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THE LEADER IN ENVIRONMENTAL TESTING

Sacramento Area Sediments Survey for Pharmaceuticals, Personal Care Products, and Other Endocrine Disruptors

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Technical Director

August 8, 2011

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PPCPs and Endocrine Disruptors Are Often in the News

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featuring Today Show Nightly News Dateline Meet the Press MSN

Kids and parenting

Calif. weighs chemical ban in baby bottles

Bill would restrict bisphenol A in products designed for children under 3

AP Associated Press

updated 7:37 a.m. PT, Mon., Aug. 11, 2008

SACRAMENTO, Calif. – Responding to growing consumer anxiety, California lawmakers are considering enacting what could be the first statewide restrictions on a chemical found in plastic baby bottles and infant formula cans.

The bill would require that all products or food containers designed for children 3 years and younger contain only trace amounts of the chemical, bisphenol A.

There is little dispute that bisphenol A can disrupt the hormonal system, but scientists

Kids and parenting videos

A very special summer camp

Aug. 7: At Camp Great Rock, kids with epilepsy can enjoy summer fun and have life-changing experiences. NBC's Tiki Barber reports.

Too much unmarried sex on TV, says group

A not-so-Happy Meal?

Study looks at kids, fast food

Tighter laws take toll on Chinese adoption rates

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of July 17, 2008 Text: Normal - Larger | Print

iosolids a 'disaster waiting'

first in a special series looking pth at the practice of ading treated human waste rm fields

ola Vyhnak pendent

lids are rife with contaminants tially harmful to humans, livestock, e, crops, soil and groundwater. tested or regulated, biosolids may in thousands of toxic chemicals the s of which we know little about. lines for spreading biosolids on nd are outdated and inadequate.

y biosolid opponents.

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The Independent / Need Our Help?

Canada Declares BPA, a Chemical in Plastics, to Be Toxic

By IAN AUSTEN

Published: October 13, 2010

Potential for ecological and human health impacts is driving public health concern and pre- regulatory assessments

Common Emerging PPCP Contaminants

Antibiotics
- Azithromycin
- Lincomycin
- Sulfamethoxazole
- Trimethoprim
- Tyolsin

Anti-inflammatories
- Ibuprofen
- Naproxen

Analgesic and Antipyretic
- Acetaminophen

Antibacterials
- Triclocarban
- Triclosan

Fibrates
- Gemfiborzil

Stimulants

Caffeine

Aniticonvulsants

Carbamazepine

Antidepressants

Cotinine

Fluoxetine

Benzothiazepines

Diltiazem

Contrast Media

Iopromide Isomers

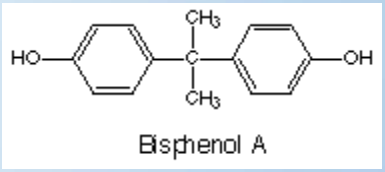
Plastics Manufacturing

Bisphenol A

Surfactants
- Octylphenol
- Nonylphenol
- Nonylphenol Monoethoxylate
- Nonylphenol Diethoxylate

Steroids and Hormones
- 17a-Estradiol
- 17a-Ethynyl Estradiol
- 17b-Estradiol
- Equilenin
- Estriol
- Estrone
- Progesterone
- Testosterone

