Public Hearing (12/15/10)
CEC – Recycled Water
Deadline: 1/10/11 by 12 noon

CONSTITUENTS OF EMERGING CONCERN (CEC) MONITORING FOR RECYCLED WATER

December 15, 2010

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MWH Laboratories is the largest lab in the U.S. that is focused solely on water analysis, specifically for CECS in water. In 2010 we have tested well over 500 samples for CECs from water samples across the United States. Our analytical method allows the analysis of nearly 90 CECs in a sample, as opposed to focusing on a short list of analytes (as recommended by the Blue Ribbon Panel and CDPH in their comments on the Blue Ribbon Panel Report. The fact that we have amassed a large database of occurrence of a number of CECs makes us recommend an alternative to the shortlist proposed by the Blue Ribbon Panel.

We will not address issue of relative toxicity of different CECs compared to concentration, but instead focus on the use of CECs as indicator compounds, which could prompt other actions. The important characteristics of a CEC for monitoring as an indicator of either treatment efficiency or the presence of wastewater in a receiving water include the following:

1. High frequency of occurrence in the source water (wastewater influent)
2. Relatively poor removal efficiency by conventional wastewater treatment processes (or conversely frequent occurrence in wastewater effluents)
3. Ideally relatively small variation in concentration over time (so that the source function is relatively constant).
4. High enough concentration to allow measurement in samples that have undergone substantial dilution.

Our experience in looking at multiple wastewater effluent samples, particularly in a recent California study sponsored by the Santa Ana Watershed Project Authority (SAWPA), leads us to the conclusion that RESTRICTING testing to a short list of compounds risks losing valuable information on occurrence and also potential site specific indicators. In this study there were more than 20 dischargers sampling for CECs. MWH analyzed samples for 17 of those dischargers, providing a relatively robust database from a single lab (thus eliminating interlab variability). SAWPA requested analysis of 11 CECs (of which 4 were also in the Blue Ribbon Panel report). These results have been submitted to the Board in a recent SAWPA report. However, the majority of the 17 dischargers elected to analyze not just for the SAWPA compounds, but also to obtain data on the full suite of ~90 CECs in order to have a broader sense of CEC occurrence.

This longer list provides an opportunity to directly compare occurrence using various "lists". This comparison shows that there are numerous CECs that are not on the Blue Ribbon Panel list (or the SAWPA list) that occur in more than 90% of these wastewater effluents, and some of them occur at much higher concentrations and frequency than a few of the indicators recommended by the Blue Ribbon panel. Selected comparisons follow.

Blue Ribbon Panel indicators

Sucralose is an excellent indicator compound (and is on the Blue Ribbon Panel list). It occurs in 100% of wastewater effluents we have tested so far and is at typical concentrations of 15-25 ppb in these samples. Variation over time is <50%.

Iopromide is a poor potential indicator compound. Although many people have tested for it, the frequency of occurrence is actually relatively low, because it is not commonly used as an X-ray contrast medium. Instead Iohexol (Iohexal) occurs much more frequently and at higher concentrations. (as much as 100X higher). There were several examples in this data set where iopromide was ND while iohexal was up to 1 ppb.

Caffeine is potentially a poor indicator compound because it is detected in only about 50% of effluent samples, even at detection levels of 5 ppt and is also subject to extensive biodegradation. Concentrations varied by more than a factor of 100 among plants, and the vast majority of detects were less than 10X the reporting level. We have seen two caffeine degradates – 1,7-dimethylanxthine and theobromine often at concentrations exceeding those of caffeine. If one is going to use this as an indicator it is therefore also important to also include the degradates.

DEET shows variations of as much as a factor of 10 among different treatment plants and over time from the same treatment plant, but it is detected in more than 90% of effluents.

Gemfibrozil was only observed in about 40% of the effluents and concentrations varied by two orders of magnitude. Thus using this compound as an indicator of treatment performance would run the risk of measuring a compound that was frequently not present at all (concentrations among plants varied from <5 ng/L to >2,000 ng/L.

Thus of the Blue Ribbon Panel recommended analytes only two, **Sucralose** and **DEET**, would seem to be reliable general indicators that could be used to assess treatment efficiency.

CDPH recommendations for CECs

In the CDPH response to the Blue Ribbon Panel report, 3 additional CECs were recommended – BPA, TCEP, and carbamazepine. Each of these was part of the SAWPA study so there is extensive data available on occurrence.

BPA was detected in less than 20% of effluent samples and the highest concentration was <5 times the reporting limit of 10 ppt. Thus it is not clear how valuable monitoring of BPA would be. Additionally in an ongoing Water Research Foundation study of interlab variability, BPA was one of the "poorer" performing compounds.

TCEP is a very commonly occurring CEC which is also very difficult to remove. Because of this it was detected in the SAWPA study in 100% of samples. However the concentrations vary widely (10X) among plants and over time at a single plant.

Carbamazepine was detected in more than 80% of effluent samples and is generally considered to be difficult to remove by conventional treatment. Concentrations vary by less than a factor of five.

Thus at least two of the compounds recommended by CDPH for CEC indicators are indeed desirable candidates based on occurrence frequency and concentration range.

Other Potential compounds

Based on evaluation of the 90 compound list for more than 10 of these plants, there are several other compounds that are not widely analyzed but occurred in 100% of tested effluent samples at concentrations that are well above typical reporting limits. The Table below (Table 1) shows those compounds that we detected in more than 90% of SAWPA effluent samples. All of the ones that are detected frequently and have small variation in concentration are potential good indicators of wastewater presence in recycled water and should be considered for monitoring. More importantly this suggests that the Board should not restrict the list of compounds being monitored, but encourage dischargers to identify the best indicators for their specific scenario and thus allow greater flexibility so that dischargers can maximize the value of measurements. Using

only a small subset of the analytes picked up by CEC methods risks loss of significant information.

Some of these, most notably primidone, have been proposed by others as good wastewater indicators, but we urge the Board to be open to broader conceptual views of the monitoring needs.

Table1. Results of snapshot survey of SAWPA dischargers for CECs

List	compound	Ratio Max concentration/ Min concentration	90th % concentration (ng/L)	Frequency of occurrence
Blue Ribbon	Sucralose	2	28900	100%
	Dehydronifedipine	3	592	100%
	Butalbital	4	78	100%
	Primidone	5	242	100%
	Dilantin	6	306	100%
	Meprobamate	11	1146	100%
sawpa	TCEP	12	448	100%
	DACT	15	166	100%
	Theobromine	31	352	100%
	2,4-D	32	115	100%
	Simazine	34	59	100%
	Carisoprodol	39	678	100%
	Atenolol	46	776	100%
	1,7-Dimethylxanthine	79	128	100%
	Iohexal	97	3770	100%
sawpa	DEET	Huge	304	94%
	Lopressor	Huge	220	92%

Evaluation of PPCP Occurrence in Wastewater Effluents, Are We Looking for the Right Things?

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11/4/10

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Our Primary Theses….

- Many of the "Lists" that have been developed are insufficiently broad to pick up the best indicators of wastewater influence

- Precise, accurate, simple multi-analyte screening methods offer a cost-effective approach to the problem.

