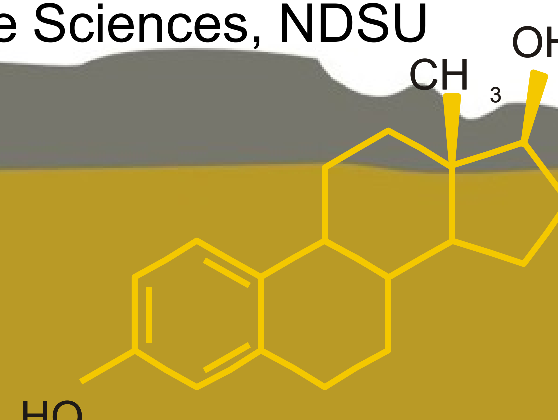
Fate and Transport of Estrogenic Hormones in Subsurface Waters

Francis X.M. Casey

Professor and Director, School of Natural Resource Sciences, NDSU



17β-Estradiol

Shepherd (online) EXPRESS

Cover Story - Volume 19, Issue 3 - ©1998

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What the Frogs Are Trying to Tell Us

BY BRIAN LAVENDEL

DECCAN HERALD

Saturday November 22, 2003

Declining male fertility

PIONEER PRESS

Published on June 28, 2003

ESTROGEN IN LAKE BENDS THE GENDER OF MALE FISH IN TEST

Source: SETH BORENSTEIN

PIONEER PRESS

Published on September 10, 1989

THE FIGHT OVER FOOD//HORMONES ...WORRY ABOUT THE SAFETY OF RESIDUES IN THEIR FOOD.

Lee Egerstrom, Staff Writer

The Washington Times

Published on February 15, 1998

Number of gators falling again

MIAMI - hormonal problem

BBC NEWS

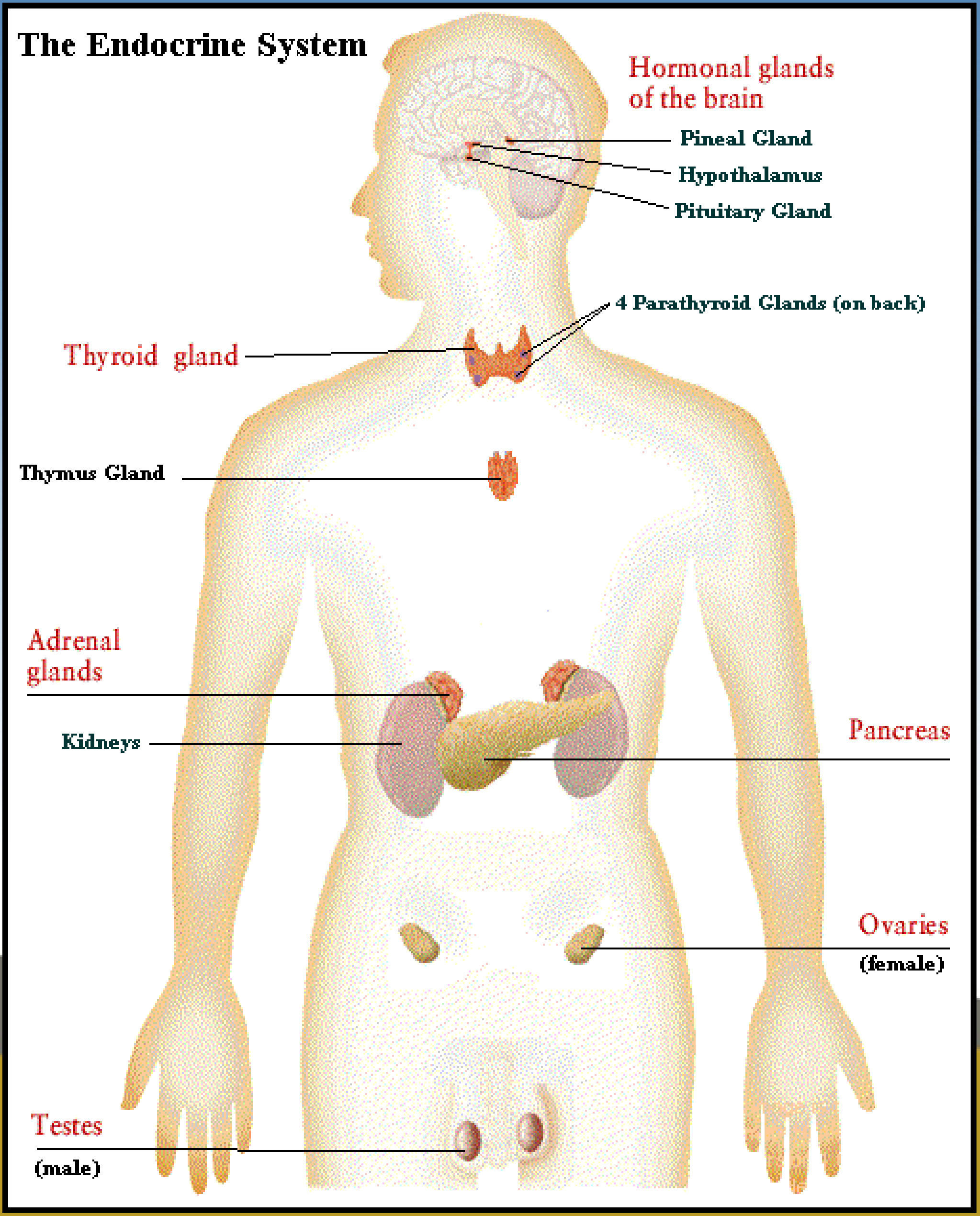
'Gender-bender' threat to marine life

By Helen Briggs, science reporter

Endocrine
Disrupting
Compounds
EDCs

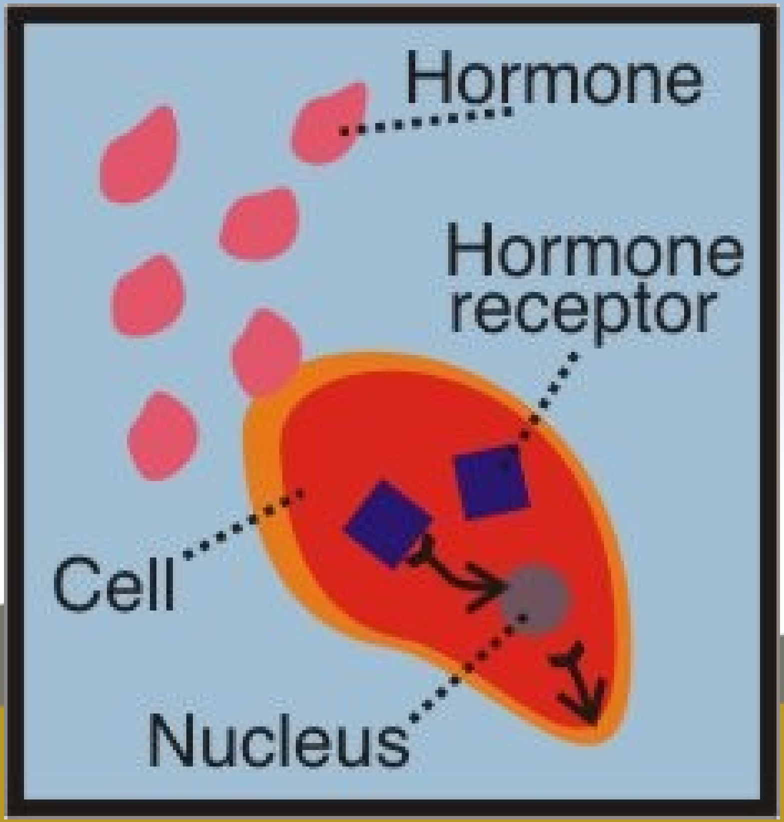
"chemicals that can induce adverse health effects by disruption of an organism's endocrine system or normal development"

(Ashby et al., 1997)

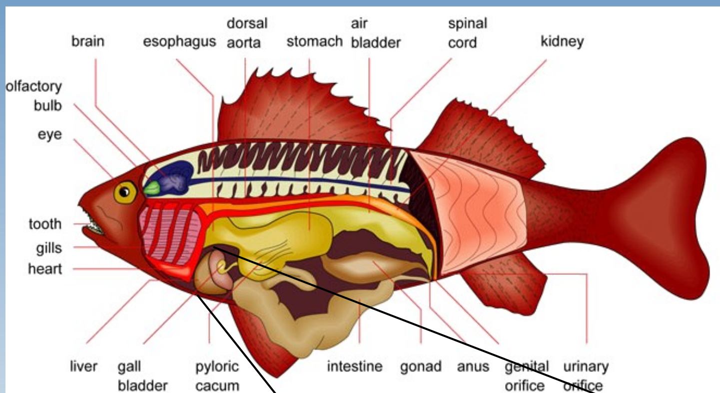


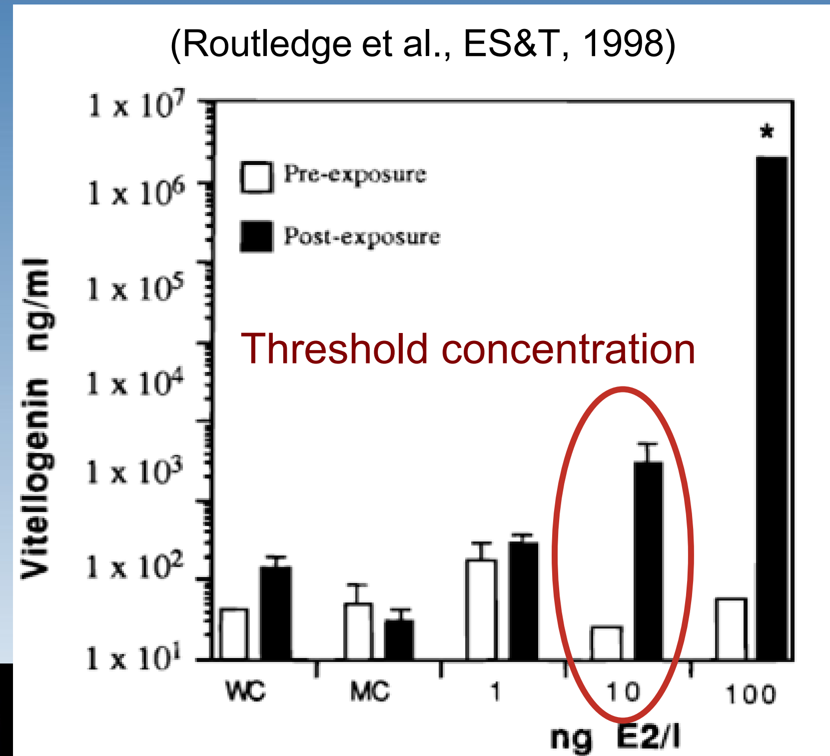
Exogenous Hormones are EDCs

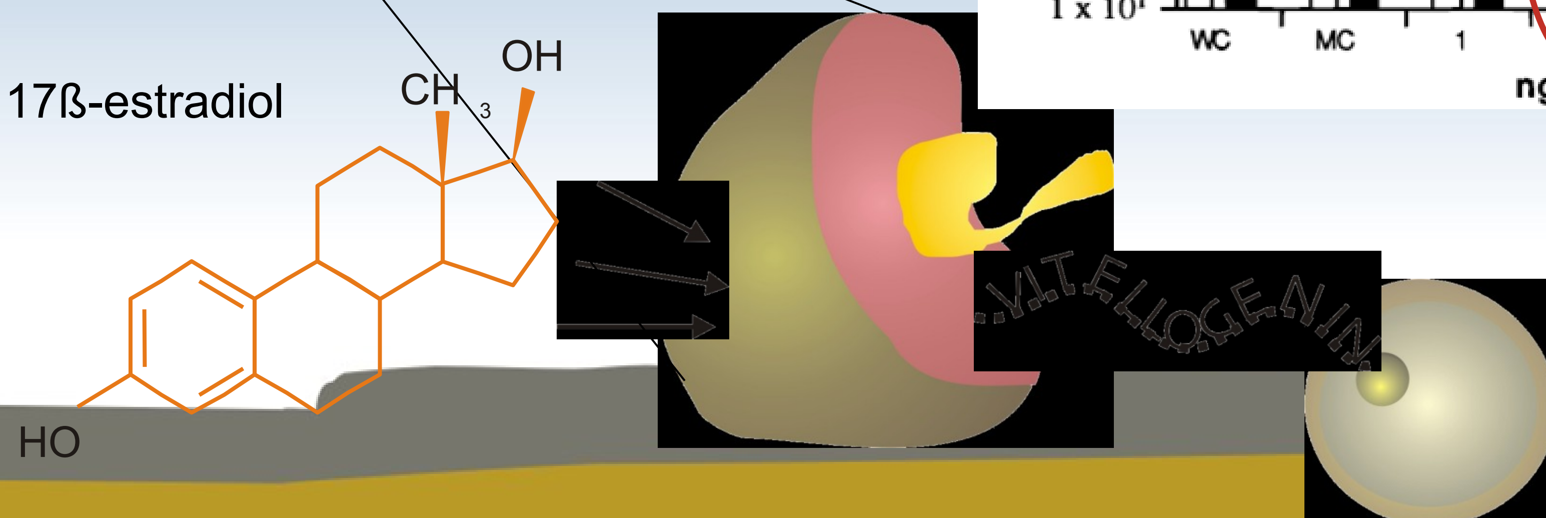
- Exogenous Hormones mimic an endogenous hormone and bind strongly to hormone receptors.
- Fish are especially susceptible to EDCs b/c of their special sexual adaptive strategies