Example- Bisphenol A



Bisphenol A

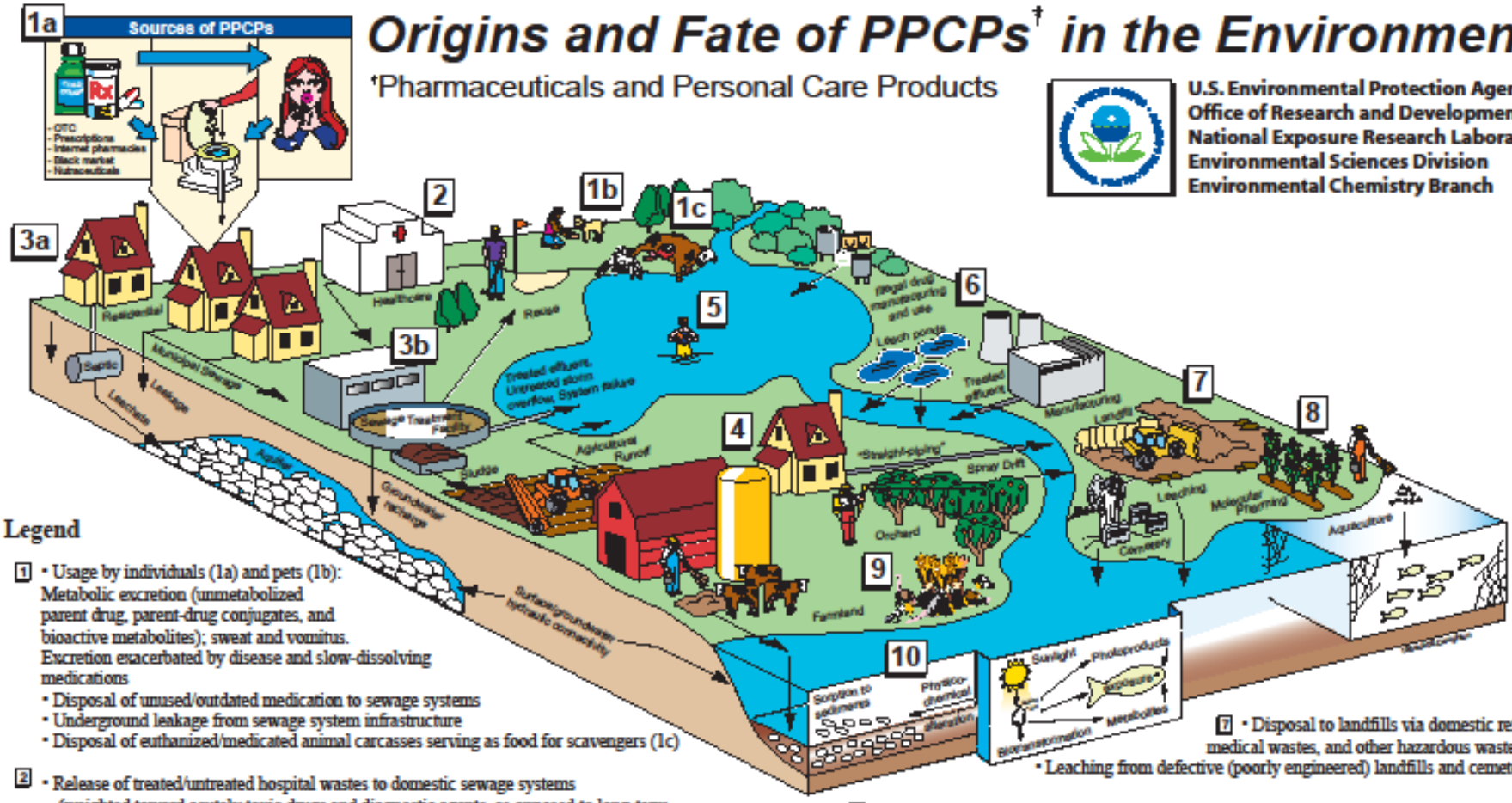
- 400 million tons world production in 2009
- 5% of US BPA used in food contact applications
- Recent Studies found BPA in 93% of 2,500 people surveyed (>6yrs old.)
- Labeled an estrogenic compound

Plastics	Epoxy Resins	Carbonless Paper
Water Bottles	Canned Foods	Receipts
Medical Equipment	Soda Cans	
Food Storage Cont.	Dental Sealants	

Origins and Fate of PPCPs† in the Environment

†Pharmaceuticals and Personal Care Products

U.S. Environmental Protection Agency
Office of Research and Development
National Exposure Research Laboratory
Environmental Sciences Division
Environmental Chemistry Branch



Legend

1 • Usage by individuals (1a) and pets (1b): Metabolic excretion (unmetabolized parent drug, parent-drug conjugates, and bioactive metabolites); sweat and vomitus. Excretion exacerbated by disease and slow-dissolving medications
- Disposal of unused/outdated medication to sewage systems
- Underground leakage from sewage system infrastructure
- Disposal of euthanized/medicated animal carcasses serving as food for scavengers (1c)

2 • Release of treated/untreated hospital wastes to domestic sewage systems (weighted toward acutely toxic drugs and diagnostic agents, as opposed to long-term medications); also disposal by pharmacies, physicians, humanitarian drug surplus

