Developing Surrogate Measurements for the Analysis of Produced Water

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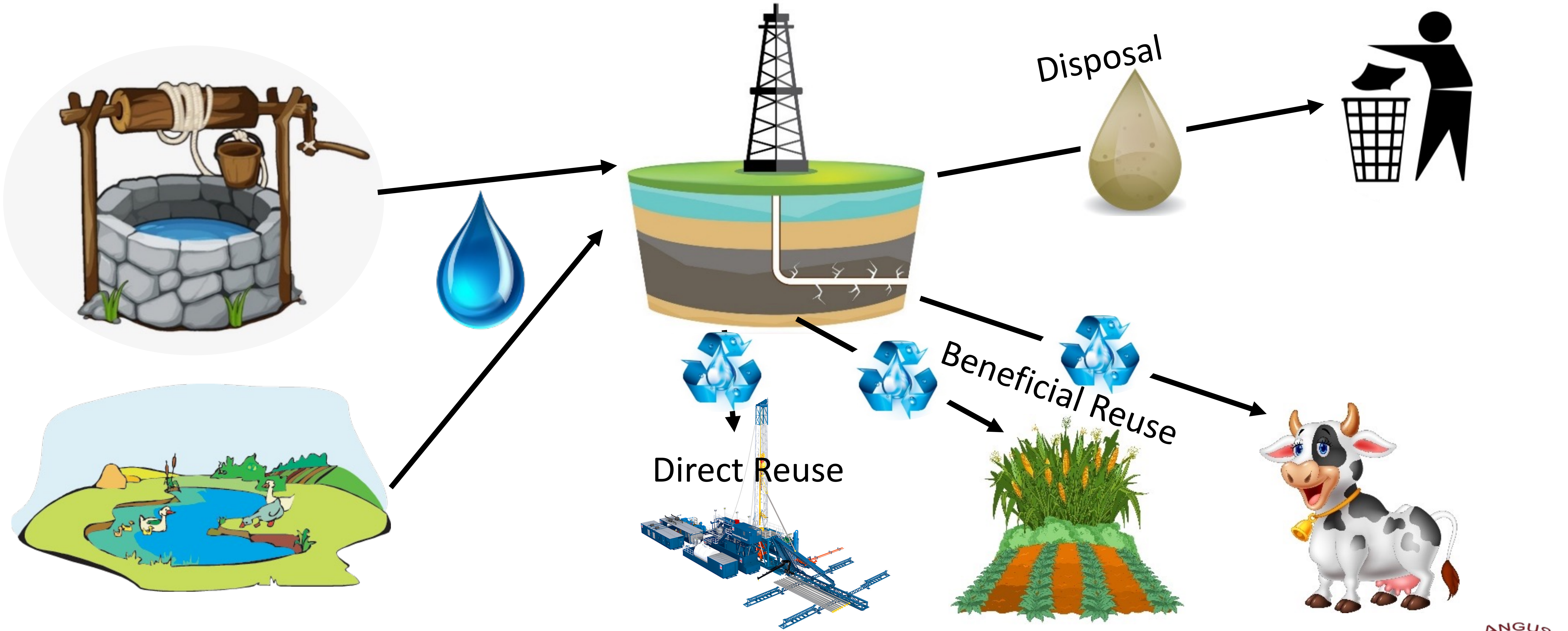
OIL FIELD WATER MANAGEMENT SYMPOSIUM
MARCH 29-30, 2023