17ß-estradiol



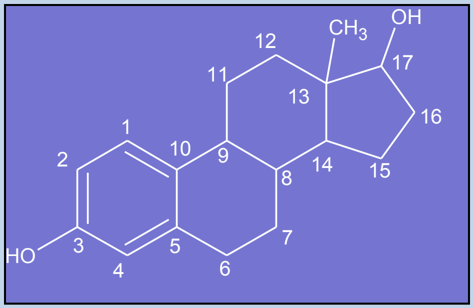




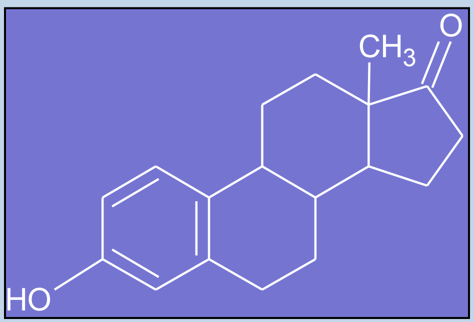
Panter et al. (ES&T 2002) intermittent exposure (alternate days, 1 day in 4, or 3 days in 6) to 0.120 □g L^{-1} E2 = significant vitellogenin induction in fathead minnows (*Pimephales promelas*).

Natural Hormones

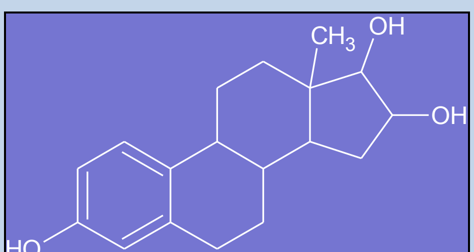
Structural differences occur in the arrangement of functional groups at the C-16 and C-17 on the D-ring structure



17β-Estradiol (E2)

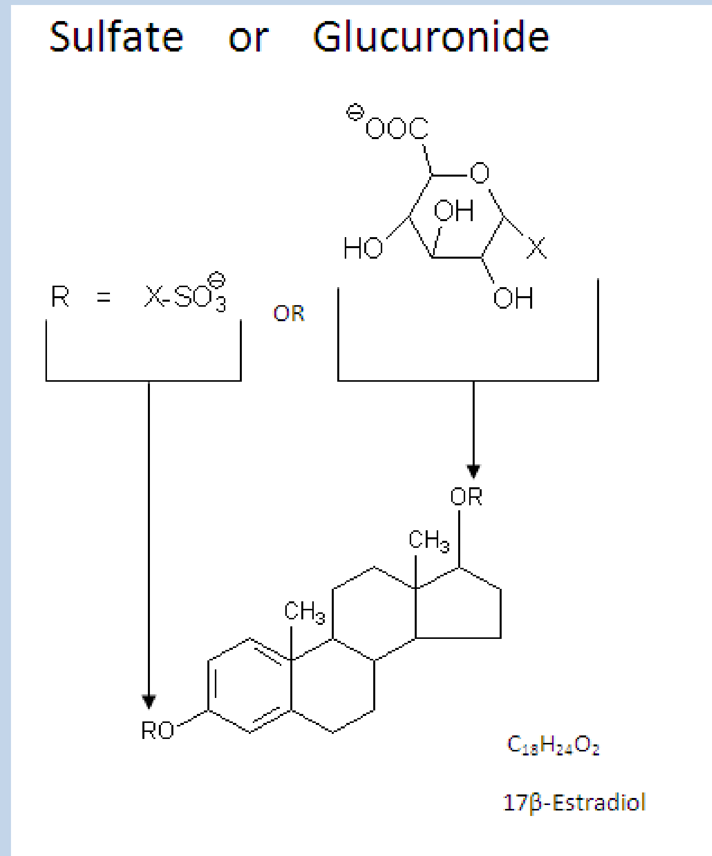


Estrone (E1)



Estriol (E3)

Majority of excreted estrogens are conjugated considered to be biologically inactive



Animal Estrogen Excretion Dwarfs Humans

- 6.7 billion humans = 26.8 metric tons/year estrogen
- US+EU Animals = 82 metric tons/year

Potential for Contamination

- Shore et al. (1998) measured 30 ng g^{-1} 17β-estradiol in poultry litter.
- 1997 U.S. poultry produced over ten billion kg of broiler litter
  - 90% applied to fields
  - Potentially contained 270 kg 17β-estradiol.
- Worse case, 27,000,000,000,000 L of water contaminated at 10 ng L^{-1}.
  - Enough to cover North Dakota in nearly 3” of rain.

Analyzing the Ignored Environmental Contaminants

The U.S. Geological Survey reports some of the first monitoring data on pharmaceuticals and other emerging organic wastewater contaminants in U.S. streams.

BRITT E. ERICKSON

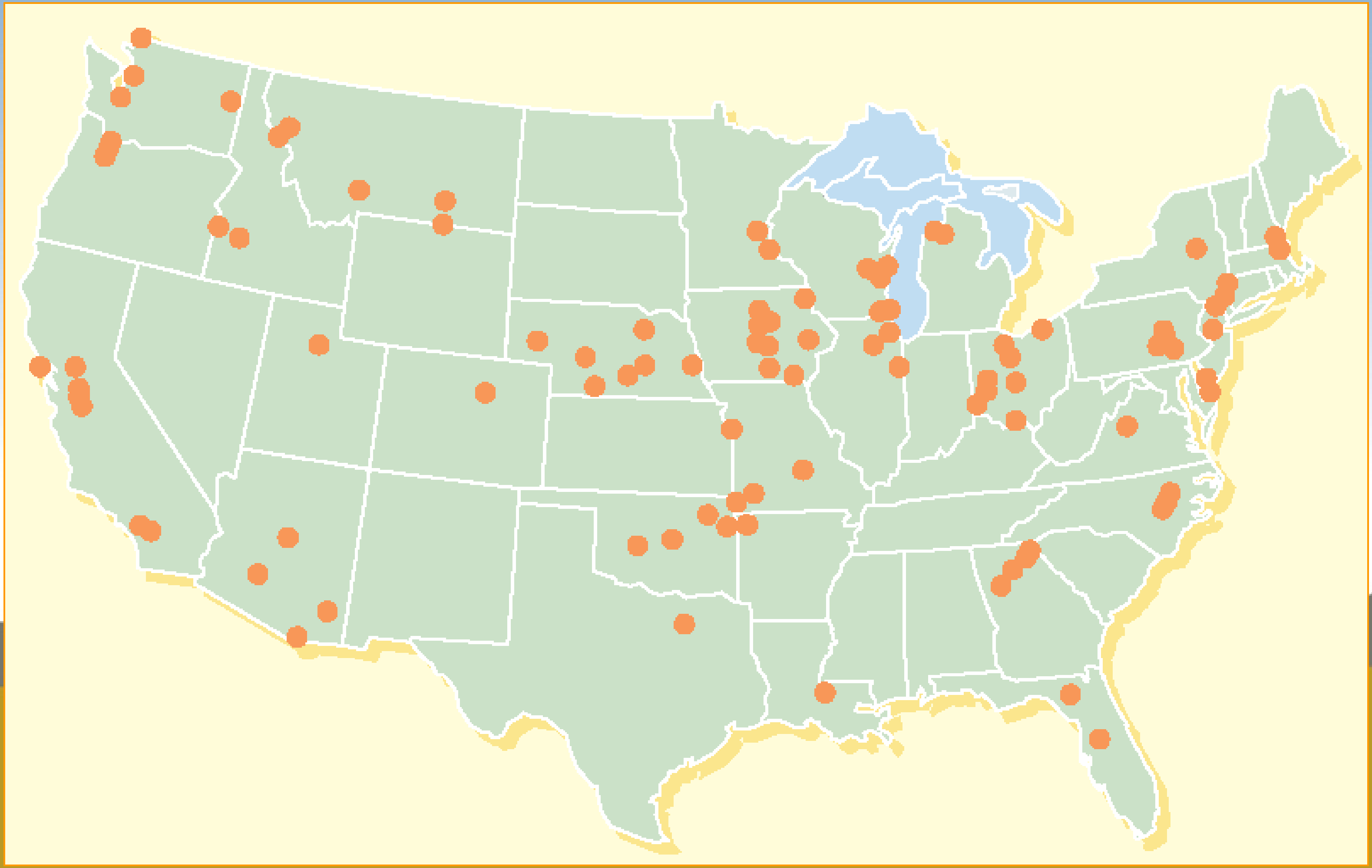
As analytical chemists develop new tools for detecting organic wastewater contaminants, the number of compounds they find in the environment continues to grow. Low levels of reproductive hormones, steroids, antibiotics, and numerous other prescription and nonprescription drugs, as well as some of their metabolites, have been detected in European waters and, more recently, in U.S. streams. Along with pharmaceuticals, products used in everyday life, such as detergents, disinfectants, fragrances, insect repellants, fire retardants, and plasticizers, are turning up in aquatic environments.

© 2002 American Chemical Society

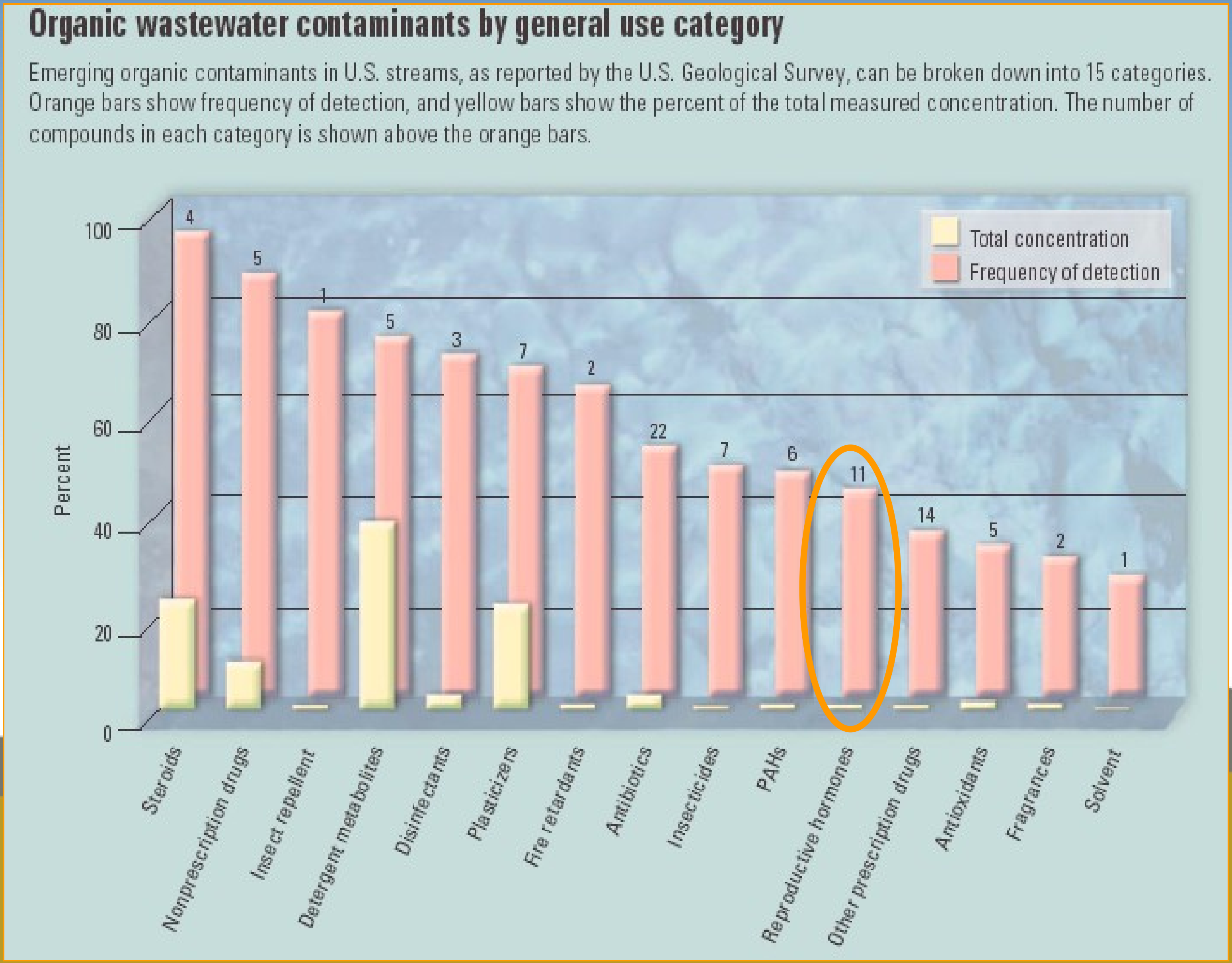
A National Reconnaissance by Koplin et al. (2002)

Reference 777 times since 2002

139 streams in 38 states were tested for pharmaceuticals, reproductive hormones, and other organic compounds.