3 • Release to private septic/leach fields (3a)
- Treated effluent from domestic sewage treatment plants discharged to surface waters, re-injected into aquifers (recharge), recycled/reused (irrigation or domestic uses) (3b)
- Overflow of untreated sewage from storm events and system failures directly to surface waters (3b)

4 • Transfer of sewage solids ("biosolids") to land (e.g., soil amendment/fertilization)
- "Straight-piping" from homes (untreated sewage discharged directly to surface waters)
- Release from agriculture: spray drift from tree crops (e.g., antibiotics)
- Dung from medicated domestic animals (e.g., feed) - CAFOs (confined animal feeding operations)

5 • Direct release to open waters via washing/bathing/swimming

6 • Discharge of regulated/controlled industrial manufacturing waste streams
- Disposal/release from clandestine drug labs and illicit drug usage

7 • Disposal to landfills via domestic refuse, medical wastes, and other hazardous wastes
- Leaching from defective (poorly engineered) landfills and cemeteries

8 • Release to open waters from aquaculture (medicated feed and resulting excreta)
- Future potential for release from molecular pharming (production of therapeutics in crops)

9 • Release of drugs that serve double duty as pest control agents:
examples: 4-aminopyridine, experimental multiple sclerosis drug → used as avicide; warfarin, anticoagulant → rat poison; azacholesterol, antilipidemics → avian/rodent reproductive inhibitors; certain antibiotics → used for orchard pathogens; acetaminophen, analgesic → brown tree snake control; caffeine, stimulant → *coqui* frog control

10 Ultimate environmental transport/fate:
- most PPCPs eventually transported from terrestrial domain to aqueous domain
- phototransformation (both direct and indirect reactions via UV light)
- physicochemical alteration, degradation, and ultimate mineralization
- volatilization (mainly certain anesthetics, fragrances)
- some uptake by plants
- respirable particulates containing sorbed drugs (e.g., medicated-feed dusts)

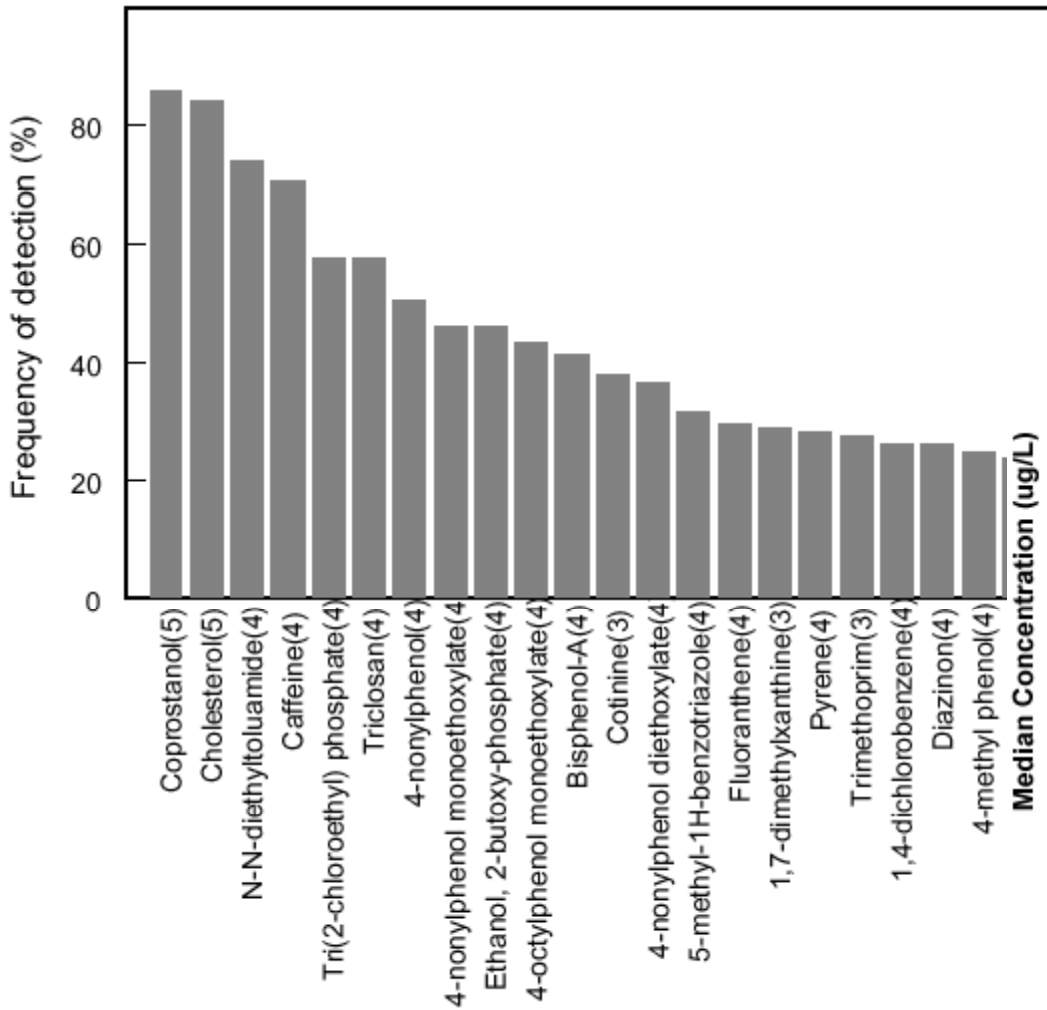
Christian G. Daughton, U.S. EPA-Las Vegas

