Contaminants of Emerging Concern: Environmental Fate and Transport

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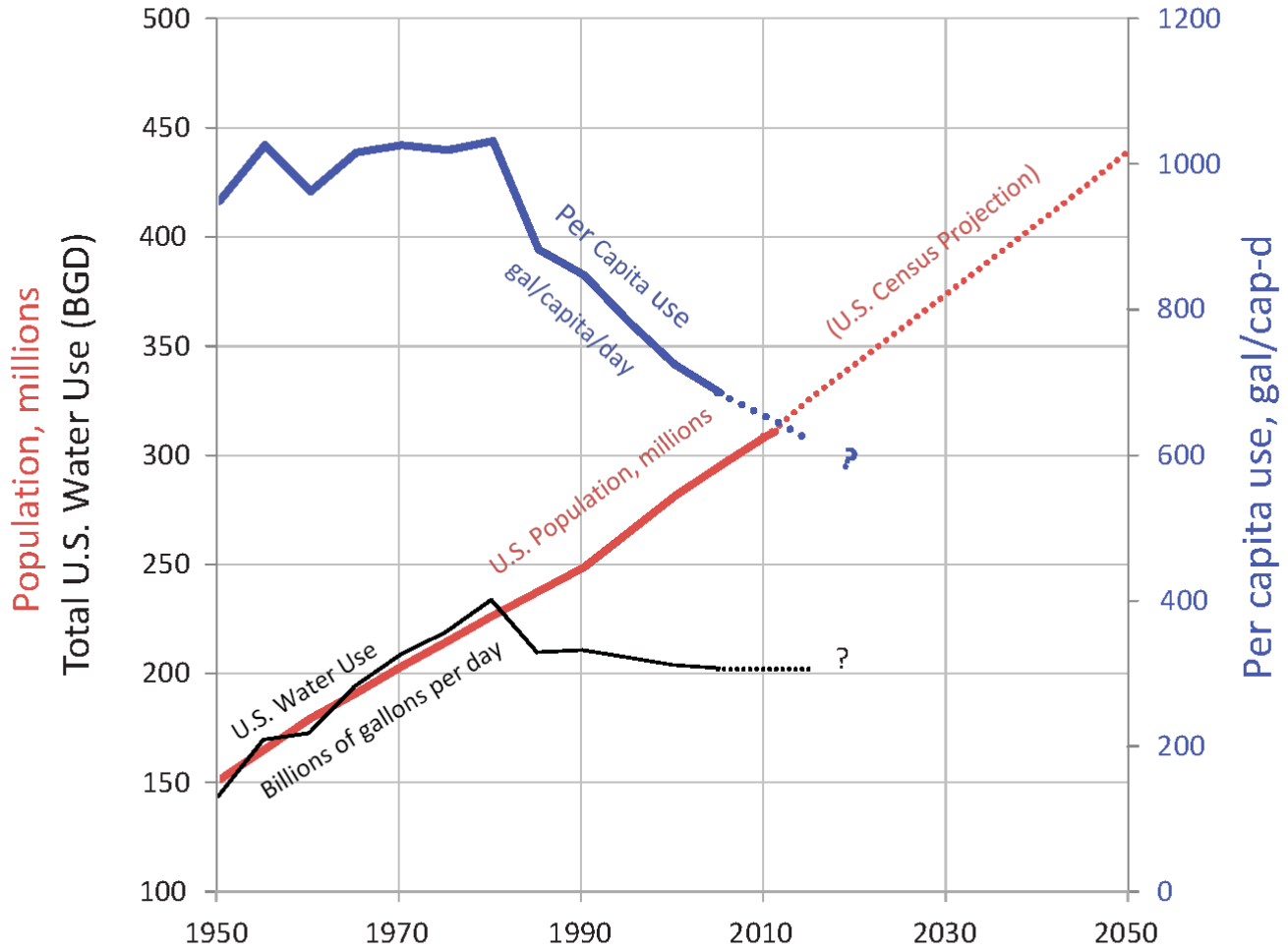
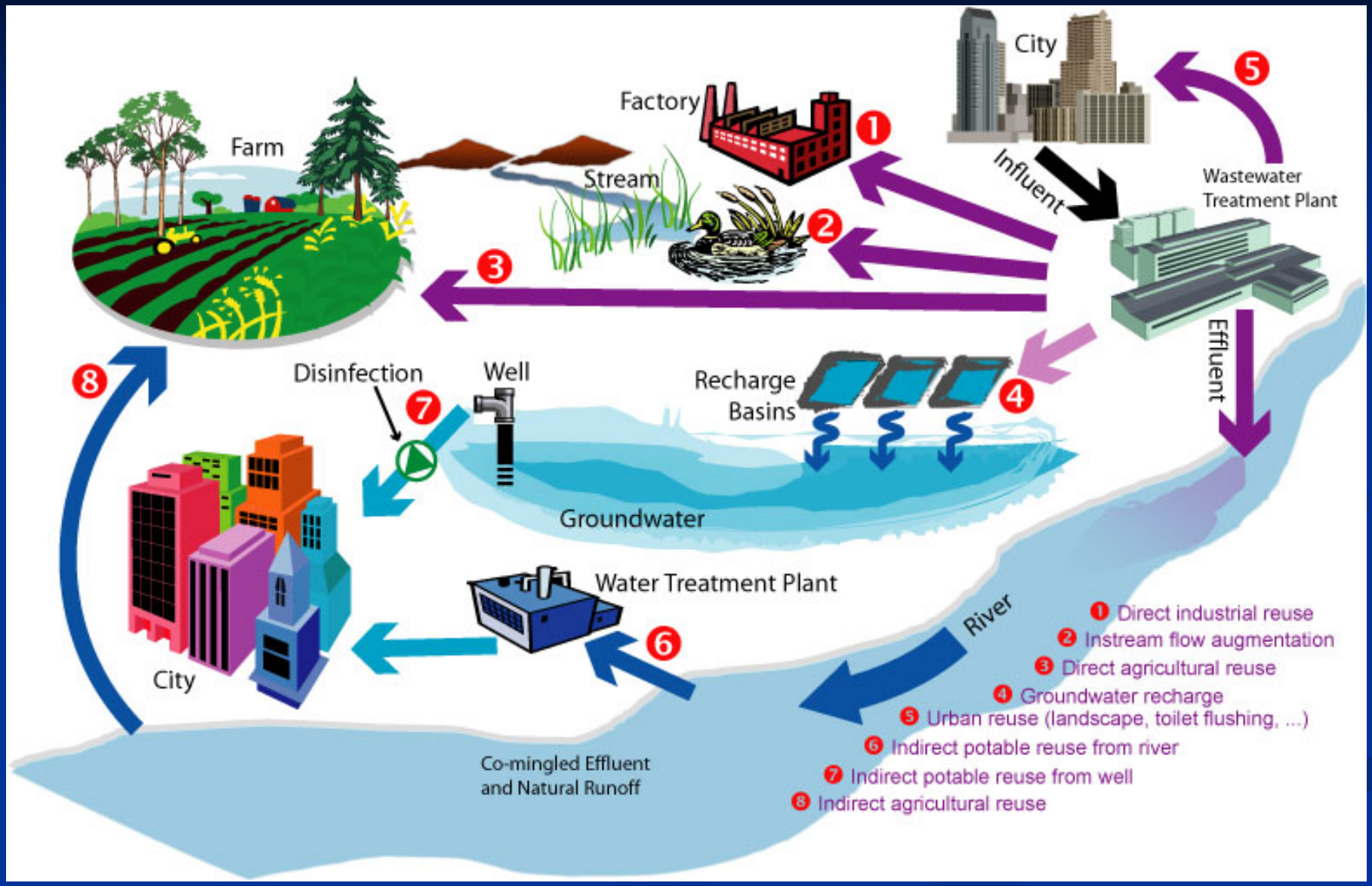
USDA-ARS
Maricopa, AZ


Population, millions
Total U.S. Water Use (BGD)
Per capita use, gal/cap-d
500
450
400
350
300
250
200
150
100
1200
1000
800
600
400
200
0
1950
1970
1990
2010
2030
2050
Per Capita use
gal/capita/day
(U.S. Census Projection)
U.S. Population, millions
U.S. Water Use
Billions of gallons per day
?
?