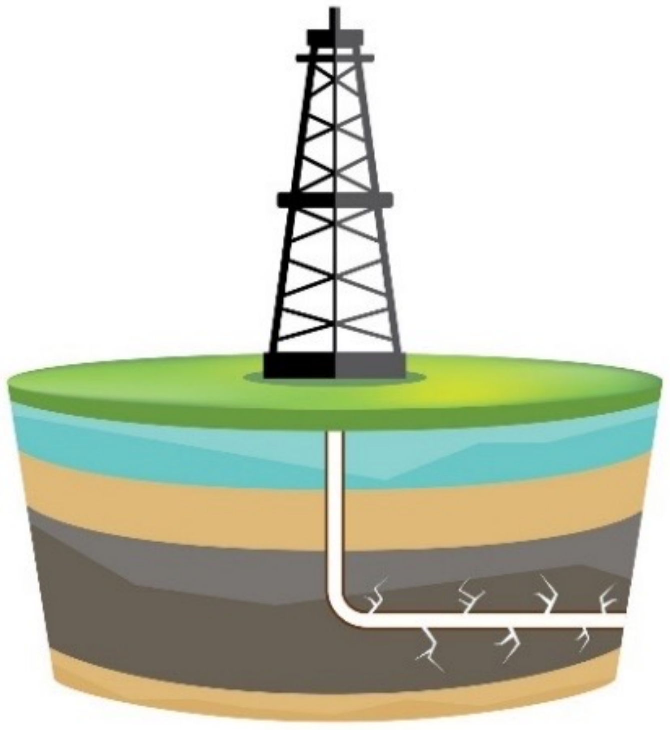
Killing Two Birds



3.4 x 10^8 bbl surplus of Produced water!
~15,714 Olympic swimming pools/year

Liden et al., Sci. Tot. Environ. 2018

Treated Water Applications



Cost

X | 3X | 6X

Quality

TSS and HC removal, bacterial kill, pertinent metals

Additional metals and TDS NORM

SDWA

Tech

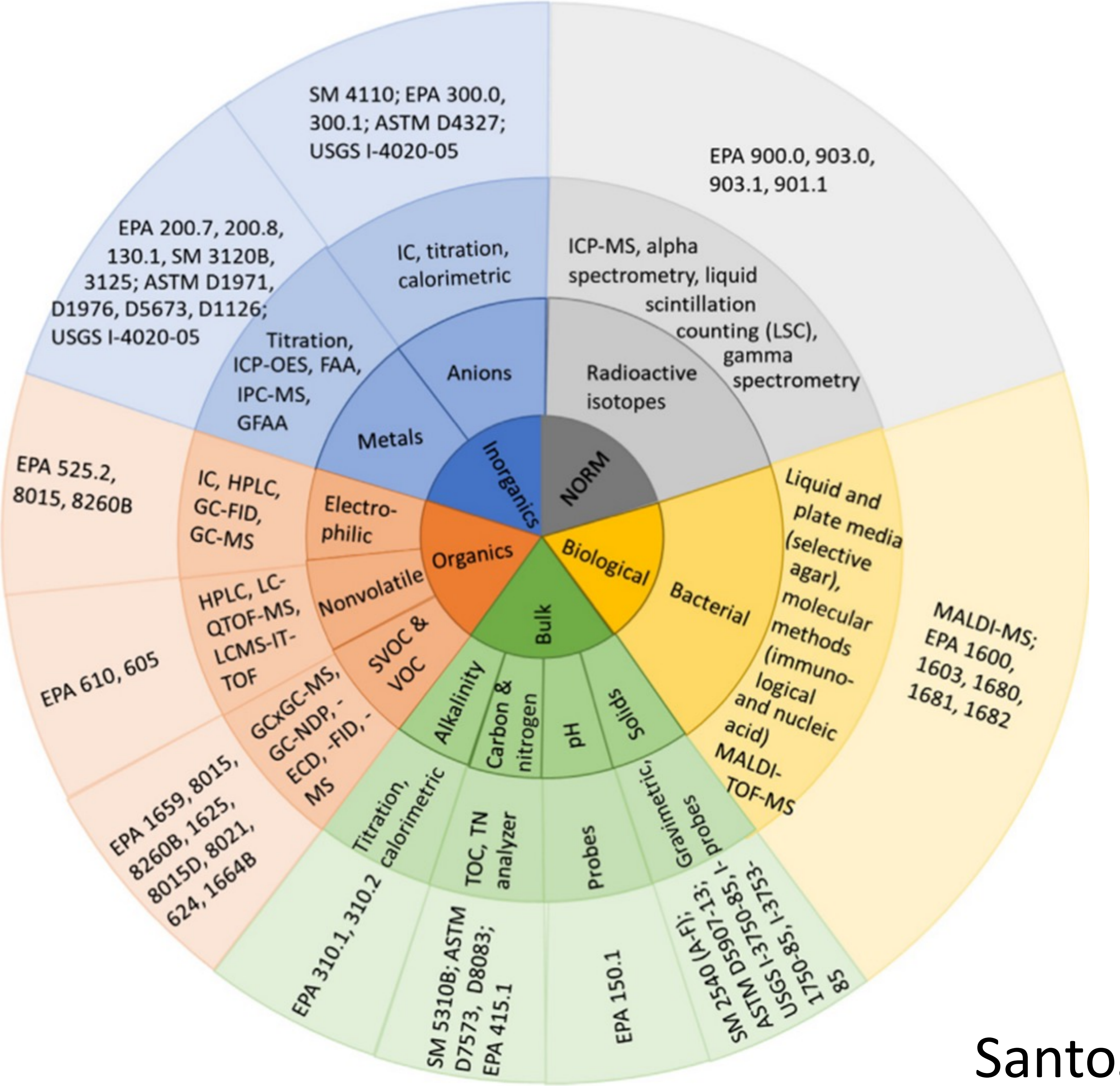
2-5 modalities required

+Desalination

+Additional polishing

Liden et al., Water 2019

Treated Water Applications

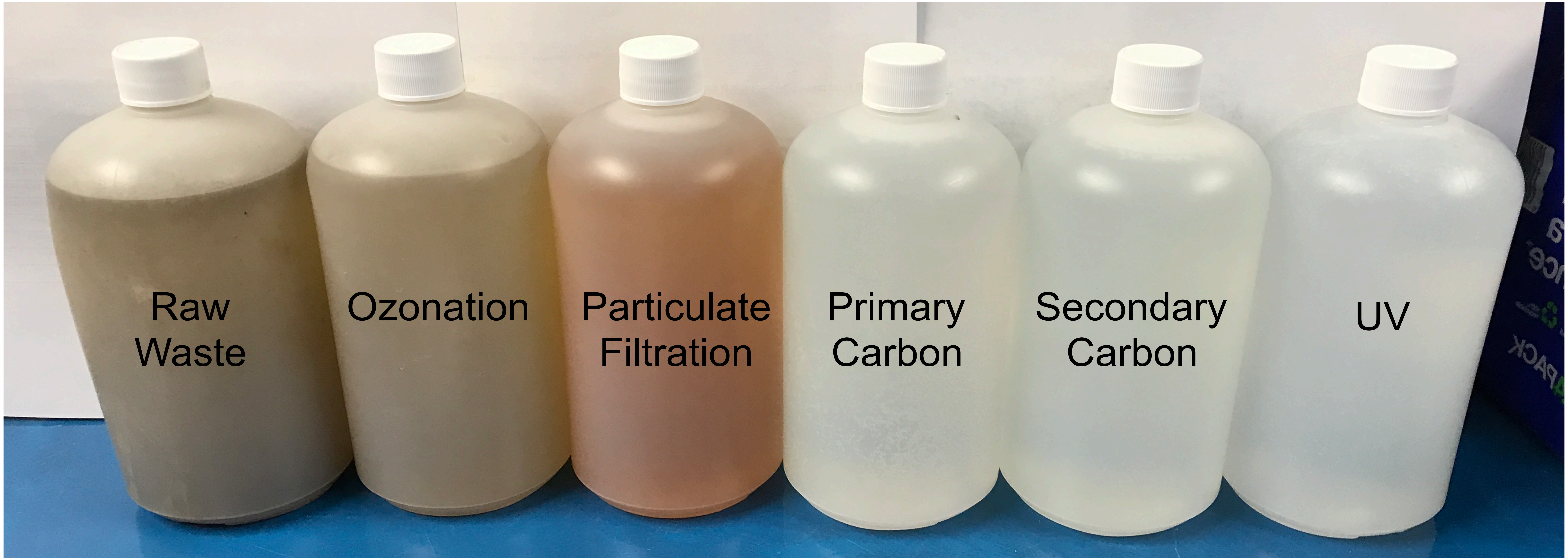


Santos et al., Analytical Chemistry 2018
Liden et al., Sep. Sci. Tech. 2019

SPL
ANGUS MEASUREMENT

Objectives of this Study

1) Determine how 'how clean is clean enough' for the beneficial reuse application



Hildenbrand et al., Sci. Tot. Environ. 2018

Comprehensive Analyses

1) Basic water quality (YSI multimeric probe)
   pH, TDS, conductivity, salinity, ORP, TSS, turbidity
2) Anions (Liquid Chromatography, Inductively Coupled Plasma Optical Emission Spectroscopy)
   Br, Ca, Cl, Fe, K, Mg, Na, Sr, and SO_4
3) Metals (Inductively Coupled Plasma Mass Spectrometry)
   41 different ions including As, Ba, Fe, Ni, Sr, Pb, etc.
4) Total organic carbon / total nitrogen (TOC/TN Analyzer)
   Organic carbon, inorganic carbon, nitrogen
5) Volatile and semi-volatile organic compounds (Gas Chromatography Flame Ionization Detection, Head Space Gas Chromatography Flame Ionization Detection)
   Alcohols, alkyl hydrocarbons, aromatic hydrocarbons (i.e., BTEX)
6) **Untargeted analysis of (Liquid Chromatography - Quadrupole Time of Flight Mass Spectrometry, Gas Chromatography Mass, Spectrometry w/ Vacuum Ultraviolet Detection, Thin Film Solid Phase Microextraction - Chromatography)**
