

# Using QuEChERS for Measuring Contaminants of Emerging Concern (CECs) in Sediments



SANITATION DISTRICTS OF LOS ANGELES COUNTY

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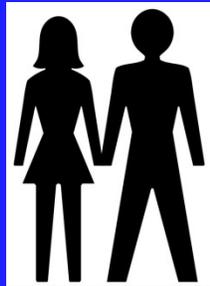
**Sanitation Districts of Los Angeles County**

San Jose Creek Water Quality Laboratory, Whittier, CA

# What are Contaminants of Emerging Concern (CECs)?

- Terminology that includes many classes of chemicals
  - Endocrine Disrupting Compounds (EDCs)
  - Pharmaceuticals and Personal Care Products (PPCPs)
  - Formulation Additives
  - Disinfection Byproducts
  - Nanomaterials
- Most are not currently regulated in wastewater effluent and/or drinking water
- Incomplete knowledge of environmental toxicity/fate
- Most of these chemicals are not new

# CEC Sources



- Human, animal and synthetic hormones (estrogens, androgens, thyroid)
- Pharmaceuticals (prescription, over-the-counter, X-ray contrast)
- Flame retardants (chlorinated, brominated)
- Personal care products (surfactants, fragrances, sunscreens, bug spray)
- Food components (caffeine, artificial sweeteners)
- Formulation compounds (perfluorinated organics, bisphenol A)

