

# Endocrine disrupting activity associated with unconventional oil and natural gas operations

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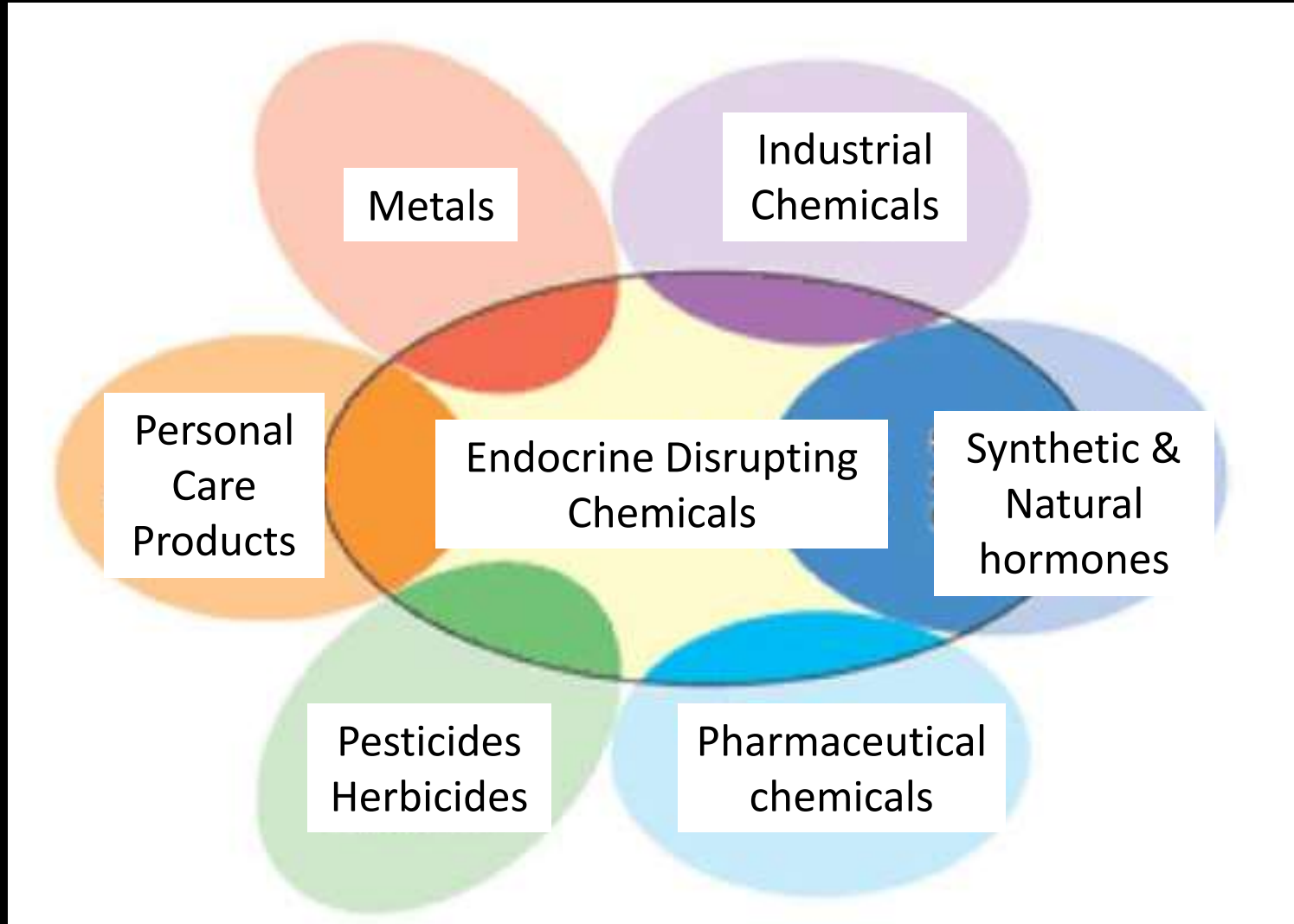
University of Missouri

# Endocrine Disrupting Chemicals (EDC)

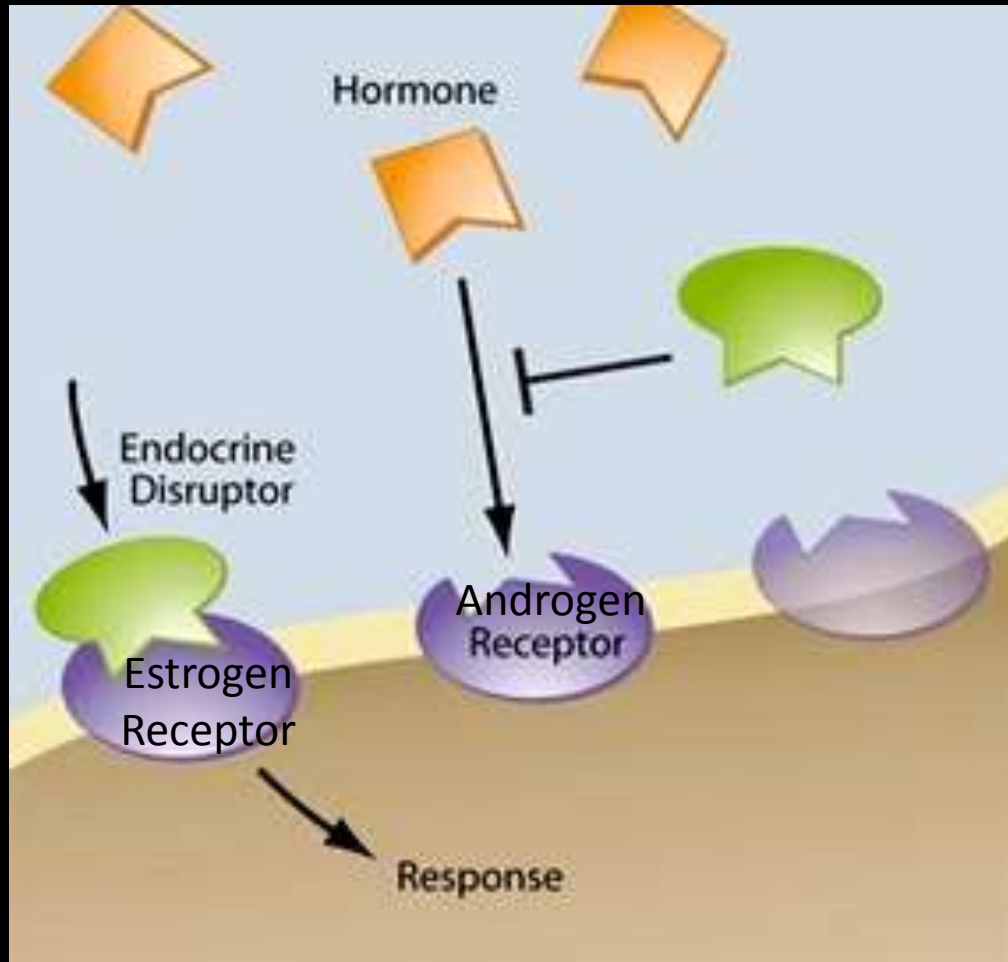
“A chemical, or mixture of chemicals, that interferes with any aspect of hormone action.”



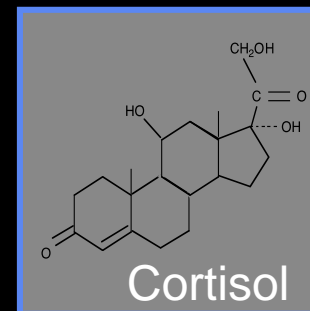
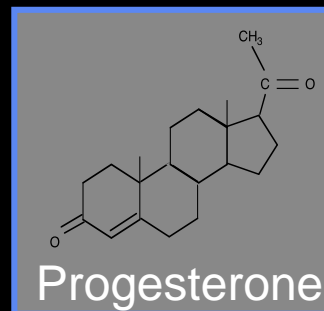
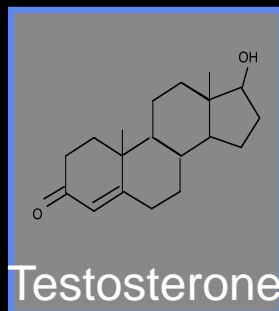
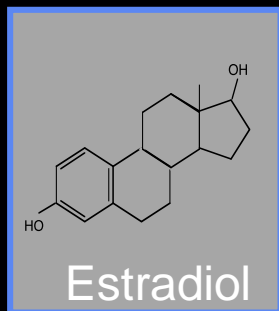
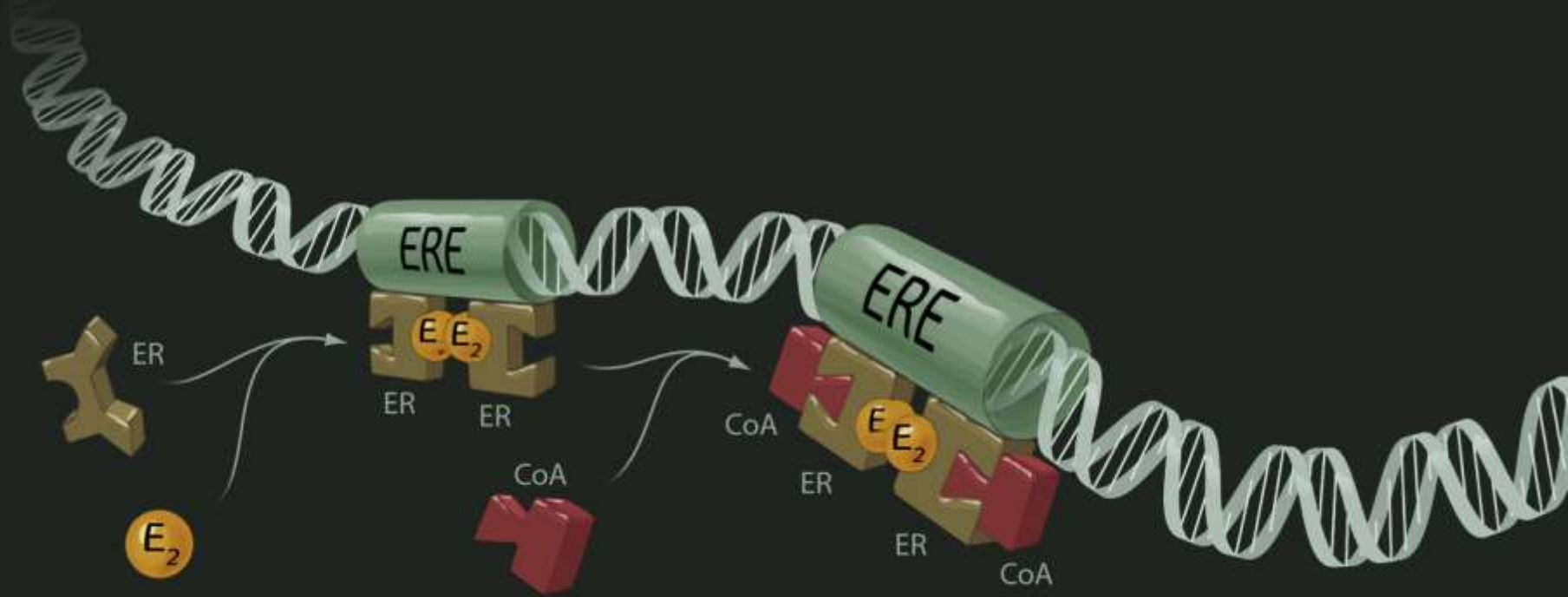
# EDCs are found in many products

