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# CEE 697z

## Organic Compounds in Water and Wastewater

PPCPs in Natural Systems

Lecture #19

For Background see:

<http://www.ecs.umass.edu/eve/background/chemicals/PPCPs/PPCP%20natural%20systems.html>

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## Paper 1: Sengupta et al., 2013

Environmental Toxicology and Chemistry, Vol. 33, No. 2, pp. 350-358, 2014  
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### THE OCCURRENCE AND FATE OF CHEMICALS OF EMERGING CONCERN IN COASTAL URBAN RIVERS RECEIVING DISCHARGE OF TREATED MUNICIPAL WASTEWATER EFFLUENT

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(Submitted 2 July 2013; Returned for Revision 15 August 2013; Accepted 2 November 2013)

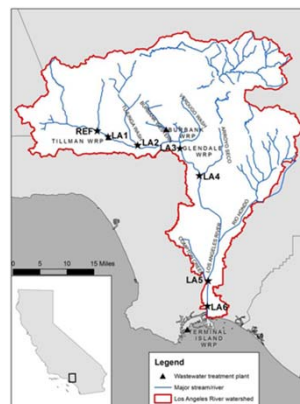
**Abstract:** To inform future monitoring and assessment of chemicals of emerging concern (CECs) in coastal urban watersheds, the occurrence and fate of more than 60 pharmaceuticals and personal care products (PPCPs), commercial/household chemicals, current-use pesticides, and hormones were characterized in 2 effluent-dominated rivers in southern California (USA). Water samples were collected during 2 low-flow events at locations above and below the discharge points of water reclamation plants (WRPs) and analyzed using gas chromatography–mass spectrometry and liquid chromatography–tandem mass spectrometry. Approximately 50% of targeted CECs were detectable at stations downstream from WRPs, compared with <31% and <10% at the reference stations above the WRPs. Concentrations of chlorinated phosphate flame retardants were highest among the CECs tested, with mean total aggregate concentrations of tris(2-chloroethyl) phosphate (TCEP), tris(1-chloro-2-propyl) phosphate (TCPP), and tris(1,3-dichloro-2-propyl) phosphate (TDCPP) of 3400 ng/L and 2400 ng/L for the 2 rivers. Maximum in-stream concentrations of pyrethroids (bifenthrin and permethrin), diclofenac, and galatolide exceeded risk-based thresholds established for monitoring of CECs in effluent-dominated receiving waters. In contrast, maximum concentrations of PPCPs commonly detected in treated wastewater (e.g., acetaminophen, N,N-diethyl-metha-toluamide [DEET], and gemfibrozil) were less than 10% of established thresholds. Attenuation of target CECs was not observed downstream of WRP discharge until dilution by seawater occurred in the tidal zone, partly because of the short hydraulic residence times in these highly channelized systems (<3 d). In addition to confirming CECs for future in-stream monitoring, these results suggest that conservative mass transport is an important boundary condition for assessment of the input, fate, and effects of CECs in estuaries at the bottom of these watersheds. *Environ Toxicol Chem* 2014;33:350–358. © 2013 SETAC

Sengupta, A., Lyons, J.M., Smith, D.J., Drewes, J.E., Snyder, S.A., Heil, A. and Maruya, K.A. (2013) [The Occurrence and Fate of Chemicals of Emerging Concern in Coastal Urban Rivers Receiving Discharge of Treated Municipal Wastewater Effluent](#). *Environmental Toxicology and Chemistry* 33(2), 350-358.

:ckhow

**The occurrence and fate of chemicals of emerging concern in coastal urban rivers receiving discharge of treated municipal wastewater effluent**

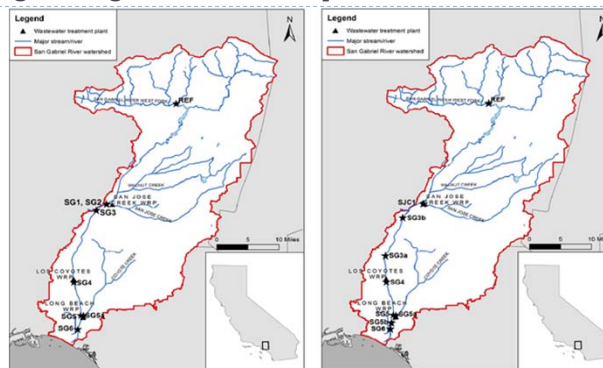
Sampling stations for the Los Angeles River (LA1–6) watershed. River water samples were collected during 2 events (July 2011 and October 2011) during low-flow conditions. REF = reference station; WRP = water reclamation plant.