   Various volatile, semi-volatile, nonvolatile organic compounds, PFAS/PFOA
7) Microbial (Matrix Assisted Laser Desorption Ionization Time of Flight Mass Spectrometry, DNA sequencing, and ATP assay)
   2,500+ different microbial species and overall microbial counts
8) Toxicological (MicroTox and ecotoxicity assays)
   Measurements of acute and chronic toxicity

PFAS/PFOA Analysis

Name	Abbreviation	Carbon number	Molecular weight (g/mol)	log P	pKa
Perfluoro-n-butanoic acid	PFBA	C4	214.0	2.31	1.07
Perfluoro-n-pentanoic acid	PFPeA	C5	264.0	3.01	0.34
Perfluoro-n-hexanoic acid	PFHxA	C6	314.0	3.71	-.078
Perfluoro-n-heptanoic acid	PFHpA	C7	364.0	4.41	-2.29
Perfluoro-n-octanoic acid	PFOA	C8	414.0	5.11	-4.2
Perfluoro-n-nonanoic acid	PFNA	C9	464.0	5.81	-6.51
Perfluoro-n-decanoic acid	PFDA	C10	514.0	6.51	-5.2
Perfluoro-n-undecanoic acid	PFUdA	C11	564.0	7.22	-5.2
Perfluoro-n-tridecanoic acid	PFTrDA	C13	664.0	8.62	-5.2
Perfluoro-n-tetradecanoic acid	PFTeDA	C14	714.0	9.32	-5.2
Perfluorobutanesulfonic acid	PFBS	C4	338.2	2.63	-3.31
Perfluorooctanesulfonic acid	PFOS	C8	522.1	5.43	-3.32
N-methylperfluoro-1-octanesulfonamidoacetic acid	MeFOSAA	C11	571.2	4.78	1.23
N-ethylperfluoro-1-octanesulfonamidoacetic acid	EtFOSAA	C12	585.2	5.14	1.34
Hexafluoropropylene oxide dimer acid	GenX (HFPO-DA)	C6	330.1	4.0	-0.77
Internal standard	Molecular weight (g/mol)				
$^{13}C_3$ GenX	287				
$^{13}C_8$ PFOA	421				
$^{13}C_8$ PFOS	507				
$^{13}C_2$ PFUdA	565				

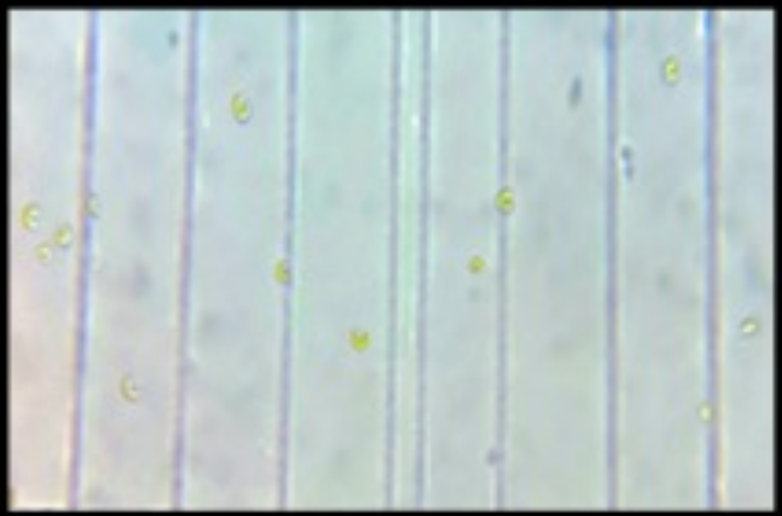
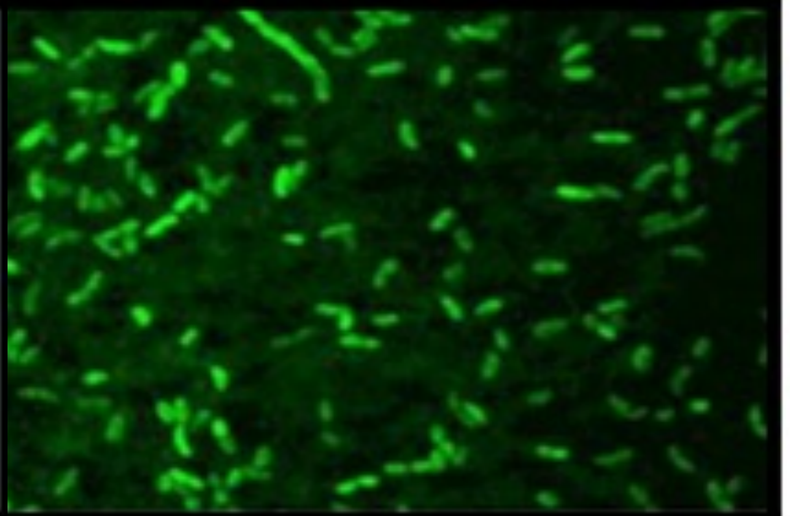
LOQs ~ 5ng/L