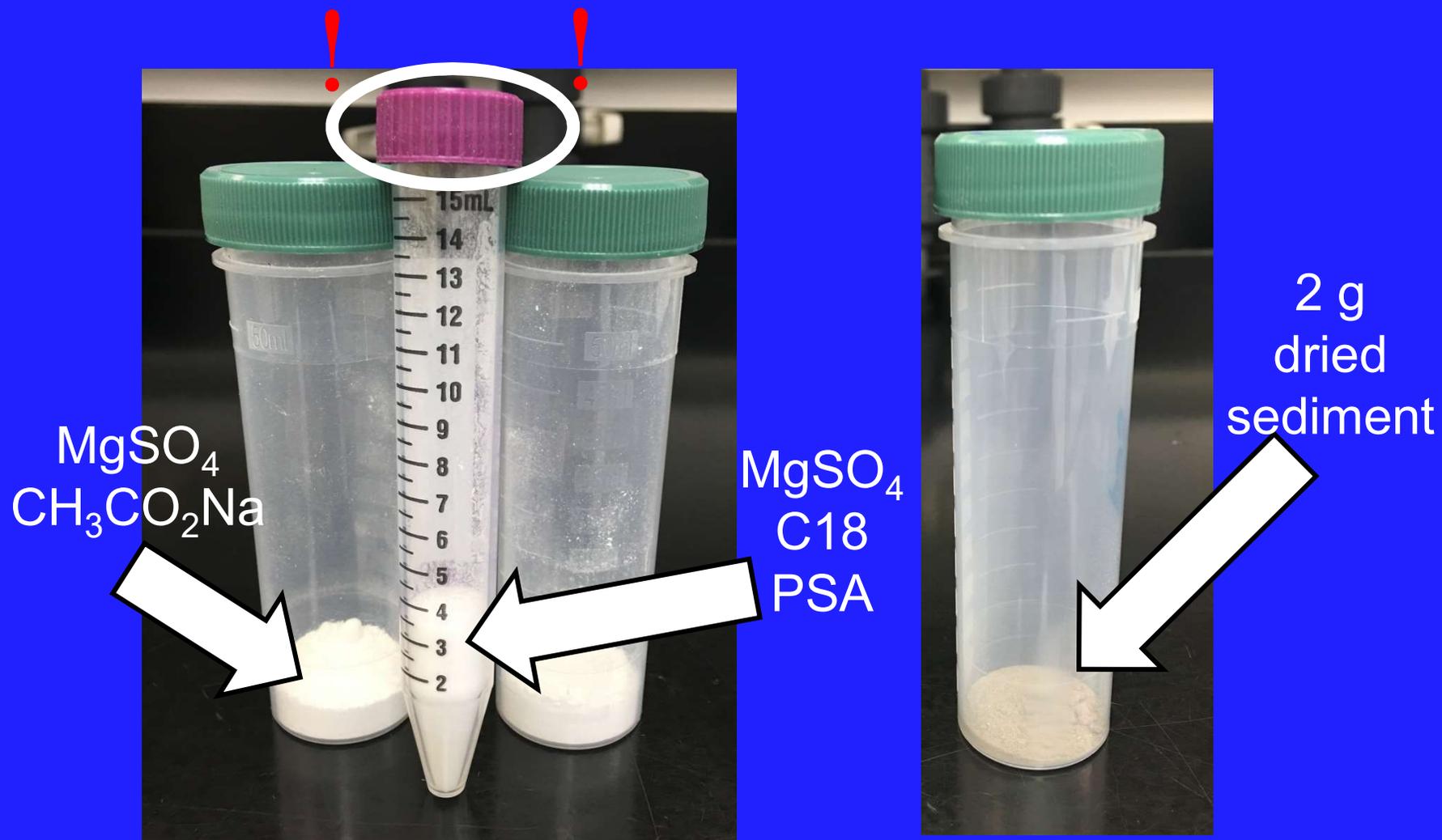
# Previous LACSD Work

- Validated SPE methods using 3 different SPE extractions in water (extractions for 5 analyses including PPCP, steroids, alkylphenols and pyrethroid pesticides)
- PPCP method has been published in *Standard Methods for the Examination of Water and Wastewater*
- CEC monitoring data from 9 treatment plant effluents spanning 8+ years.
- Our lab has established a method using Accelerated Solvent Extraction (ASE) for POPs in sediments requiring a GPC clean-up, looking for organochlorine pesticides, PCBs and PAHs (EPA 8270), using GC/MS

# QuEChERS?

- QuEChERS
  - Quick, Easy, Cheap, Effective, Rugged, Safe
- Two Steps
  - Liquid/solid extraction with acetonitrile, buffer and water using vortex and centrifuge
  - Clean-up with dispersive SPE and drying agent using vortex and centrifuge
- Uses less solvent than ASE (start with 10 mL acetonitrile, finish with ~5 mL to reduce)
- Up to 20 samples can be extracted/cleaned-up/concentrated in one work day
- Have been used effectively for pesticides for at least 10 years

# QuEChERS?



# QuEChERS?

	QuEChERS	Soxhlet	ASE	Sonication (EPA 1694)
<b><i>Solvent Used (mL)</i></b>	<b><u>200</u></b>	<b>1600-3000</b>	<b>400-3000</b>	<b>1000</b>
Extraction (min)	20	480-840	300	1800
Centrifuge (min)	10	NA	NA	NA
Clean-up (min)	20	600-780	600-780	600-780
Centrifuge (min)	5	NA	NA	NA
Reduction (min)	180	200-350	200-250	200-250
Total time (hours)	3.9	21.3 - 26.8	18.3 - 22.2	40.3 – 47.2

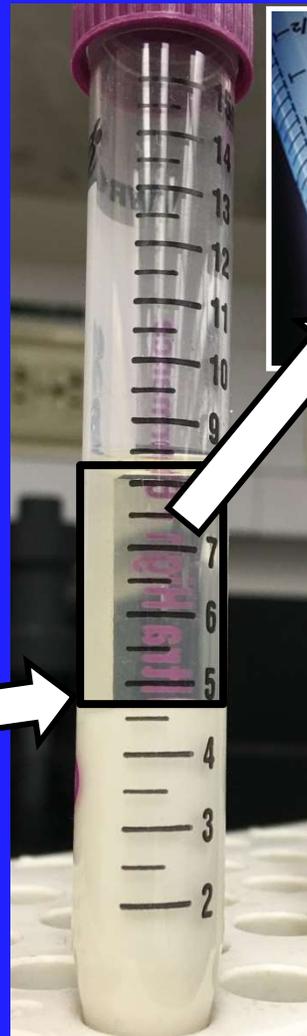
Calculations based on a set of 20 samples

# Our QuEChERS

- Standard US set-up (sodium acetate, 1% acetic acid)
- Reduced  $\text{MgSO}_4$  (from 6 g to 2 g)  
lower temperature: less thermal degradation or loss of deuterium labels on IS
- Can freeze sample for easier transfer
- 1 mL final volume, MeOH:H<sub>2</sub>O (1:1)
- 4 analyses on one extract (+1, PPCP+ on other)
- Isotope dilution technique, using as many labeled compounds as possible