Environmental Toxicology and Chemistry  
Volume 33 Issue 2, pages 350-358, 7 JAN 2014 DOI: 10.1002/etc.2457  
<http://onlinelibrary.wiley.com/doi/10.1002/etc.2457/full#etc2457-fig-0001>

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**The occurrence and fate of chemicals of emerging concern in coastal urban rivers receiving discharge of treated municipal wastewater effluent**



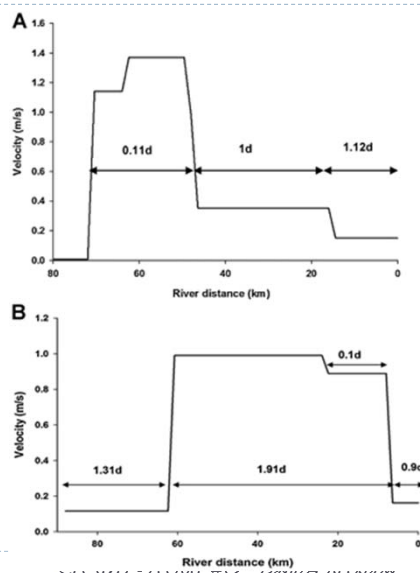
Sampling stations for the San Gabriel River (SG1–6) watershed. River water samples were collected during 2 events during low-flow conditions. The left map is for event 1 in July 2011, and the right map is for event 2 in October 2011. The location of station SG3 differed between events because of managed flow diversions. REF = reference station; SJCI = San Jose Creek targeted station; WRP = water reclamation plant.

Environmental Toxicology and Chemistry  
Volume 34 Issue 2, pages 350-358, 7 JAN 2014 DOI: 10.1002/etc.2457  
<http://onlinelibrary.wiley.com/doi/10.1002/etc.2457/full#etc2457-fig-0002>

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### The occurrence and fate of chemicals of emerging concern in coastal urban rivers receiving discharge of treated municipal wastewater effluent

Modeled water velocity profiles and estimated hydraulic residence times (in days) for the (A) Los Angeles River and (B) San Gabriel River during low-flow conditions. The confluence point of the river and the ocean is considered as river kilometer = 0.

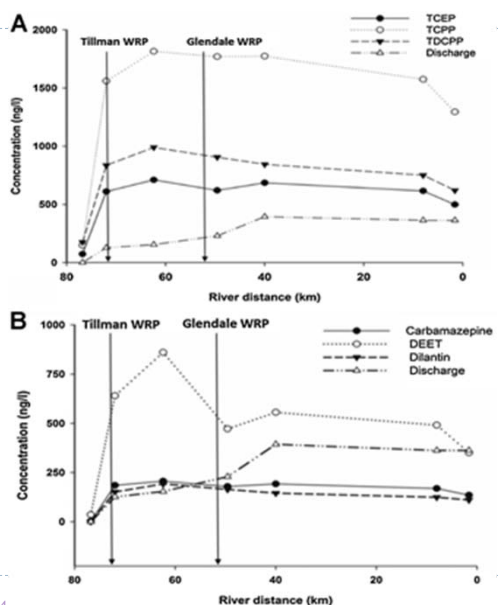


Environmental Toxicology and Chemistry  
 Volume 35 Issue 2, pages 350-358, 7 JAN 2014 DOI: 10.1002/etc.2457  
<http://onlinelibrary.wiley.com/doi/10.1002/etc.2457/full#etc2457-fig-0003>

### The occurrence and fate of chemicals of emerging concern in coastal urban rivers receiving discharge of treated municipal wastewater effluent

In-stream concentration profiles of (A) chlorinated phosphate flame retardants (TCPP, TDCPP, and TCEP) and (B) selected PPCPs for the Los Angeles River (July 2011). The confluence point of the river and the ocean is considered as river kilometer = 0. The units plotted for discharge are ( $\text{m}^3/\text{s} \times 100$ ). WRP = water reclamation plant;

- TCPP = tris(1-chloro-2-propyl) phosphate;
- TDCPP = tris(1,3-dichloro-2-propyl) phosphate;
- TCEP = tris(2-chloroethyl) phosphate;
- DEET = N,N-diethyl-meta-toluamide.

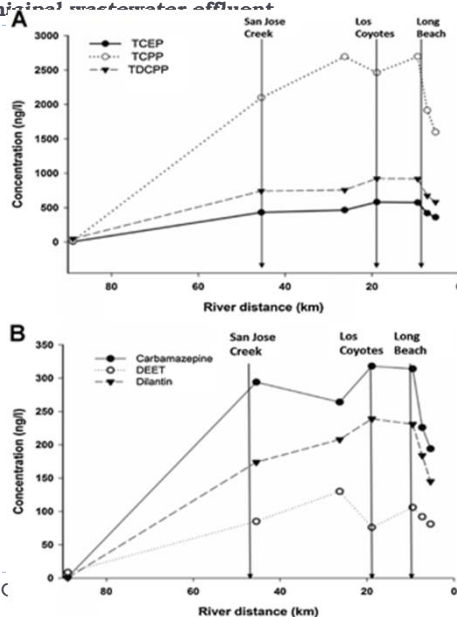


Environmental Toxicology and Chemistry  
 Volume 35 Issue 2, pages 350-358, 7 JAN 2014 DOI: 10.1002/etc.2457  
<http://onlinelibrary.wiley.com/doi/10.1002/etc.2457/full#etc2457-fig-0004>

The occurrence and fate of chemicals of emerging concern in coastal urban rivers receiving discharge of treated municipal wastewater effluent

In-stream concentration profiles of (A) chlorinated phosphate flame retarding chemicals and (B) selected pharmaceuticals and personal care products (PPCPs) for the San Gabriel River (October 2011). The confluence point of the river and the ocean is considered as river kilometer = 0.