Chemical sources include agricultural, industrial, and residential



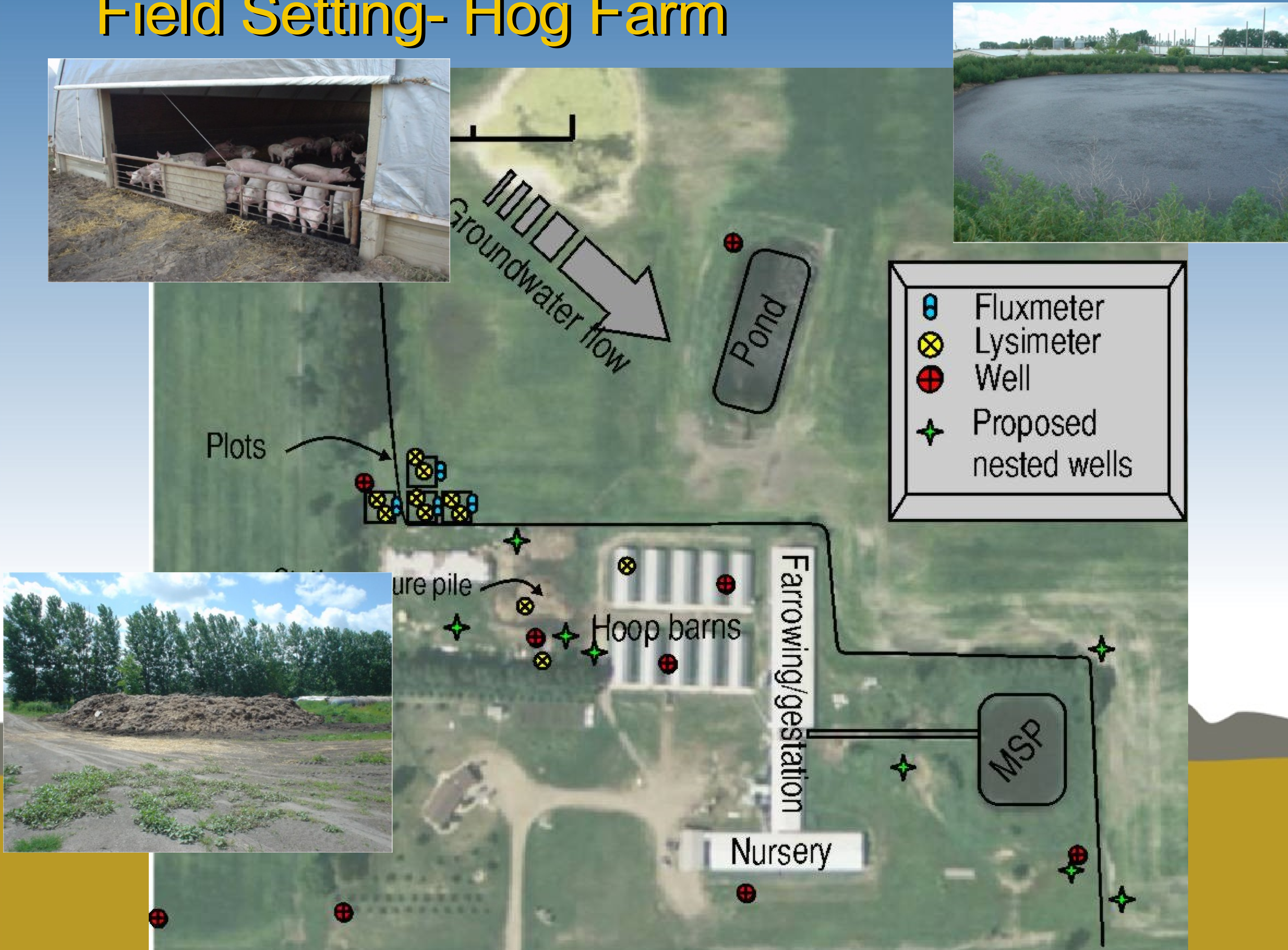
How does it get into the Environment?

- Evidence of hormone movement from manured lands into surface and ground water in concentrations that may affect wildlife (e.g., Peterson et al., 2000; Bushee et al., 1998; Nichols et al., 1997)
- Hog waste sprayed onto crop fields contains high levels of natural estrogens (Servos et al., 1998).
- On-farm measurements were enough to cause premature utter development in heifers (Shore et al., 1998)

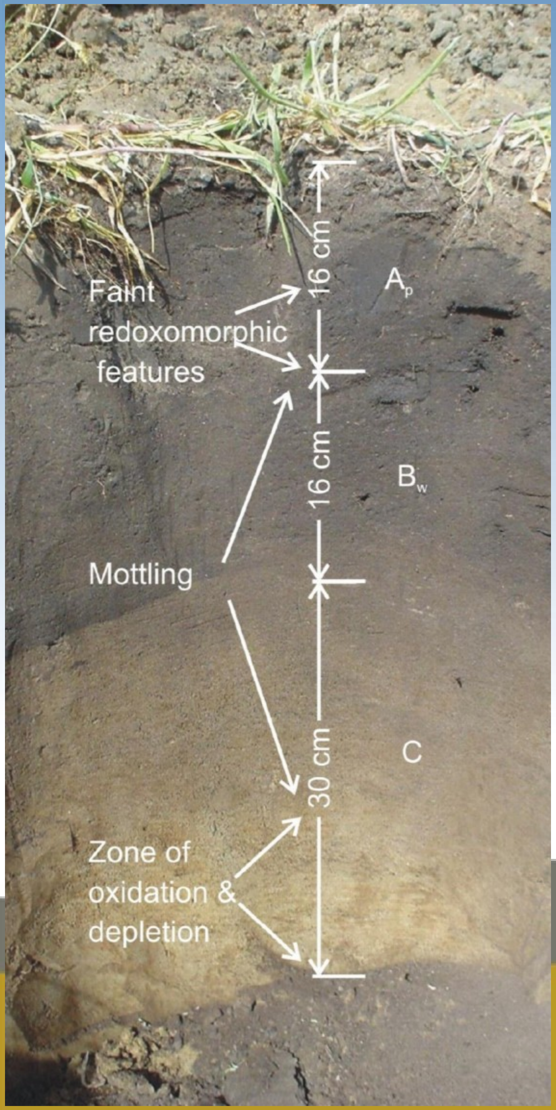
Fate and Transport

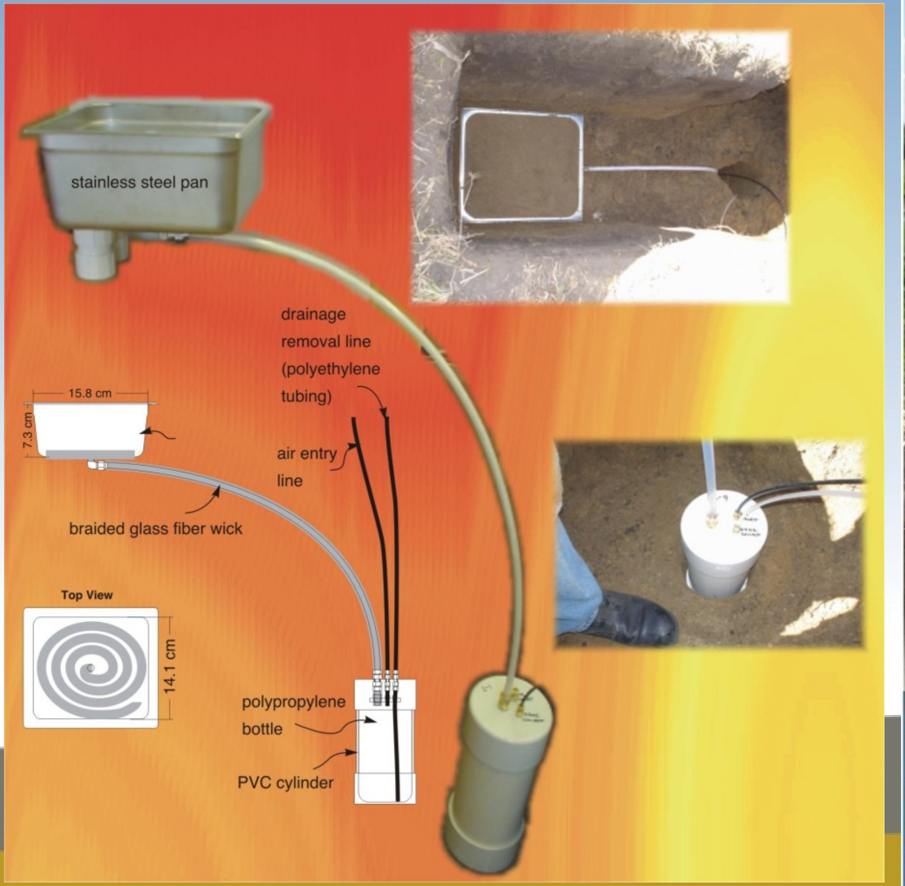
Laboratory
vs.
Field

Field Setting- Hog Farm



Hecla–Hamar Series/loamy fine sand:

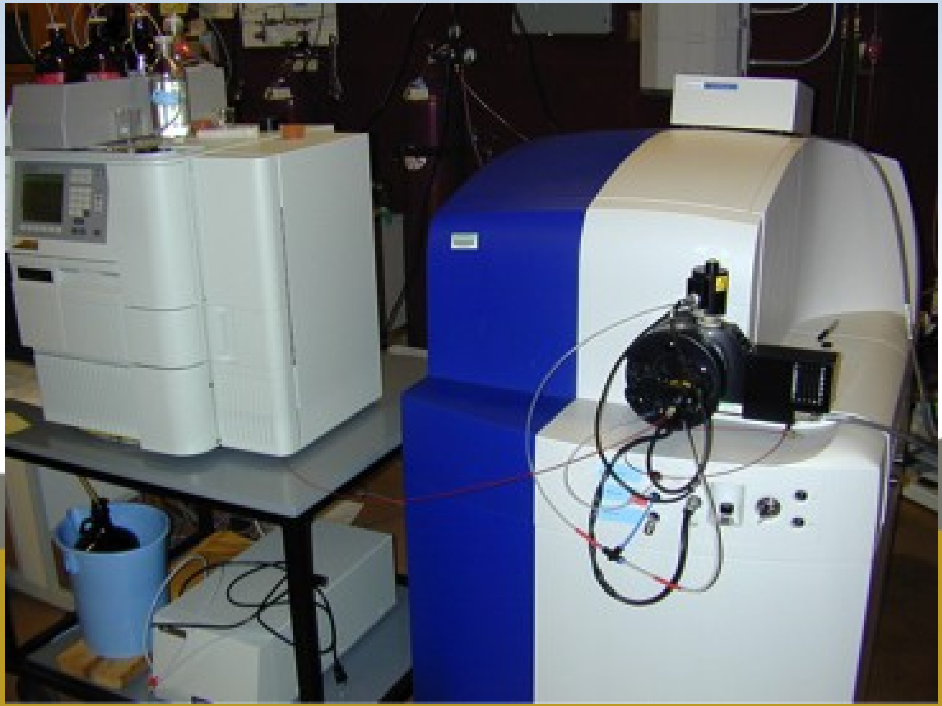




17β-Estradiol Identification and Quantification

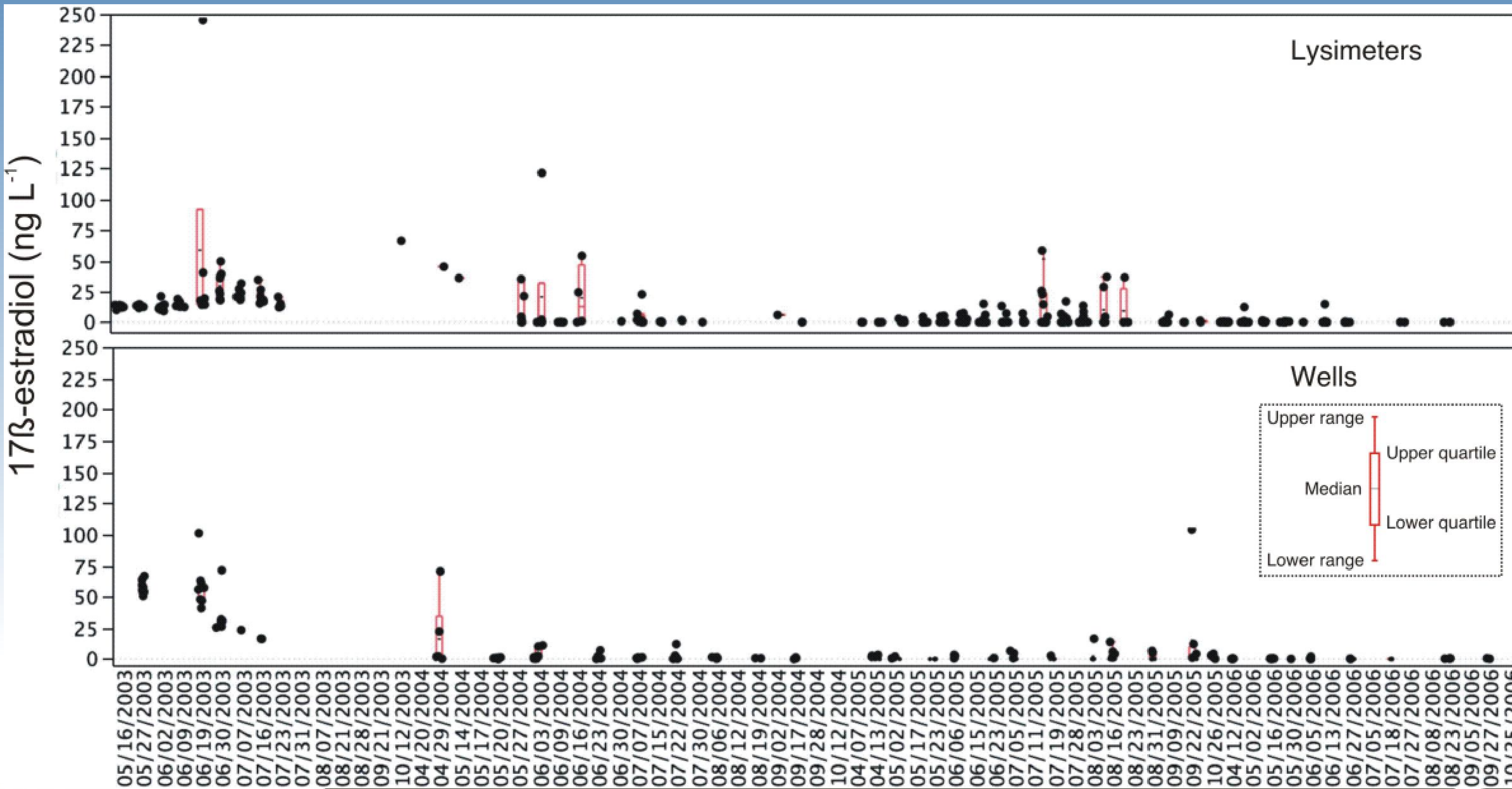
Liquid chromatography Mass spec /Mass spec

- (First MS identifies molecular ion)/(2nd MS identifies & quantifies on fragment ions)
- This is coupled with the retention times that have a drift error of +/- 5% retention time
- 25 pg mass on-column reliably detected using selected ion monitoring



Analytical Methods

- Waters Q-TOF Ultima API-US
- Negative ion mode (ES-)
- Capillary voltage = 2.33
- Cone voltages = 55
- Source temp = 120 ° C
- Desolvation temp = 400° C
- Cone gas flow= 0 L h^{-1}
- Desolvation gas flows = 500 L h^{-1}
- Injection volumes = 10 µL


17ß-estradiol (ng L-1)
Lysimeters
Wells
250
225
200
175
150
125
100
75
50
25
0
Upper range
Upper quartile
Median
Lower quartile
Lower range
05/16/2003
05/27/2003
06/02/2003
06/09/2003
06/19/2003
06/30/2003
07/07/2003
07/16/2003
07/23/2003
07/31/2003
08/07/2003
08/21/2003
08/28/2003
09/21/2003
10/12/2003
04/20/2004
04/29/2004
05/14/2004
05/17/2004
05/20/2004
05/27/2004
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06/09/2004
06/16/2004
06/23/2004
06/30/2004
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07/15/2004
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08/06/2004
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08/03/2005
08/16/2005
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08/31/2005
09/09/2005
09/22/2005
10/26/2005
04/12/2006
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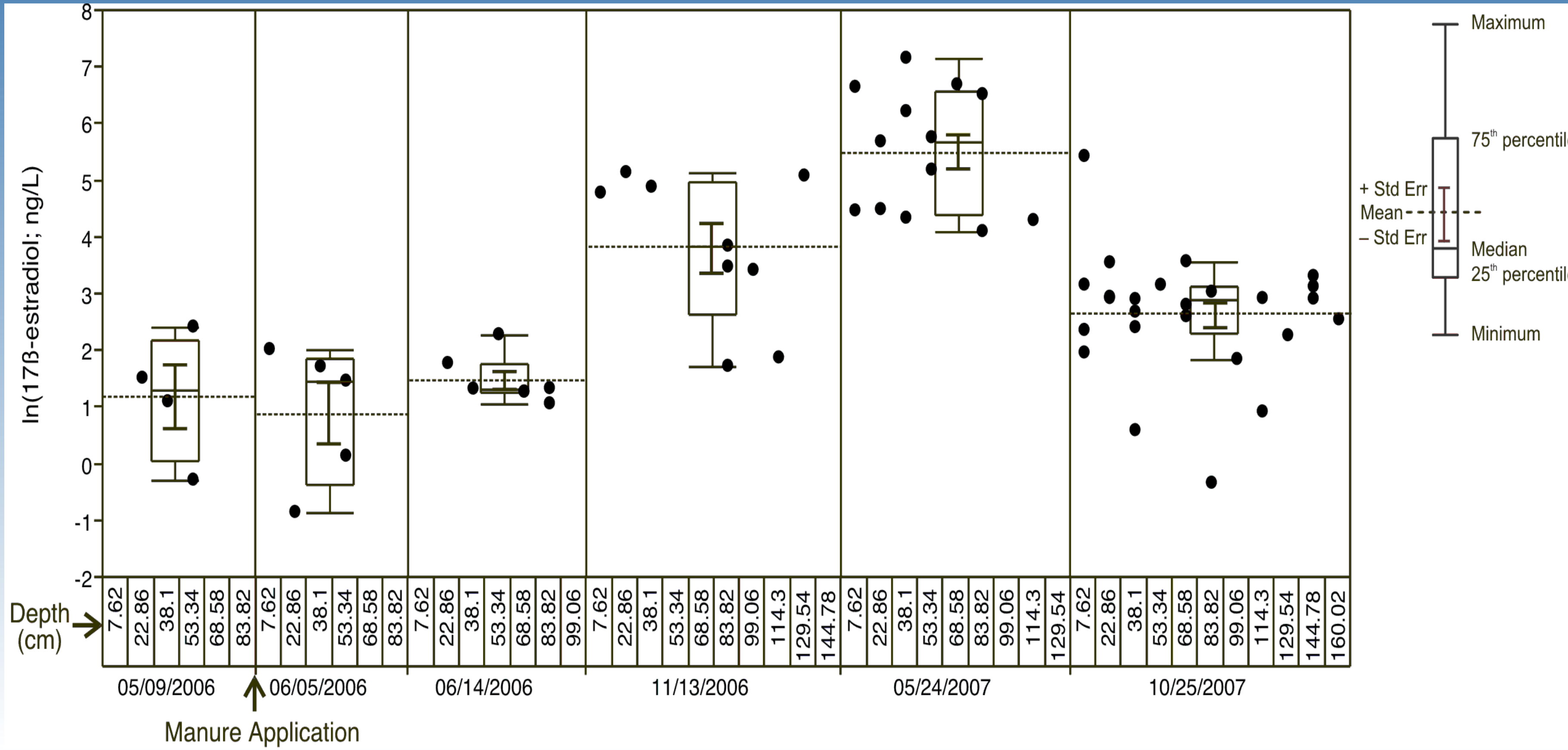
142nd Ave SE



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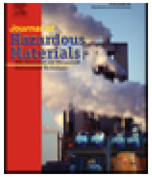
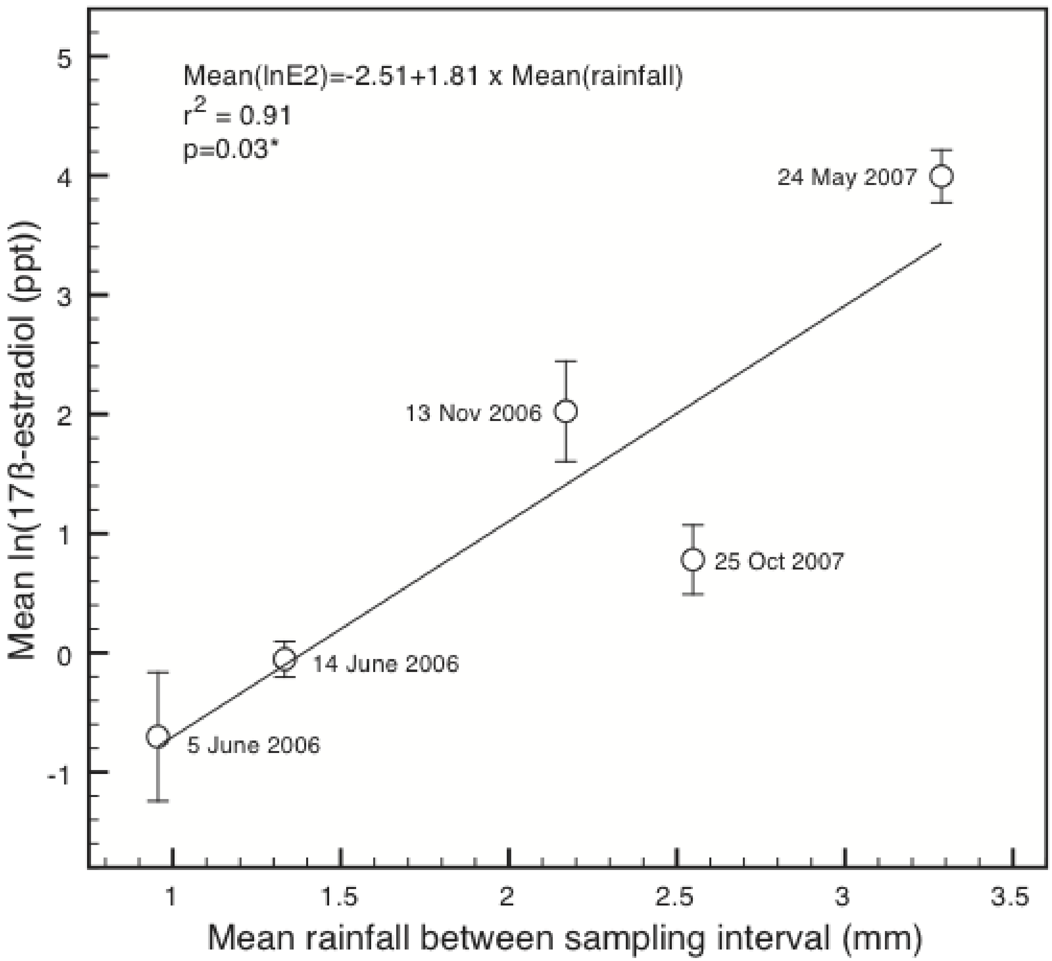