Office of Water Use and Efficiency, California Department of Water Resources

Sewer farm near Salt Lake City Utah circa 1908

WATER QUALITY
WATER QUANTITY
ENERGY

Acetaminophen for control of Brown Tree snakes

Brown Tree snakes (*Boiga irregularis*), native to eastern Indonesia, become invasive pests on Guam starting in the 1940's/1950's.

Without natural predators, the Brown Tree snake's population in Guam is estimated at upwards of 15,000 per square mile.

Have decimated certain native bird, bat, and reptile populations, as well as caused extensive economic losses (agriculture, pets, human bites, electric grid outages/repairs).

No safe and effective chemical-controls until discovery by USDA that **acetaminophen (80 mg) will effectively kill Brown Tree snakes within 3 days** of even a brief exposure to baited, dead mice.

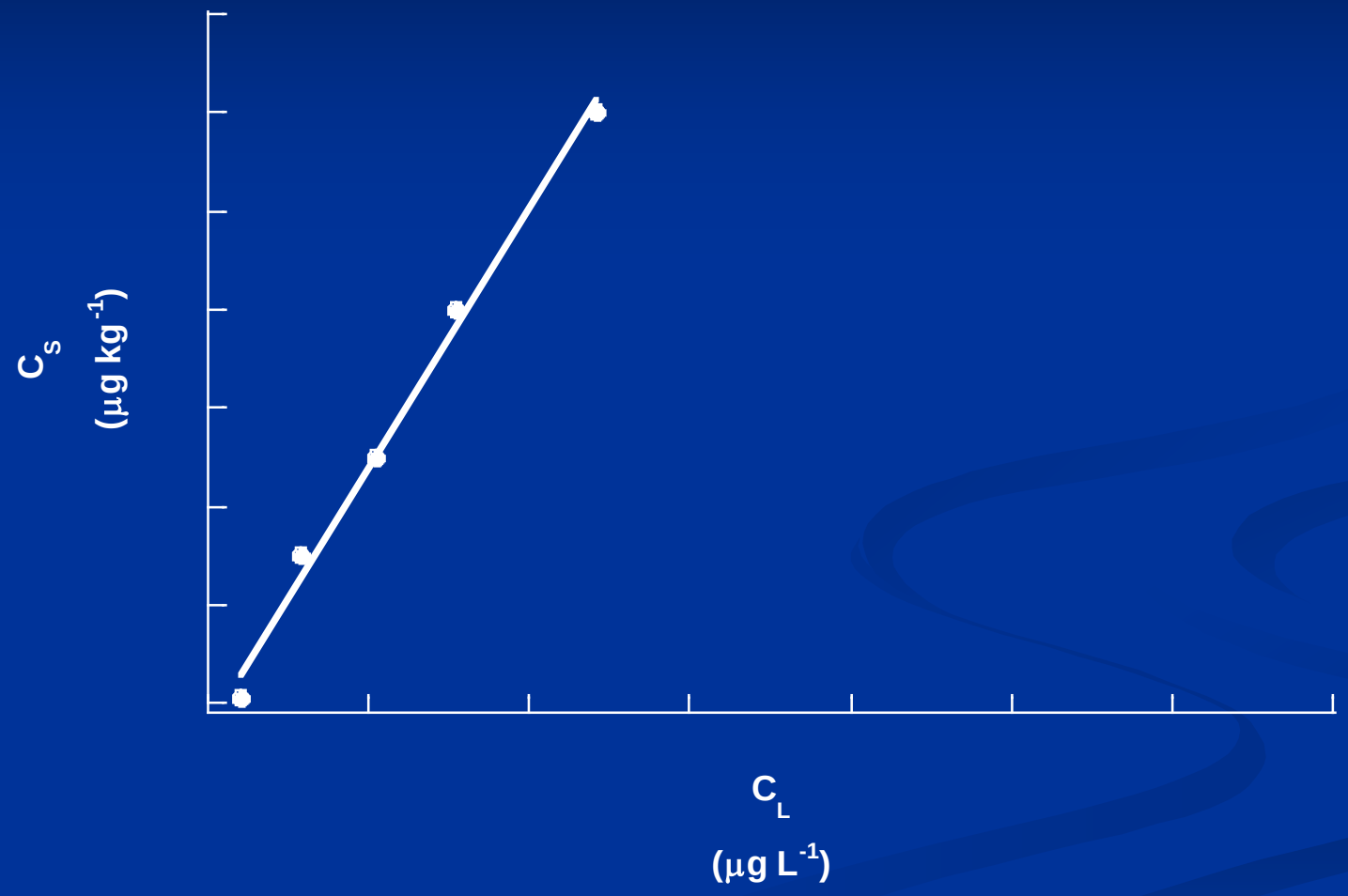
Acute effects of larger doses of acetaminophen on local non-target species have not been detected.