- DEET = N,N-diethyl-meta-toluamide;
- TCPP = tris(1-chloro-2-propyl) phosphate;
- TDCPP = tris(1,3-dichloro-2-propyl) phosphate;
- TCEP = tris(2-chloroethyl) phosphate.



Environmental Toxicology and Chemistry  
 Volume 37 Issue 2, pages 350-358, 7 JAN 2014 DOI: 10.1002/etc.2457  
<http://onlinelibrary.wiley.com/doi/10.1002/etc.2457/full#etc2457-fig-0005>

## Paper 2: [Jurgens et al., 2002](#)

SETAC PRESS

Environmental Toxicology and Chemistry, Vol. 21, No. 3, pp. 480-488, 2002  
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 0730-7268/02 \$9.00 + .00

### THE POTENTIAL FOR ESTRADIOL AND ETHINYLESTRADIOL DEGRADATION IN ENGLISH RIVERS

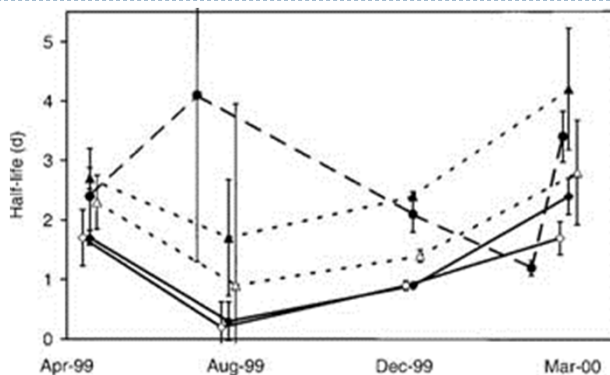
MONIKA D. JÜRGENS,† KARLIJN I.E. HOLTHAUS,† ANDREW C. JOHNSON,\*† JENNIFER J.L. SMITH,† MALCOM HETHERIDGE,‡ and RICHARD J. WILLIAMS†

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(Received 17 April 2001; Accepted 13 August 2001)

**Abstract**—Water samples were collected in spring, summer, and winter from English rivers in urban/industrial (River Aire and River Calder, Yorkshire, UK) and rural environments (River Thames, Oxfordshire, UK) to study the biodegradation potential of the key steroid estrogen 17 $\beta$ -estradiol (E2) and its synthetic derivative ethinylestradiol (EE2). Microorganisms in the river water samples were capable of transforming E2 to estrone (E1) with half-lives of 0.2 to 9 d when incubated at 20°C. The E1 was then further degraded at similar rates. The most rapid biodegradation rates were associated with the downstream summer samples of the River Aire and River Calder. E2 degradation rates were similar for spiking concentrations throughout the range of 20 ng/L to 500  $\mu$ g/L. Microbial cleavage of the steroid ring system was demonstrated by release of radiolabeled CO<sub>2</sub> from the aromatic ring of E2 (position 4). When E2 was degraded, the loss of estrogenicity, measured by the yeast estrogen screen (YES) assay, closely followed the loss of the parent molecule. Thus, apart from the transient formation of E1, the degradation of E2 does not form other significantly estrogenic intermediates. The E2 could also be degraded when incubated with anaerobic bed sediments. Compared to E2, EE2 was much more resistant to biodegradation, but both E2 and EE2 were susceptible to photodegradation, with half-lives in the order of 10 d under ideal conditions.

### The potential for estradiol and ethinylestradiol degradation in english rivers



Half-lives and standard deviations of  $17\beta$ -estradiol (E2) in water samples collected from five sites on four occasions in 1999 and 2000 (Thames Wallingford, UK —•—, Calder Brighthouse (upstream) —△—, Aire Riddlesden (upstream) —▲—, Calder Methley Bridge (downstream) —◆—, Aire Beal (downstream) —#—).