Effects of field-manure applications on stratified 17β-estradiol concentrations

Mary C. Schuh[a], Francis X.M. Casey[b,*], Heldur Hakk[c],
Thomas M. DeSutter[b], Karl G. Richards[d], Eakalak Khan[e], Peter G. Oduor[f]


Mean(lnE2)=-2.51+1.81 x Mean(rainfall)
r2 = 0.91
p=0.03*
24 May 2007
13 Nov 2006
25 Oct 2007
14 June 2006
5 June 2006
Mean ln(17β-estradiol (ppt))
Mean rainfall between sampling interval (mm)
5
4
3
2
1
0
-1
1
1.5
2
2.5
3
3.5

Shallow piezometer field samples

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Chemosphere

journal homepage: www.elsevier.com/locate/chemosphere

Occurrence and pathways of manure-borne 17β-estradiol in vadose zone water

Michael L. Thompson [a], Francis X.M. Casey [b,*], Eakalak Khan [c], Heldur Hakk [d], Gerald L. Larsen [d], Thomas DeSutter [b]

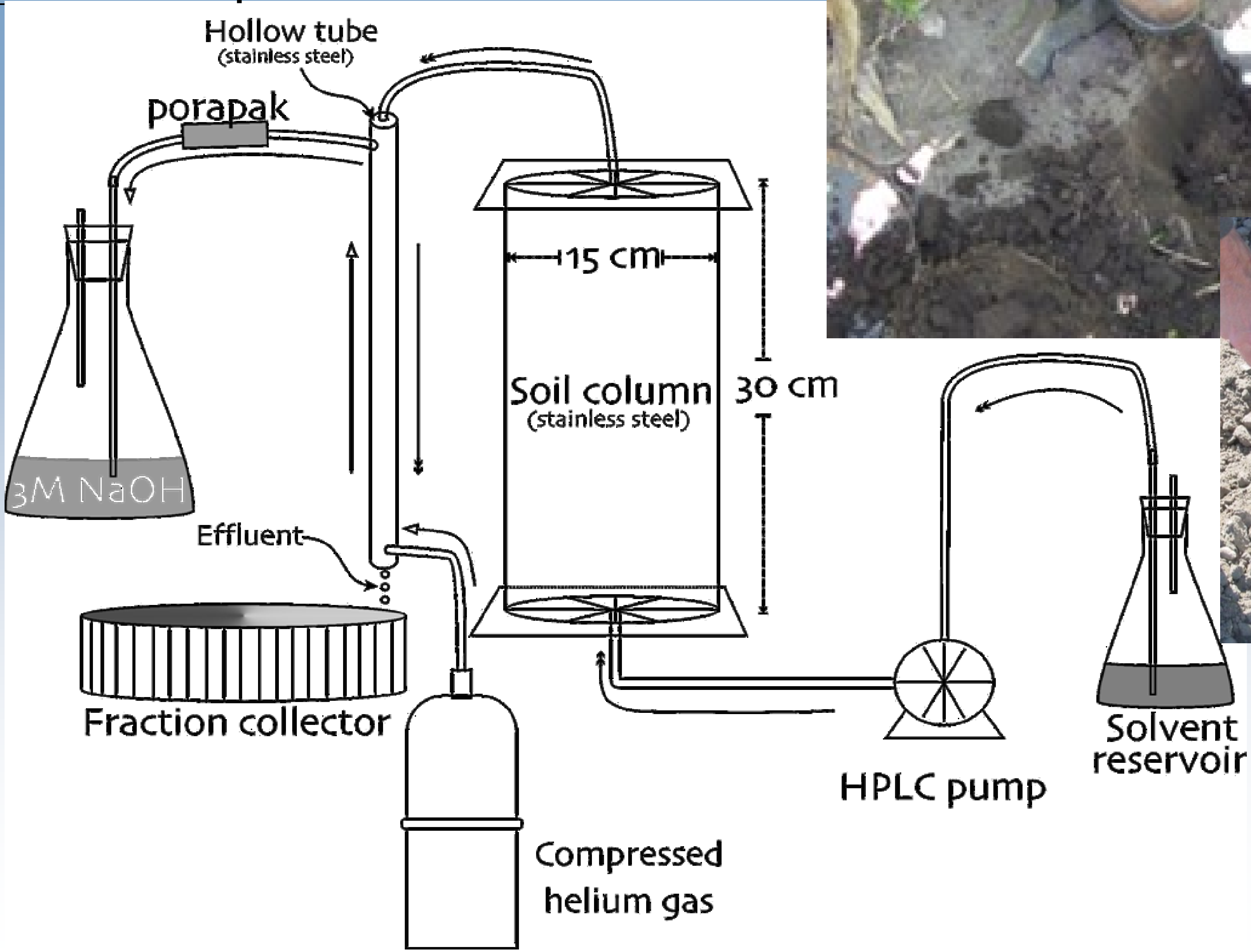
Fate and Transport

Laboratory

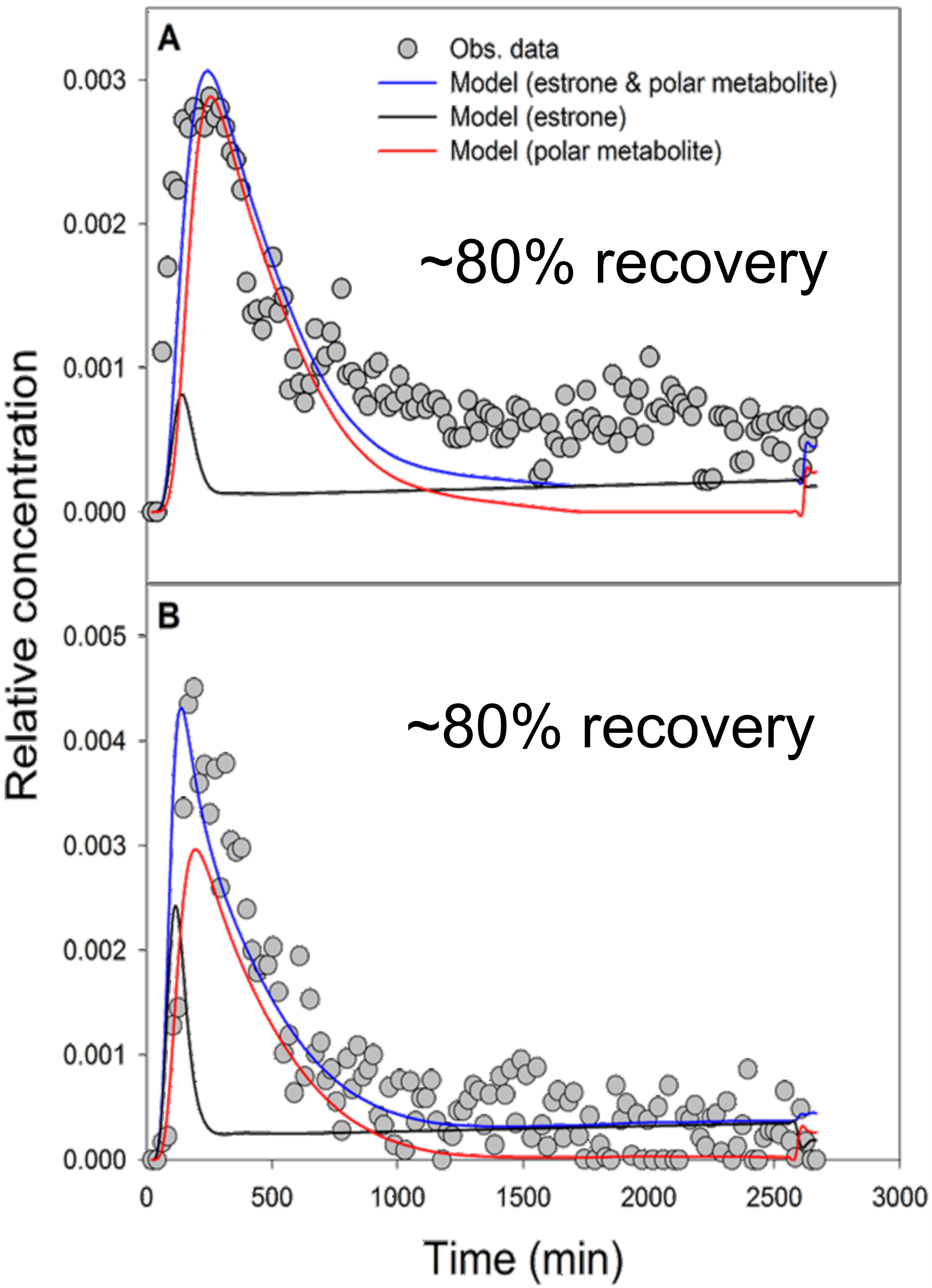
vs.