[see: J. J. Johnston et al. "Risk Assessment of an Acetaminophen Baiting Program for Chemical Control of Brown Tree Snakes on Guam: Evaluation of Baits, Snake Residues, and Potential Primary and Secondary Hazards," *Environ. Sci. Technol*. 2002, 36(17):3827-3833;].

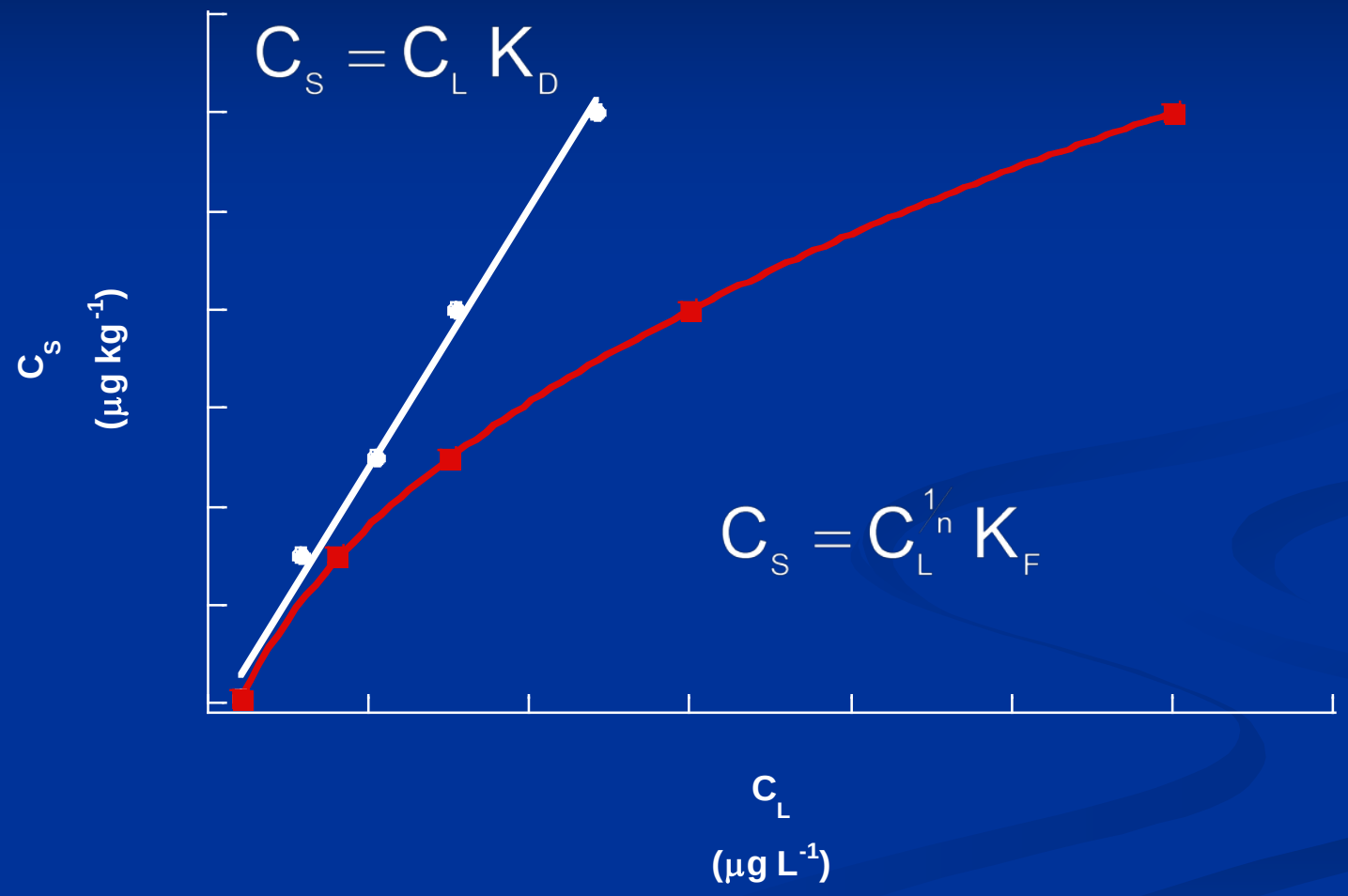
Predicting Transport

- Using equilibrium sorption isotherms
  - Mix untreated soil with contaminant solution
  - Equilibrate
- Plot aqueous vs sorbed concentration