Untargeted GC-MS Analysis

RT	NAME	MF	AREA
10.3724	Acetic acid, (acetyloxy)-	80.4	8415.2
12.706	4-Ethylcyclohexanol	88.3	61876.6
12.3936	Cyclohexanone, 2-ethyl-	83.5	110413.9
14.2738	alpha-Campholenal	80.9	193303.3
20.2992	2,2,4-Trimethyl-1,3-pentanediol diisobutyrate	75.6	58021.9
13.5343	2,5-Furandicarboxaldehyde	70.6	13950.7
9.326	Ethylbenzene	86.7	93097.1
14.0865	Ethanone, 1-(4-methylphenyl)-	80.1	18748
10.4453	2-Propanol, 1-butoxy-	88.4	27129.4
16.8146	Quinoline, 6-methyl-	73.3	60627.6
7.7099	2,4-Pentanedione, 3-methyl-	79.6	34074.3
27.8208	Methyl dehydroabietate	76.4	59699.5
22.4155	Octadecane	84.7	92405.5
22.1168	Benzenemethanamine, N-(phenylmethylene)-	75.6	88343.1
20.2042	Hexadecane	94.2	95368.1
17.917	Dodecanal	82	366059.7
9.2826	Styrene	81.1	65939.2
11.3731	1-Decene	77.4	108400.1
10.87	Benzaldehyde	98	1618260
14.7991	1-Dodecene	95.9	152856.8
22.5318	Benzenesulfonamide, N-butyl-	93.3	164235

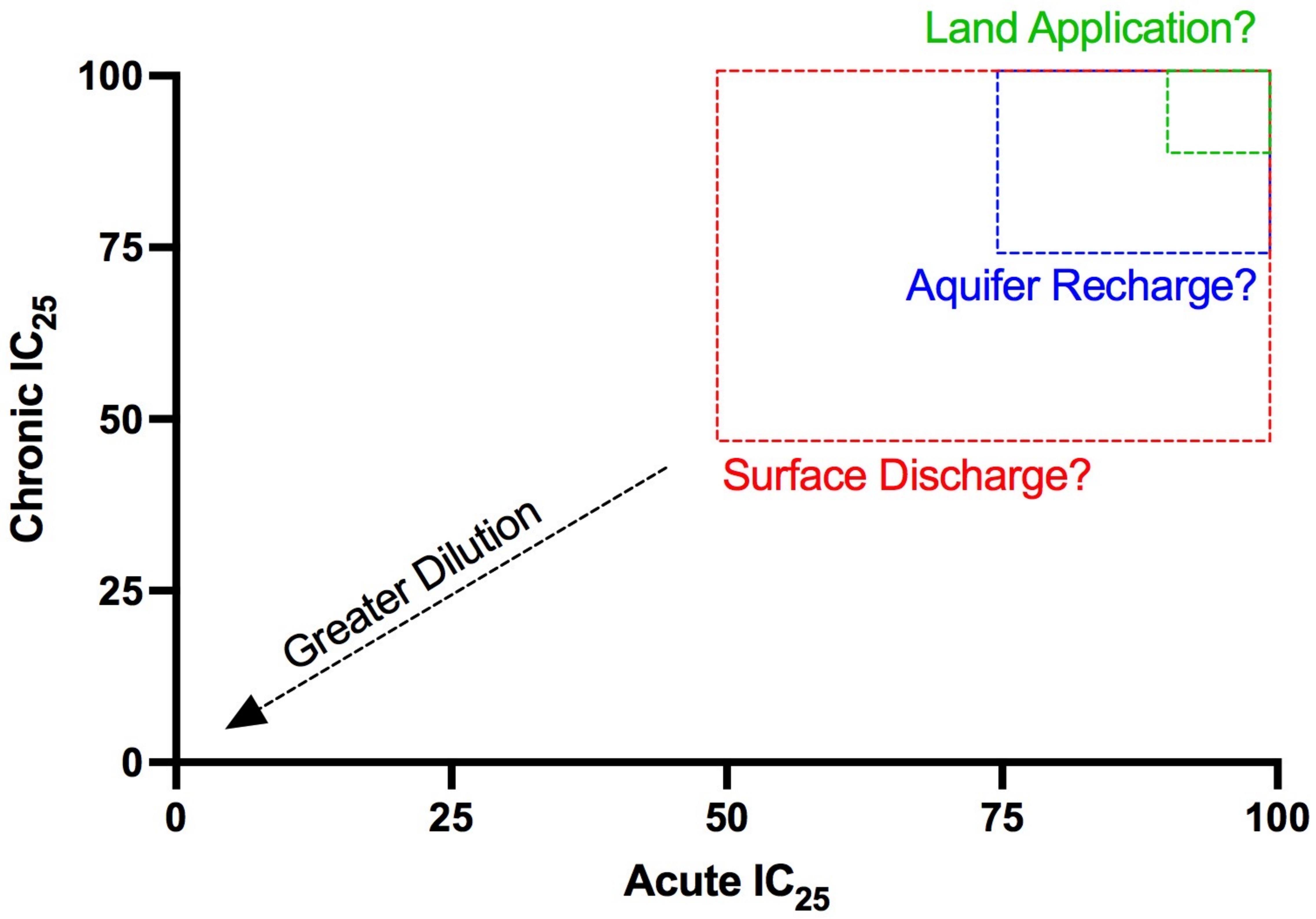
LODs < 1µg/L (ppb)