# Our QuEChERS

0.2  $\mu\text{m}$



# Analytes

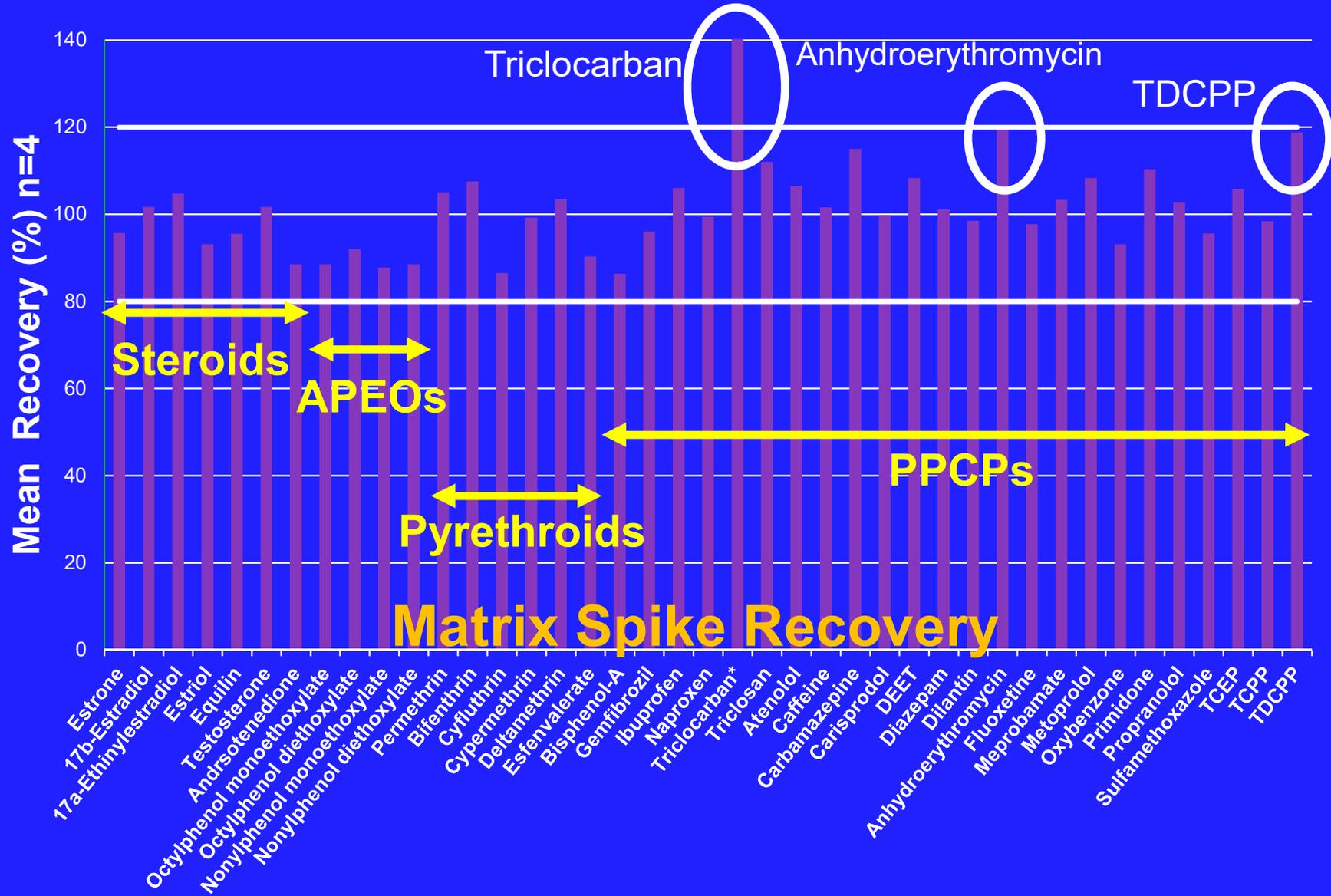
- Pyrethroids (6): permethrin, bifenthrin, cypermethrin, cyfluthrin, deltamethrin, esfenvalerate
  - Alkylphenol Ethoxylates (4): 4-*tert*-octylphenol monoethoxylate, 4-*tert*-octylphenol diethoxylate, 4-nonylphenol monoethoxylate, 4-nonylphenol diethoxylate
  - Steroids (7): estriol, estradiol, estrone, equilin, ethinylestradiol, testosterone, androstenedione
  - PPCPs (25\*): atenolol, trimethoprim, primidone, erythromycin[-H<sub>2</sub>O], sulfamethoxazole, fluoxetine, carbamazepine, metoprolol, propranolol, caffeine, phenytoin, DEET, TCEP, TCPP, TDCPP, meprobamate, carisoprodol, diazepam, oxybenzone, naproxen, ibuprofen, bisphenol A, gemfibrozil, triclosan, triclocarban
- \* PPCP+ analysis more effective with separate QuEChERS extraction