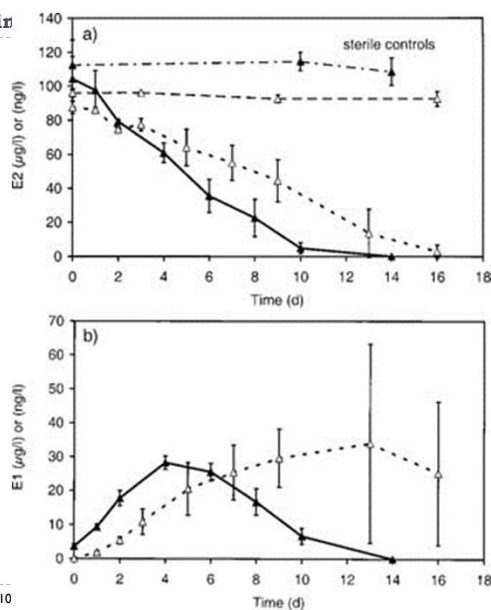
Environmental Toxicology and Chemistry

Volume 29 Issue 3, pages 480-488, 5 NOV 2009 DOI: 10.1002/etc.5620210302  
<http://onlinelibrary.wiley.com/doi/10.1002/etc.5620210302/full#fig1>

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### The potential for estradiol and ethin

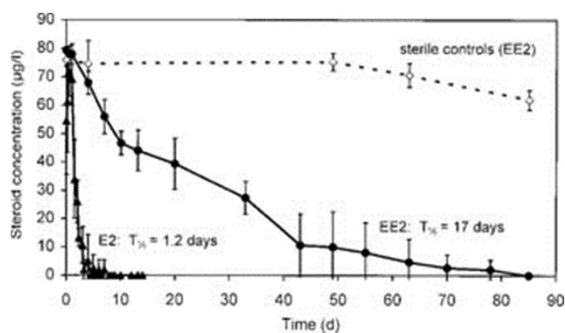
Aerobic degradation of  $17\beta$ -estradiol (E2) (100  $\mu\text{g/L}$  —△— and 100  $\text{ng/L}$  —▲—) in River Thames, UK, water (January 18, 2000), means and standard deviations of three replicates; (a) disappearance of the parent product, (b) evolution and subsequent degradation of the first metabolite estrone (E1).



Environmental Toxicology and Chemistry

Volume 29 Issue 3, pages 480-488, 5 NOV 2009 DOI: 10.1002/etc.5620210  
<http://onlinelibrary.wiley.com/doi/10.1002/etc.5620210302/full#fig2>

### The potential for estradiol and ethinylestradiol degradation in english rivers



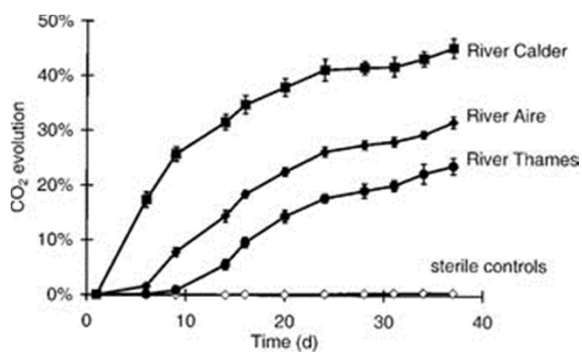
Comparison of biodegradation of 17 $\beta$ -estradiol (E2) and ethinylestradiol (EE2) in a Thames River water sample (March 2, 2000, means and standard deviations of three replicates).

Environmental Toxicology and Chemistry

Volume 28, Issue 3, pages 480-488, 5 NOV 2009 DOI: 10.1002/etc.5620210302  
<http://onlinelibrary.wiley.com/doi/10.1002/etc.5620210302/full#fig3>

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### The potential for estradiol and ethinylestradiol degradation in english rivers



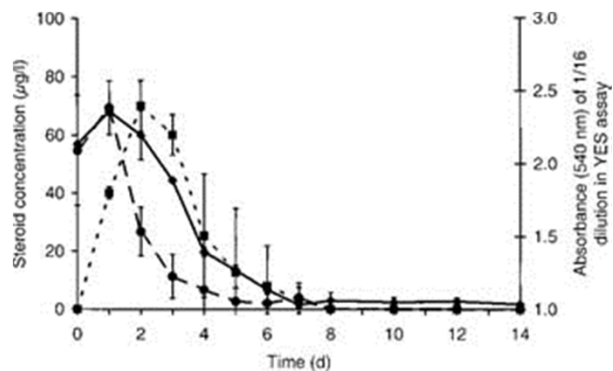
Mineralization of 17 $\beta$ -estradiol (E2) (500  $\mu$ g/L) measured by evolution of  $^{14}$ CO $_2$  from a radiolabeled analogue in river water samples taken from the rivers Aire, Calder, and Thames, UK (means and standard deviations of three replicates).