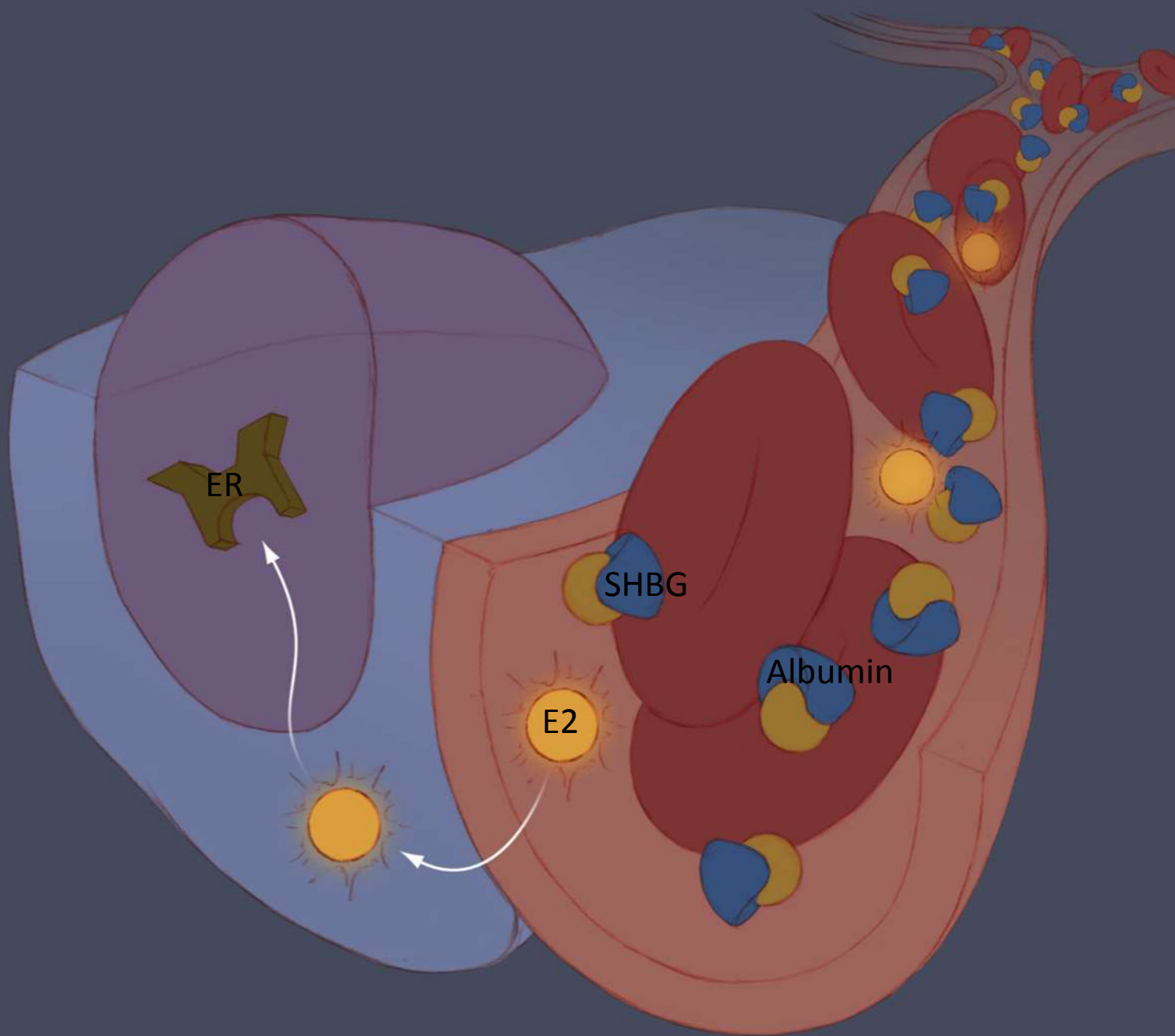


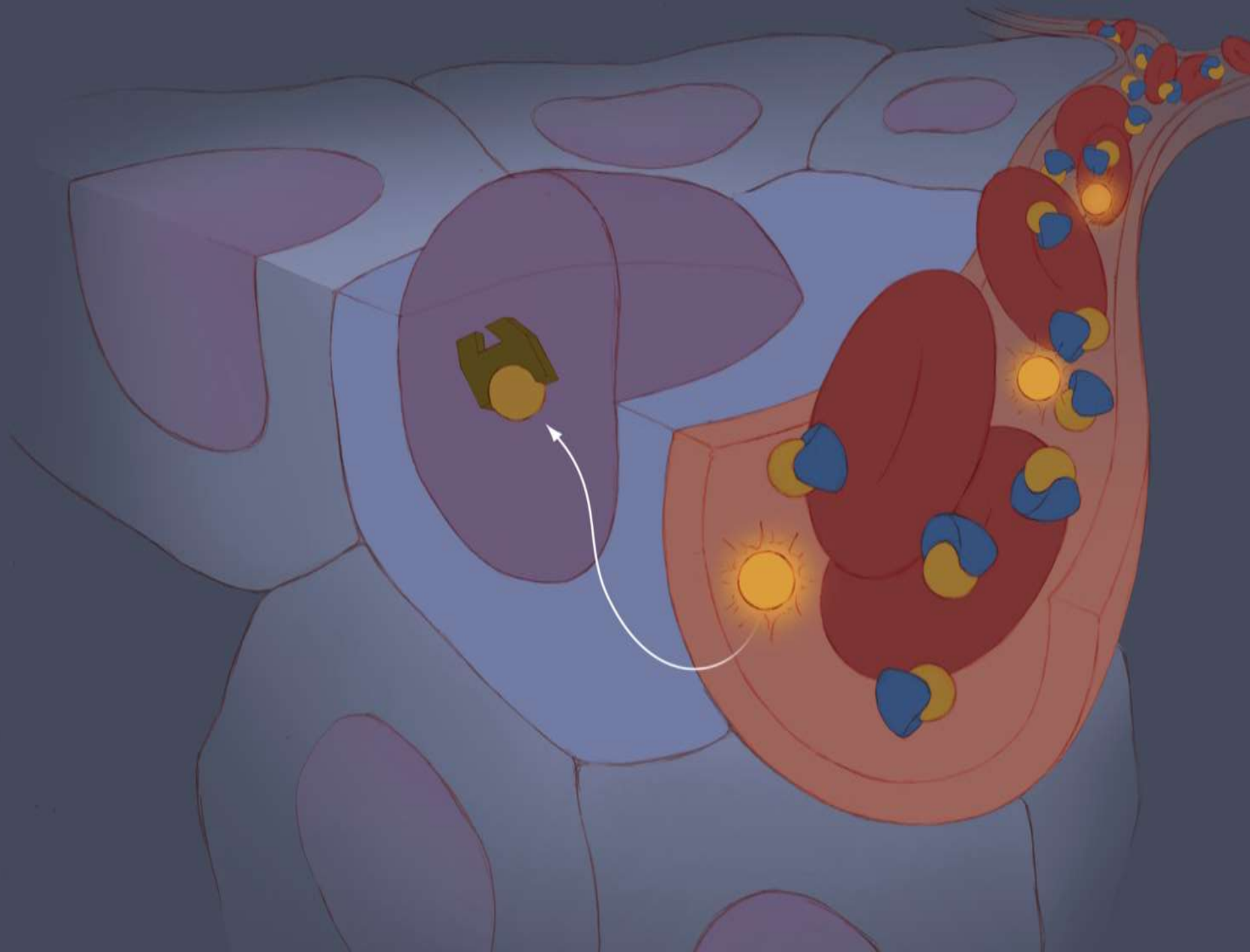
# EDCs disrupt hormone receptors





# Steroid Receptors Are Ligand activated Transcription Factors







# Why is endocrine disruption important to human health and disease?

<b>Estradiol</b>		<b>BPA</b>									
<b>1</b>	<b>10</b>	<b>100</b>	<b>1</b>	<b>10</b>	<b>100</b>	<b>1</b>	<b>10</b>	<b>100</b>	<b>1</b>	<b>10</b>	<b>100</b>
<b>(pg/ml)</b>			<b>(ng/ml)</b>			<b>(µg/ml)</b>			<b>(mg/ml)</b>		
<b>Parts Per trillion</b>			<b>billion</b>			<b>million</b>			<b>thousand</b>		

- Hormones and EDCs can act at low concentrations
- Human exposure can be within the range of bioactivity
- Developmental exposure can alter adult health & disease



# Hormones are essential for normal health and development

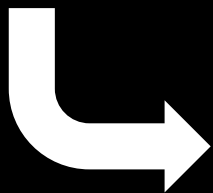


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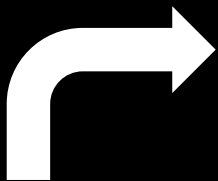
Fetal Testosterone

# Fetal and early life exposure to EDCs is associated with adult disease

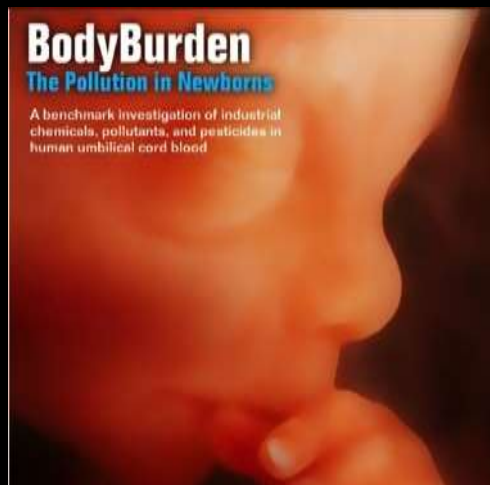
Pollutants



Nutrition



Maternal Health and Disease



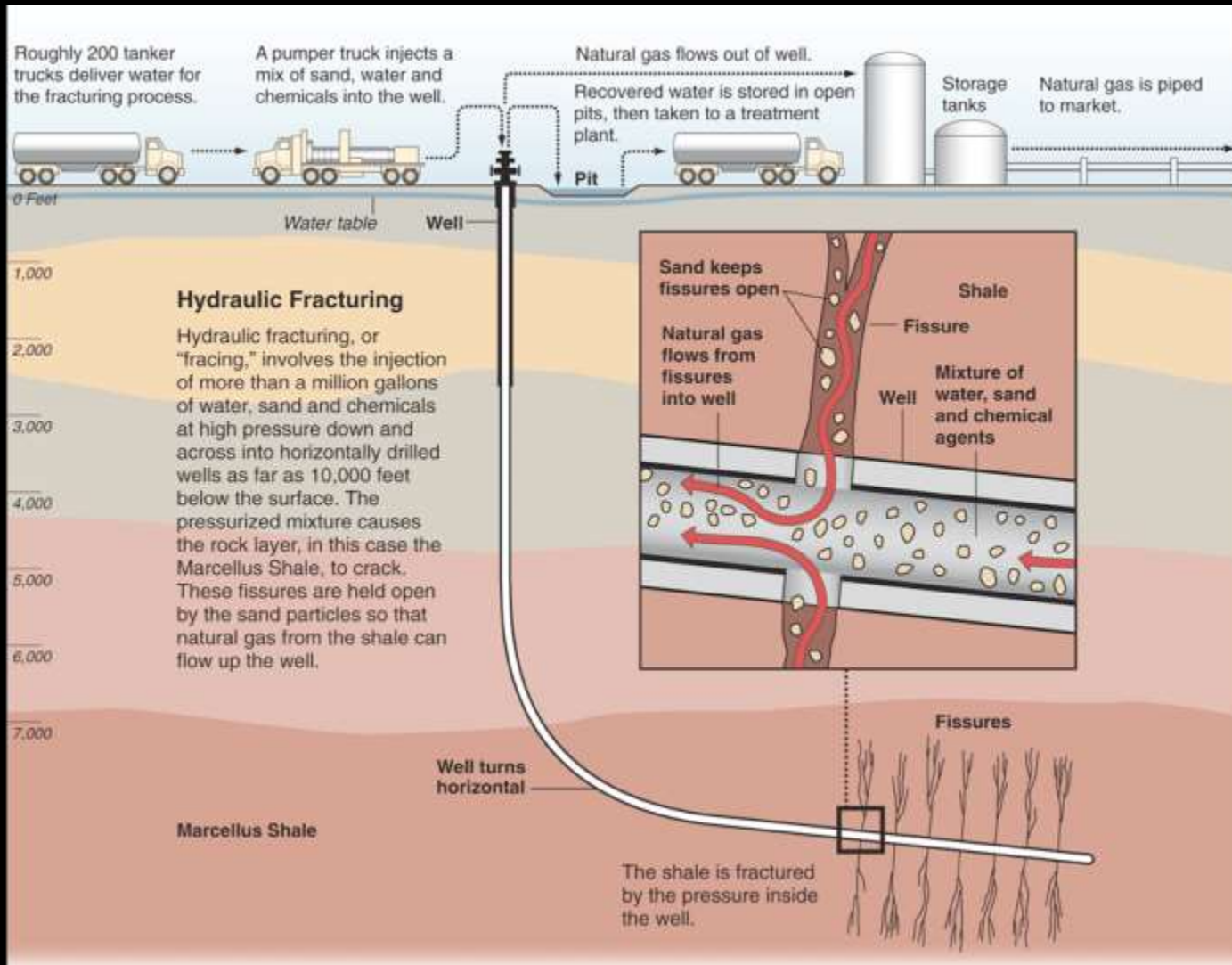
Breast Cancer  
Bone Health  
Endometriosis  
Infertility  
Obesity  
Reduced Sperm  
Heart Disease  
Diabetes  
Hypertension  
Testicular Cancer