- There are multiple unique tracers that are useful as indicators

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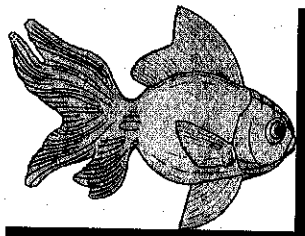
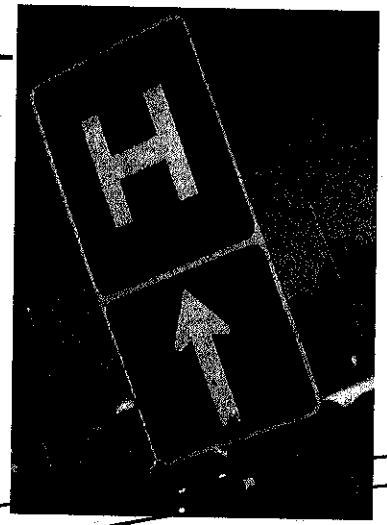
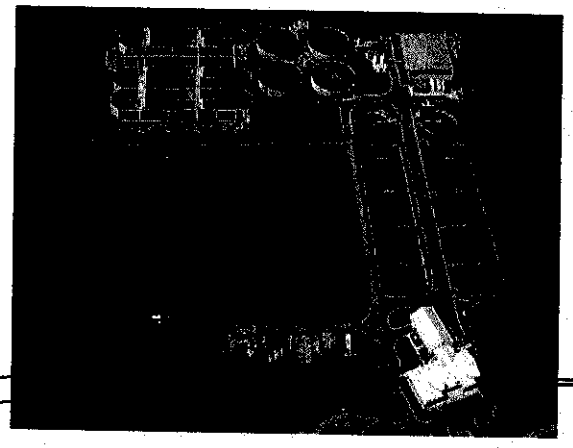
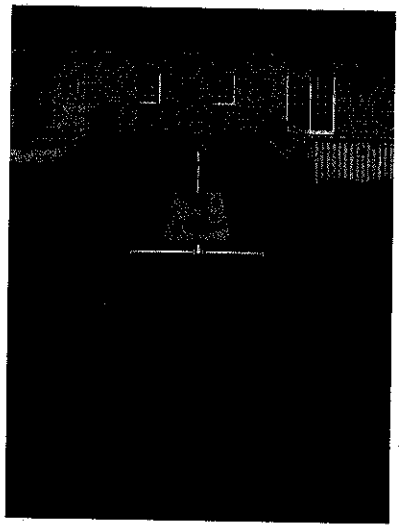


Challenge – What Do You Look For?

- Looking for appropriate tracers for assessing impact of wastewater is a fishing expedition
  - It all depends upon the ultimate WW source
  - Urban? Rural?
  - Septic? Tertiary Treated WW?
  -







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Other Challenge: What About Analytical Artifacts?

- Concentrations are in the part per trillion (ppt) range
  - Field (and lab) QA/QC becomes critical
  - Analytical Methods aren't always precise (or accurate) at these levels
- Some compounds are ubiquitous and can be problematic
  - Some labs see TCEP in blanks
  - Triclosan can be persistent
  - Some labs report false positives for EE2
  - Some labs see BPA in blind blanks

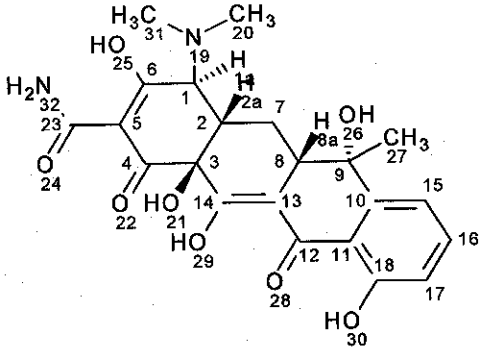
This Led Us to Explore Innovative LC-MS-MS Approaches to PPCP Analysis

- Cost Effective Screen for as Many Analytes as Possible
  - 5 to 10 ng/L reporting level targeted
- Include common target analytes based on literature
- Accuracy and precision should be comparable to drinking water methods (e.g. target 70-130% recovery)
- Use multiple ion transitions (MRM) for each analyte to minimize potential for misidentification
- Minimize potential for blank contamination

MWH Online Method for Simultaneous Extraction and Analysis of 80+ Analytes

This encompasses lots of categories of compounds (not just drugs) and 3 broad classes (pharma, ww indicators, and pest/herb)

1. Hormones
2. Pharmaceuticals:
   - Antibiotic
   - Anti-inflammatory
   - Lipid regulating agents
   - Triazides
   - Antagonists
3. Personal care products
   - Sunscreen agents
   - Preservatives
4. Pesticide/Herbicides
   - Including EPA 536 compounds -Triazines and their degradates.
5. Flame retardants
6. Stimulants
7. Sugar substitutes (sucralose, acesulfame-k)



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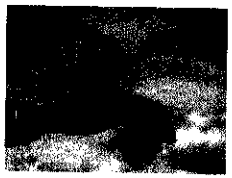
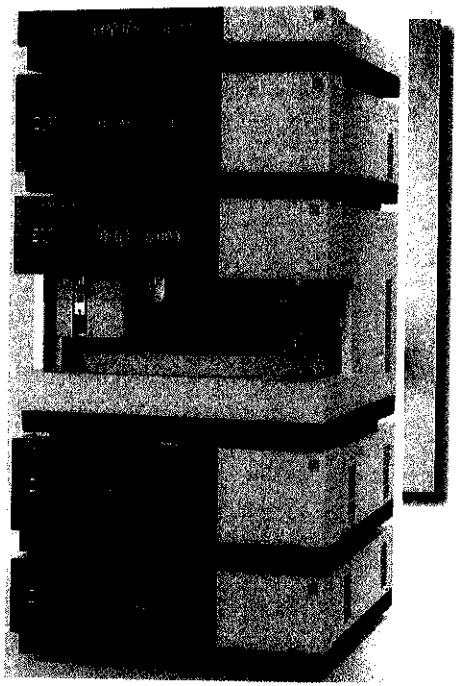
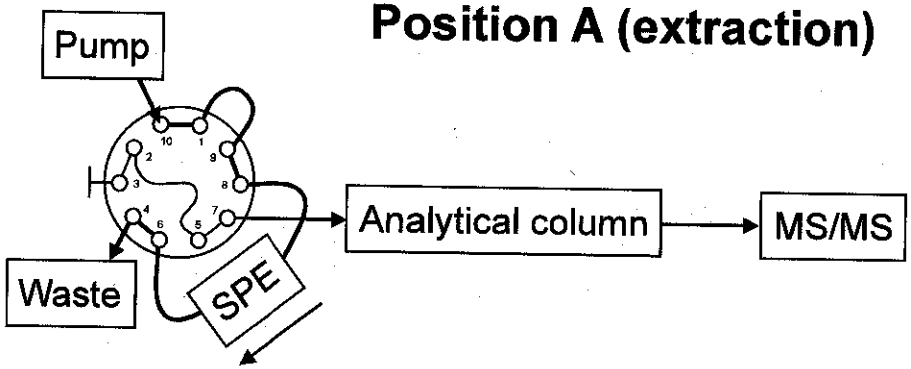
Online SPE Setup And Procedure

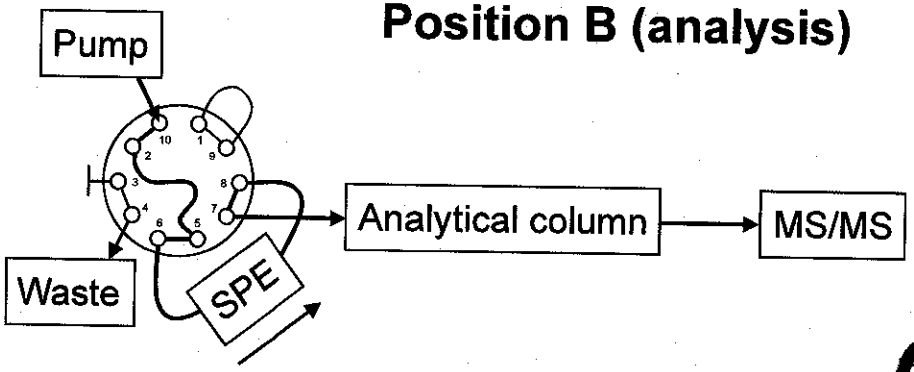


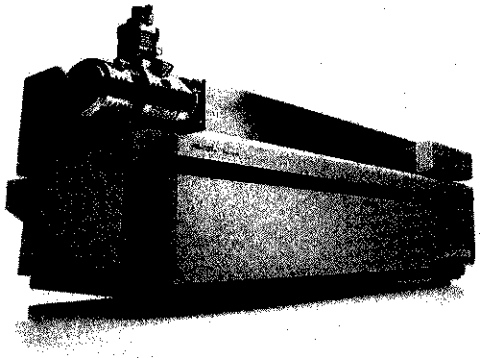


Position A (extraction)



Position B (analysis)