Environmental Toxicology and Chemistry

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<http://onlinelibrary.wiley.com/doi/10.1002/etc.5620210302/full#fig4>

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### The potential for estradiol and ethinylestradiol degradation in english rivers

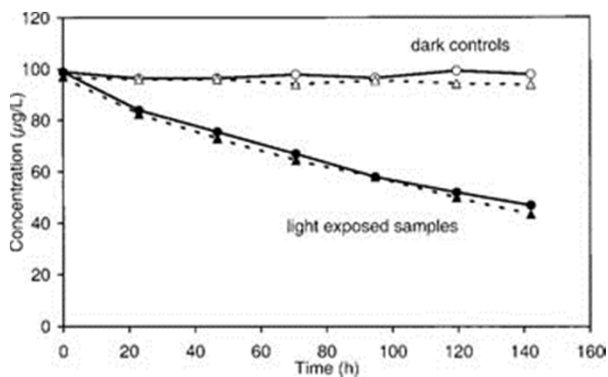


Loss of  $17\beta$ -estradiol (E2) (—•—) with formation and subsequent loss of estrone (E1) (—■—), correlated with overall estrogenicity measured by the yeast estrogen screen (YES) assay (—♦—) for river water collected from the River Thames (March 2, 2000, means and standard deviations of three replicates). Note that where E2 levels rise before falling, it is due to incomplete dissolution of the steroid at time 0.

Environmental Toxicology and Chemistry  
Volume 21, Issue 3, pages 480-488, 5 NOV 2009

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### The potential for estradiol and ethinylestradiol degradation in english rivers



Photodegradation of  $17\beta$ -estradiol (E2) (—▲—) or ethinylestradiol (EE2) (—●—) (means of two replicates; the standard deviation of the replicates was < 3%), compared to dark controls (open symbols).

Environmental Toxicology and Chemistry  
Volume 21, Issue 3, pages 480-488, 5 NOV 2009 DOI: 10.1002/etc.5620210302  
<http://onlinelibrary.wiley.com/doi/10.1002/etc.5620210302/full#fig6>

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## Occurrence in New England

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- ▶ Most work of surface waters has focused on watersheds presumed to be impacted by wastewater
  - ▶ Merrimack, Assabet
  - ▶ USGS, UMass-Amherst, Harvard SPH
- ▶ Groundwater studies have focused on the Cape
  - ▶ Silent Spring Institute
- ▶ Some studies on raw drinking waters
  - ▶ UMass WRF study
- ▶ The good news: little has been found to date



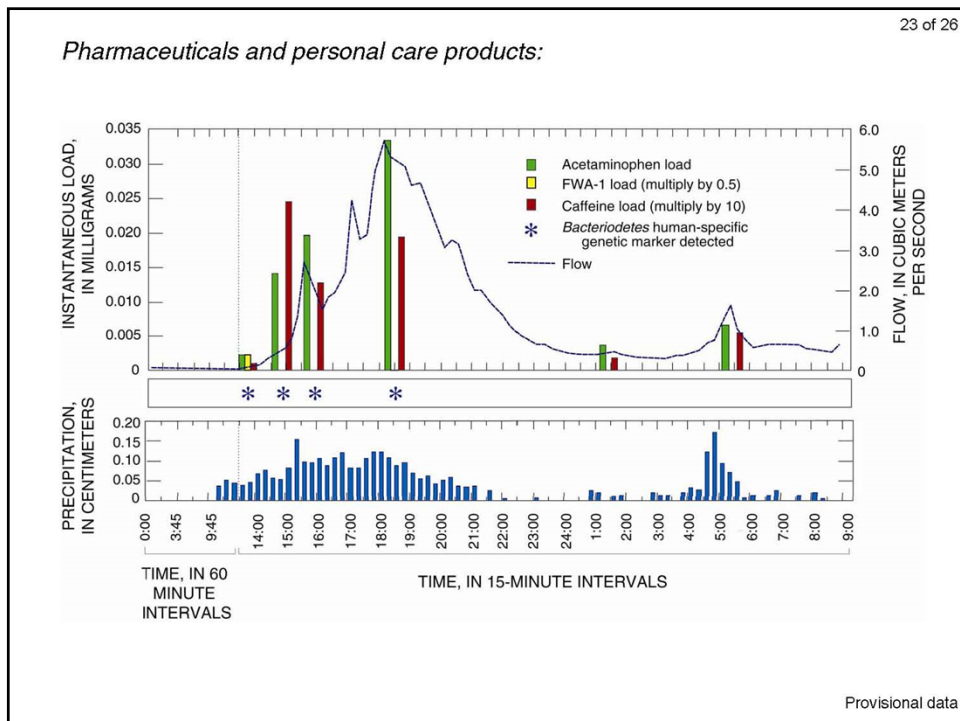
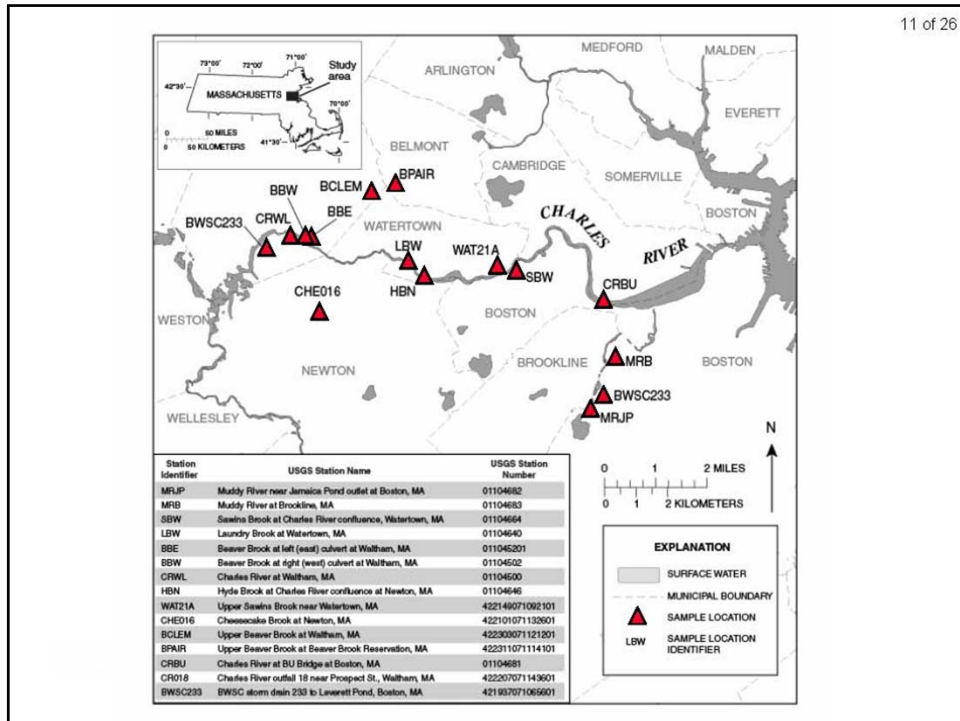
## USGS Survey