**Unconventional oil and natural gas extraction is a potential source of endocrine disrupting chemicals**

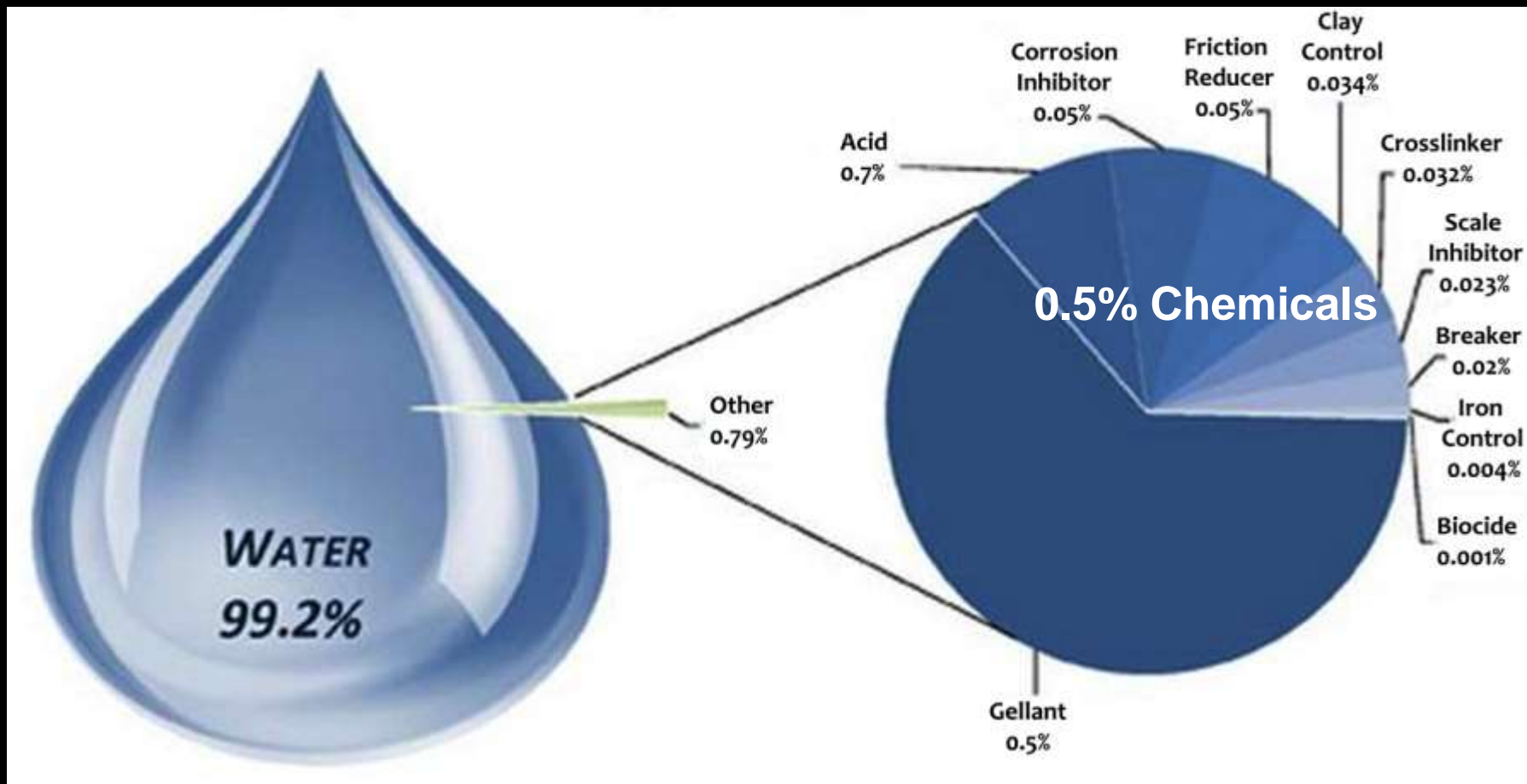


# Unconventional oil & gas (UOG) extraction: Hydraulic Fracturing + Horizontal Drilling

Feet  
0  
1000  
2000  
3000  
4000  
5000  
6000  
7000  
8000



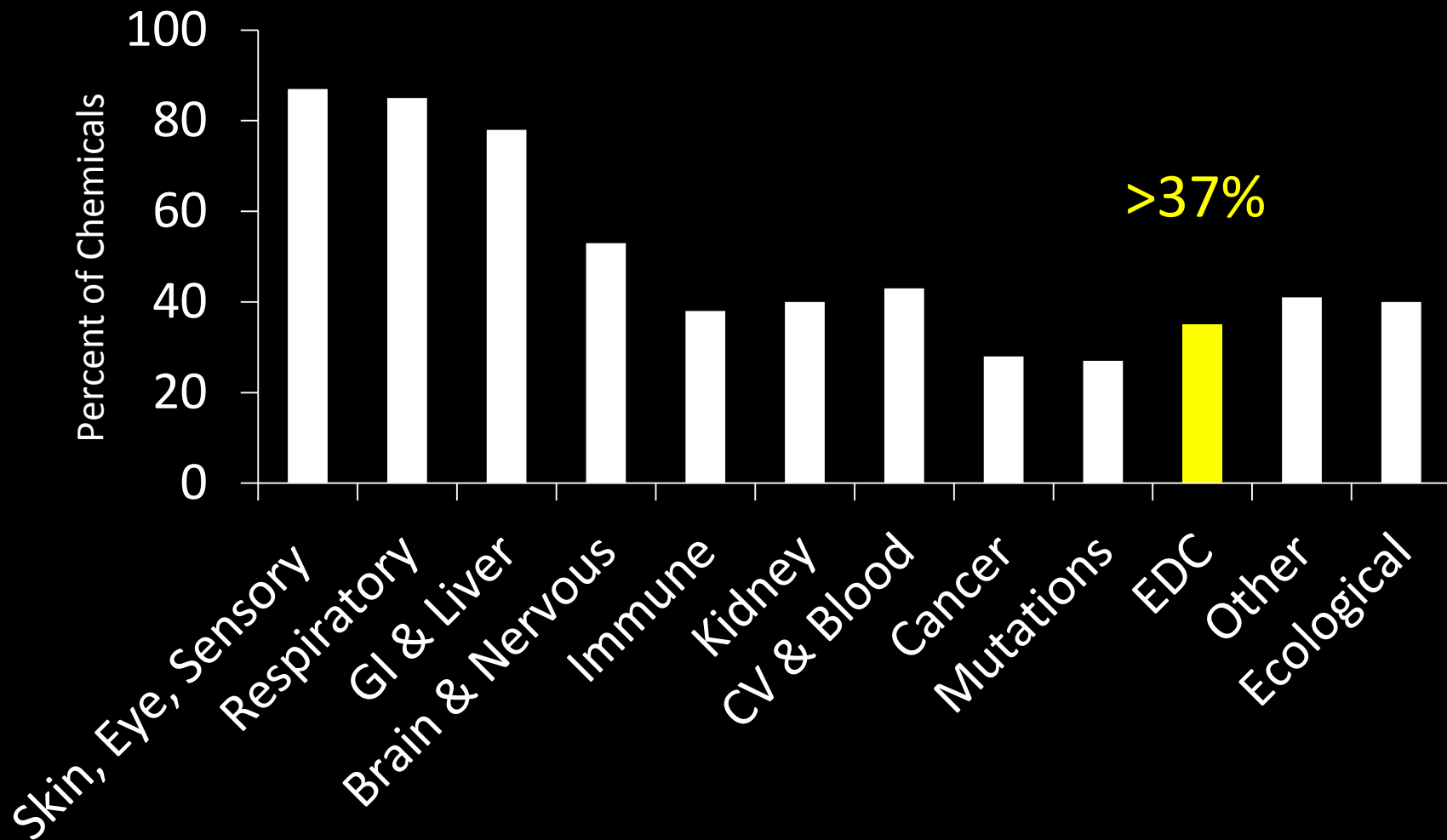
# Fracturing Fluid Composition



Millions of gallons  
of water

Thousands of gallons of  
chemicals

# Health Effects of 350 Chemicals



Colborn T, Kwiatkowski C, Schultz K, and Bachran M. 2011. Natural gas operations from a public health perspective. *Hum Ecol Risk Assess*, 17(5):1039-56.

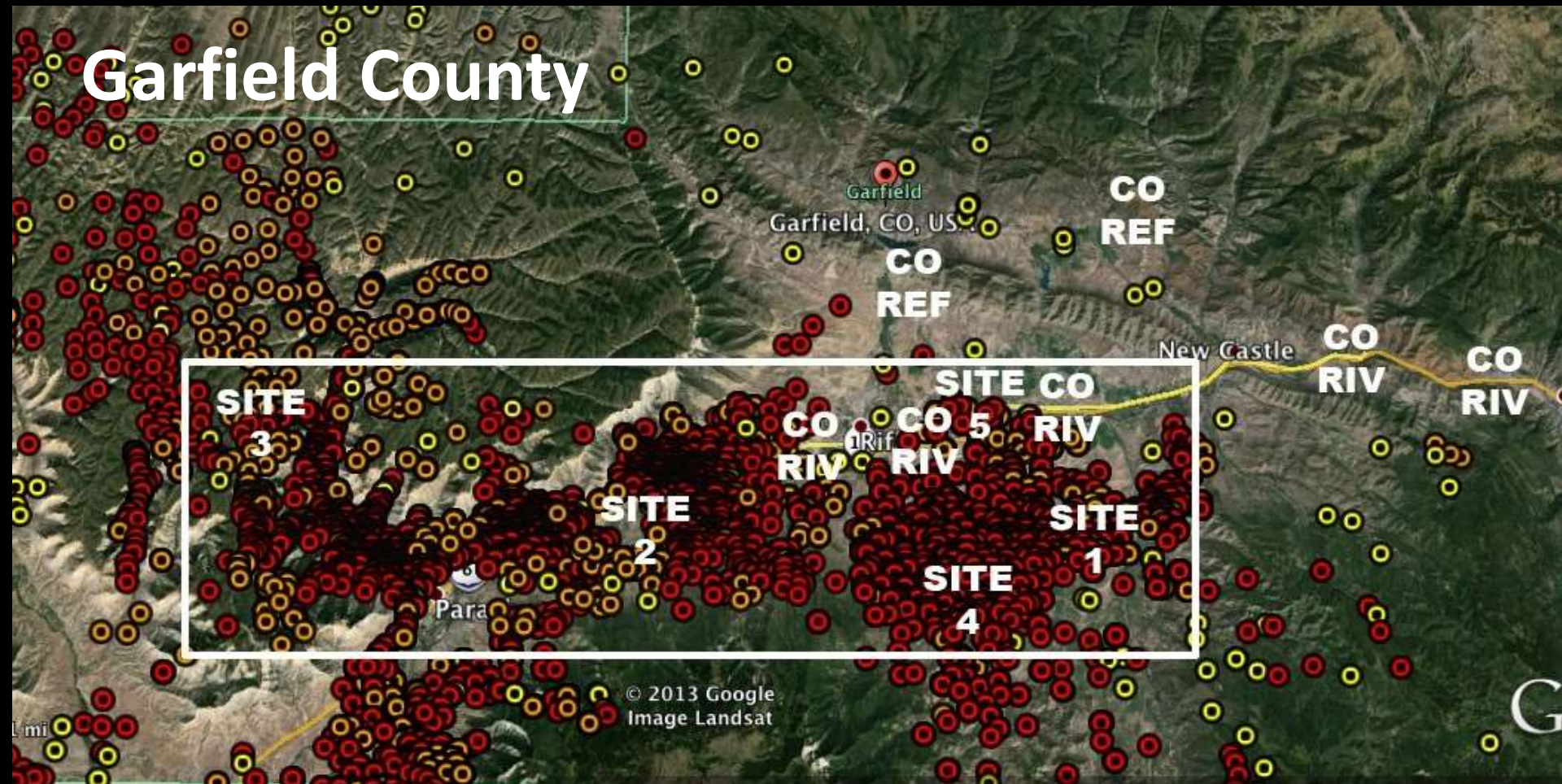
# Millions of gallons of wastewater

- “Flowback” returns immediately to surface
- “Produced water” returns over the life of the well and contains fracking chemicals, liberated salts and radioisotopes from deep underground
- Wastewater spills and leaks
- Direct disposal into surface water
- Well casing failures
- Underground migration



Hypothesis: Surface and ground water at natural gas drilling spill sites contain more endocrine disrupting activity than reference sites.