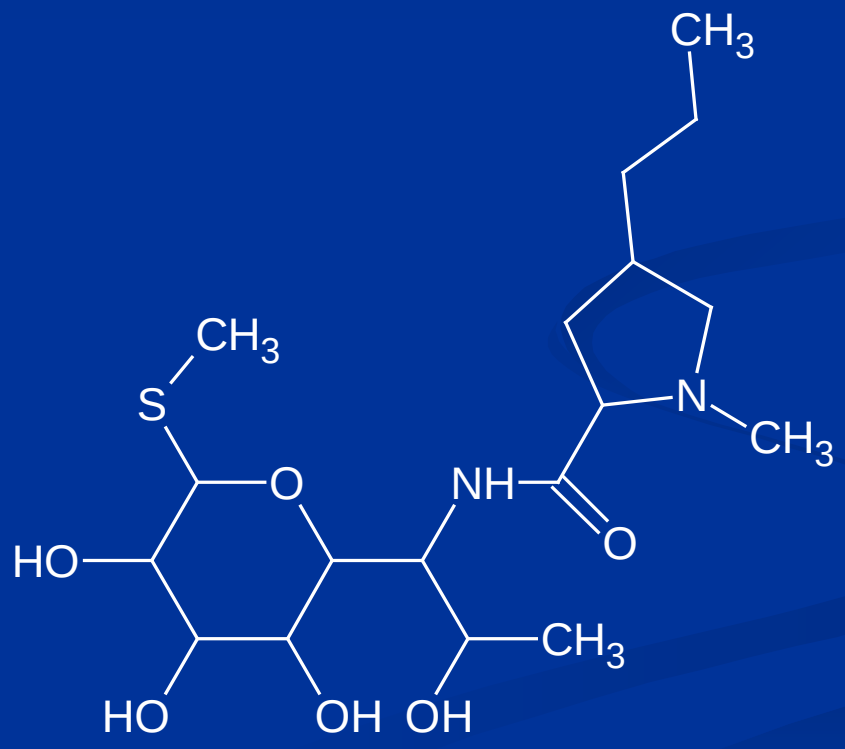
Distribution Coefficients



Distribution Coefficients