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- ▶ 138 stream sampling sites
- ▶ Kolpin et al., 2002







## A General Modeling Approach?

Plosz, B.G., Benedetti, L., Daigger, G.T., Langford, K.H., Larsen, H.F., Monteith, H., Ort, C., Seth, R., Steyer, J.P. and Vanrolleghem, P.A. (2013) Modelling micro-pollutant fate in wastewater collection and treatment systems: status and challenges. *Water Science and Technology* 67(1), 1-15.

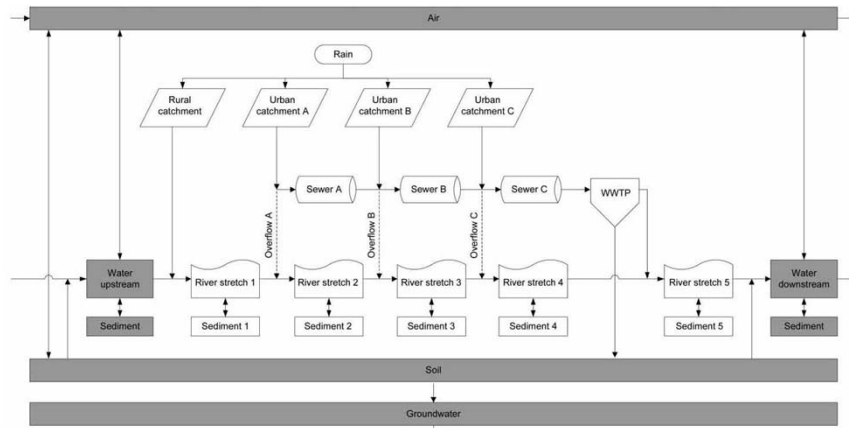
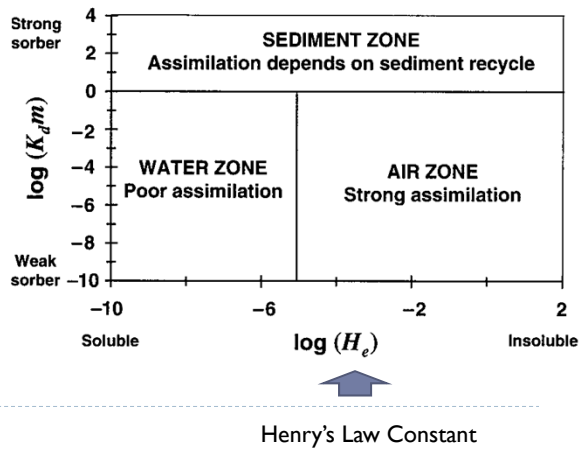


Figure 2 | Schematic representation of the integrated environmental model (IUWS model (white blocks) and MFTM (grey blocks)).