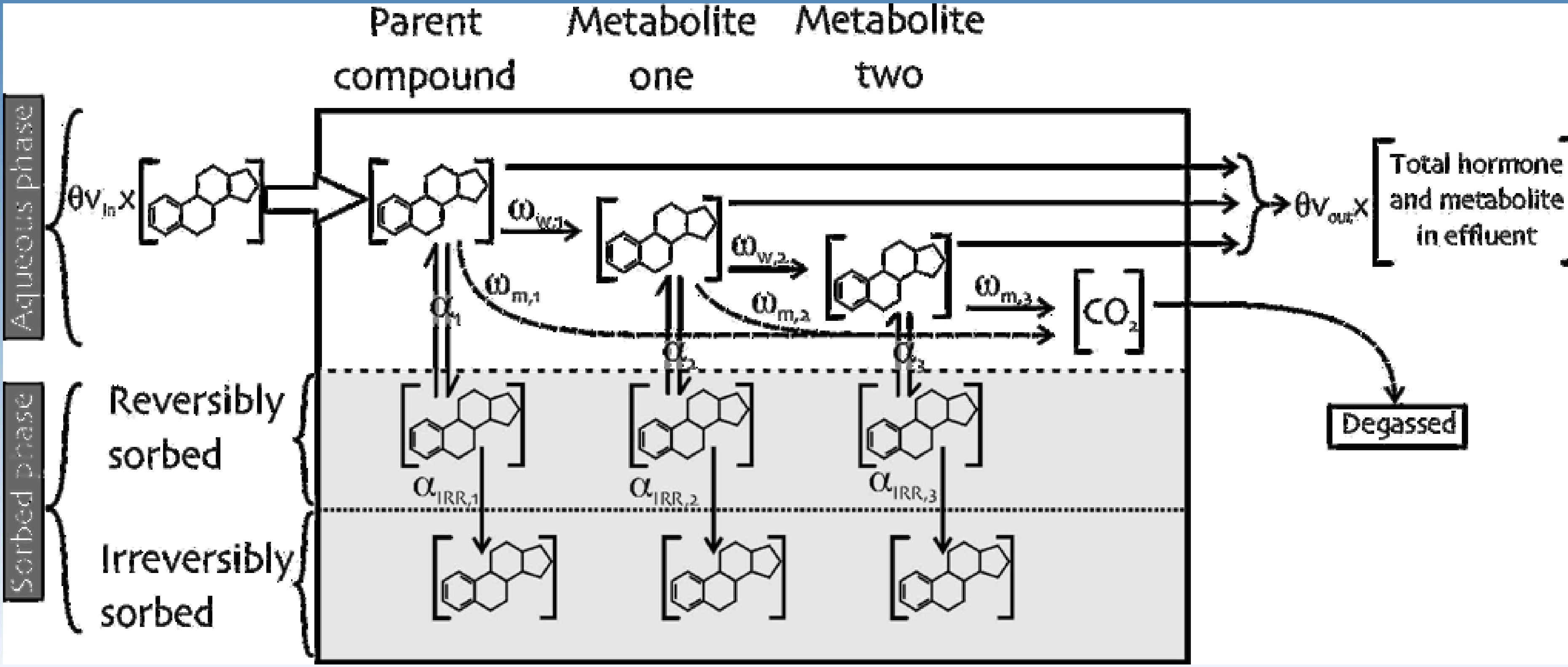
Field

- Trapped $^{14}CO_2$
- Inject $HgCl_2$ to sterilize at end of experiment



17ß-estradiol



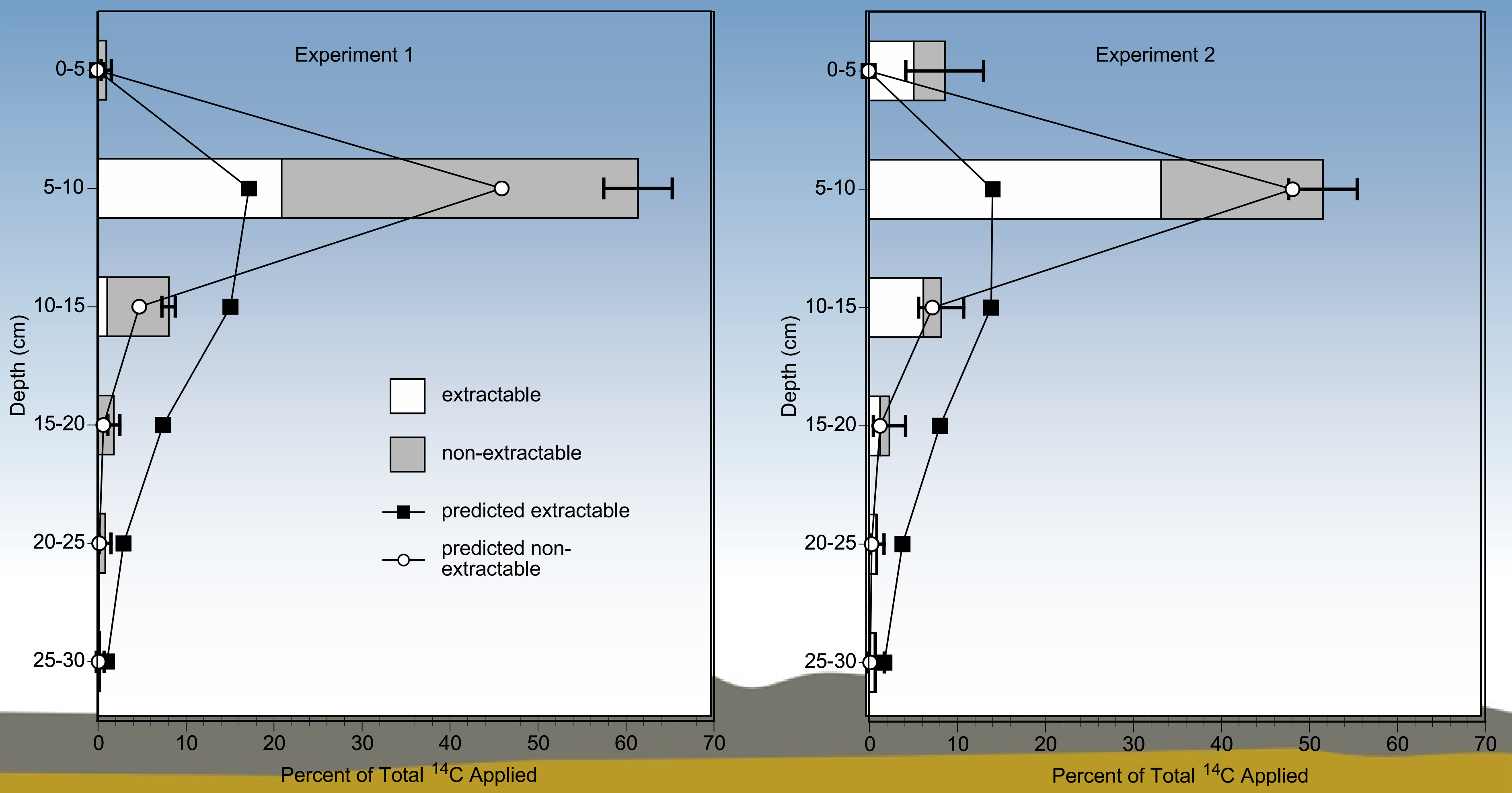


$$\theta \frac{\partial C_1}{\partial t} + \rho_b \frac{\partial S_{r,1}}{\partial t} = \theta v \lambda \frac{\partial^2 C_1}{\partial x^2} - \theta v \frac{\partial C_1}{\partial x} - (\omega_{irr,1} + \omega_{s,1})\rho_b S_{r,1} - (\omega_{w,1} + \omega_{w,2})\theta C_1$$

$$\theta \frac{\partial C_2}{\partial t} + \rho_b \frac{\partial S_{r,2}}{\partial t} = \theta v \lambda \frac{\partial^2 C_2}{\partial x^2} - \theta v \frac{\partial C_2}{\partial x} + \omega_{w,1}\theta C_1 - \omega_{irr,2}\rho_b S_{r,2} + \omega_{s,1}\rho_b S_{r,1}$$

$$\theta \frac{\partial C_3}{\partial t} + \rho_b \frac{\partial S_{r,3}}{\partial t} = \theta v \lambda \frac{\partial^2 C_3}{\partial x^2} - \theta v \frac{\partial C_3}{\partial x} + \omega_{w,2}\theta C_1 - \omega_{irr,3}\rho_b S_{r,3}$$

Concentration Distribution



17ß-estradiol Column
Fan et al. (2008)

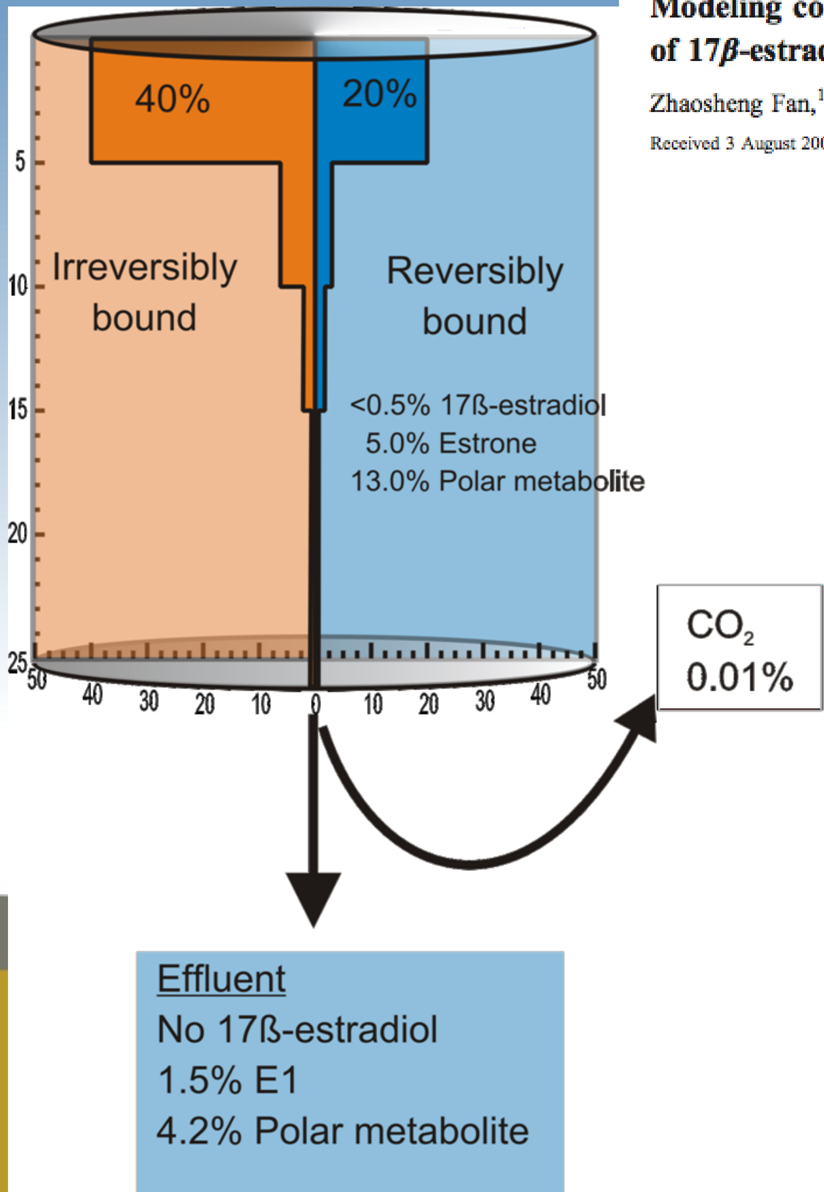
WATER RESOURCES RESEARCH, VOL. 44, W08424, doi:10.1029/2007WR006407, 2008

Click Here for Full Article

Modeling coupled degradation, sorption, and transport of 17β-estradiol in undisturbed soil

Zhaosheng Fan,[1] Francis X. M. Casey,[2] Heldur Hakk,[3] and Gerald L. Larsen[3]

Received 3 August 2007; revised 10 April 2008; accepted 9 June 2008; published 16 August 2008.



7mL/min

oil

17ß-estradiol

- Immobile – 40% irreversibly bound
- Readily degrades – < 0.5% of original E2 was recovered in soil and none in the effluent

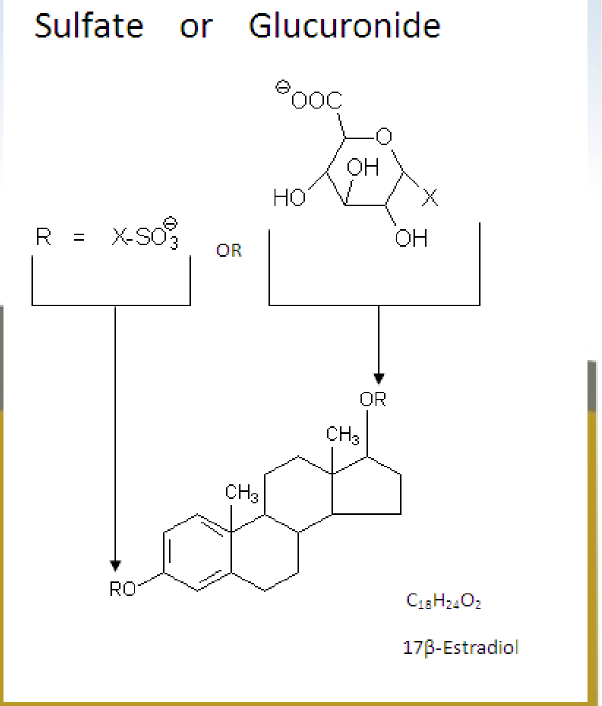
Research Questions

If estrogens are short lived (<1day) and bind readily and strongly to soil, they why are they detected so frequently in the environment?