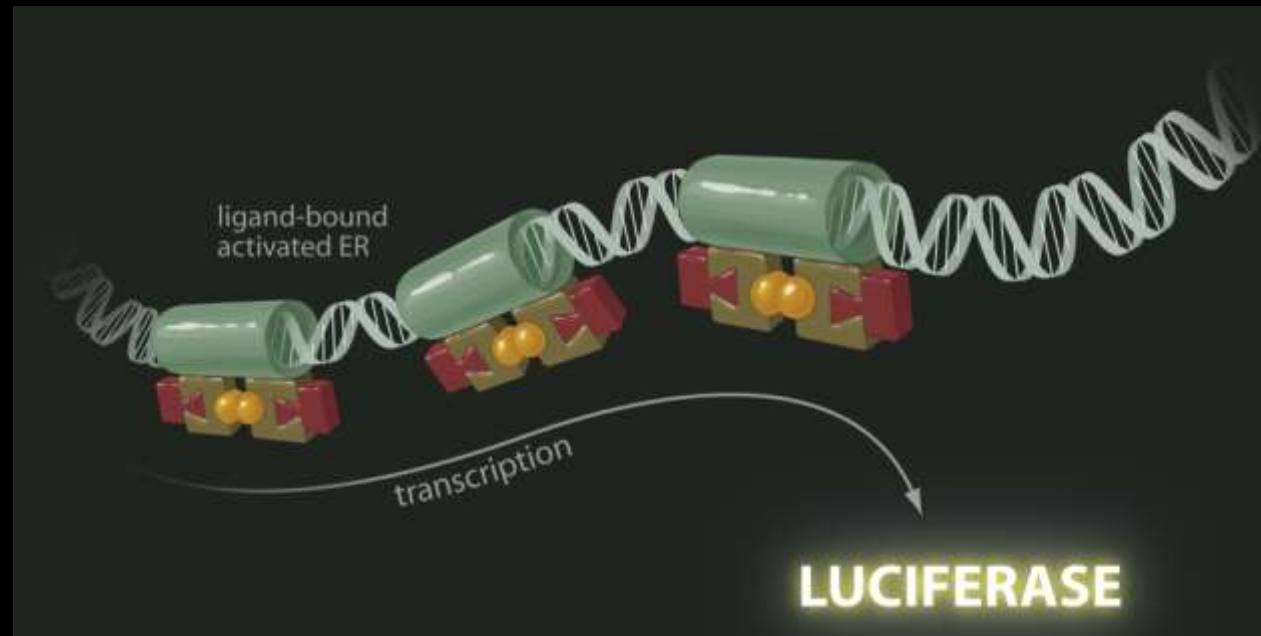
## Garfield County



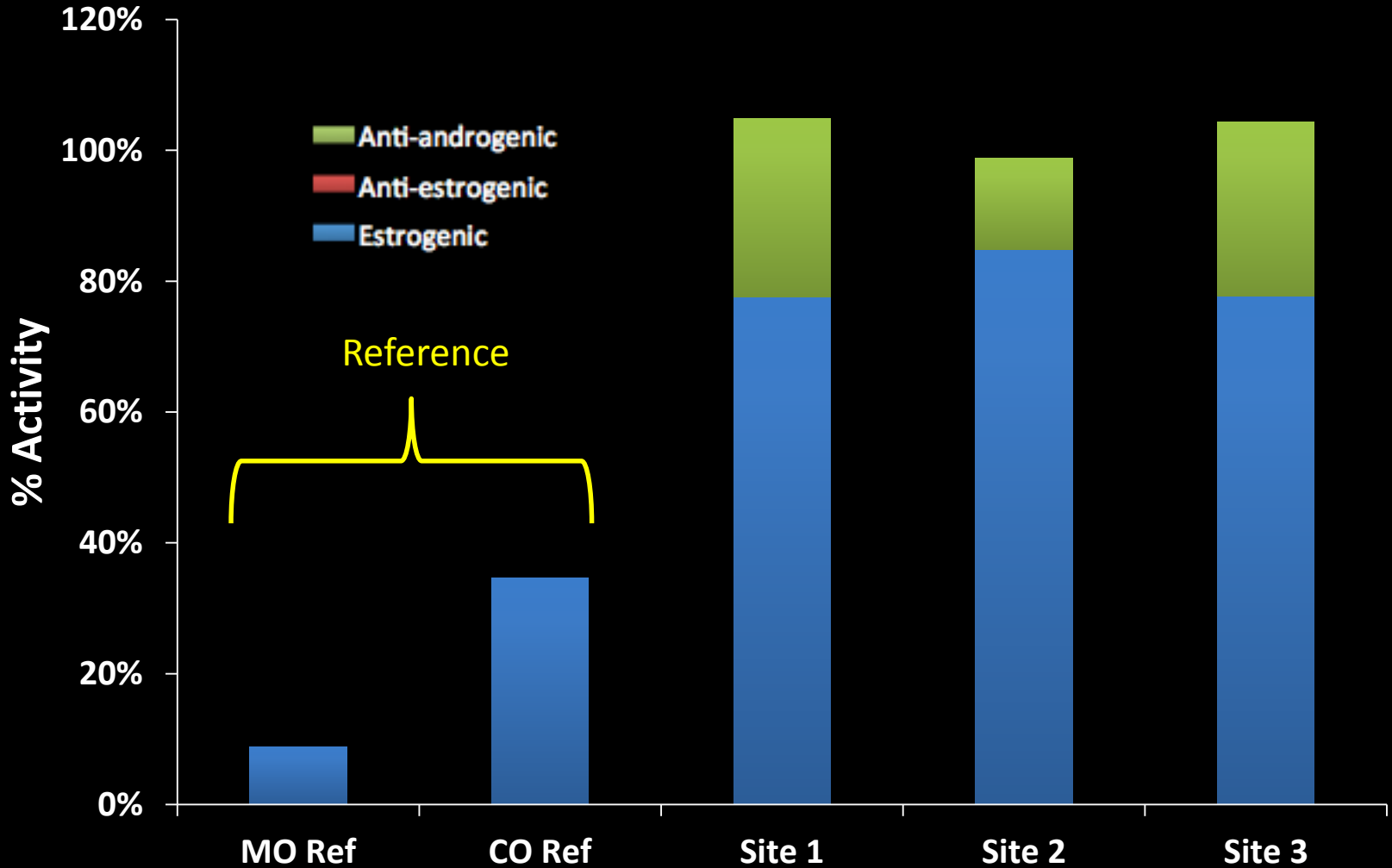
Red = Active wells, Orange = permitted wells, Yellow = Abandoned wells



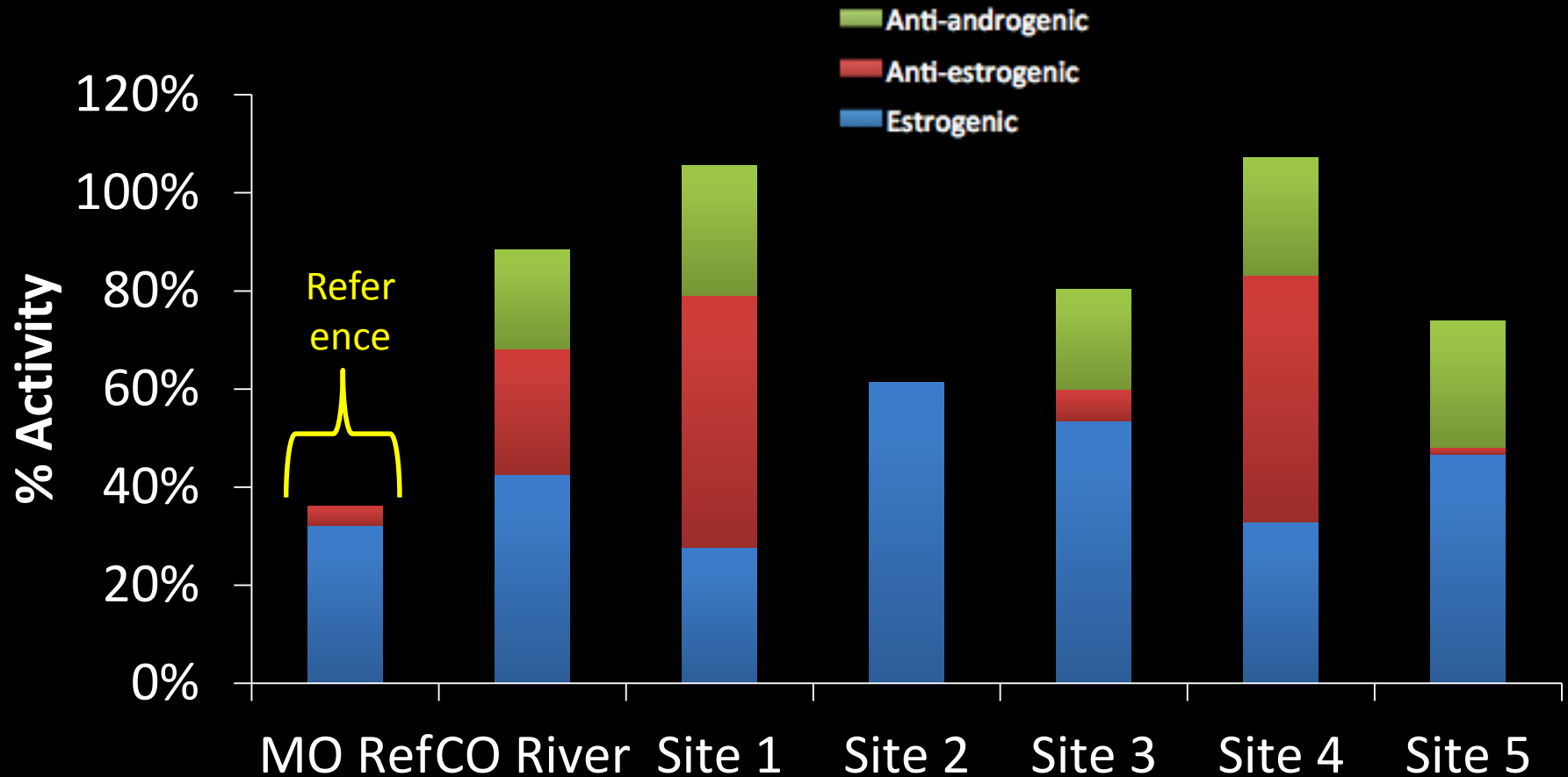
# Solid Phase Extraction & Reporter Gene Assays