# Analytes

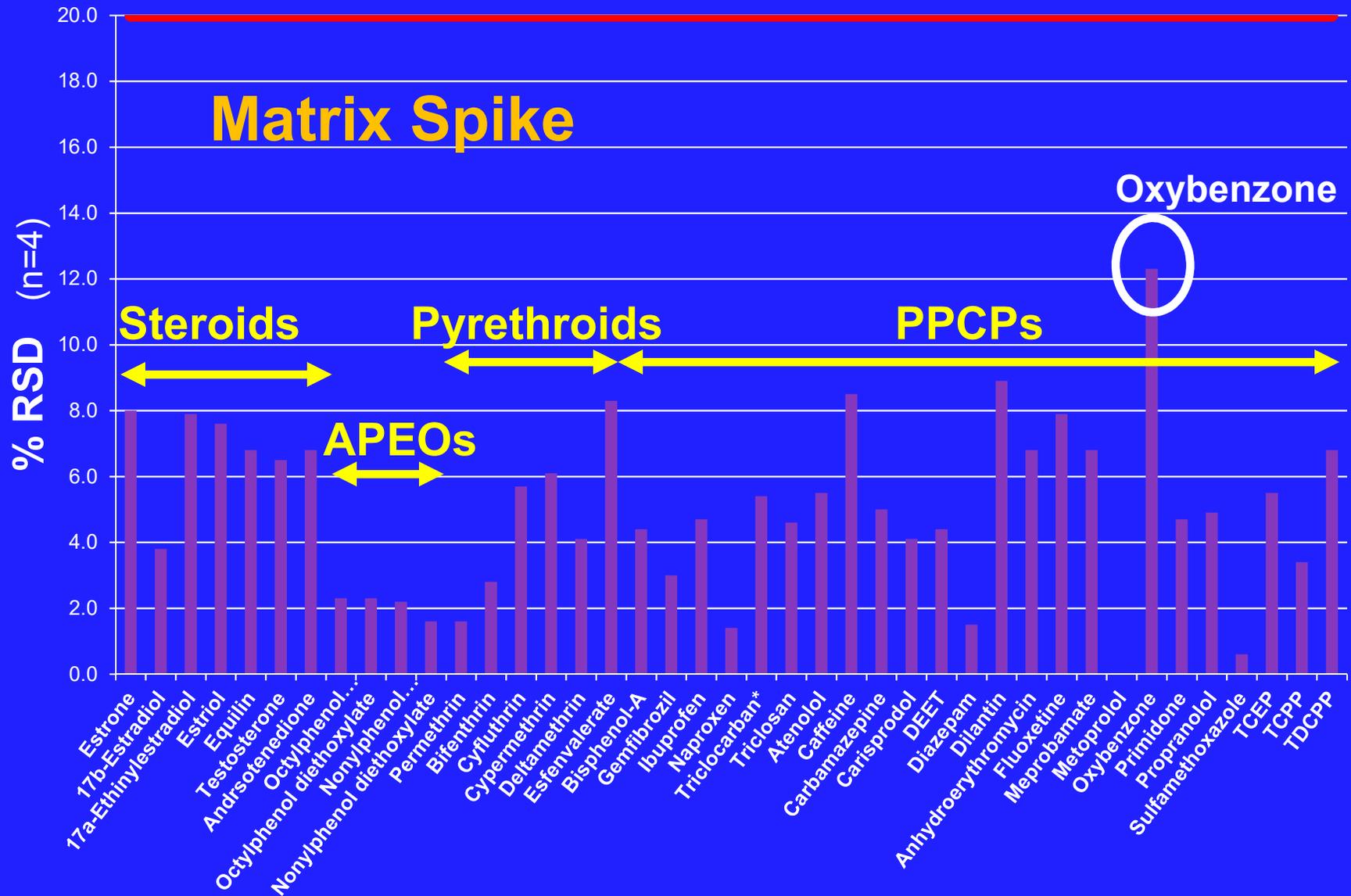
- Pyrethroids (1): lamda-cyhalothrin  
*Interference, possibly from solvent*
- Alkylphenols (2): 4-tert-octylphenol and 4-nonylphenol  
*Contamination from reagents*
- PPCPs (8\*): azithromycin, atorvastatin, iohexol, acetaminophen, sucralose, iopromide, furosemide, diclofenac
  - Binds irreversibly*
  - Too polar, associated with aqueous fraction*
  - Matrix interference*
  - Matrix Interference with labeled internal standard*