API 5000®
LC/MS/MS system

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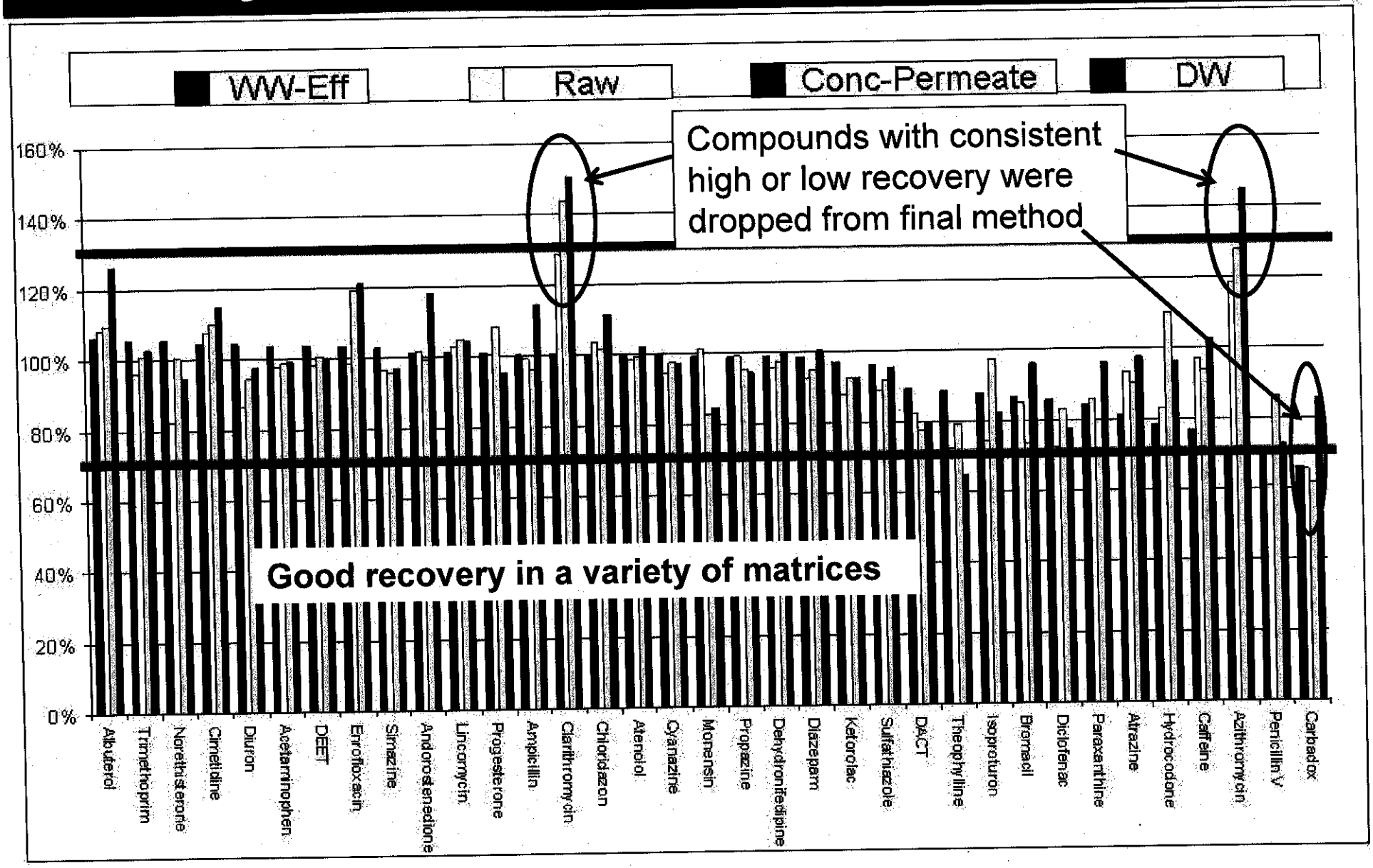
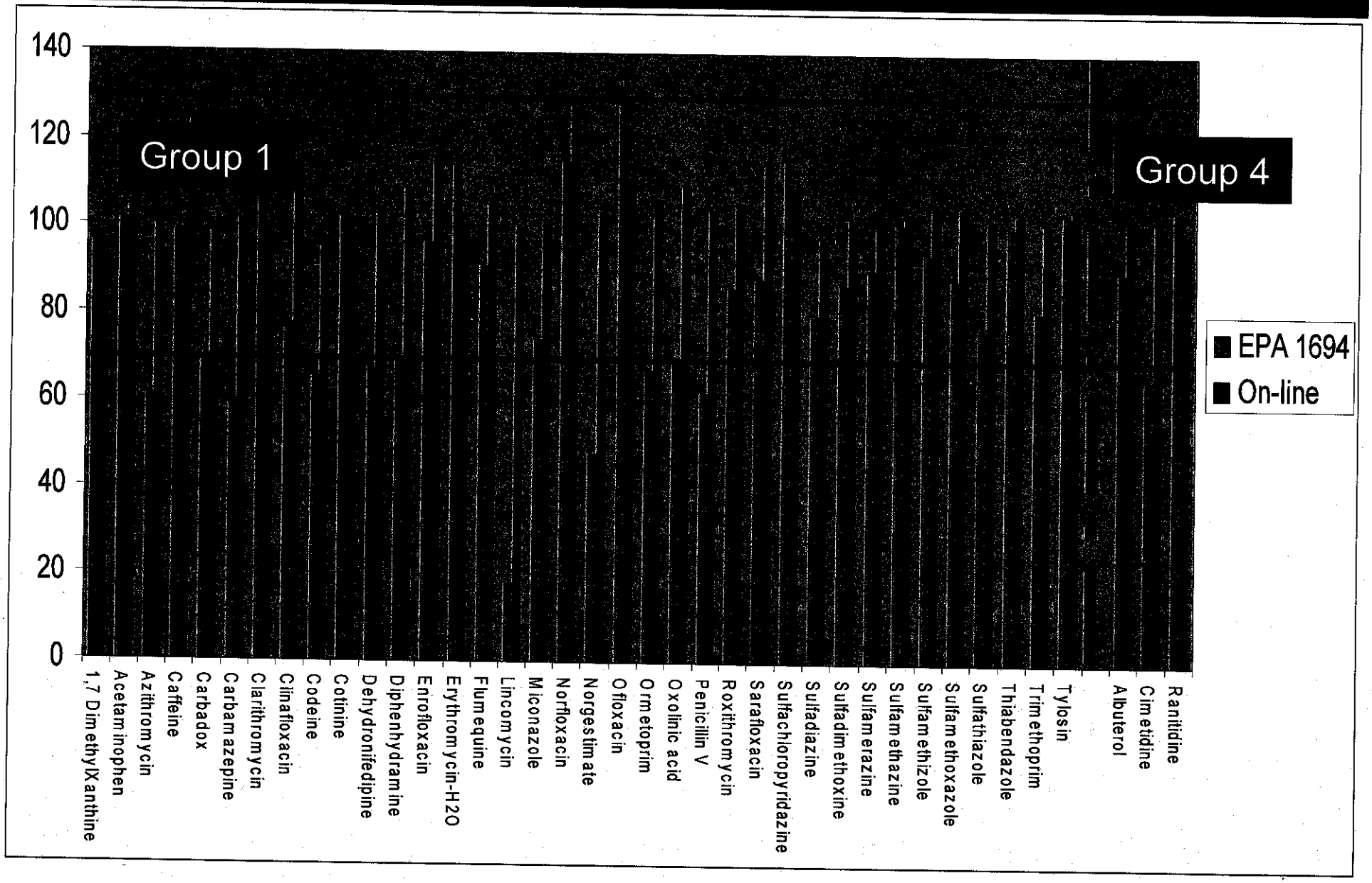
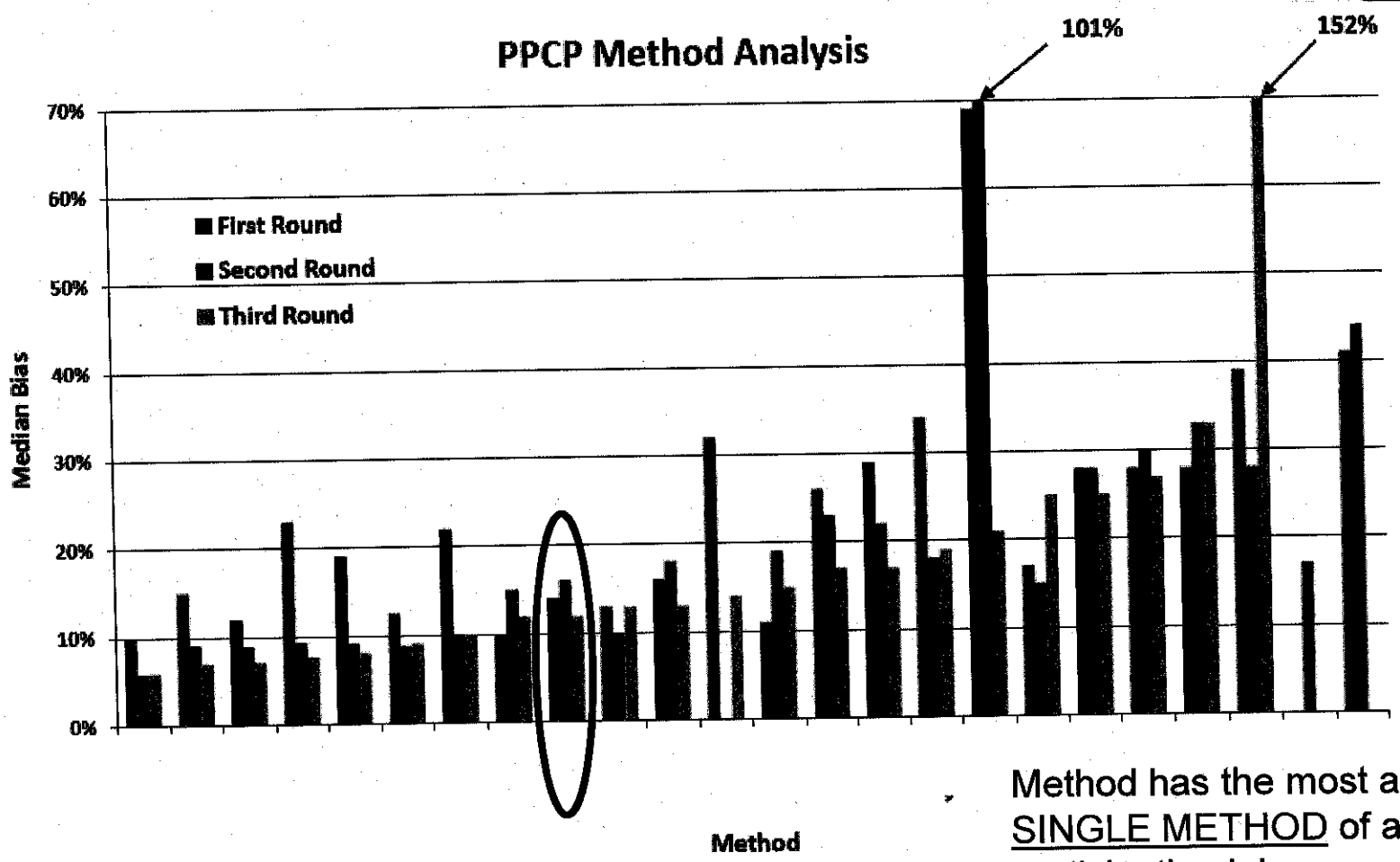
Matrix Spike Recoveries are Good in a Wide Variety of Sample Types.



