androsterone
Atenolol
Caffeine
Carbadox
Clarithromycin
Codeine
Cotinine
Desmethyldiltiazem
Oxycodone
Propoxyphene
Propranolol
Sertraline
Sulfamethoxazole
Testosterone
Contaminant

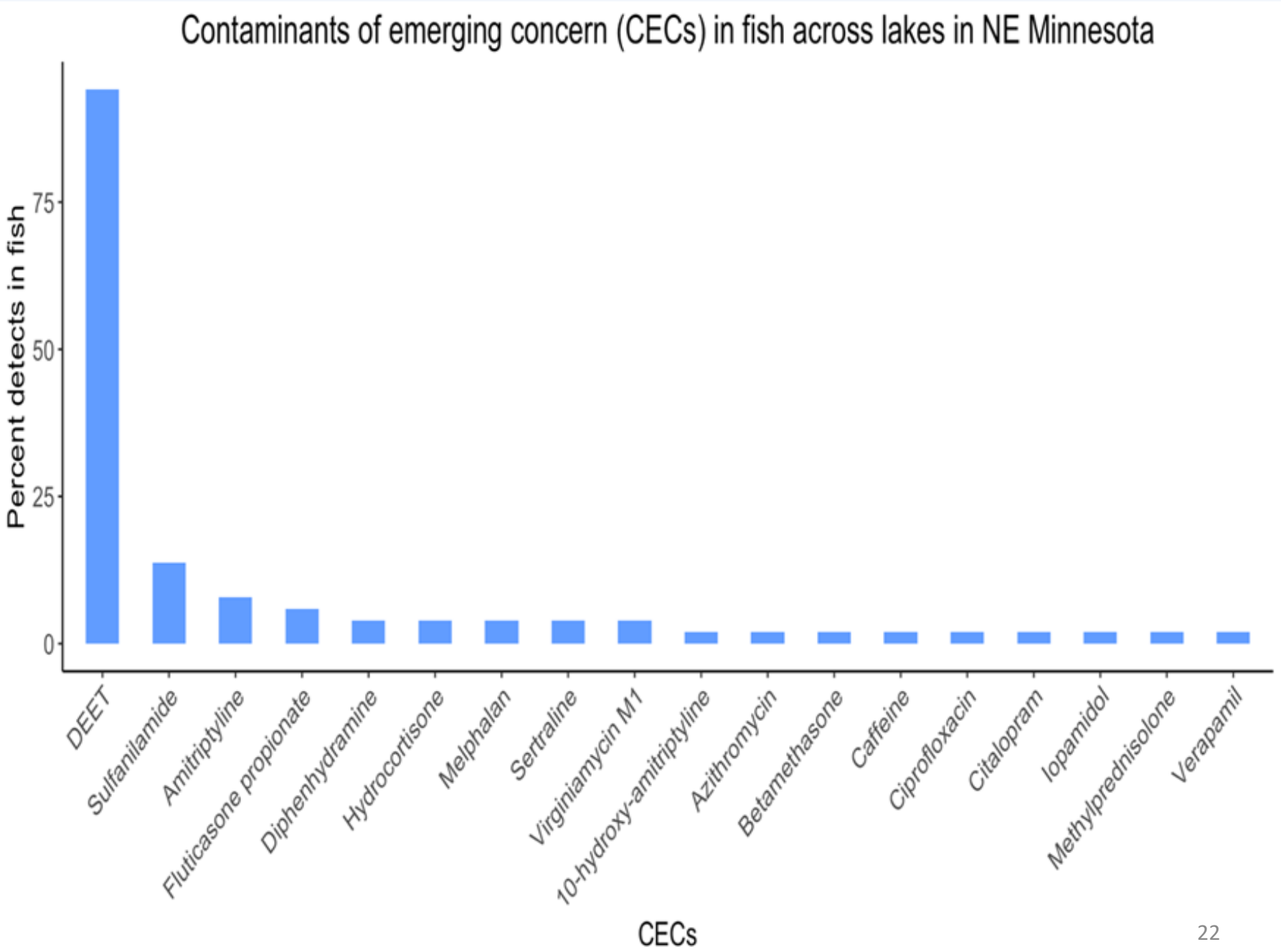

Detections of Contaminants of Emerging Concern (CECs) in Lake Superior fish samples
Percentage of sites with detections in fish
100
75
50
25
0
DEET
Virginiamycin M1
Iopamidol
Hydrocortisone
Enrofloxacin
Roxithromycin
Sertraline
Sulfamethizole
Warfarin
10−hydroxy−amitriptyline
Amitriptyline
Azithromycin
Betamethasone
Diatrizoic acid
Fluticasone propionate
Metformin
Miconazole
Prednisolone
Sarafloxacin
Sulfadimethoxine
Sulfanilamide
Venlafaxine
Contaminant