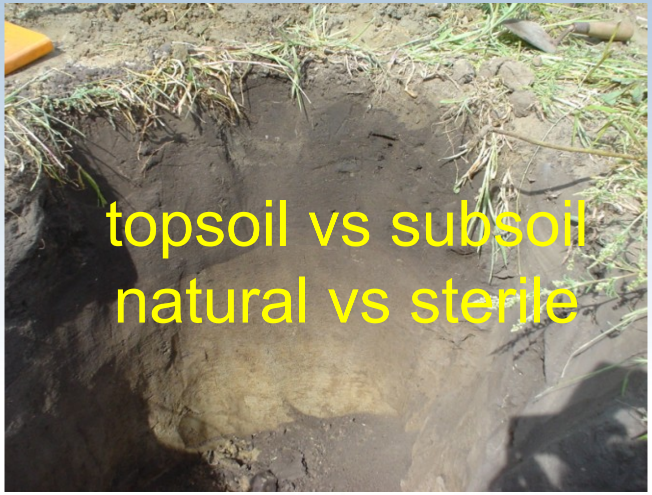
Explaining Movement and Persistence

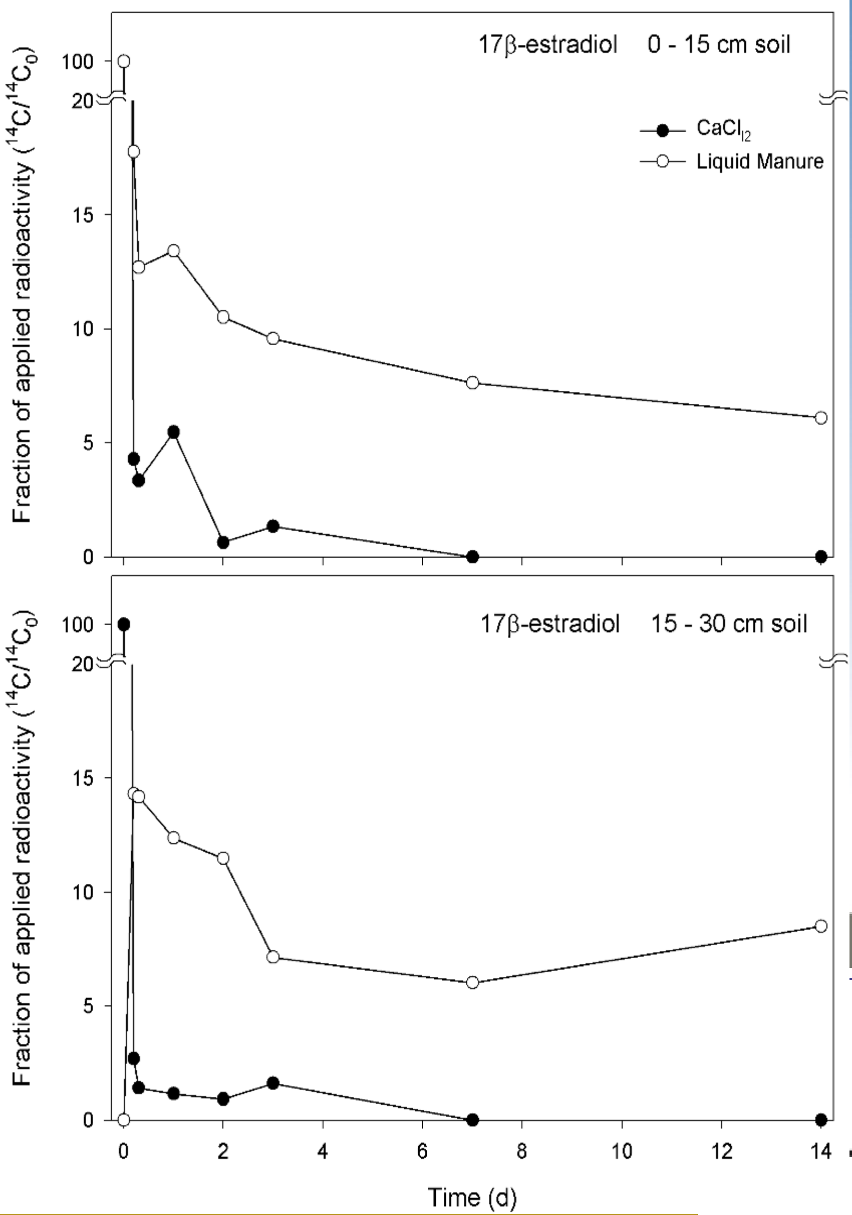
1. What is the role of dissolve and colloidal fractions?
   – Holbrook et al. (2004) indicated that up to **60% of aqueous E2** and EE2 concentrations may be **associated with organic colloids** in wastewater.

2. What is the role of hormone conjugates?



Batch studies





Batch Soil Experiment Comparing

- DOC/COC (derived from liquid swine manure) spiked with ^{14}C E2
- $CaCl_2$ (control) spiked with ^{14}C E2

Results

- E2 is gone in $CaCl_2$ solution by 7 days
- E2 persists in DOC/COC solution at least to 14 days

Conclusions

- DOC/COC causes E2 to remain suspended and inhibits E2 from binding to soil
- DOC/COC causes E2 to persist longer in solution compared to the $CaCl_2$ (control)

Kim Zitnick-Anderson's Master study, 2010

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journal homepage: www.elsevier.com/locate/jhazmat

Effects of liquid swine manure on dissipation of 17β-estradiol in soil

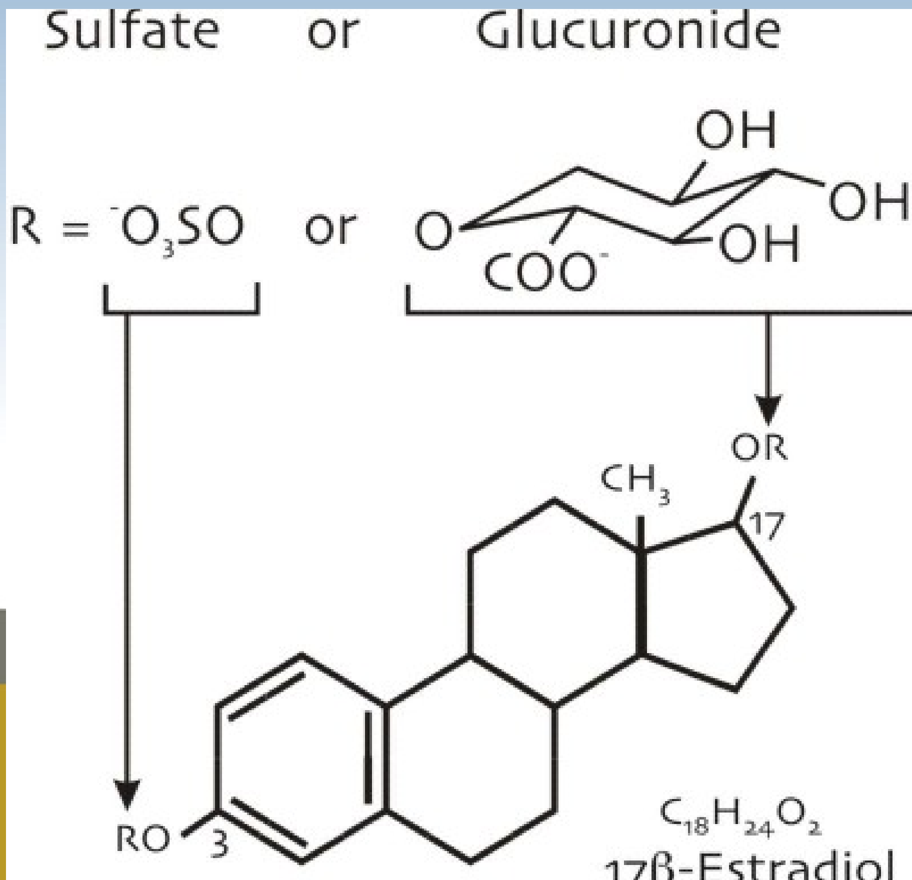
K.K. Zitnick[a], N.W. Shappell[b], H. Hakk[b], T.M. DeSutter[c], E. Khan[d], F.X.M. Casey[c,*]

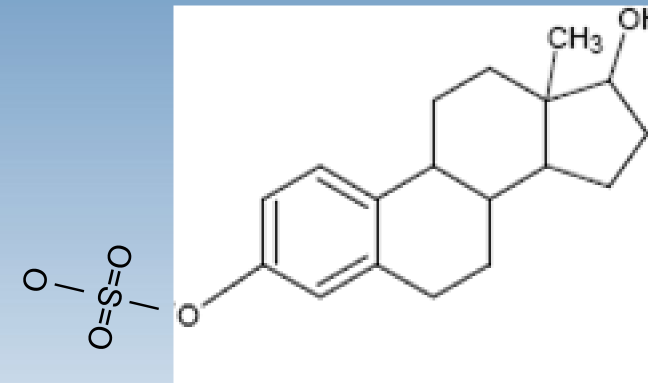
General Conclusions for DOC/COC

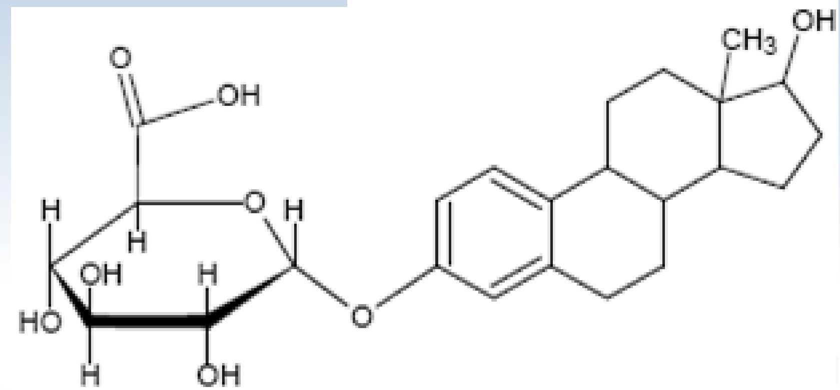
1. Manure DOC/COC solution caused E2 to persist in aqueous phase longer
   1. Reduced degradation transformation
   2. Reduced sorption
2. Likely contributed to greater than expected mobility in the field

Explaining Movement and Persistence

2. Conjugate transport

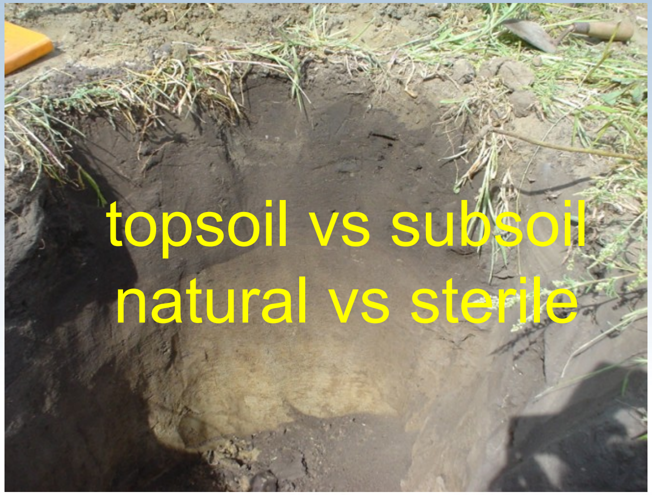




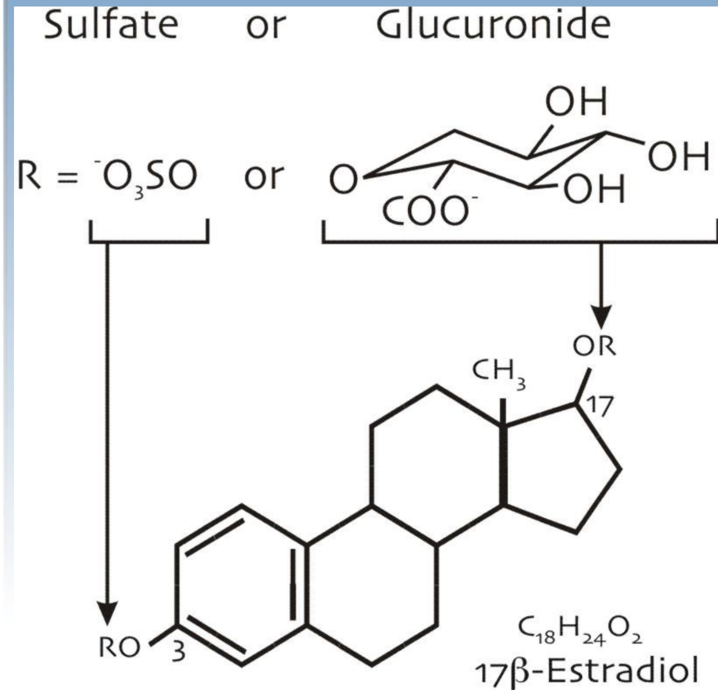


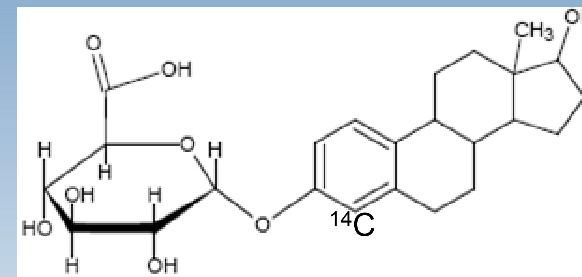
Batch studies

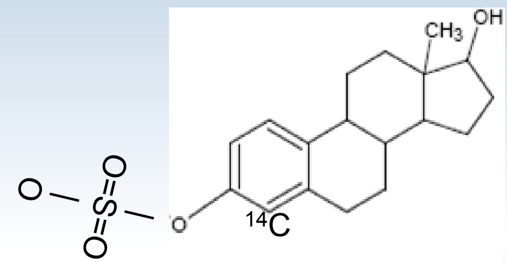
- Determine parent (i.e. E2, E2-3S, E2-3G) and metabolite concentrations through time in aqueous and bound phases