Toxicological Assays

Method Characteristics	*S. capricornutum* EPA 1003.0	*V. fischeri* Microtox ISO11348
Type	Chronic	Acute
Endpoint	Growth	Inhibition
Time:	96 h	15 min
Organism		
Role	Producer	Decomposer

Methods	*EPA-821-R-02-013, Method 1003.0*	ISO 11348:2007

Toxicological Standards



Objectives of this Study

1) Determine how 'how clean is clean enough' for the beneficial reuse application

Comprehensive biogeochemical and toxicological testing

2) Evaluate whether or not TOC/conductivity measurements could be representative indicators of overall water quality

Collectively, these measurements may allow us to distill 1,000s of pertinent water quality measurements down to two metrics, the levels of which could help determine the appropriate terminal destination for any treated produced water

Saving time, money, and other resources

Hypothetical Example

Source	Treatment*	TOC (mg/L)	SPC (mS/cm)	# VOCs & SVOCs	# Untargeted Compounds	Bacteria (CFU/mL)	Toxicity (1-10)	Terminal Destination
Raw Permian	Raw	2,300	140	85	21	5,000,000	10	Disposal
Partially Treated	OX, PF	100	130	15	5	2,000,000	5	Direct Reuse
Partially Treated	OX, PF, CF	25	110	5	3	1,500,000	4	Direct Reuse
Fully Treated	OX, PF, CF, RO	10	1	2	1	<1,000	2	Agricultural Discharge
Fully Treated	OX, PF, CF, FD	5	0.5	1	0	<1,000	2	Agricultural Discharge
Fully Treated	OX, CAV, SD	2.5	0.4	0	0	<1,000	1	Agricultural Discharge

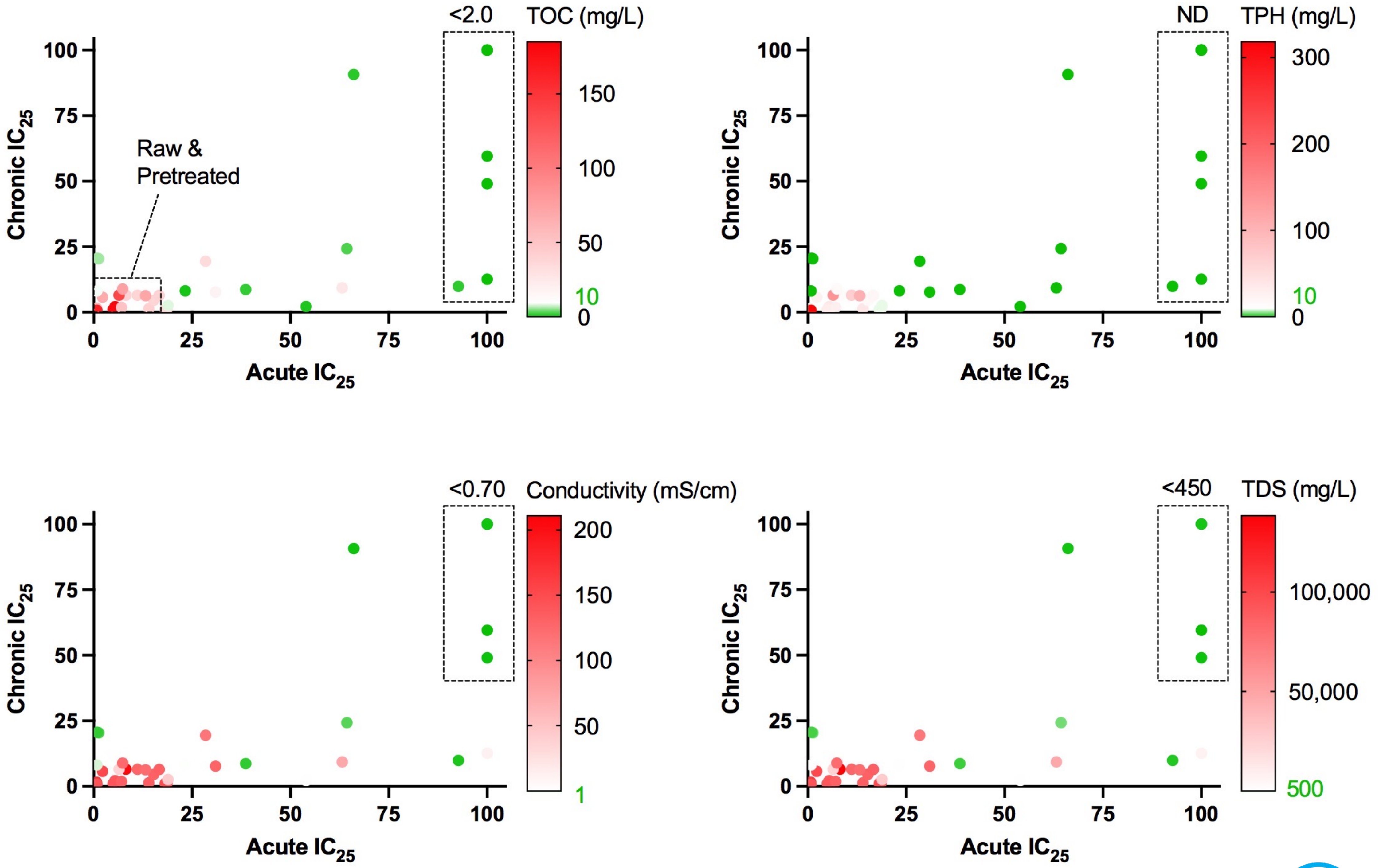
* OX=Oxidizing Agent, PF=Particulate Filtration, C=Carbon Filtration, RO=Reverse Osmosis, FD= Flash Distillation, CAV=Cavitation, SD=Solar Distillation