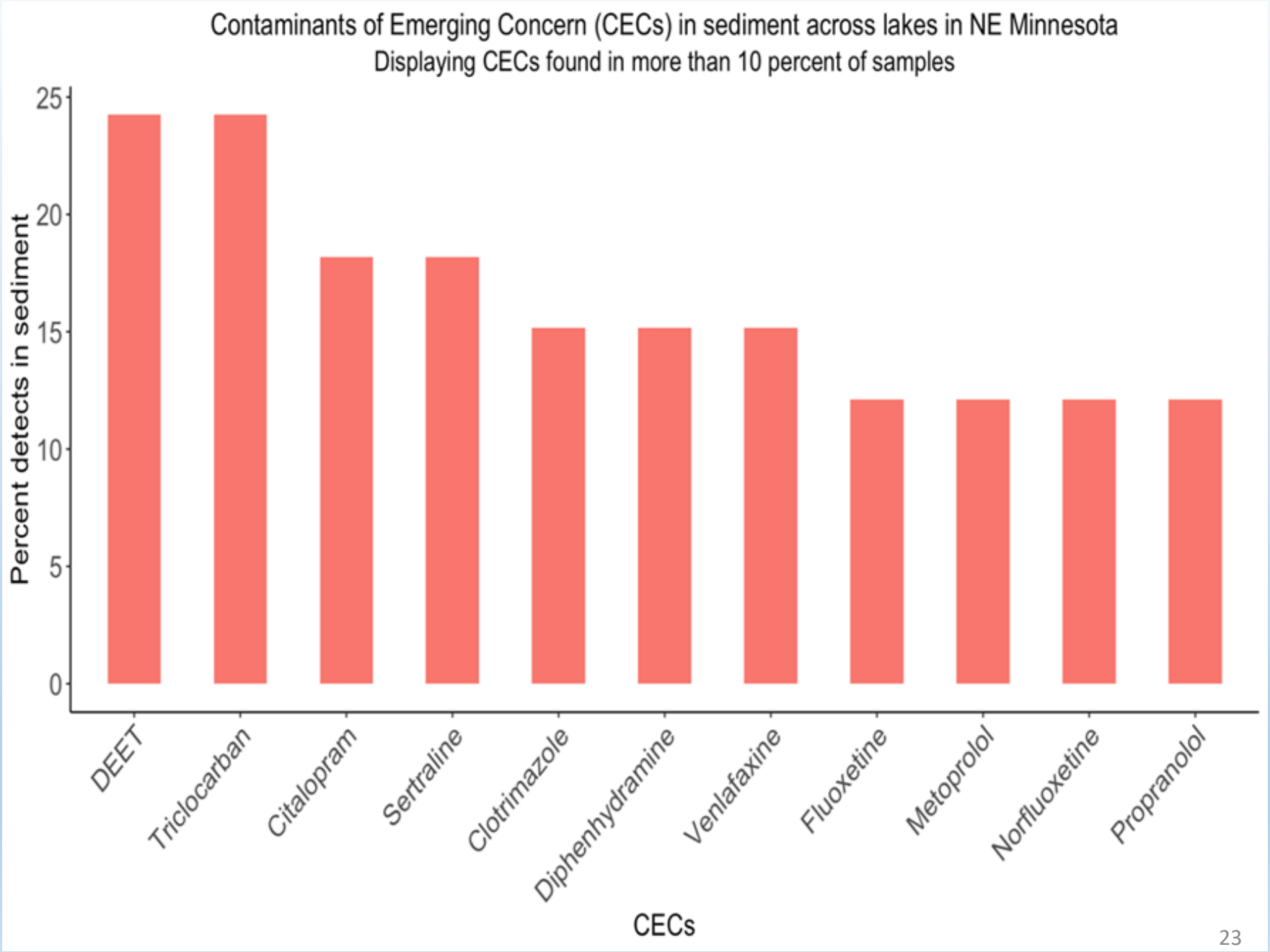

Contaminants of emerging concern (CECs) in
Lake Superior water samples in 2016−2018
Number of detected CECs
60
40
20
0
Developed
Undeveloped
Lake Superior sites