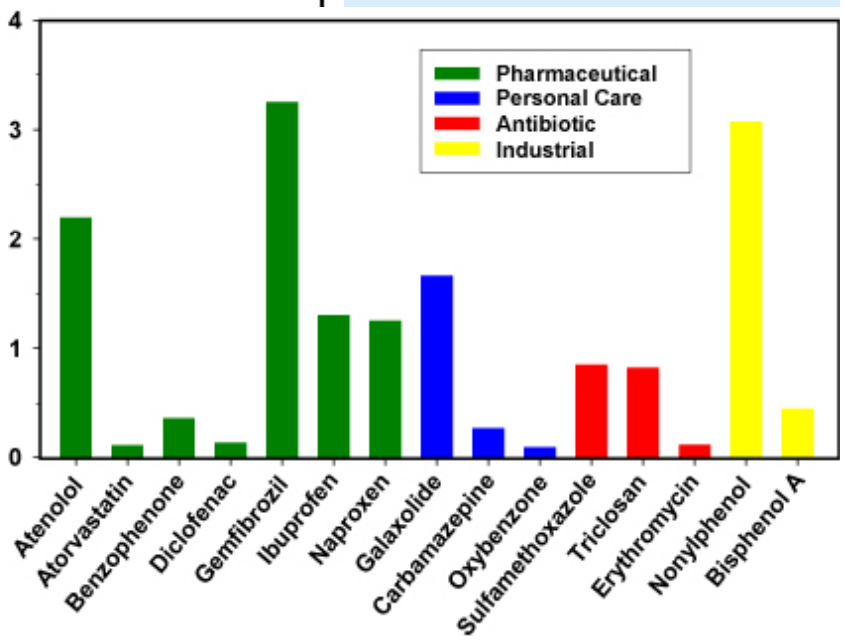
March 2006
(original February 2001)

http://epa.gov/nerlesd1/chemistry/pharma/images/drawing.pdf
from: http://epa.gov/nerlesd1/chemistry/pharma/

Ongoing Studies ….

- Seminal ‘streams’ study by USGS- 2002
  - 80% streams contain steroids
- California coastal estuary study





Impacted Sites Requesting Analytical Support

Programs Requesting PPCP & EDC Analysis:

- *Public Drinking Water Systems*
- *Research & Method Development Programs (EPA, USGS, CSC, CDC, USDA, etc)*
- *Municipal POTW/Sewage effluent monitoring.*
- *Biosolids/Sewage sludge land use programs.*
- *CSO (sewage outflow monitoring programs).*
- *Confined Animal Feed Operations (CAFO)/Agricultural operations.*

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Why the new concerns?

Increasing use

Ecological impacts

Detection capabilities

- **1980's – Parts per Million**
- **1990's – Parts per Billion**
- **Today – Parts per Trillion (aq)**
- **Soon – Parts per Quadrillion**

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Regulatory Framework for PPCPs

- Regulations non-existent or under development for most PPCP compounds from non-point sources
- EPA coordinating > 100 active studies on presence, fate, treatment and impact of PPCPs
- EPA Methods 1694 and 1698 for PPCPs published in early 2008 (1699 for low-level pesticides)
- Other Federal, State and local agencies also sponsoring studies
- PPCPs have been added to EPA-CCL3 and UCMR3

EPA FAQ - EPA Method 1694

Is it necessary to analyze for all the chemicals?