\* PPCP+ analysis

# Results



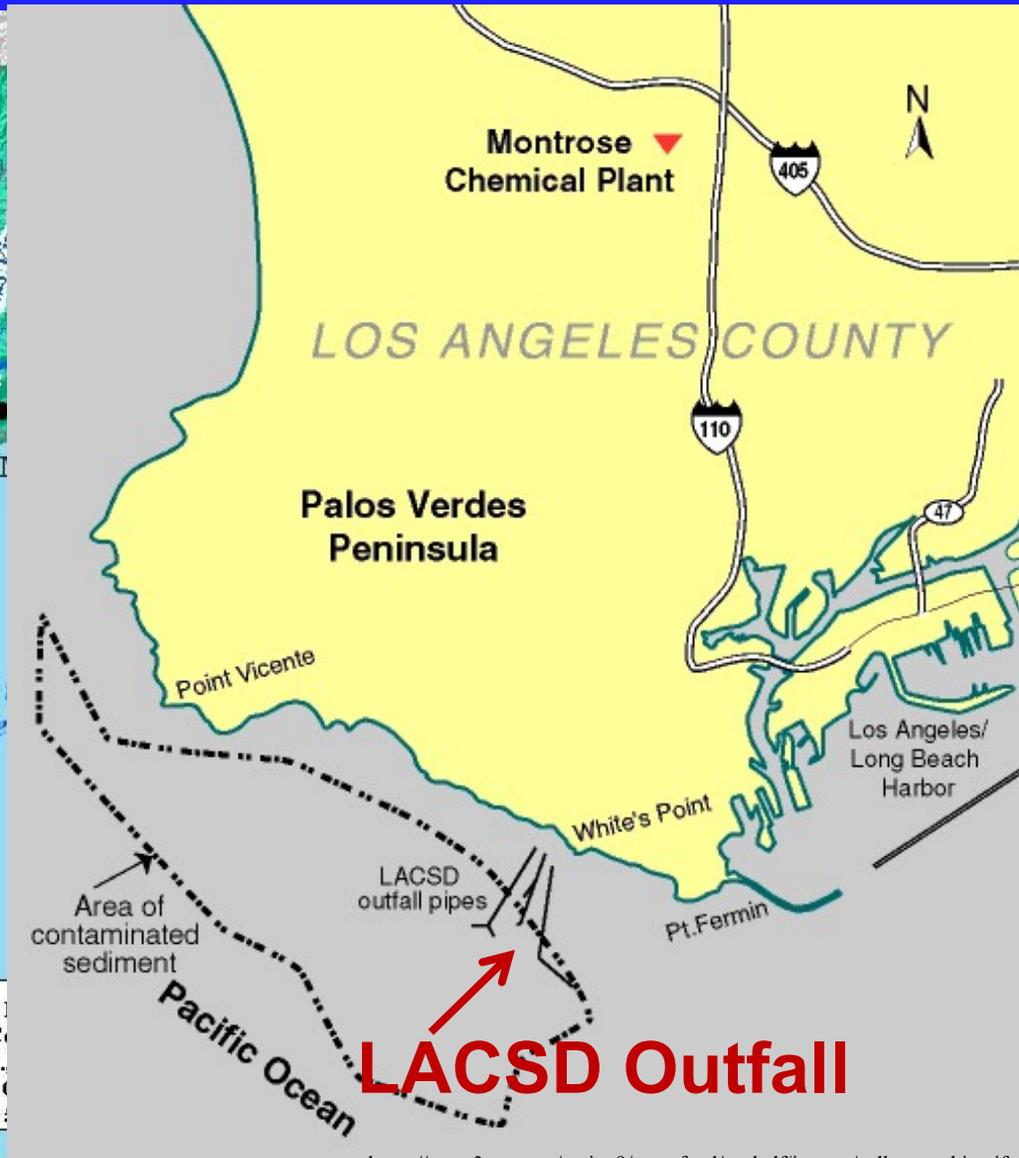
# Results



# Results

- Some compounds don't work
  - iohexol, iopromide, sucralose, furosemide: too polar
  - azithromycin, atorvastatin: too sticky
  - acetaminophen, diclofenac, cyhalothrin: interferences
- Nonylphenol/octylphenol contamination in reagents
- Some suppression of pyrethroids, but not a big problem
- Low RLs with only 2 g and small inject volumes (more than 2 g, suppression for pyrethroids)
- Have also used these methods successfully with surface water particulate collected on glass fiber filters.