The Method is Simpler and Performs Better Than EPA 1694



The Method Stacks Up Well in Interlab Comparisons (WaterRF 4167)



Method has the most analytes IN A SINGLE METHOD of any participating lab

How Can One Use This Analytical Tool?

- It can be used for occurrence monitoring for contaminants.
- Used for tracer monitoring
- Allows comparison of "lists" that have been developed for the PPCP with tracers.
  - Santa Ana Watershed Project Authority (SAWPA) list
  - CA SWRCB Blue Ribbon Panel List
  - Primidone (NWRI study)
  - WaterRF 4167
  - Others (literature studies)

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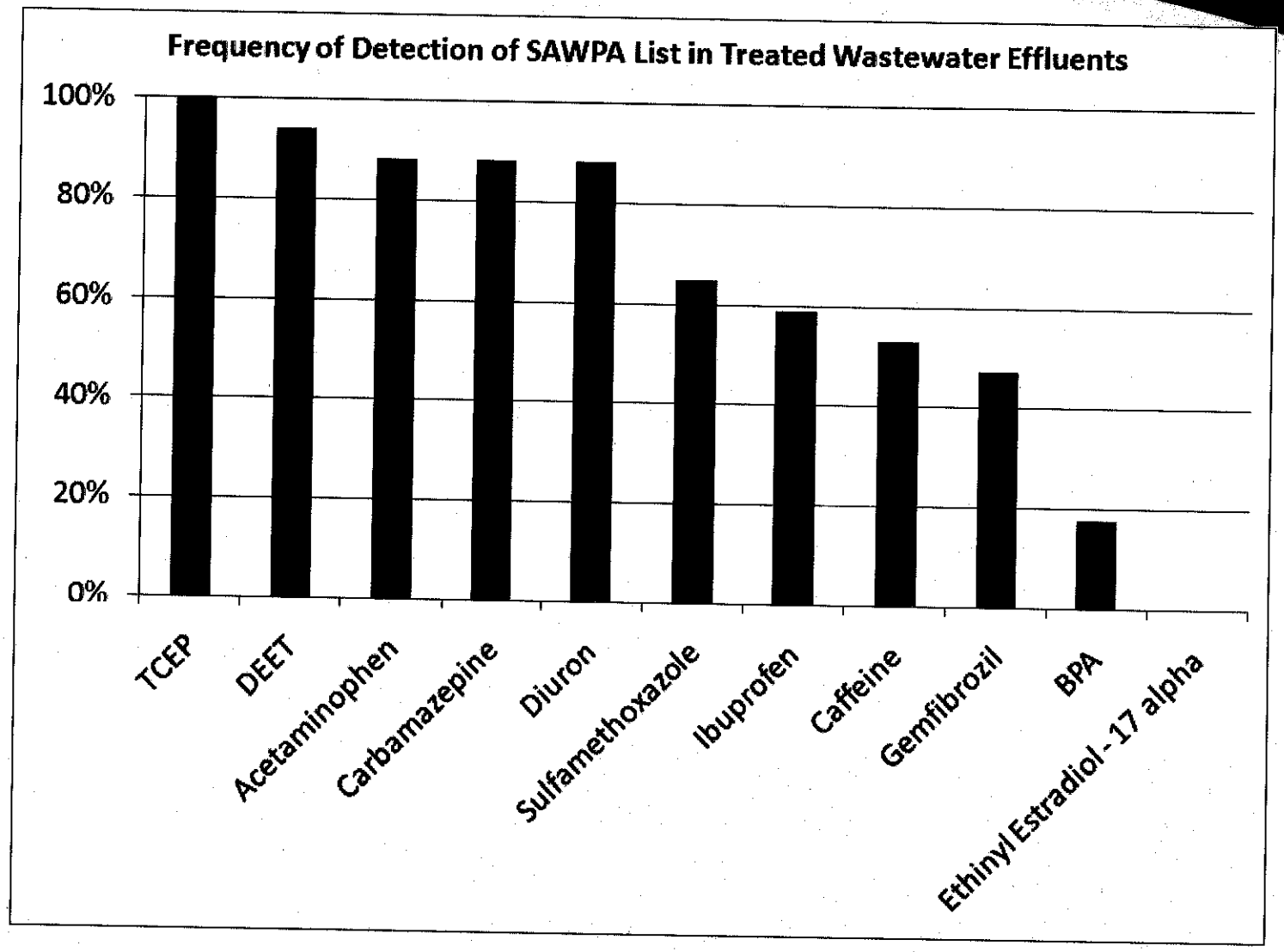
SAWPA Identified a "Short" List of Potential Targets and Conducted a Snapshot Survey