Samples to Date

	Collected To Date (n=44)			*En Route* (n=4)		
Region	Raw	Treated-Clean Brine	Treated-Desal	Raw	Treated-Clean Brine	Treated-Desal
Control Samples			6			
Permian	4	18	6			4
Eagle Ford		1				
Arkhoma		1				
San Juan	2		2			
Marcellus	1		2			
Haynesville		1				
TOTALS	7	21	16	0	0	4

Hildenbrand et al., *unpublished preliminary data*

How Clean is Clean Enough?



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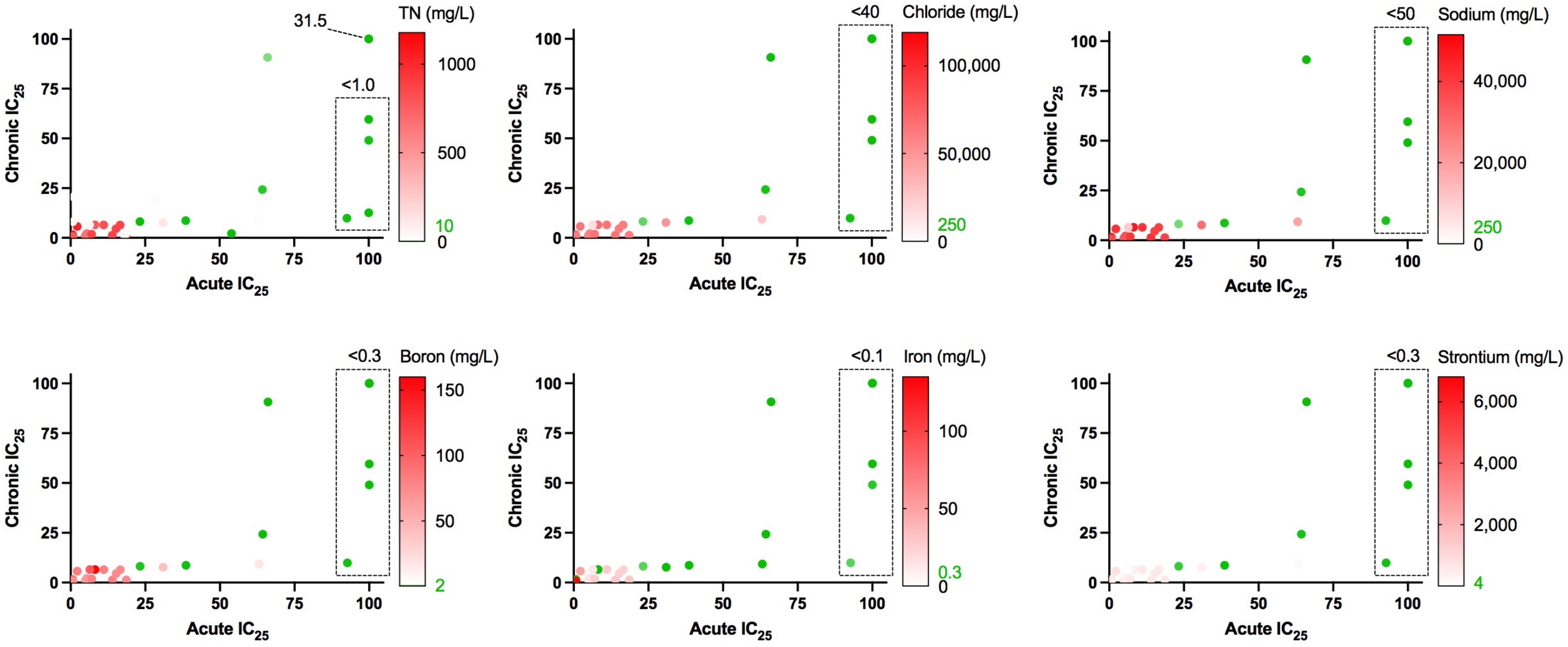