Estrogen conjugates synthesis







Research Article

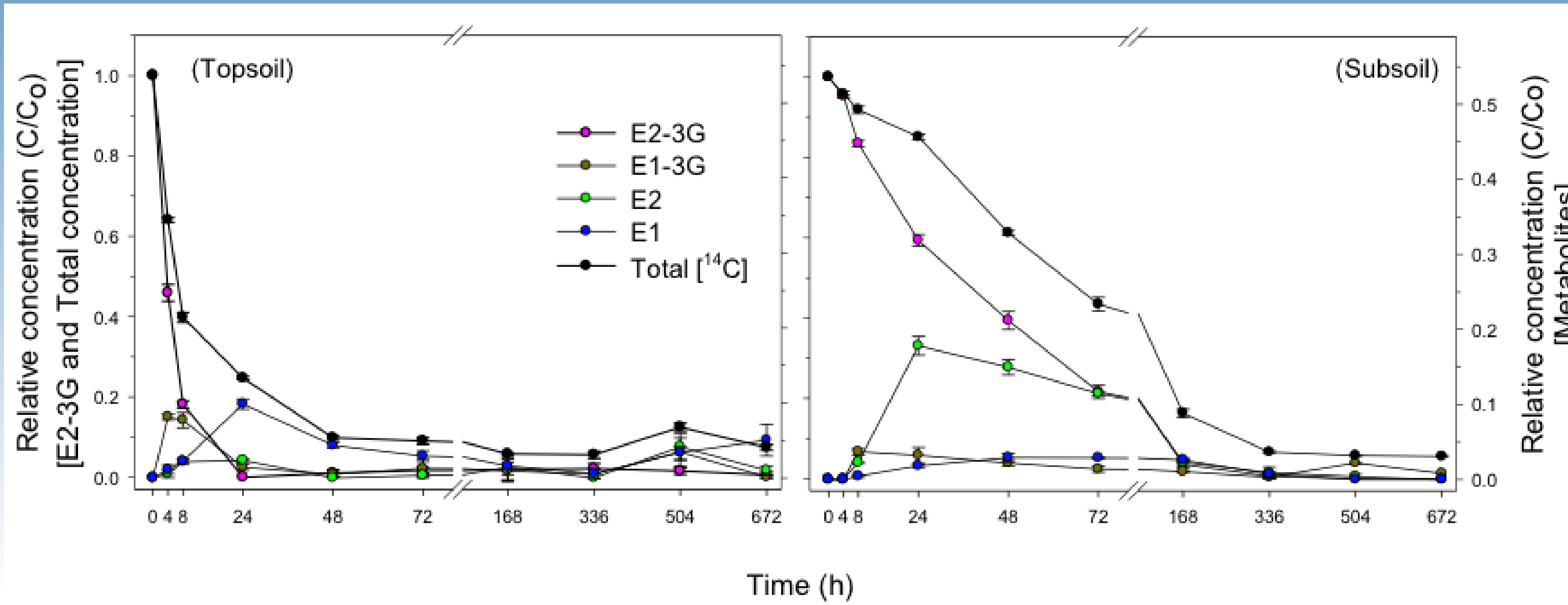
Journal of Labelled Compounds and Radiopharmaceuticals

Received 24 June 2010, Revised 20 October 2010, Accepted 24 November 2010 Published online 17 February 2011 in Wiley Online Library (wileyonlinelibrary.com) DOI: 10.1002/jlcr.1864

Synthesis and characterization of radiolabeled 17β-estradiol conjugates

Suman L. Shrestha,[a] Xuelian Bai,[b] David J. Smith,[c] Heldur Hakk,[c*] Francis X. M. Casey,[b] Gerald L. Larsen,[c] and G. Padmanabhan[a]

Aqueous phase-E2-3G



Environmental Science & Technology

Article

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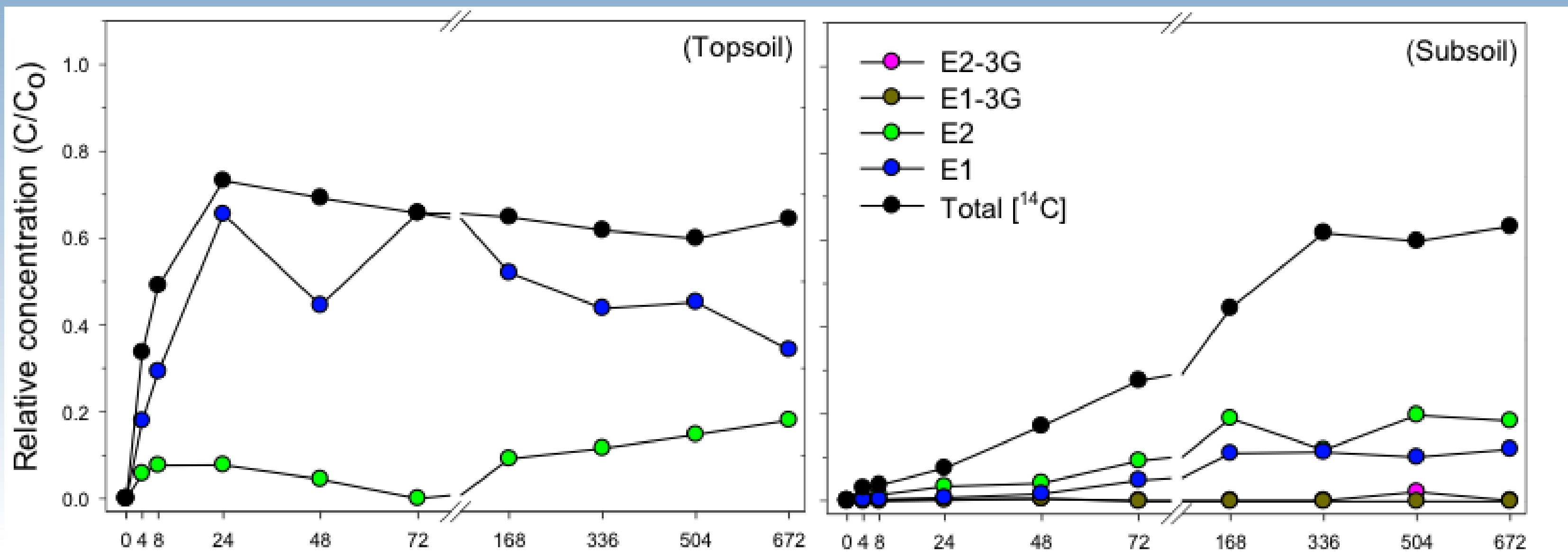
Fate and Transformation of an Estrogen Conjugate and Its Metabolites in Agricultural Soils

Suman L. Shrestha,[†] Francis X. M. Casey,*[,†] Heldur Hakk,[‡] David J. Smith,[‡] and G. Padmanabhan[§]

Sorbed phase-E2-3G



Environmental Science & Technology

Article

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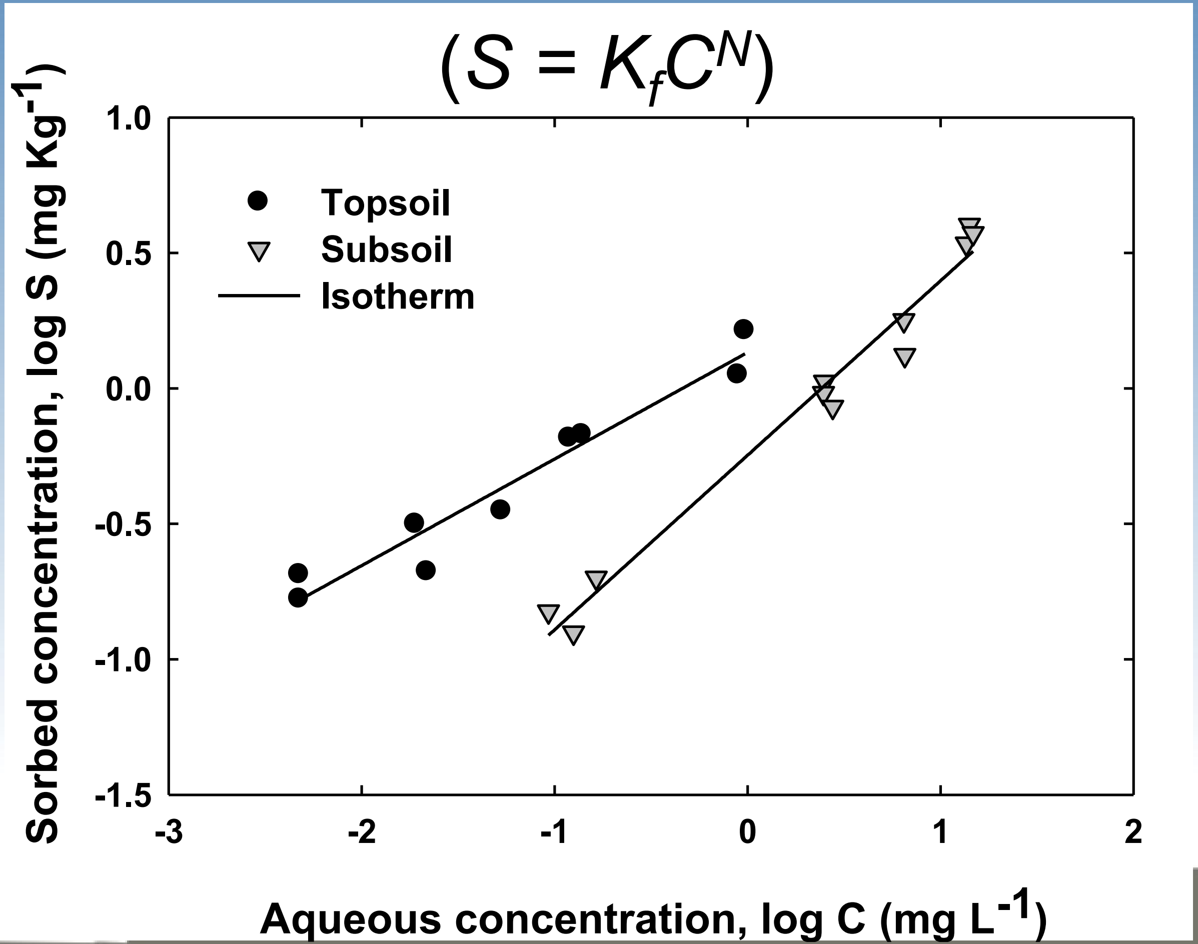
Fate and Transformation of an Estrogen Conjugate and Its Metabolites in Agricultural Soils

Suman L. Shrestha,[†] Francis X. M. Casey,*[,†] Heldur Hakk,[‡] David J. Smith,[‡] and G. Padmanabhan[§]

Freundlich Sorption isotherms of E2-17S



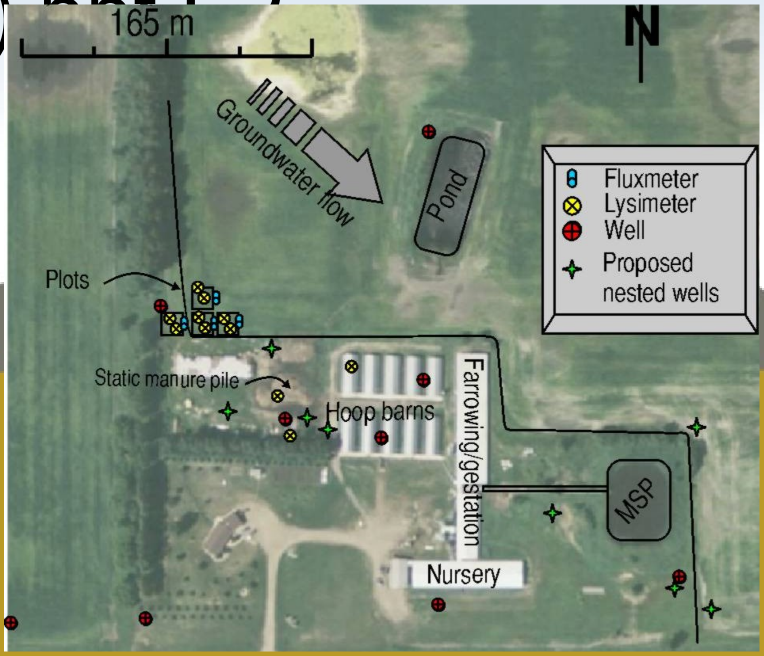
log K_{OC} for E2 = 3.12[1]

log K_{OC} for E1-3S = 1.73 to 2.08[2]

[1]Sarmah et al. (2008); [2]Scherr et al. (2009)

Field conjugate detection (E2-3G)

- E2-3G detected in well 6.5–8.1 m deep
- Average conc = 425 (± 63) ng L^{-1} (ppt), which if hydrolyzed, would produce 258 (± 38) ppt E2



Estrogen Research Highlights

- Field Results
  - Detected frequently in the environment

- Laboratory Results
  - Degrade readily
  - Bind strongly and irreversibly
  - Immobile

- Colloidal and Dissolved Fractions
- Sulfate/Glucuronide Conjugates
  - Enhanced persistence
  - Enhanced mobility