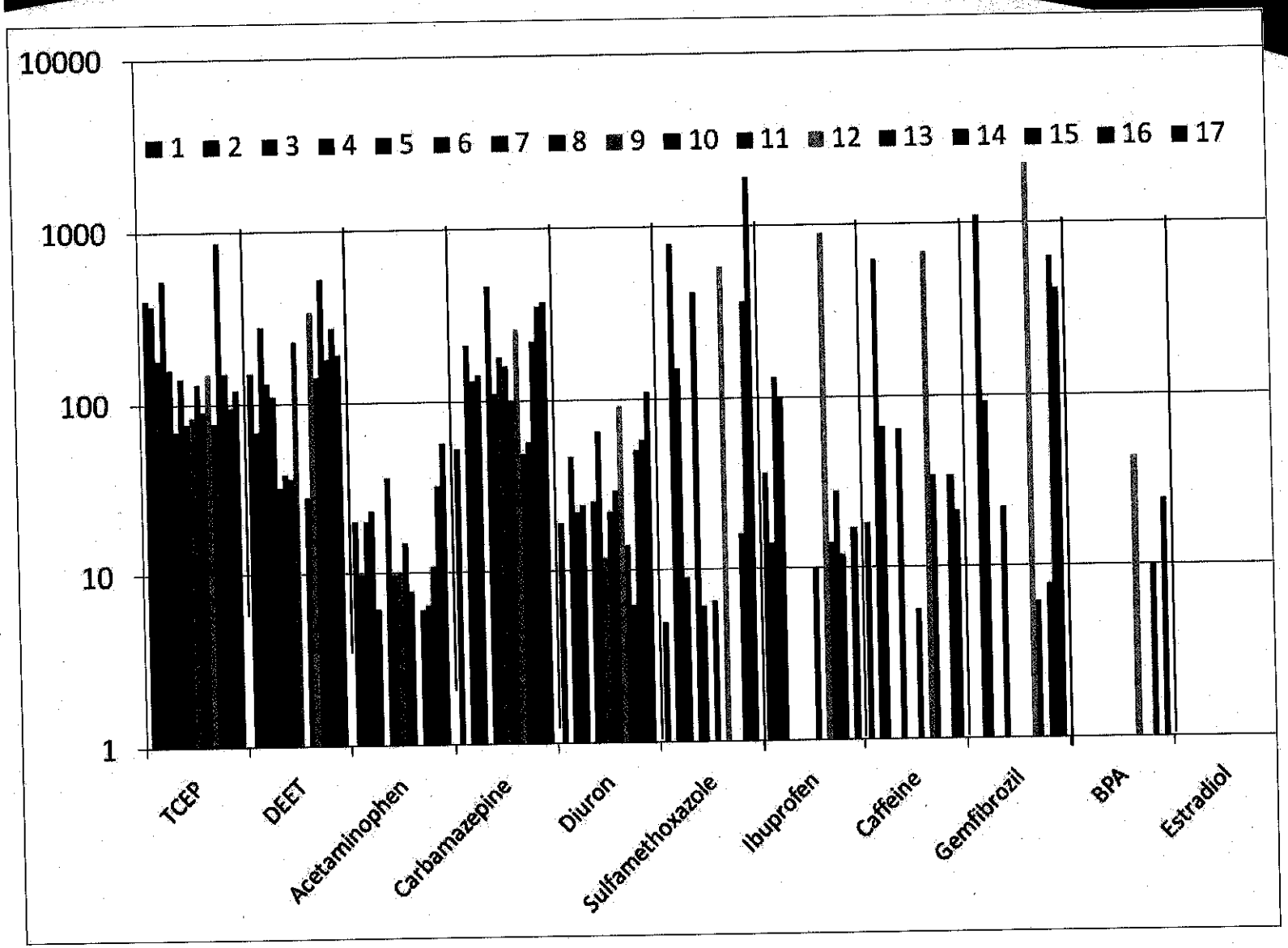
- List developed by a consensus process
- Snapshot Survey with Specific Field and Lab QC required.
- We analyzed effluent from 17 plants discharging to the Santa Ana River (single lab eliminates lab to lab variability).
- SAWPA 11 analytes were measured + number of other analytes (in some samples).

Looking at Occurrence – SAWPA Target List. 5 of 11 Compounds Detected in >80% of Samples.



Frequency suggests this is a reasonable "starter" list.

However the Concentration Range on the SAWPA List Varies Widely For Some Compounds and Between Compounds



Note that scale is a log scale (ng/L)

Compounds sorted by frequency of detection

CA SWRCB Panel Developed Another "List"

Compound	SAWPA?	CA SWRCB?
Acetaminophen	X	
BPA	X	
Caffeine	X	X
Carbemazepine	X	
DEET	X	X
Diuron	X	
Ethinyl Estradiol	X	
Gemfibrozil	X	X
Ibuprofen	X	
Sucralose		X
Sulfamethoxazole	X	
TCEP	X	
Triclosan		X
Iopromide		X
17β-Estradiol		X

The CA Panel List is much shorter and includes four compounds not on the SAWPA list.

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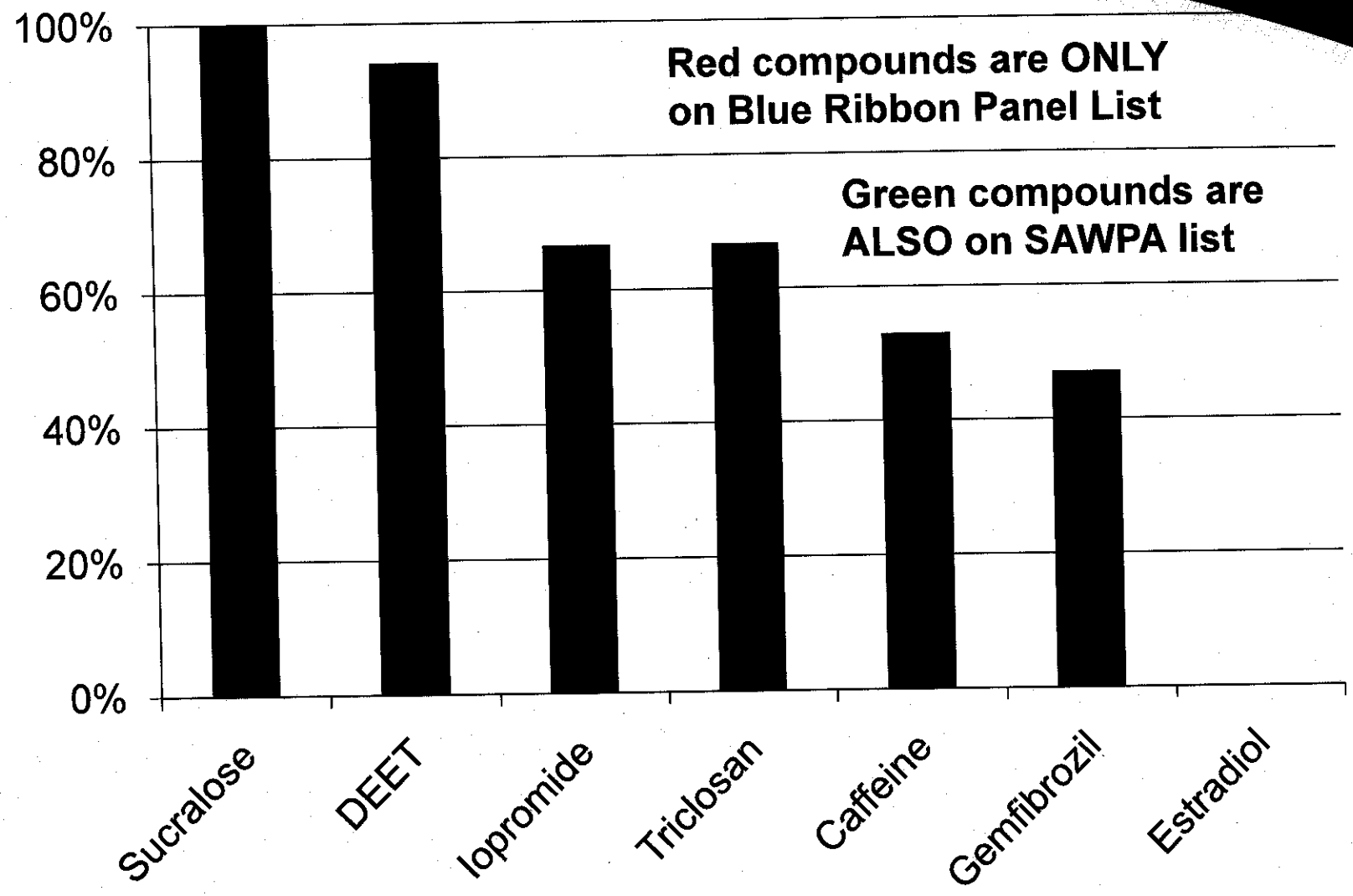
2 of 7 "Blue Ribbon Panel" Analytes Occur in >80% of Samples



WaterRF 4167 – Another "List" Developed Based on Literature Review.