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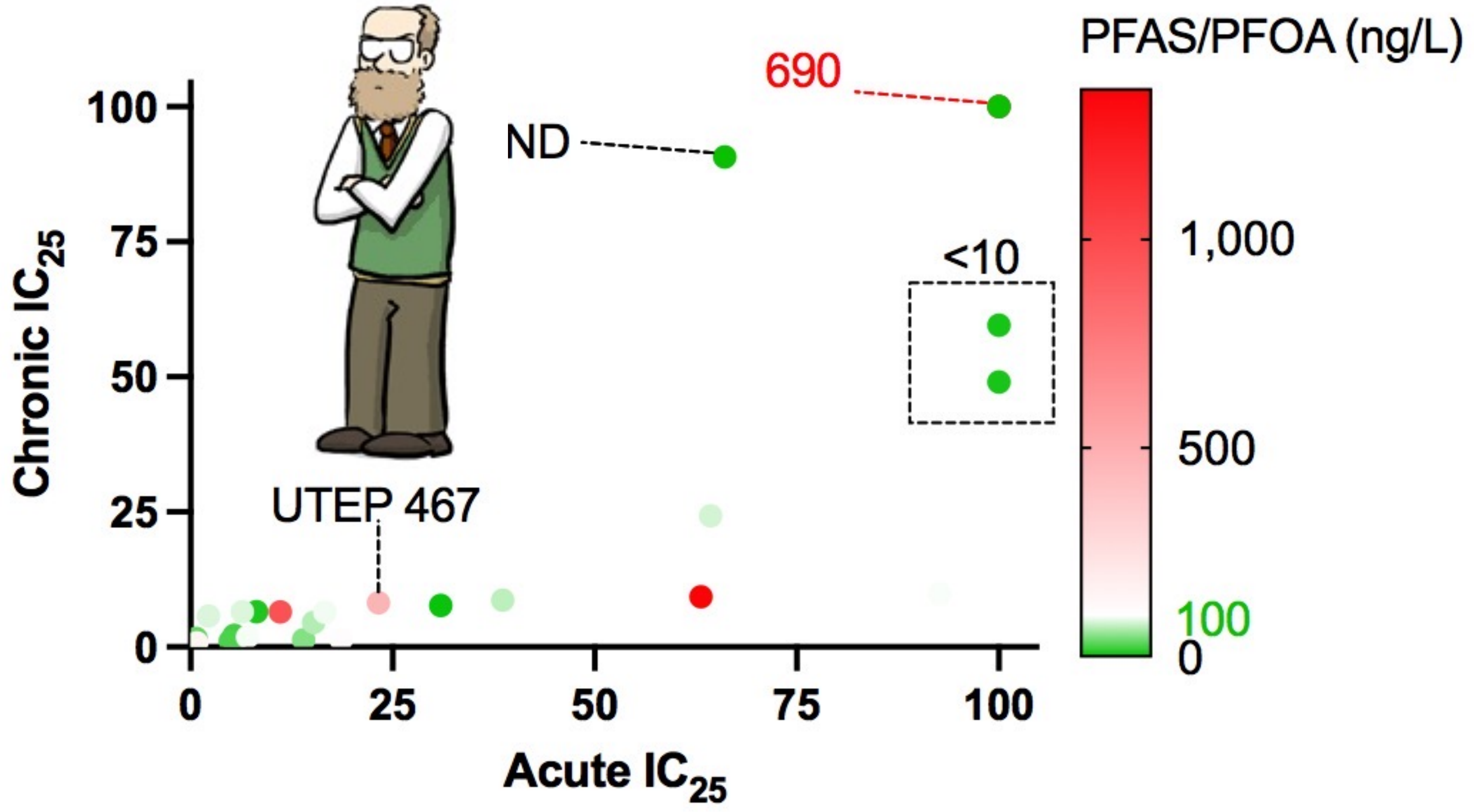