## A simple partition model based on sorption & volatilization effects

### Assumptions

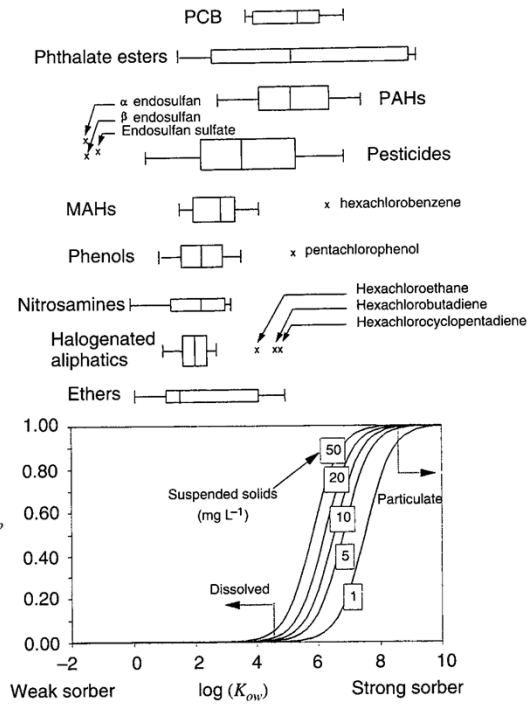
- ▶  $T_a = 283 \text{ K}$
- ▶  $M = 200 \text{ g/mole}$
- ▶  $U_w = 5 \text{ mph}$
- ▶  $v_s = 91 \text{ m/yr}$



## Sorption

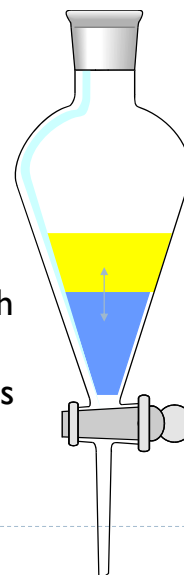
- ▶ Summary of  $K_{ow}$  and TSS effects
- ▶ From Chapra, pg. 722

Fraction particulate  $\rightarrow F_p$



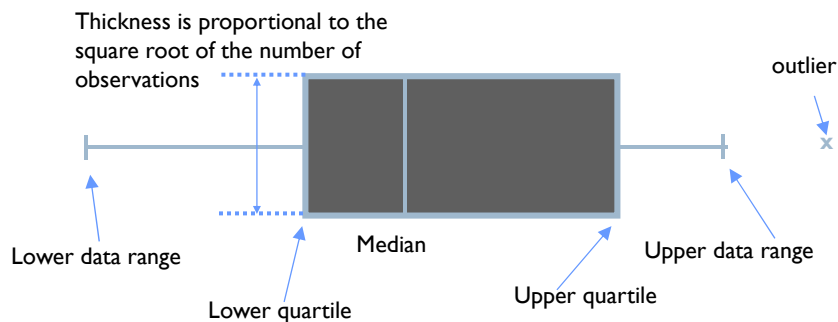
## Octanol:water partitioning

- ▶ 2 liquid phases in a separatory funnel that don't mix
  - ▶ octanol
  - ▶ water
- ▶ Add contaminant to flask
- ▶ Shake and allow contaminant to reach equilibrium between the two
- ▶ Measure concentration in each ( $K_{ow}$  is the ratio)



## Box and Whisker Plots

- ▶ Useful for summarizing non-ideal data distributions



## Classification based on partitioning

- ▶ In terrestrial (soil) systems
  - ▶  $m = 10^5$  to  $10^6$  mg/L
  - ▶ Immobile:  $K_d > 50$  L/kg
  - ▶ Slightly mobile:  $K_d = 5-50$  L/kg
  - ▶ Medium to highly mobile:  $K_d < 5$  L/kg
- ▶ In aqueous systems
  - ▶ @ $m = 100$  mg/L
  - ▶ Particulate based:  $K_d > 10,000$  L/kg
  - ▶ Solution based:  $K_d < 10,000$  L/kg

## Estimation of ( $K_d$ ) partition coefficients

$f_{oc}$  = Fraction of particle that is organic material

- ▶ Relationship to organic fraction

$$K_d = f_{oc} K_{oc} \longrightarrow \left( \frac{mg\text{-tox./g-C}}{mg\text{-tox./m}^3} \right) \text{ or } \left( \frac{m^3}{g-C} \right)$$

- ▶ and properties of organic fraction

$$K_{oc} = 6.17 \times 10^{-7} K_{ow} \longrightarrow \text{Octanol:water partition coefficient}$$

- ▶ combining, we get:

$$K_d = 6.17 \times 10^{-7} f_{oc} K_{ow} \left( \frac{mg\text{-tox./m}^3\text{-Oct.}}{mg\text{-tox./m}^3\text{-H}_2\text{O}} \right)$$

▶ Karickhoff et al., 1979; [Wat. Res. 13:241](#)

## Other correlations

### $K_{oc}$ units

- ▶ Karickhoff, 1979

[Karickhoff et al., 1979; Wat. Res. 13:241](#)

$$K_{oc} = 6.17 \times 10^{-7} K_{ow} \left( \frac{mg\text{-tox./g-C}}{mg\text{-tox./m}^3} \right) \text{ or } \left( \frac{m^3}{g-C} \right)$$

$$K_{oc} = 0.617 K_{ow} \left( \frac{mg\text{-tox./Kg-C}}{mg\text{-tox./L}} \right) \text{ or } \left( \frac{L}{Kg-C} \right)$$