No. When screening complex matrices, such as WWTP wastewaters and solids, monitoring for a subset of 15- 20 chemicals may produce better results, if cleanup procedures are tailored for those chemicals in your matrix, and especially if the subset pairs a target chemical with an isotopic analog. The 73 chemicals in Method 1694 include several classes of chemicals from which one or two chemicals representative of each class could be selected, and several of which have commercially available isotopes.

May I alter the extraction and clean up techniques?

Yes, modifications that improve the accuracy and precision associated with individual subsets of compounds or individual matrices are encouraged. The modifications should be documented and provide performance equal or better than that specified in the method.

Is Method 1694 a useful template for developing a custom PPCP method?

Yes, the information in 1694 or similar LC/MS/MS methods may be used as a starting point to develop an analytical method tailored to specific matrices or compounds.

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Analytical Challenges for Laboratories

Add new PPCP/EDC compounds of interest without proliferating number of methods or compromising efficacy for existing target analytes

Expand analytical technique to include more complex matrices (sediments, tissue, etc)

Improve reliability and performance of the method in routine high production laboratory environment

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Analytical Challenges of Sediments

Interferences include bacteria, organisms as well as other organic material

Some target analytes may be soluble and trapped in the water and while others may be tightly bound to sediment material

The Solution:

Gently apply energy to extract / release the bound target compounds without destroying them

Survey Details

Survey the sediments and water above and below the Sacramento WWTP discharge.

- SRCSD serves ~2M people
- Treats and releases 150M gallons of wastewater each day.
- Discharge point is just south of the Freeport Bridge
- Related studies underway for small subsets of target analytes

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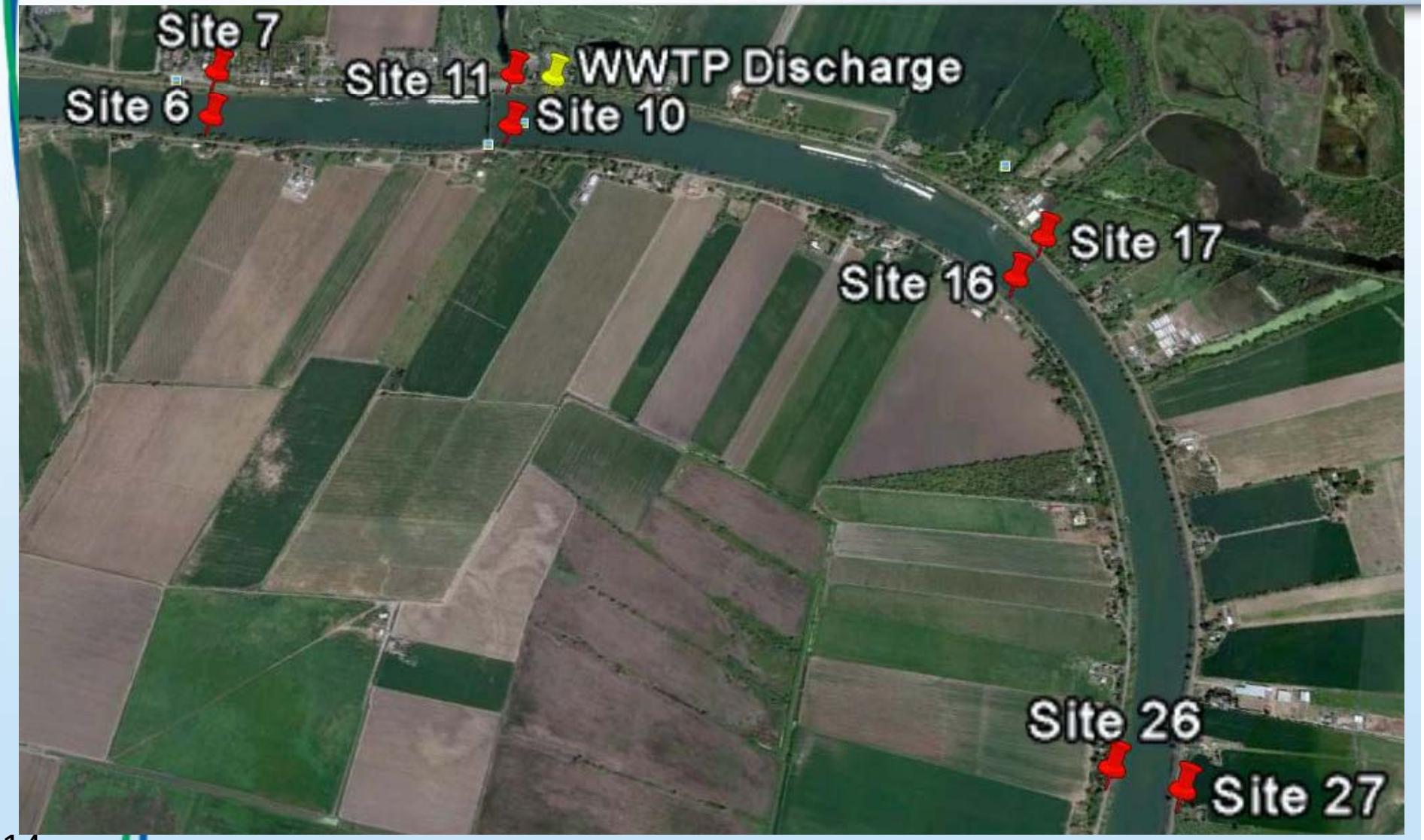
Grab Sampling Points