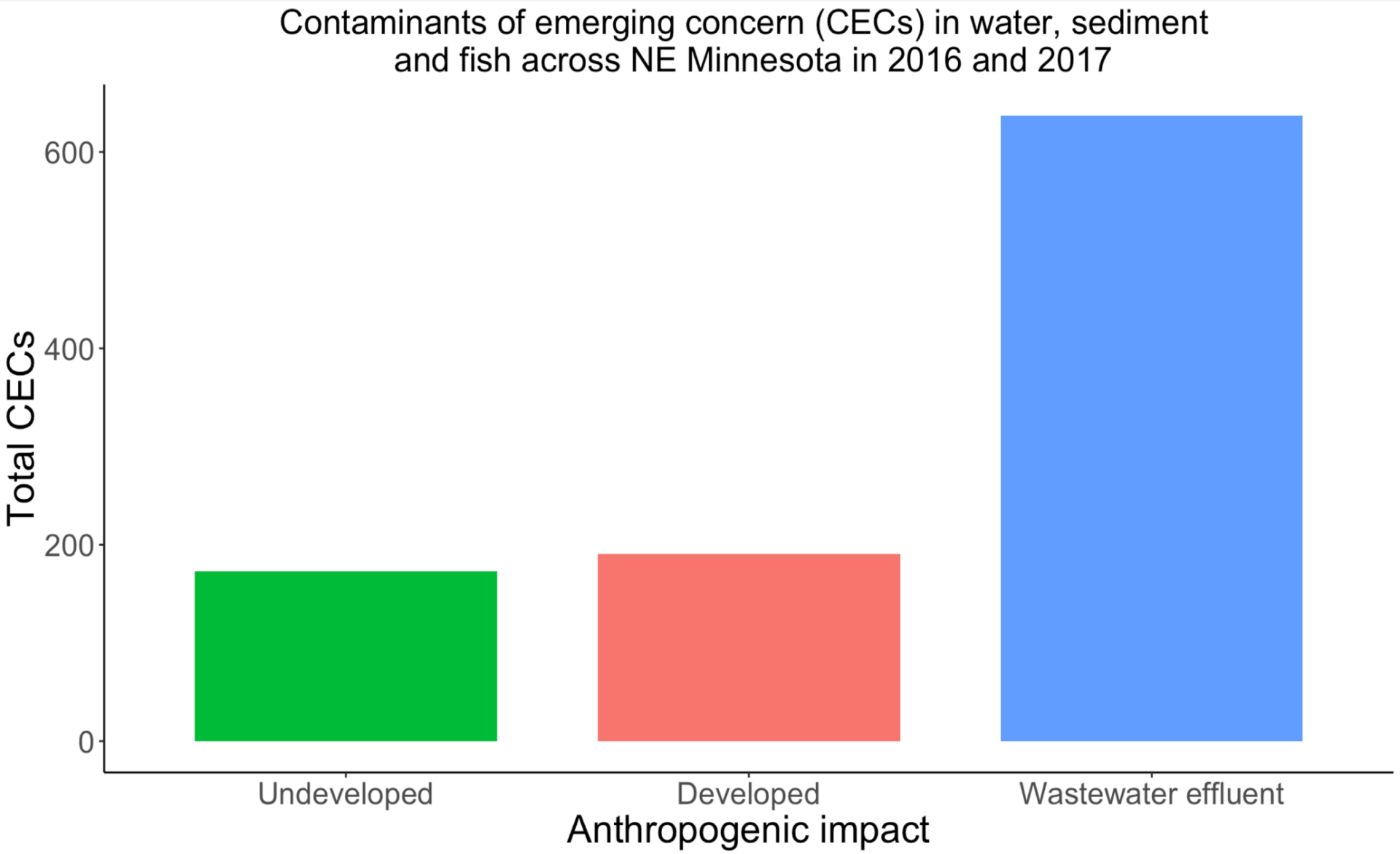

Contaminants of emerging concern (CECs) in
Lake Superior fish samples in 2016−2017
Number of detected CECs
20
10
0
Developed
Undeveloped
Lake Superior sites