# Ground Water Activity By Site



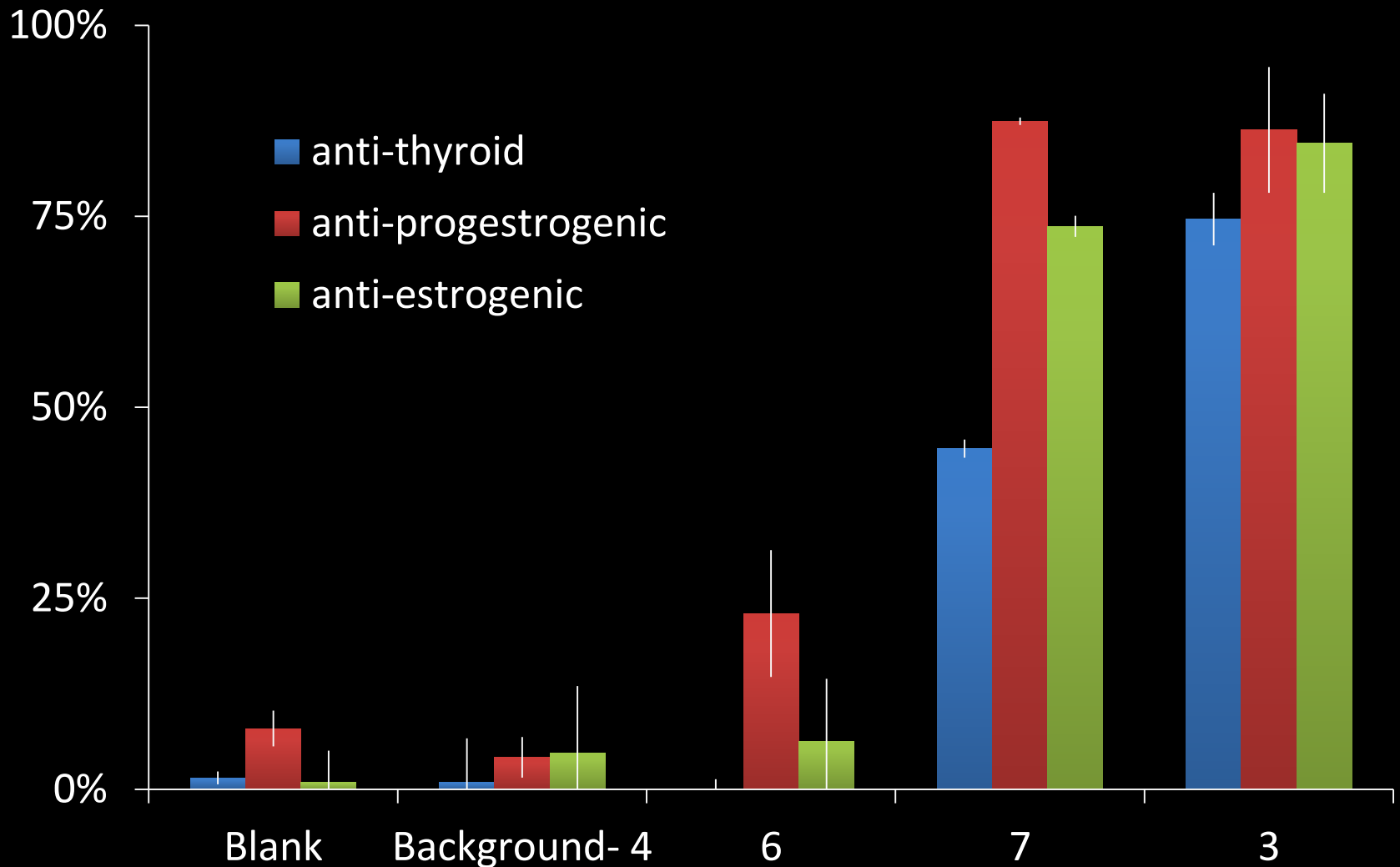
# Surface Water Activity By Site



# Disposal Facility in West Virginia



# Hormone Blocking Activity Associated with Injection/Disposal Well



# Our hypothesis: Chemicals used in hydraulic fracturing will disrupt hormone receptors

Estrogen

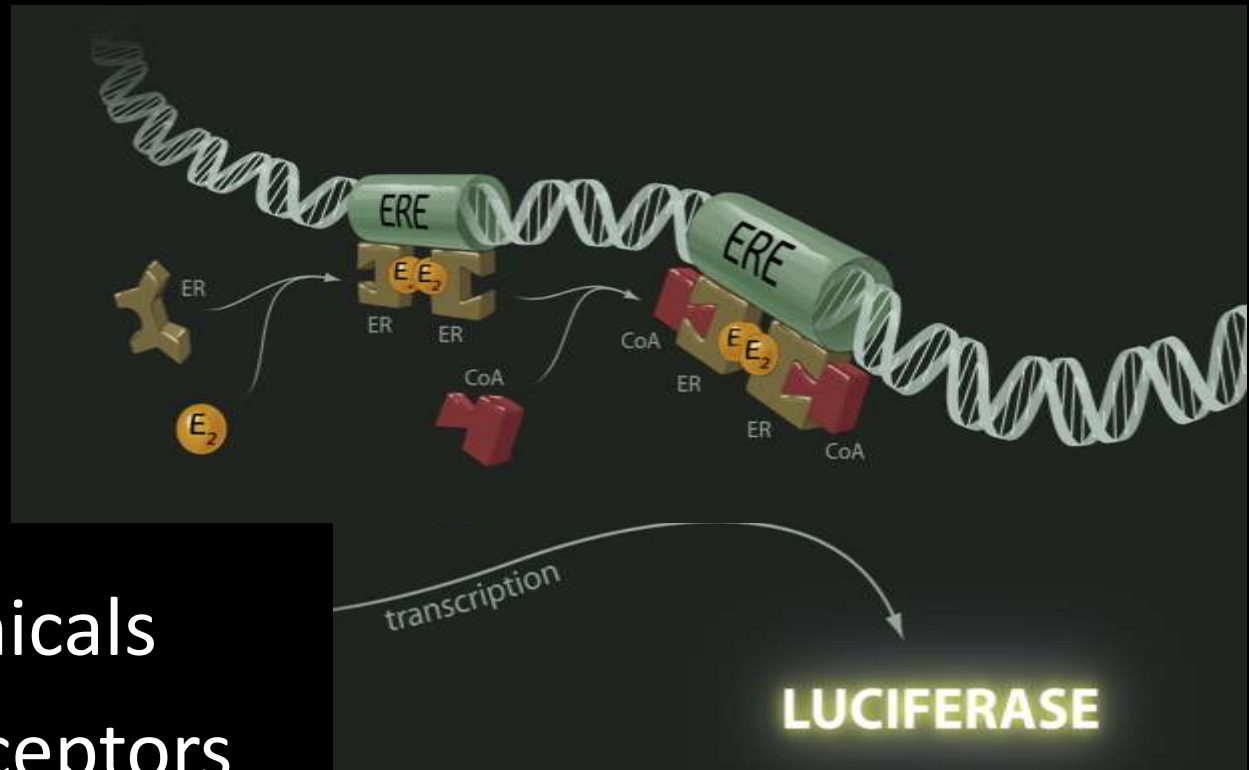
Androgen

Glucocorticoid

Progesterone

Thyroid

# Hydraulic Fracturing and EDCs



- Tested 24 chemicals
- Five nuclear receptors
- Measured receptor activation
- Measured receptor inhibition