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Study Details

Co-located aqueous and sediment grab samples from each location, collected Spring 2011

During summer/fall, Sacramento River at Freeport is tidal

During late winter/spring, Sacramento River flow is high, with significant suspended sediment load

Method 1694 – 69 PPCPs

Method 1698 – 8 Steroids & Hormones

Method 1668 – 209 PCB Congeners

Method 1613B – 17 Dioxin/Furan Isomers

1694 Analysis Details

Analysis included parameters not described in 1694 (DEET, Bisphenol-A, Morphine)

Acid extraction fraction only

Quality Control Parameters -

- Method Blanks
- Laboratory control samples
- Matrix spikes (for sediments)
- 2g/10g extraction replicates (for sediments)
- Internal Standard/Surrogates

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PPCP Water Results (ng/L)

	RL	SR-06	SR-07	SR-10	SR-11	SR-16	SR-17	SR-27	SR-26
Acetaminophen	10	6.24	1.92	ND	7.13	1.94	5.99	1.19	**108.84**
Cotinine	10	ND	**31.48**	**14.54**	**24.32**	**23.81**	**30.06**	**30.58**	**17.4**
Salicylic Acid	10	40.14	**23.94**	**15.28**	**23.31**	**21**	**18.22**	**25.71**	**27.55**
Caffeine	10	**56.53**	11.51	14.16	7	**62.51**	**11.76**	9.72	**41.68**
Trimethoprim	10	1.48	1.28	1.36	0.84	1.53	3.62	4.1	**64.04**
Sulfamethoxazole	10	**2.41**	**3.62**	**2.11**	**2.7**	**3.04**	**5.8**	**4.01**	**61.08**
Bisphenol A	200	22.4	**843.28**	**751.31**	**263.34**	**918.96**	**411.33**	**503.66**	20.37
tris(2-chloro-2-propyl)phosphate (TCPP)	50	8.46	11.67	9.88	6.88	15.78	37.03	**74.25**	**94.79**
Diphenhydramine	10	8.75	2.42	2.73	0.32	2.19	3.82	7.18	**38.43**

1694 Aqueous QC Results

- Method Blanks
  - 68 of 69 target analytes below established RL (Salicylic Acid at 12 vs RL of 10 ng/L), multiple analytes detected at conc < RL.
- Laboratory Control Samples
  - 68 of 69 target analytes recovered in range 30-150%, with 63 recovered in range 60-140%
  - Roxithromycin only 13%
  - Avg recovery for all analytes 88% with .23 stdev
- Internal Standard/Surrogates
  - 25 of 34 labeled internal standards (IS) showed recovery > 30%
  - 3 IS with very low recovery < 1% in samples, but OK in MB/LCS (azithromycin, ciprofloxacin, cotinine)