PPCPs		Potential EDCs	
Carbamazepine	Erythromycin	**17β-Estradiol**	Bisphenol A
Sulfamethoxazole	Acetaminophen	17α-Ethynylestradiol	Octylphenol
Trimethoprim	Fluoxetine	Estrone	Nonylphenol
Naproxen	**Triclosan**	Progesterone	
Diclofenac	Primidone	Testosterone	
Ibuprofen	**Caffeine**		
Gemfibrozil	Ciprofloxacin		

Compounds in red are also on the SAWPA list. (8)
Ones in green or **red bolded** are also on the Blue Ribbon Panel List (4)

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Its Clear there are Multiple Potential Indicators…..

- Are the ones proposed necessarily the right ones?
  - Since there has been limited broad screen monitoring, "you only find what you look for"

- The broad spectrum analytical method allows comparison of a) SAWPA List; b) Blue Ribbon Panel list; c) individual compounds (e.g. primidone); d) WaterRF 4167 list e) others (literature suggested)…

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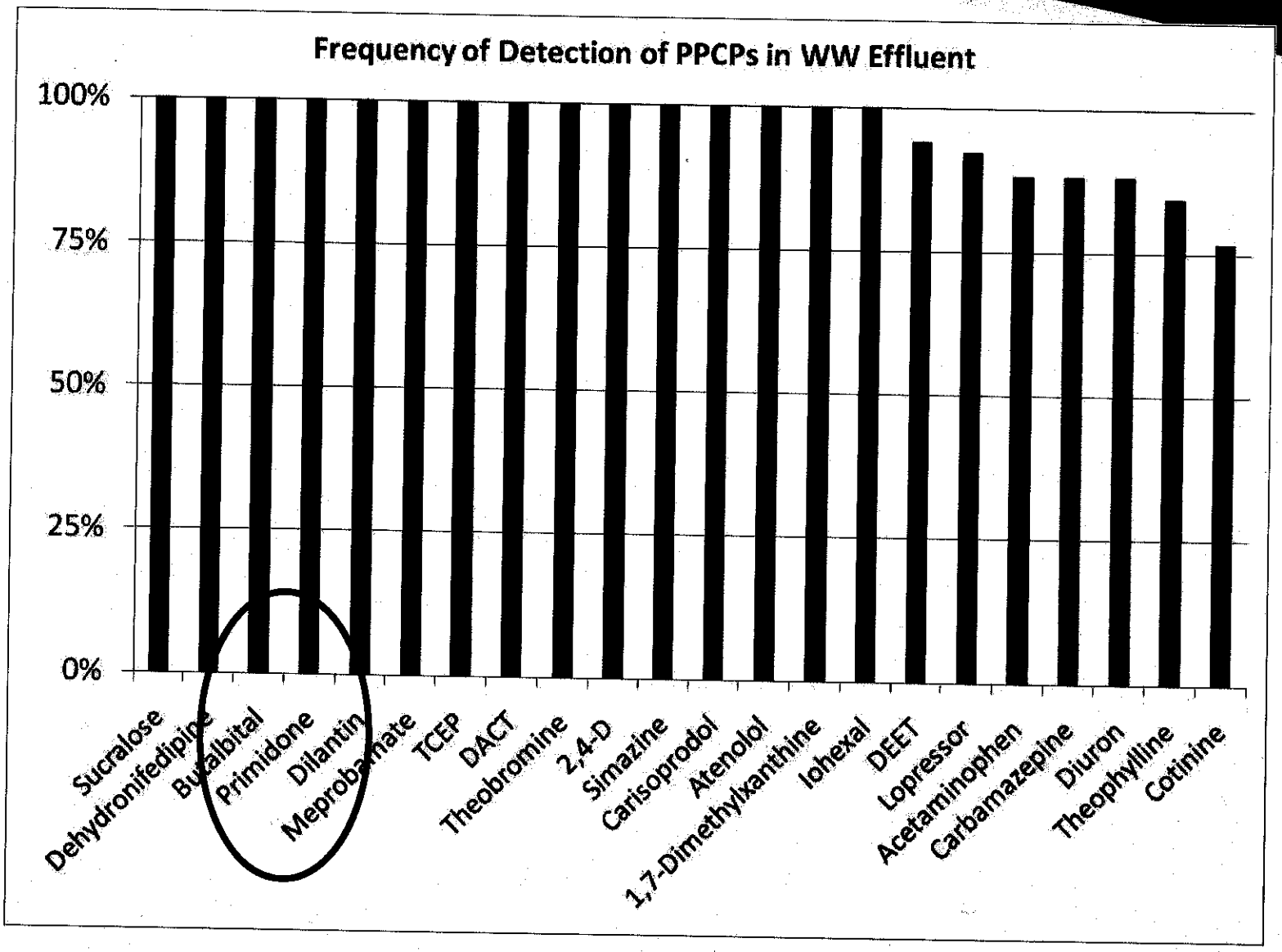
Analyzing the "Long List" Shows that the current agreed upon lists may miss other potential indicators