# Fracking Chemicals We Tested

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1,2,4-trimethylbenzene

2-(2-methoxyethoxy) ethanol

2-ethylhexanol

Acrylamide

Benzene

Bisphenol A

Bronopol

Cumene

Diethanolamine

Dimethyl formamide

Ethoxylated nonylphenol

Ethoxylated octylphenol

Ethylbenzene

Ethylene glycol

Ethylene glycol butyl ether

Methyl-4-isothiazolin

Naphthalene

Phenol

Propylene glycol

Sodium tetraborate decahydrate

Styrene

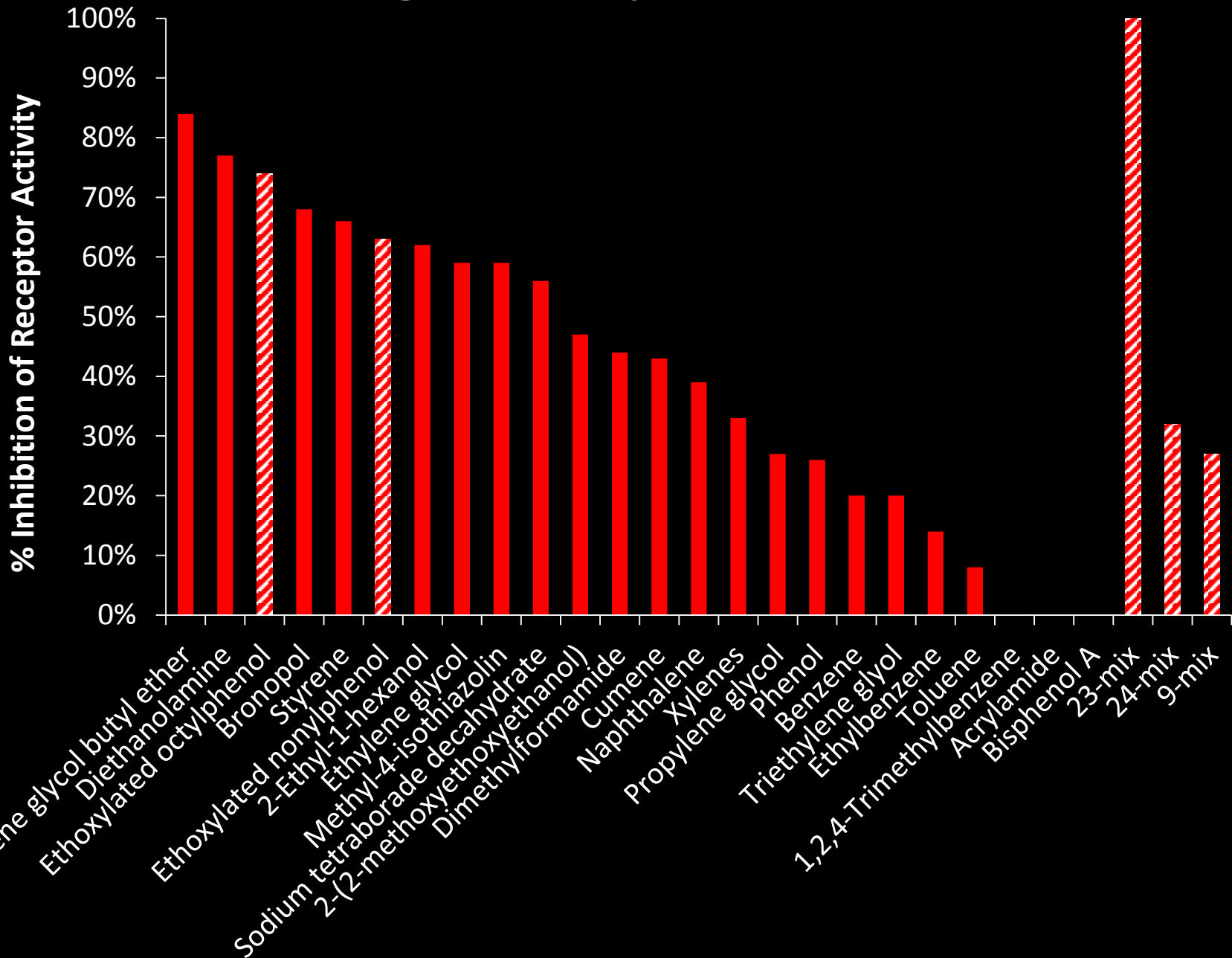
Toluene

Triethylene glycol

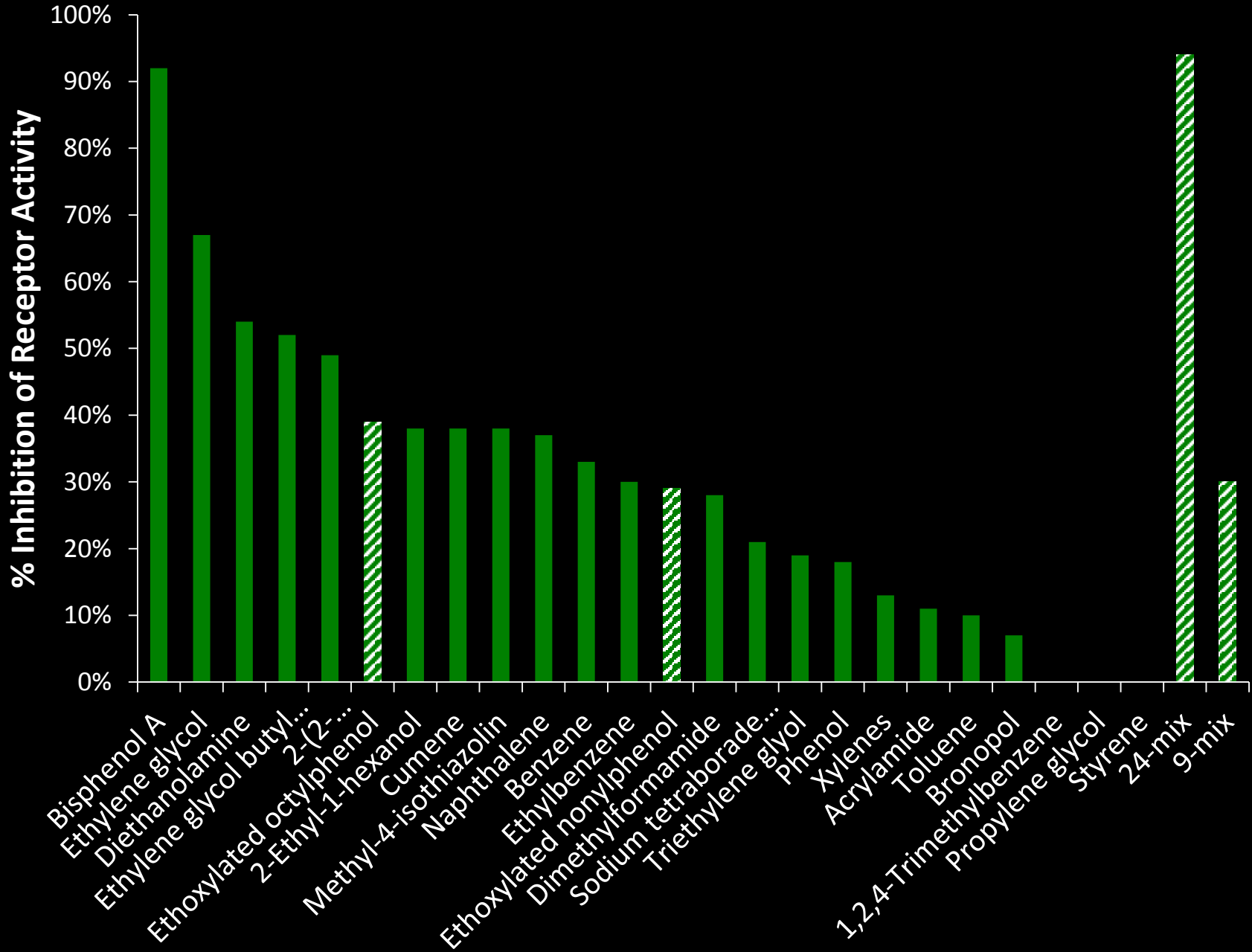
Xylenes



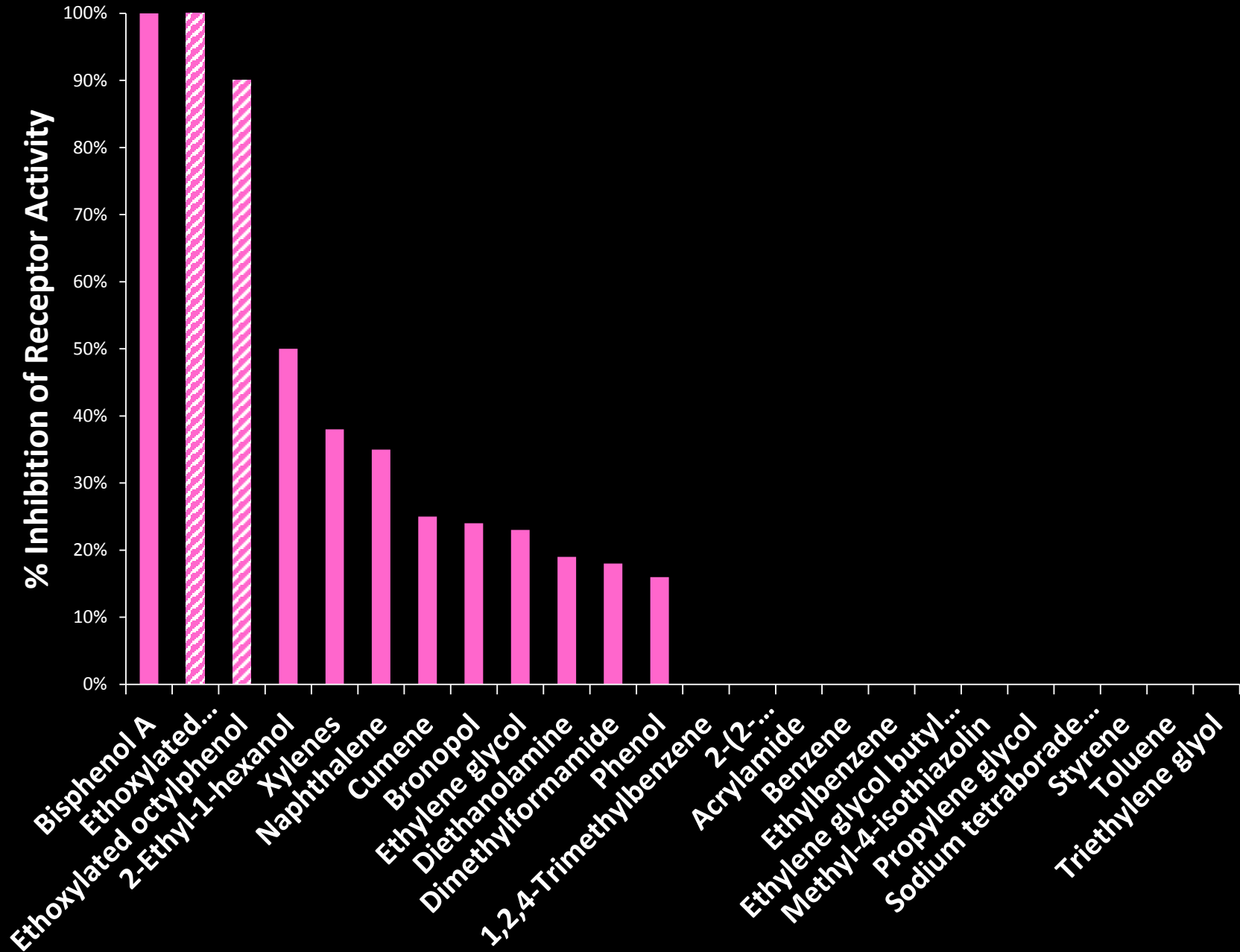
# Estrogen Receptor Inhibition



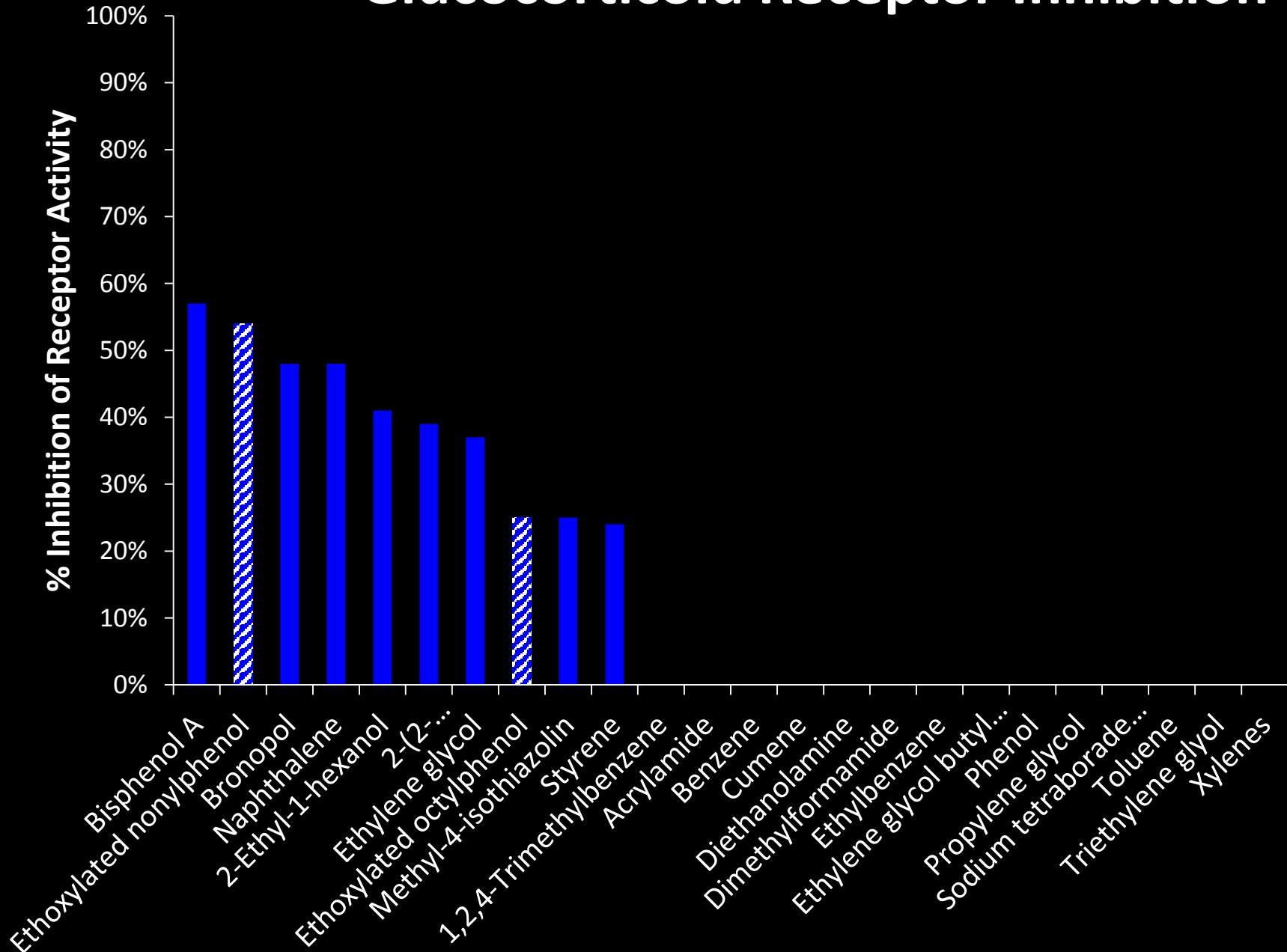
# Androgen Receptor Inhibition



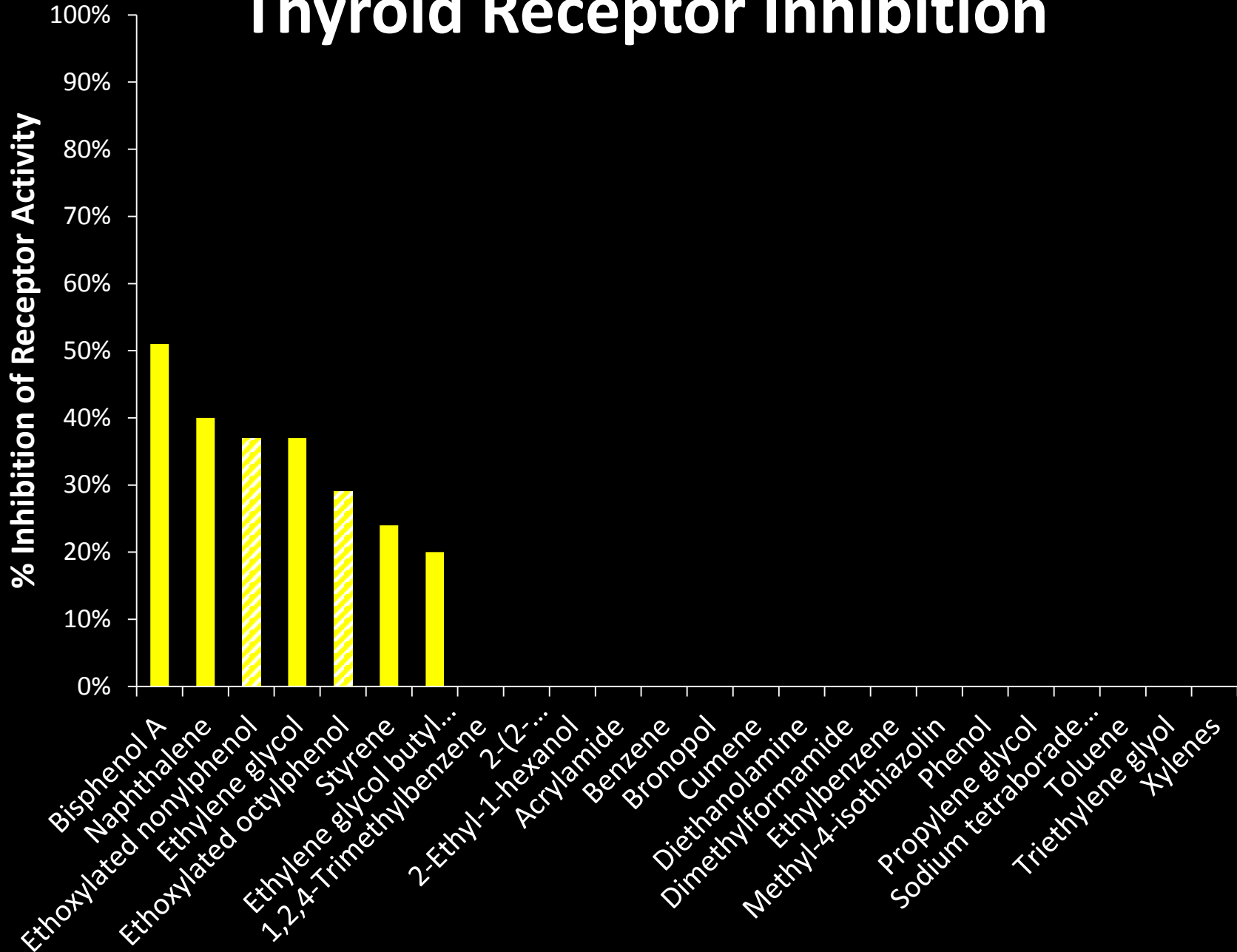