Sediment Results

	RL	SRS-06	SRS-07	SRS-10	SRS-11	SRS-16	SRS-17	SRS-27	SRS-26
Salicylic Acid	5	**86.61**	**21.37**	**22.61**	**58.67**	**25.77**	**30.2**	**24.88**	**43.15**
Caffeine	5	ND	1.26	**11.57**	1.6	1.67	2.39	2.22	1.46
TeCB-61/70/74/76	20	**22.17**	9.86	**32.41**	**16.1**	**18.17**	**15.66**	**42.76**	**21.02**
PeCB-95	20	ND	ND	**22.13**	ND	ND	0.26	43.13	**ND**
PeCB-90/101/113	20	**13.13**	ND	**35.42**	**18.51**	ND	ND	**60.78**	**22.82**
PeCB-86/87/97108/119	20	9.66	7.92	**23.25**	**11.09**	**12.05**	**12.24**	**44.96**	**13.85**
PeCB-85/110/116/117	20	21.37	0.91	**55.45**	**28.26**	1.5	1.55	**95.08**	**40.26**
PeCB-118	2	**16.99**	ND	**42.98**	**20.82**	ND	ND	**64.91**	**26.7**
HxCB-147/149	20	15.53	ND	**45.92**	**32.24**	1.35	1.01	**53/19**	**36.13**
HxCB-153/168	20	2.92	2.5	**64.35**	**41.98**	4.36	3.89	**50.22**	**94.02**
HxCB-129/138/163	20	30.19	24.96	**85.58**	**48.43**	**45.53**	**34.82**	**83.34**	**110.29**
HpCB-180/193	20	**15.3**	**13.34**	**51.5**	**33.75**	**19.13**	**17.82**	**20.81**	**76.97**

1694 Sediment QC Results

- Method Blanks
  - 66 of 69 target analytes below established RL
  - Salicylic acid, lorezapam, and albuterol slightly above RL of 1 ng/g.
- Laboratory Control Samples
  - 47 of 69 target analytes recovered in range 30-150%
  - 10 analytes (primarily cyclines) with recovery < 5%.
  - Avg recovery for all analytes 61%
- Internal Standard/Surrogates
  - 25 of 34 labeled internal standards (IS) showed recovery > 30%
  - 5 IS with very low recovery < 1% in both samples and QC
  - Average IS recovery 54% in QC, 24% in 10g sample, and 40% in 2g sample

1694 Sediment QC Results

- Matrix spikes/spike duplicates (for 2 g sample size)
  - 48 of 69 target analytes recovered in range 30-150%
  - 9 analytes (primarily cyclines) with recovery < 5%.
  - RPD in the range 0-30% for 48 analytes with good recovery
- 2g vs 10g Replicates
  - 10g replicates showed more evidence of matrix impacts, with lower IS recovery and increased variability in matrix spike recovery and RPD.

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Conclusions from Study Results

- Sacramento River aqueous and sediment samples near the regional WWTP discharge show evidence of PPCP and POP impacts
- Aqueous and sediment sample collection at high flow and at the high water line may not fully characterize PPCP and POP impacts
- Method modifications to include additional analytes of interest were successful for these parameters, but may have compromised method performance for other target analytes
- Method performance appeared most significantly compromised for those target analytes without labeled analogs as IS

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Path Forward

- Continue to optimize acid/base extraction procedures for expanded analyte list.
- Refine extract clean-up procedures for expanded list
- Increase number of labeled internal standards and optimize analyte correspondence
- Recently completed MDL studies show significant improvement in overall method performance

Resources

- **USGS - Water-Quality Data for Pharmaceuticals, Hormones, and Other Organic Wastewater Contaminants in U.S. Streams, 1999-2000**
- Environ Health Perspect. 2008 January; 116(1): 32–38.Published online 2007 October 5. doi: 10.1289/ehp.10587.**Direct Evidence Revealing Structural Elements Essential for the High Binding Ability of Bisphenol A to Human Estrogen-Related Receptor-γ**
- US News - Studies Report More Harmful Effects From BPA **Chemical in plastics may hurt heart and fertility, researchers say** Posted: June 10, 2009
- **epa.gov/safewater/ccl/pdfs/ccl3_docs/pre-fr_ccl3**

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