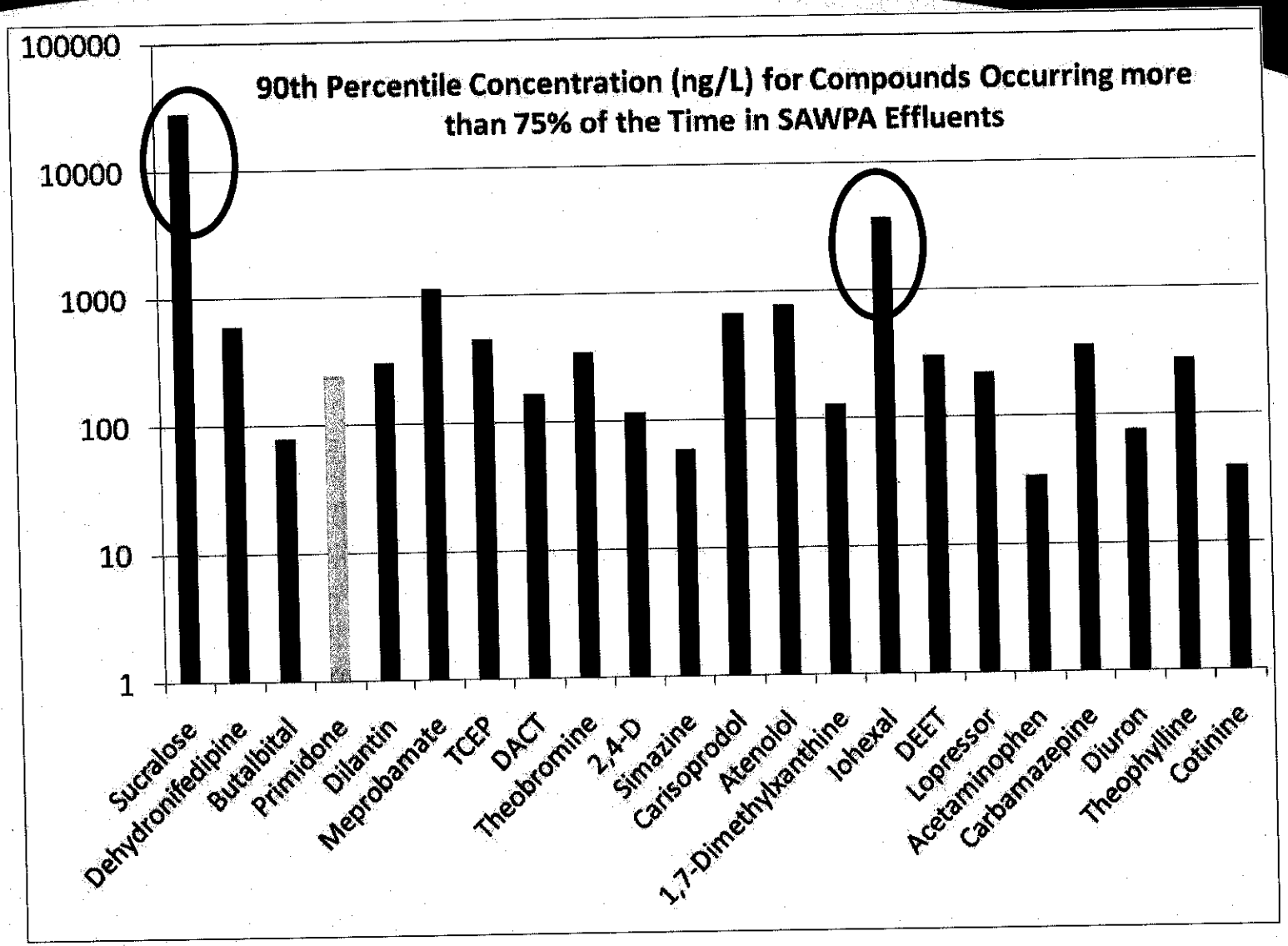


Green analytes are SAWPA targets.

Red analytes are Blue Ribbon Panel targets.

Primidone from 4167

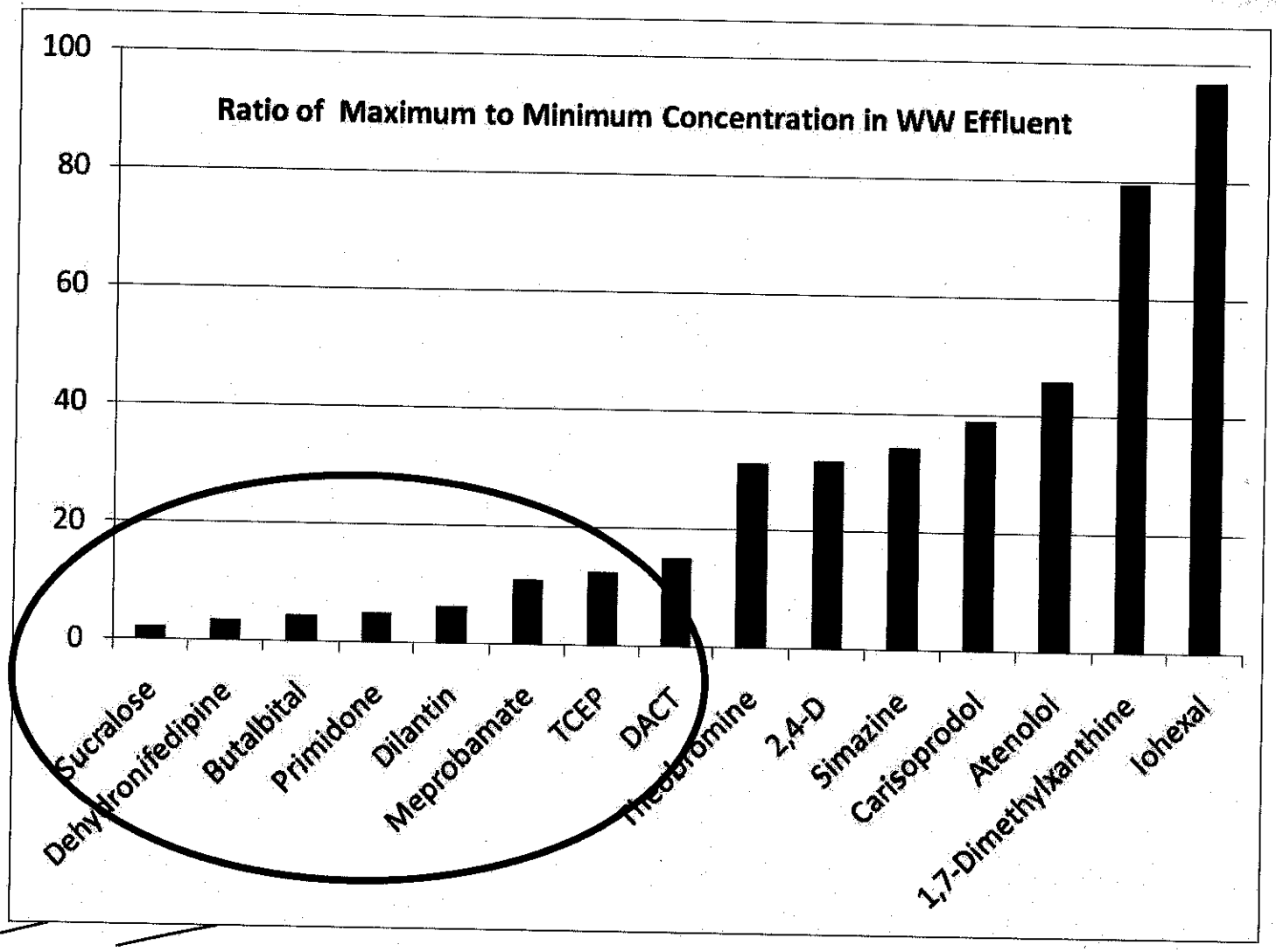
What If One Looks at the Relative Concentrations (ng/L) in WW Effluents?



Sucralose and Iohexal both are very high compared to other compounds

Note log scale for conc.

But a "Really" Good General Indicator Should Have Only Small Variation in Concentration



Sucralose has very small variation. Good generic indicator. Primidone also fits this category.

Iohexal may be a very specific source indicator (e.g. hospitals)

Comparing Lists Suggests That We May be Missing A Number of Indicators

- SAWPA – has a good indicator, TCEP
- Blue Ribbon Panel – has a good indicator, Sucralose
- WaterRF 4167 – has a good indicator- Primidone.
- Long list –includes these 3 good indicators as well as many more.
- Long list – May be able to separate different wastewater types as well as specific influences.

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So How Do the Indicators Compare Locally vs Nationally for Wastewater Effluents

- 20 additional wastewater effluents from across the US
  - Analyzed for the "long list"
- Frequency of detection information
  - Do we see the same compounds as locally?
- Concentration levels
  - Are concentration ranges similar?