# Progesterone Receptor Inhibition



# Glucocorticoid Receptor Inhibition



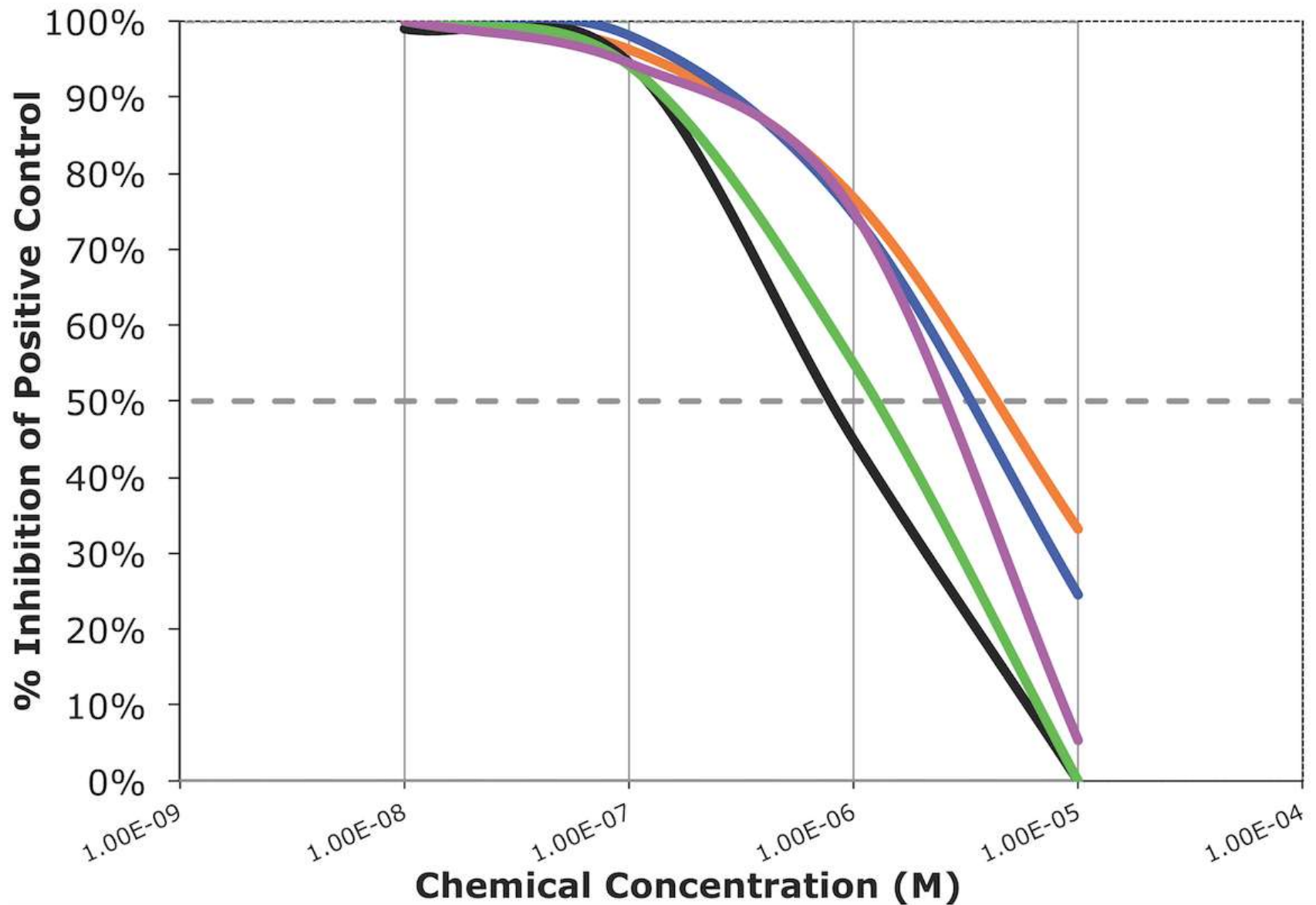
# Thyroid Receptor Inhibition



# EDC Activity of 24 Fracking Chemicals

Receptor	Activation	Inhibition
Estrogen	1	21
Androgen	0	21
Progesterone	1	12
Glucocorticoid	0	10
Thyroid	2	7

# Inhibitory Activity of a Mixture of 23 UOG Chemicals



— EC50

— Androgen

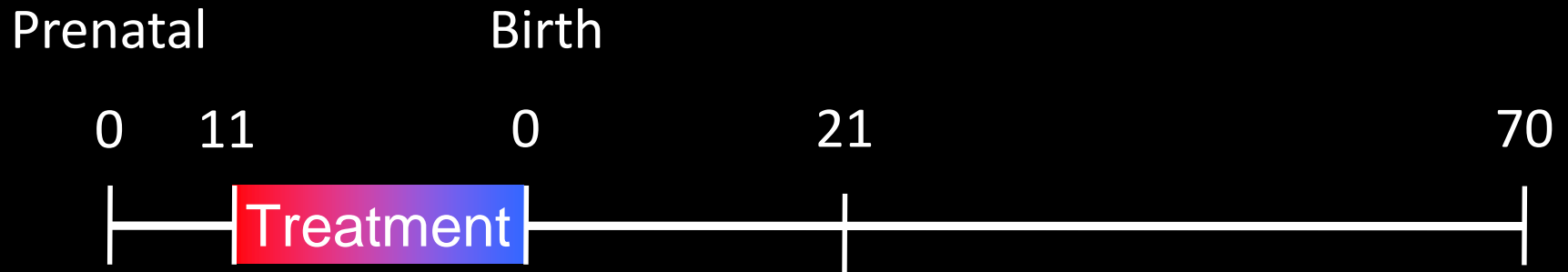
— Glucocorticoid

— Progesterone

— Estrogen

— Thyroid

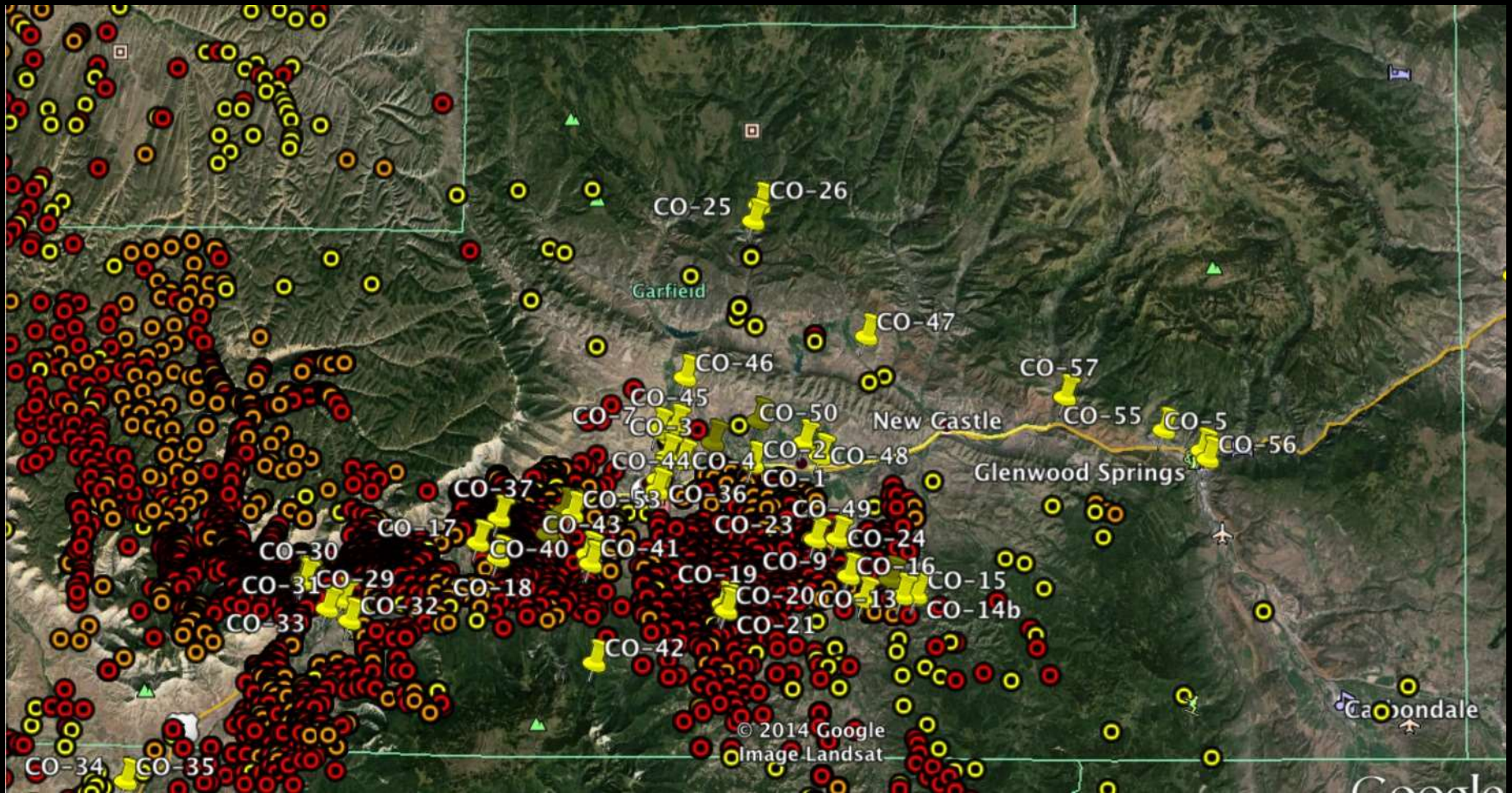
# Developmental exposure to a mixture of 23 UOG chemicals via drinking water



- 3000  $\mu\text{g}/\text{kg}$  Mix 1
- 300  $\mu\text{g}/\text{kg}$  Mix 2
- 30  $\mu\text{g}/\text{kg}$  Mix 3
- 3  $\mu\text{g}/\text{kg}$  Mix 4
- 0 Vehicle