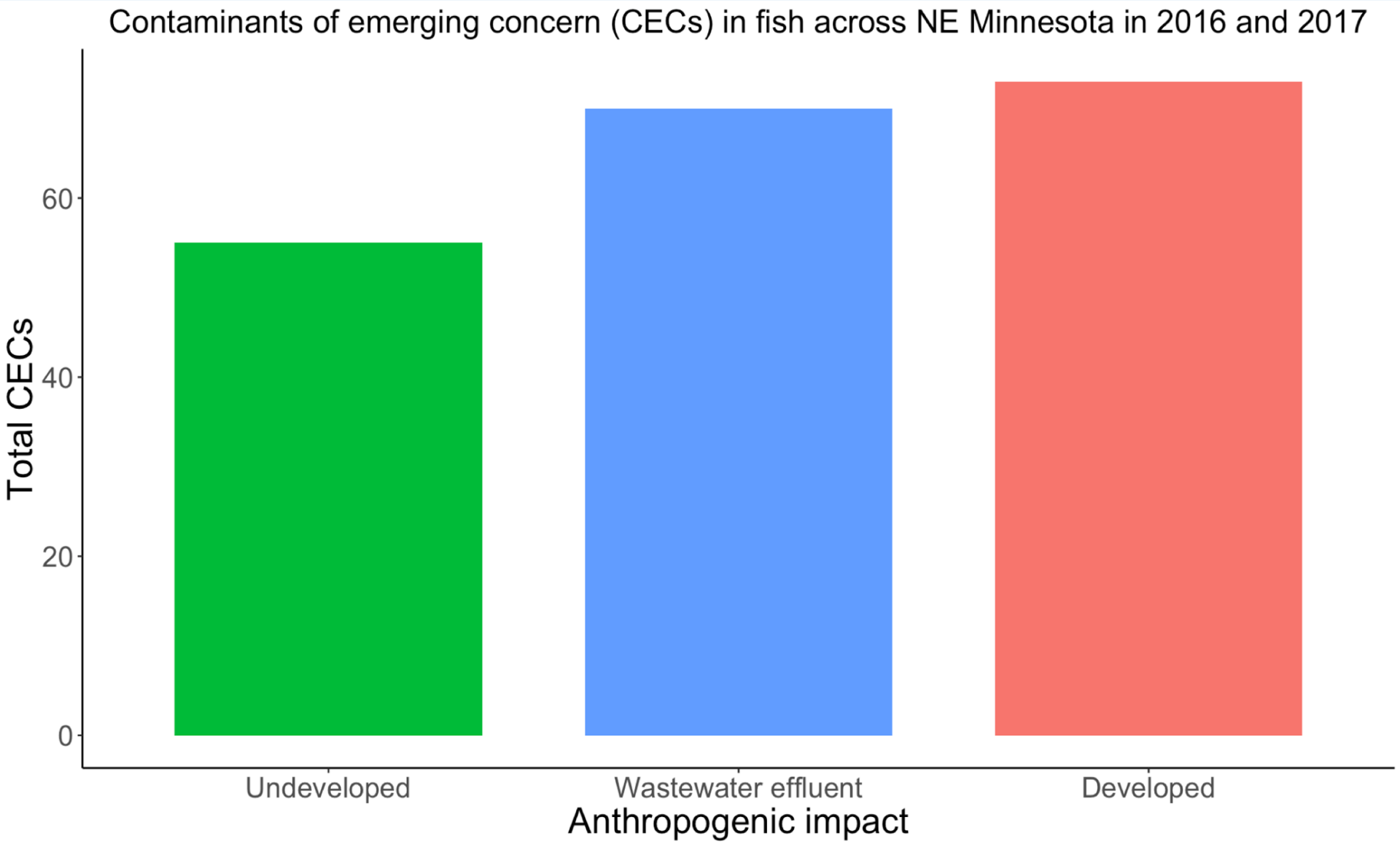

Contaminants of emerging concern (CECs) in Lake Superior fish in 2017
Fish species
Cisco
Lake Trout
Percent detects
100
75
50
25
0
DEET
Virginiamycin M1
Diatrizoic acid
Enrofloxacin
Hydrocortisone
Iopamidol
Metformin
Miconazole
Prednisolone
Roxithromycin
Sarafloxacin
Sertraline
Sulfamethizole
Sulfanilamide
Venlafaxine
Warfarin
Contaminant