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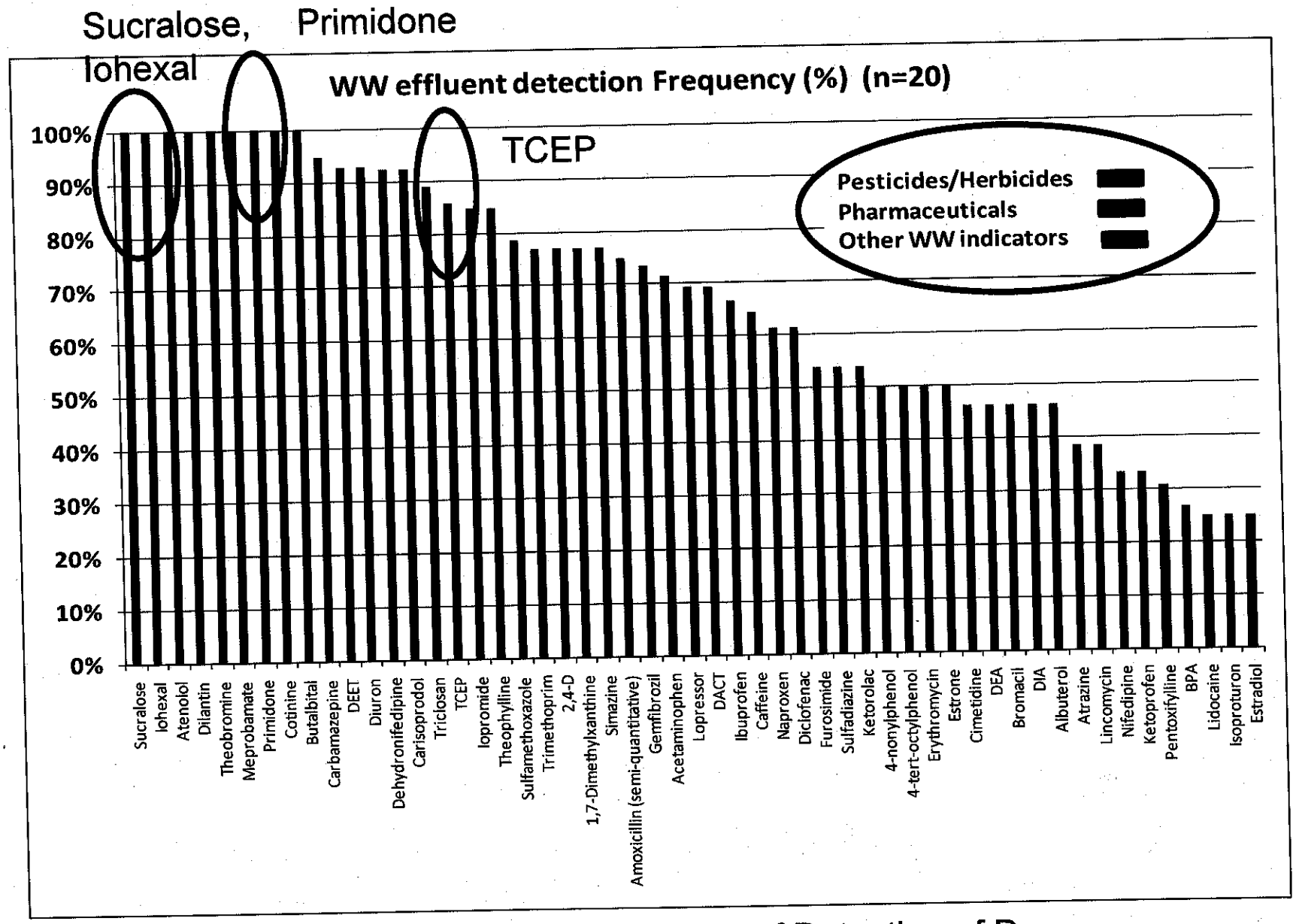
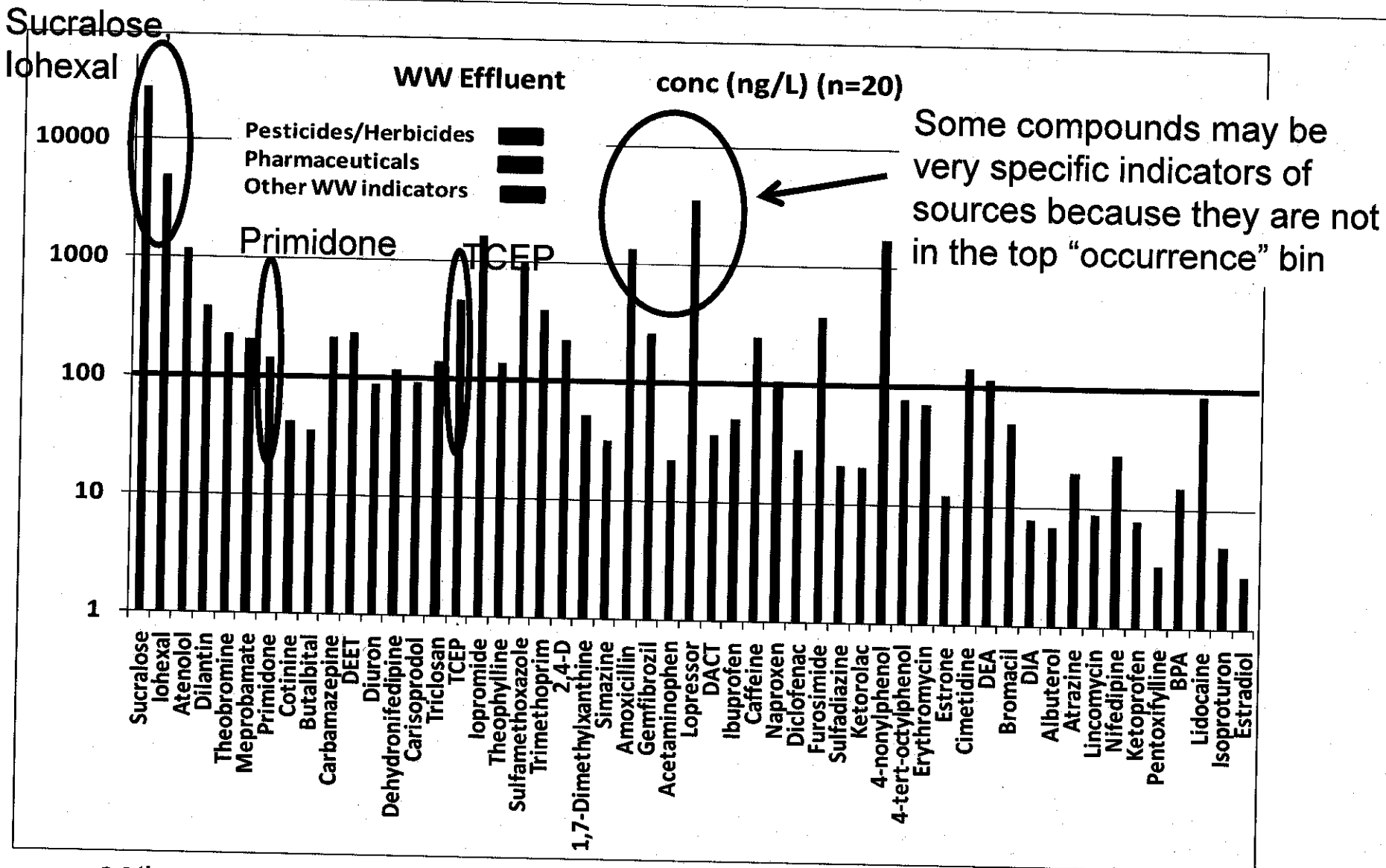


Lots of Hits; High Frequency of Detection of Drugs



90th percentile concentration (ng/L) of PPCPs in Wastewater effluents. *Concentration in log scale.* Compounds with 90th percentile concentration exceeding 100 ng/L are shown by dark line.

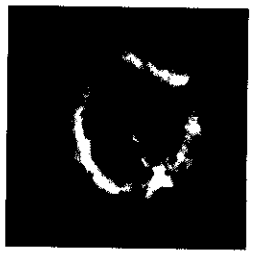
So Do the Analytes Compare?

- Yes with respect to occurrence
  - We generally see the same compounds occurring with the greatest frequency
    - But the larger the database the more variability
- Less so with respect to concentration
  - Sucralose – generally the same 20-30 ppb
  - Primidone – a little more variable, 0.05-0.3 ppb
  - TCEP – more variability as database gets larger
  - Iohexal – very localized in terms of concentration

So We Have Some Good Indicators of Impacted Sources (poorly removed).. And Use Varies

- Sucralose – Artificial Sweetener
  - Excellent conservative tracer

- Iohexol (Iohexal) or Iopromide – X-ray Contrast media
  - Good indicators of hospital wastewater influence



- TCEP- Flame Retardant
  - Resistant to treatment, but much less common and lower concentrations.

So non-pharmaceuticals are better indicators than pharmaceuticals

- Primidone – Anticonvulsant
  - Common in WW but not in finished water

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Our Primary Theses.... Validated

- Most PPCP Methods aren't picking up the best indicators because they focus on drugs only.
  e.g. Most of what we see is NOT pharmaceuticals
- A precise, accurate, simple multi-analyte screening method offers a cost-effective approach to the problem.
  The direct Injection pre-concentration LC-MS-MS method is effective, accurate, and precise
- There are multiple unique tracers of different sources
  Acesulfame-K, Sucralose, Iohexal, Primidone, TCEP, Triazine degradates

So Remember

- Each of these lists is good, but they are short, thus potentially limited.
- A longer list, with more tracers, can be used to better identify the source of the impacted water.
- Any Questions?

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Adequate Field and Lab QC is Critical as Demonstrated from Lab Results

- Compounds sometimes detected in field blanks
  - TCEP
  - Acetaminophen
  - BPA
- What are sample concentrations relative to field blanks?
  - If >10X: no issue with false positives (TCEP)
  - But if 1-2X: potential for false positive (Acetaminophen)

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