# Measurement



# Measurement

- *Reporting limits for PPCPs are 1 ng/g for most analytes. Most PPCPs were absent in sediments except for high concentrations of triclocarban (140 ng/g) and some triclosan (10 ng/g).*
- *Reporting limits for pyrethroid pesticides ranged from 0.1- 0.5 ng/g. Permethrin was detected in sediments at ~ 1.5 ng/g.*
- *Reporting limits for steroids are 0.125 ng/g. Estrone and androstenedione were detected at ~0.2 and 0.3 ng/g, respectively.*

# Measurement

- *Reporting limits for APEOs are 2.5 ng/g. NP1EO and NP2EO were abundant in sediments at 175 and 174 ng/g, respectively. OP1EO and OP2EO were slightly above reporting limits at 6 and 4.4, respectively*
- CEC sediment values are consistent with those measured previously by other methods/researchers including Southern California Coastal Water Research Project.

# Conclusions

- QuEChERS is an effective method for extraction of CECs from sediments. The technique requires minimal time, cost and solvent.
- Only minor modifications to well established methods are needed to accommodate 42 analytes with a wide range of chemical properties
- One extraction may be used for the analyses of steroids, alkylphenols, PPCPs and pyrethroids. An additional extraction (without C18 clean-up) is used to optimize PPCPs analyzed using ESI+