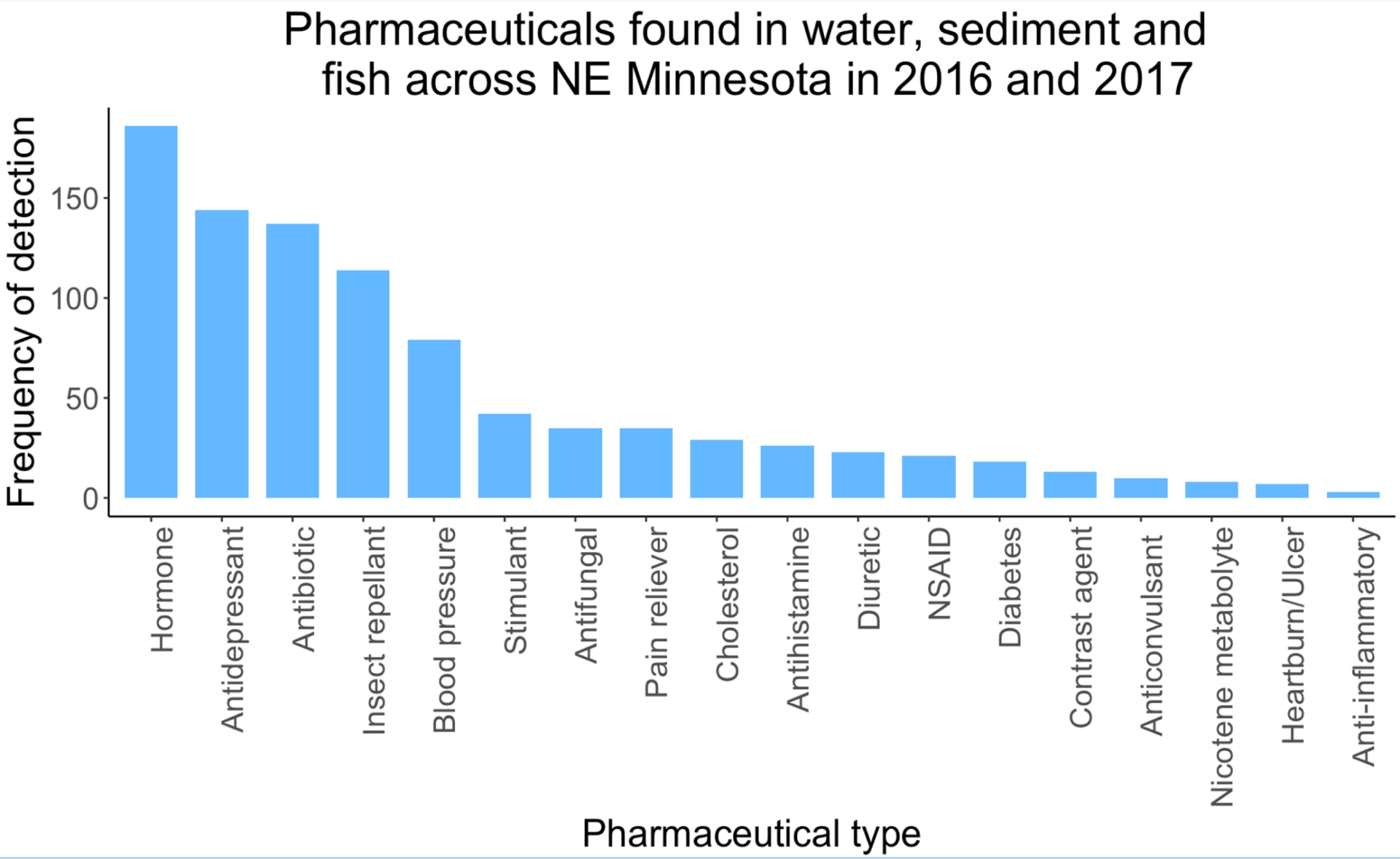

Detections of Contaminants of Emerging Concern (CECs) in Lake Superior sediment samples
Percentage of sites with detections in sediment
0
25
50
75
Androsterone
DEET
Mestranol
Clotrimazole
Miconazole
Triclocarban
Amitriptyline
Erythromycin−H2O
Sertraline
Venlafaxine
Contaminant


Contaminants of emerging concern (CECs) in fish across lakes in NE Minnesota
Percent detects in fish
0
25
50
75
DEET
Sulfanilamide
Amitriptyline
Fluticasone propionate
Diphenhydramine
Hydrocortisone
Melphalan
Sertraline
Virginiamycin M1
10-hydroxy-amitriptyline
Azithromycin
Betamethasone
Caffeine
Ciprofloxacin
Citalopram
Iopamidol
Methylprednisolone
Verapamil
CECs