- ▶ Karickhoff, 1981

[Karickhoff 1981; Chemosphere 10:833](#)

$$K_{oc} = 2.57 K_{ow}^{0.84} \left( \frac{mg\text{-tox./Kg-C}}{mg\text{-tox./L}} \right) \text{ or } \left( \frac{L}{Kg-C} \right)$$

- ▶ Schwarzenbach

[Schwarzenbach & Westall 1981; Env. Sci. Techn. 15:1630](#)

$$K_{oc} = 3.09 K_{ow}^{0.72} \left( \frac{mg\text{-tox./Kg-C}}{mg\text{-tox./L}} \right) \text{ or } \left( \frac{L}{Kg-C} \right)$$

▶ Based on neutral organic compounds

## Tetracycline

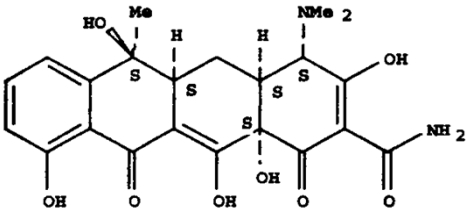
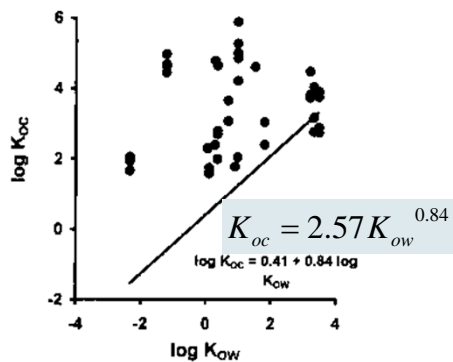
Compound / CAS-Nr / MW	Structure	Physical-chemical properties:
Tetracycline 60-54-8 MW: 444.43		$\log K_{OW}: -1.19^1$ $S: 1.7 \text{ g/L}^2$ $pK_{a,1}: 3.30^2$ $pK_{a,2}: 7.68^2$ $pK_{a,3}: 9.69^2$ $\log K_f(Al^{3+}): 10^{12.5}^3$ $\log K_f(Fe^{3+}): 10^{13.4}^3$
	Tolls, 2001; <a href="#">Env. Sci. Technol.</a> , 35(17)3397	

TABLE 2. Overview of Literature Data on Sorption of VPs to Soils or Soil Constituents <sup>a</sup>			
compound/corollary information	$K_{d,solid}$ (L/kg)	$K_{oc}$ (L/kg)	ref
<b>Tetracycline</b>			
pure Na-bentonite, Langmuir iso, pH dependency, $C_{s,max}$ at pH 6.1: 78 $\mu\text{mol/g}$ , $K_L$ not specified			30
pure Ca-bentonite, Langmuir iso, $C_{s,max}$ at pH 6.1: 200 $\mu\text{mol/g}$ , $K_L$ not specified			30
bentonite modified with cationic surfactant (C <sub>12</sub> -trimethylammonium), Langmuir iso, $C_{s,max}$ at pH 6.1: 38 $\mu\text{mol/g}$ , $K_L$ not specified			30
bentonite modified with tannic acid, Langmuir iso, $C_{s,max}$ at pH 6.1: 210 $\mu\text{mol/g}$ , $K_L$ not specified			30
pure montmorillonite clay mineral, Langmuir iso, $C_{s,max}$ at pH 5.0: 540 $\mu\text{mol/g}$ , $K_L$ not specified			31
clay loam, Topeka, KS <sup>b</sup>	> 400		57
soil organic matter (peat), Nova Scotia; pH 4.55	1 620		24
soil organic matter (peat), Nova Scotia; pH 6.14, iso's nonlinear	1 140		24

▶ Tolls, 2001; [Env. Sci. Technol.](#), 35(17)3397

- Nearly all values fall above Karickhoff's relationship



► Tolls, 2001; *Env. Sci. Technol.*, 35(17)3397

## Structure and sorption

- Enrofloxacin and Decarboxy Enro

Compound / CAS-Nr / MW	Structure	Physical-chemical properties:
Enro - CO <sub>2</sub> MW: 315.20 131775-99-0	 Enro - CO <sub>2</sub> = Decarboxylated enrofloxacin	log $K_{ow}$ : n.a. S: n.a. p $K_{a,1}$ : ca 8.3 <sup>8</sup>
Enrofloxacin 93106-60-6 MW: 359.40		log $K_{ow}$ : 1.1 <sup>6</sup> 130 g/L <sup>7</sup> p $K_{a,1}$ : 6.27 <sup>7</sup> p $K_{a,2}$ : ca 8.3 <sup>8</sup> log $K_f$ : n.a.

$K_d$  (L/Kg)

7.7

500

Both based on same soil (8% clay fraction, montmorillonite)

Tolls, 2001; *Env. Sci. Technol.*, 35(17)3397

► [To next lecture](#)