# Thanks

Syljohn Estil, Arnold Tesoro, Chris Wissman  
and Dr. Steve Carr

LACSD Laboratory  
and Technical Services Management

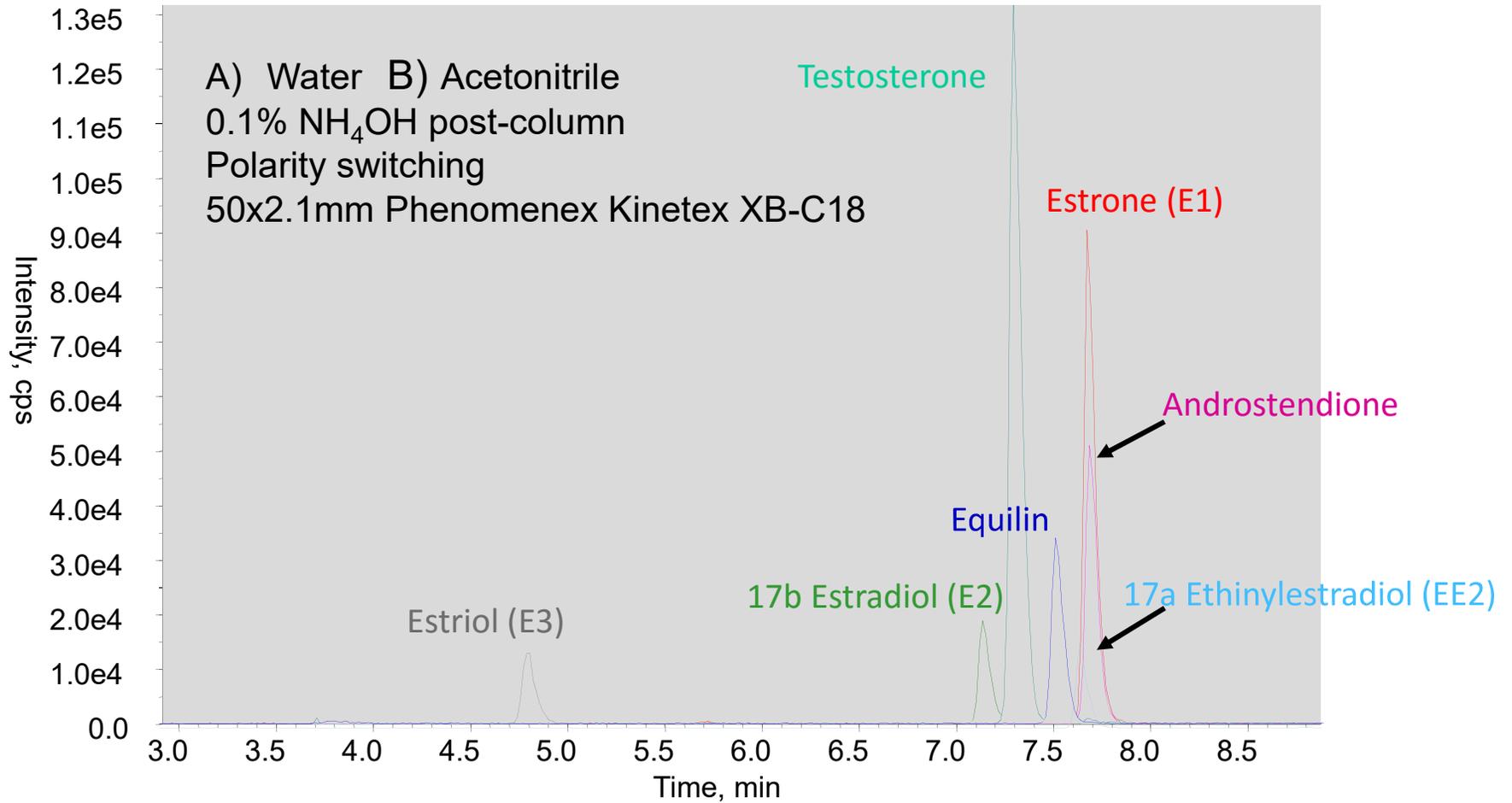


*Note:*

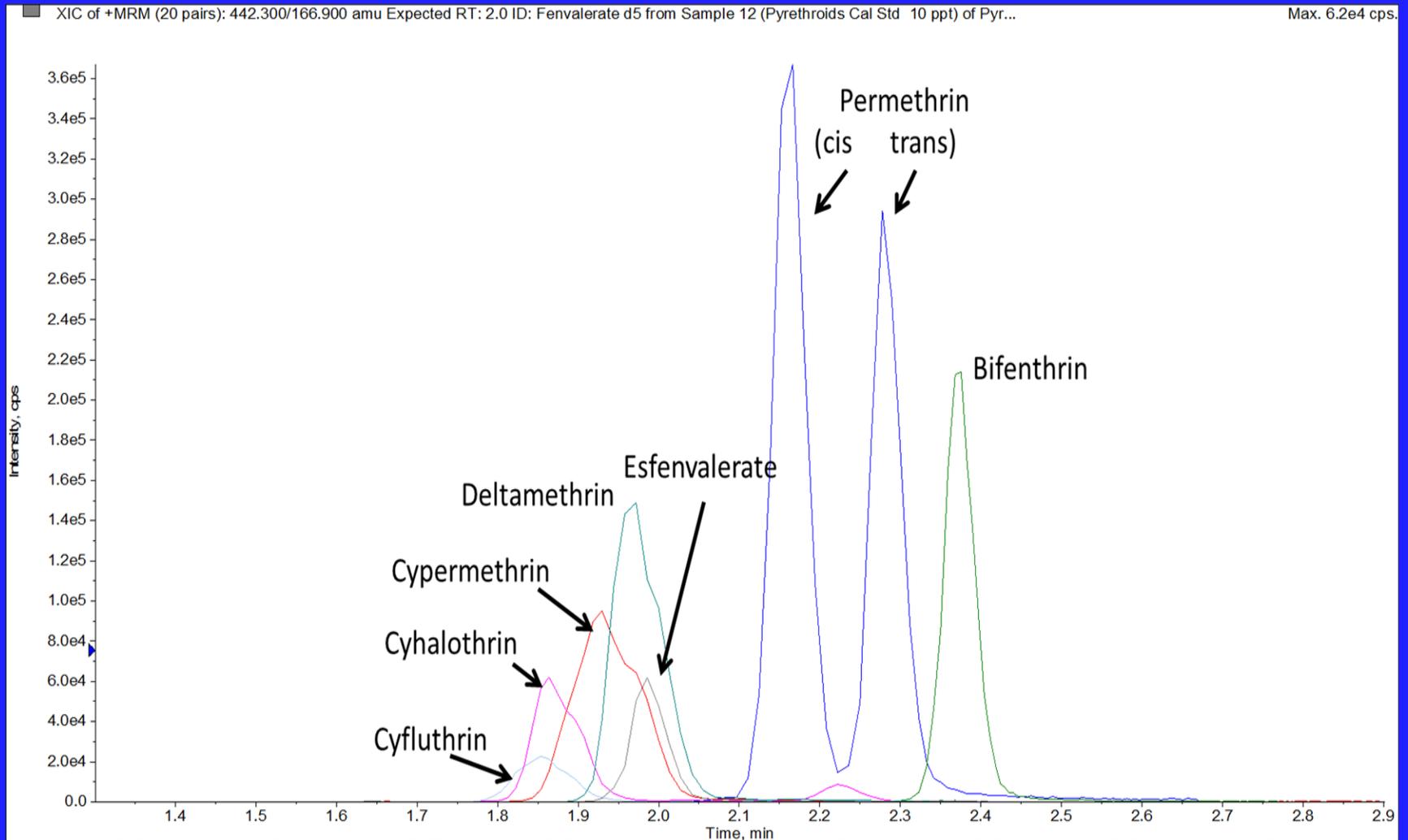
Extra slides showing analytical chromatography if there are questions