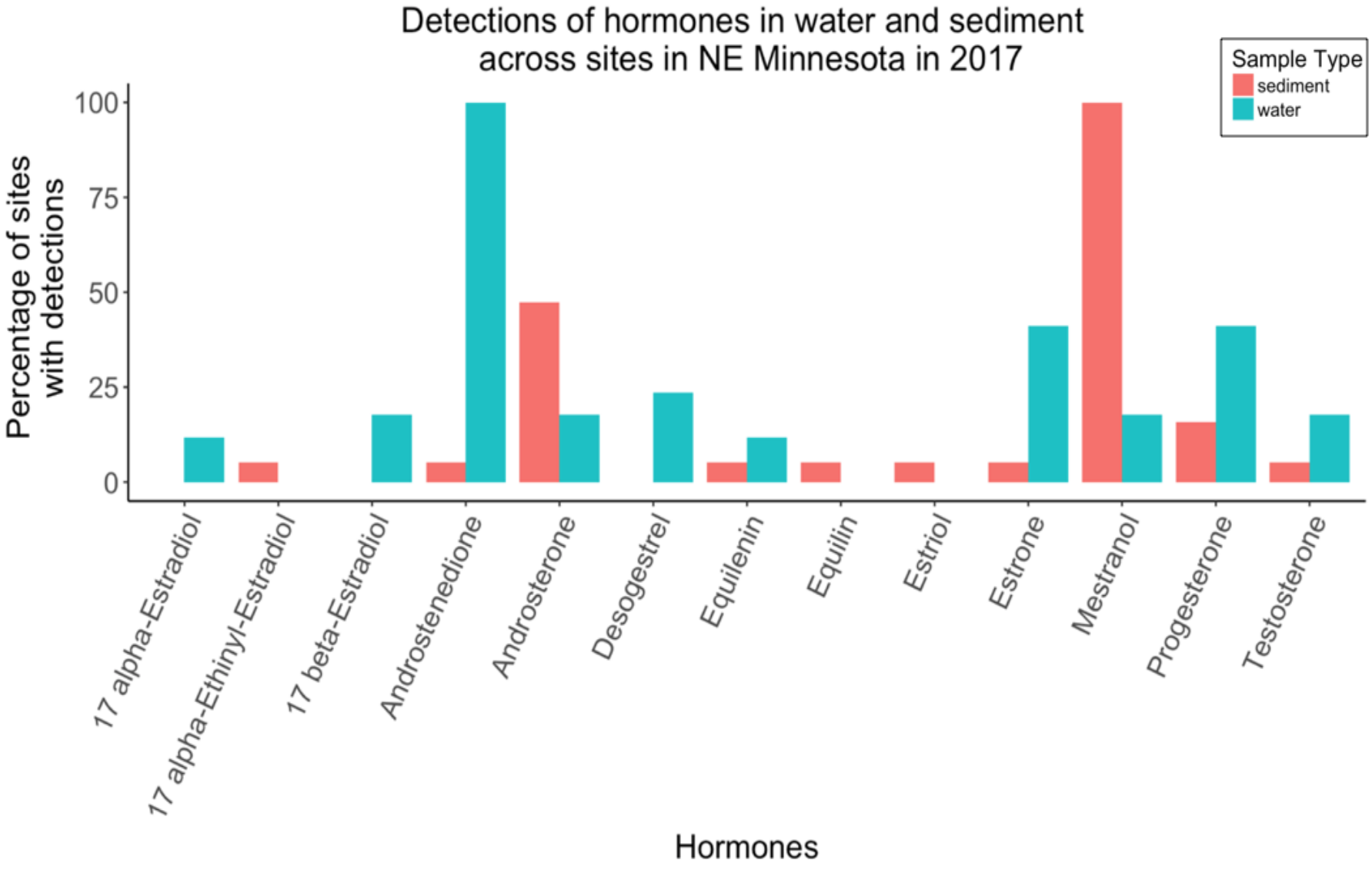

Contaminants of Emerging Concern (CECs) in sediment across lakes in NE Minnesota
Displaying CECs found in more than 10 percent of samples
Percent detects in sediment
25
20
15
10
5
0
DEET
Triclocarban
Citalopram
Sertraline
Clotrimazole
Diphenhydramine
Venlafaxine
Fluoxetine
Metoprolol
Norfluoxetine
Propranolol
CECs


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


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


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

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

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

- Tank studies to test what we find on fish in a lab setting
- Trend over time to identify trends in CEC's over time
- Wild Rice (at a regional scale)
- Wildlife subsistence species (moose, deer, bear, partridge)
- Index species