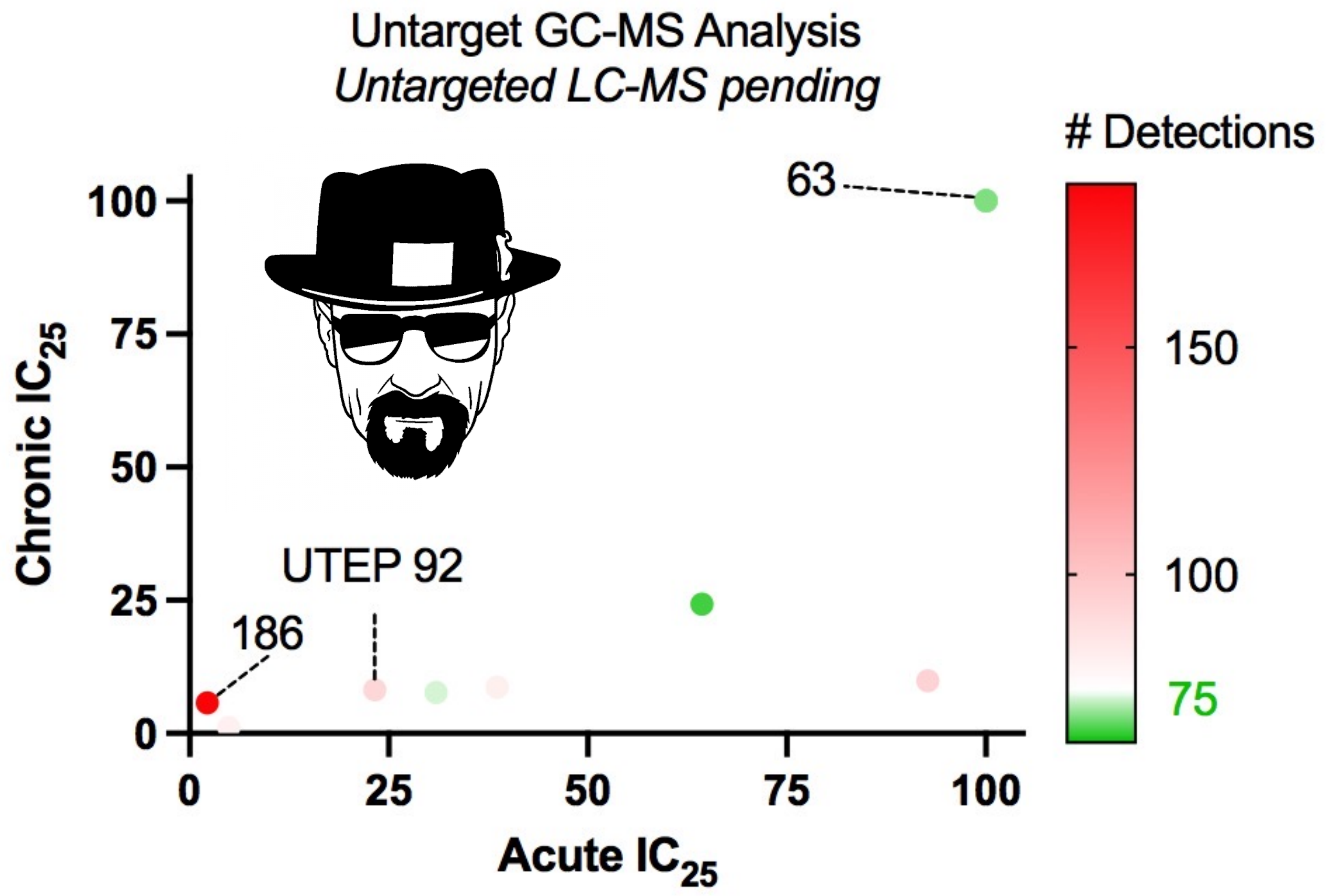

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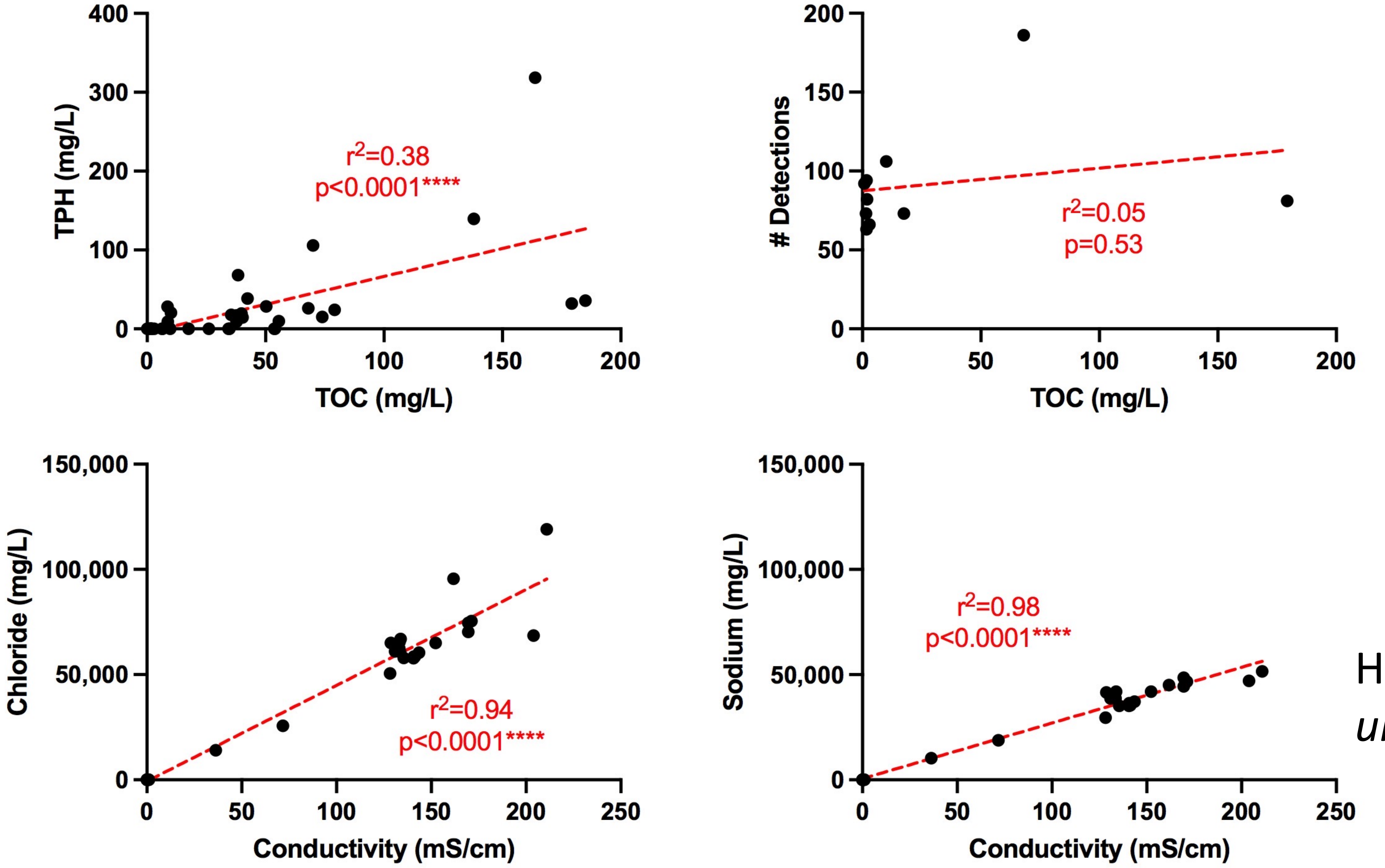
Reliable Surrogates?



Hildenbrand et al.,
unpublished preliminary data

What we've Learned so far

Source	Treatment*	TOC (mg/L)	SPC (mS/cm)	# VOCs & SVOCs	# Untargeted Compounds	Bacteria (CFU/mL)	Toxicity (1-10)	Terminal Destination
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Partially Treated	OX, PF, CF	25	110	5	3	1,500,000	4	Direct Reuse
Fully Treated	OX, PF, CF, RO	10	1	2	1	<1,000	2	Direct Reuse
Fully Treated	OX, PF, CF, FD	5	0.5	1	0	<1,000	2	Direct Reuse
Fully Treated	**VARIOUS**	**<2.0**	**<0.7** **<400 mg/L TDS**	**0**	**<75**	**<100**	**<20%**	**Beneficial Reuse?**

Hildenbrand et al., *unpublished preliminary data*

Acknowledgements

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- TTI Environmental

ARIS WATER

Questions?
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