Not part of platform presentation

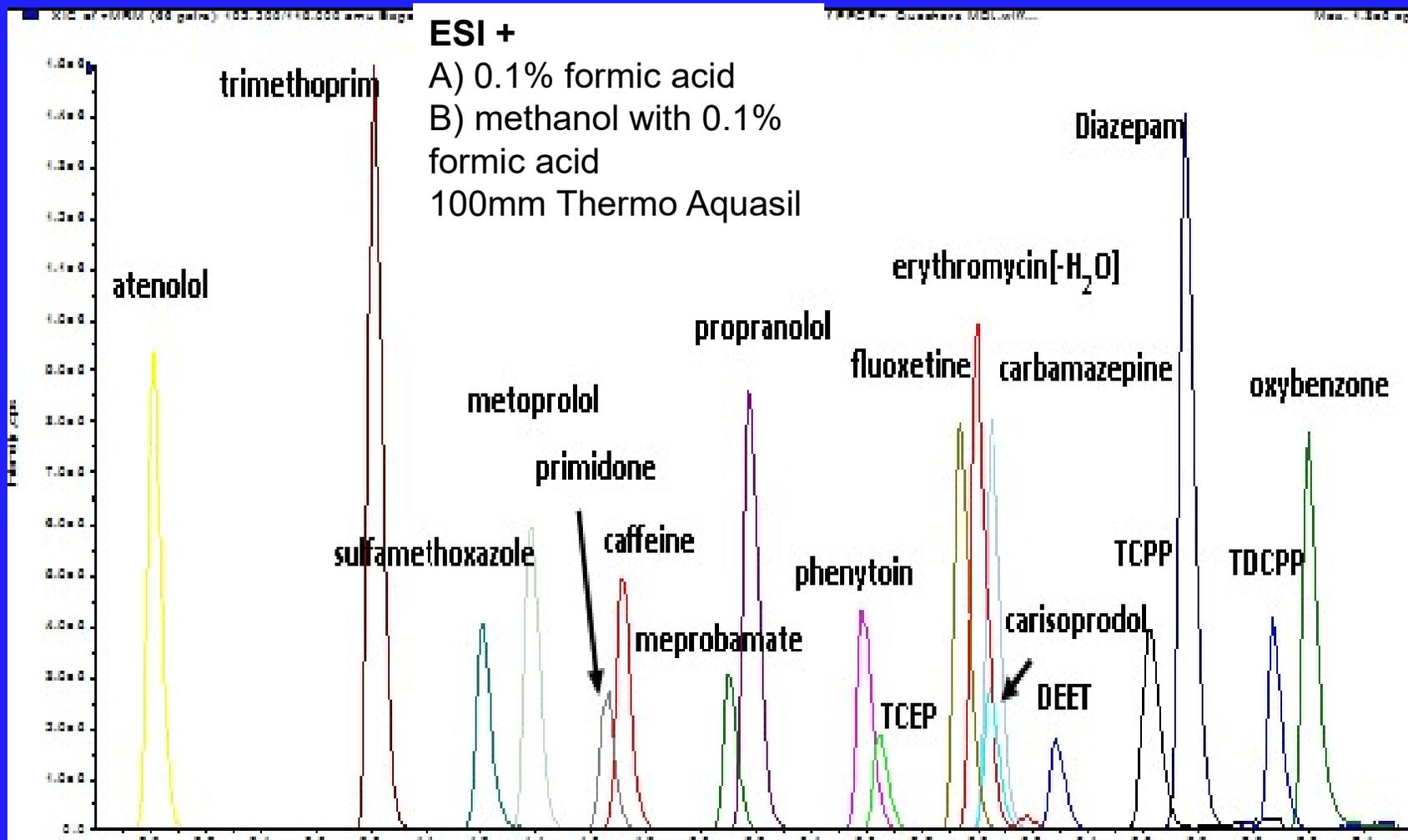
# Analytical Methods



# Analytical Methods



# Analytical Methods



# Analytical Methods