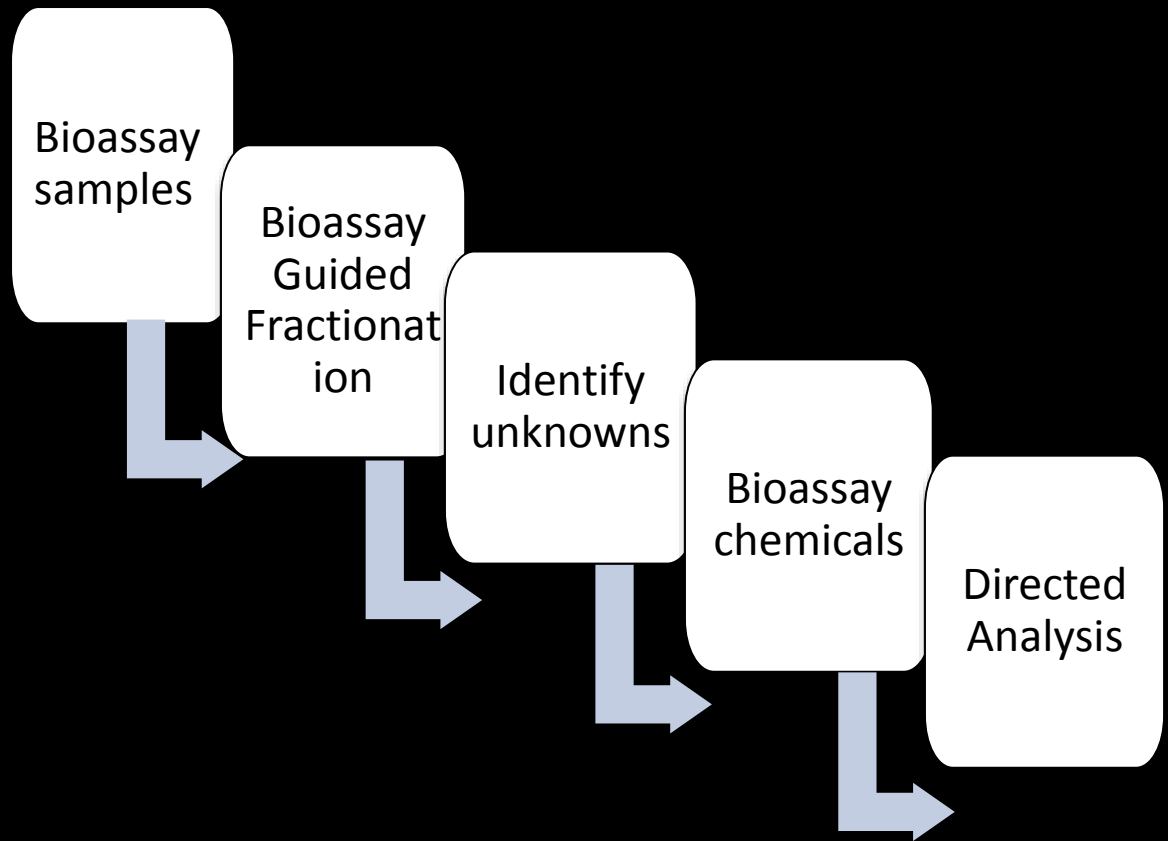


# 2014 Colorado Trip: 48 Sites Sampled



# Identify chemicals in water responsible for EDC activity

- Estrogen
- Androgen
- Glucocorticoid
- Progesterone
- Thyroid



# Preliminary results: Chemicals we found in wastewater

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1,2,4-trimethylbenzene

2-(2-methoxyethoxy) ethanol

2-ethylhexanol

Acrylamide

Benzene

Bisphenol A

Bronopol

Cumene

Diethanolamine

Dimethyl formamide

Ethoxylated nonylphenol

Ethoxylated octylphenol

Ethylbenzene

Ethylene glycol

Ethylene glycol butyl ether

Methyl-4-isothiazolin

Naphthalene

Phenol

Propylene glycol

Sodium tetraborate decahydrate

Styrene

Toluene

Triethylene glycol

Xylenes

# Conclusions

1. Hormones and EDCs work at low concentrations
2. EDCs are associated with disease in people
3. Of 24 fracking chemicals tested, 23 are EDCs
4. All five hormone receptors tested were disrupted by fracking chemicals
5. Surface and ground water from hydraulic fracturing “preventable discharge” sites had greater endocrine disrupting activity than control sites



# Research Team



Kassotis



Davis



Nagel



McElroy



Lin



Tillit



Vengosh



Balise



Funding: The Passport Foundation, University of Missouri, EPA STAR Fellowship to Kassotis

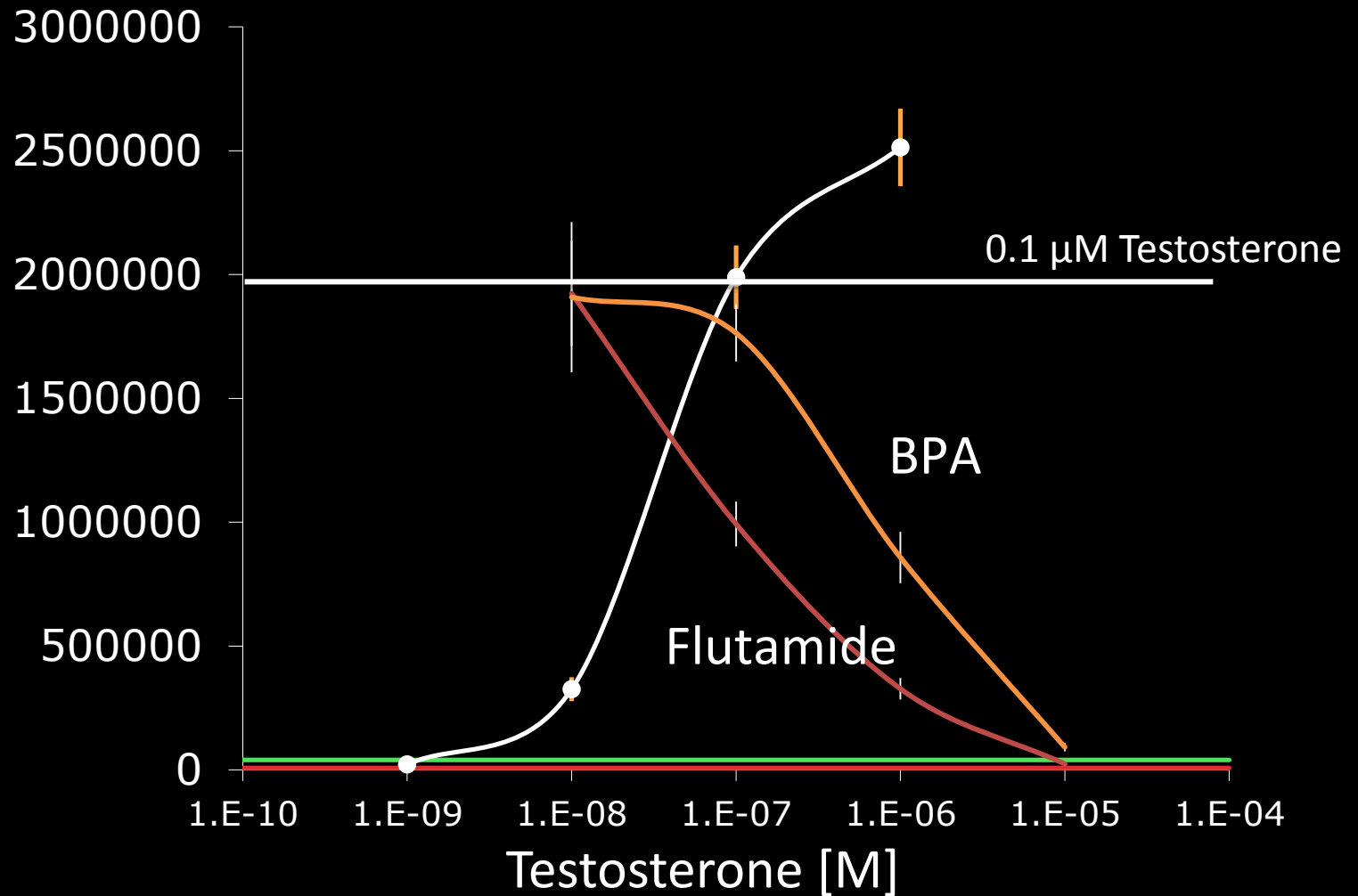
Thank you



# 2010 Sample Collection Sites

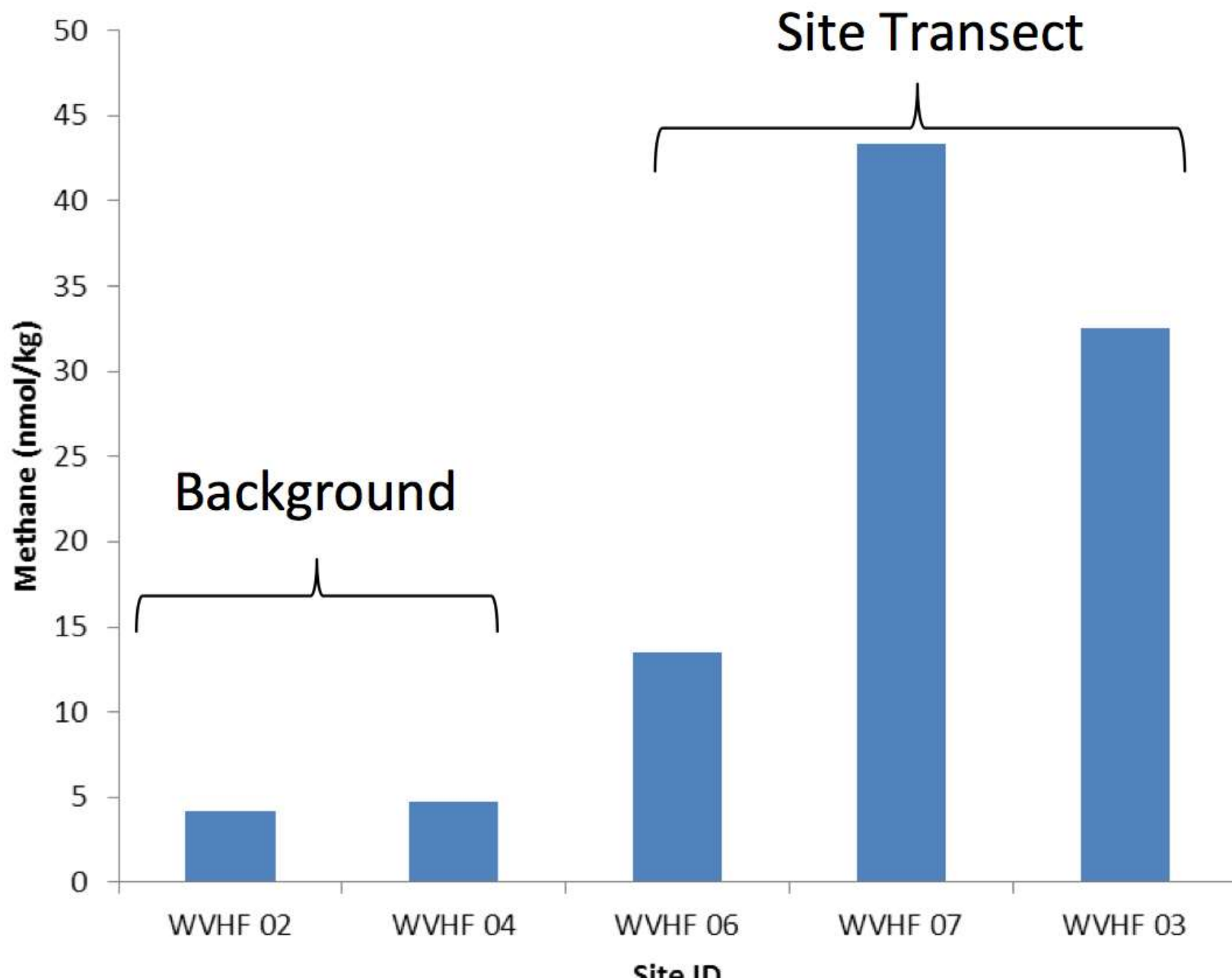
<b>Site #</b>	<b># of Samples</b>	<b>Wells within 1 mile</b>	<b>Incident</b>	<b>Year</b>
Control	5	0	-	-
1	8	43	Natural gas upwelling	2008
2	8	78	Discharge into stream	2009
3	5	69	Fuel or produced water spill	2008
4	8	136	Produced water tank leak	2004
5	9	95	Produced water line leak	2010

# Steroid Receptor Reporter Gene assay





# Methane



# Analytical Measurement of Selected Chemicals in Produced Water

Chemicals	CAS #	PW1 Aqu	PW1 Org	PW2	PW3
Naphthalene	91-20-3	3.5	264.5	0.1	0.2
Styrene	100-42-5	<LOD	52.0	<LOD	<LOD
Benzene	71-43-2	0.9	331.5	1.8	4.6
Ethylbenzene	100-41-4	7.3	1099.0	0.1	1.0
Cumene	98-82-8	4.2	128.9	0.0	0.2
2-ethylhexanol	104-76-7	<LOD	<LOD	<LOD	<LOD
trimethylbenzene	95-63-6	78.5	5873.0	0.3	2.7
Toluene	108-88-3	27.3	1410.0	4.8	11.8
m-xylene	108-38-3	<LOD	885.5	1.6	8.2
p-xylene	106-42-3	40.1	1172.0	(m+p)	(m+p)
o-xylene	95-47-6	15.0	396.4	0.9	2.7
2-butoxyethanol	111-76-2			77.5	