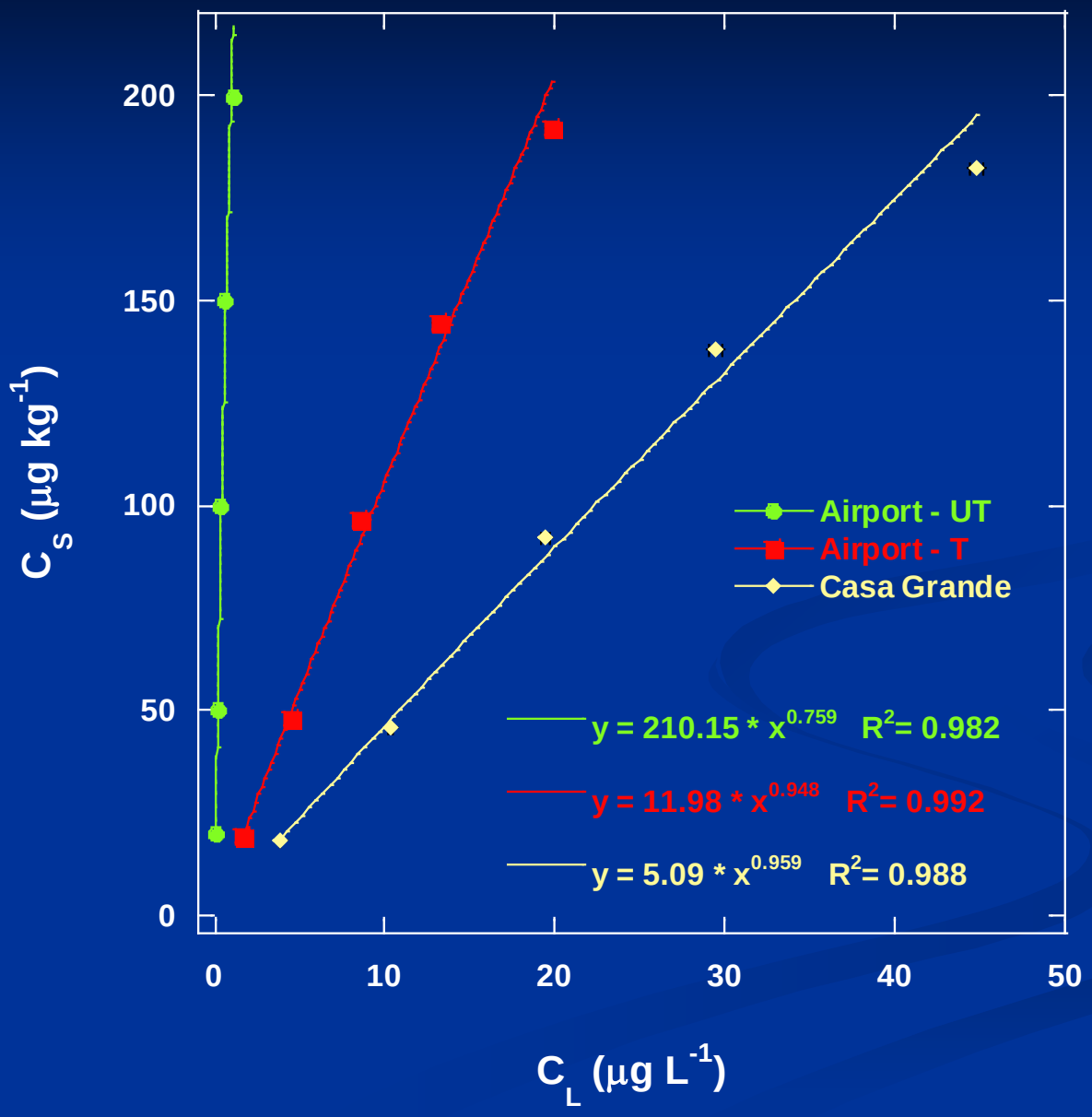
Sorption of Lincomycin to Soils Receiving Reclaimed Water

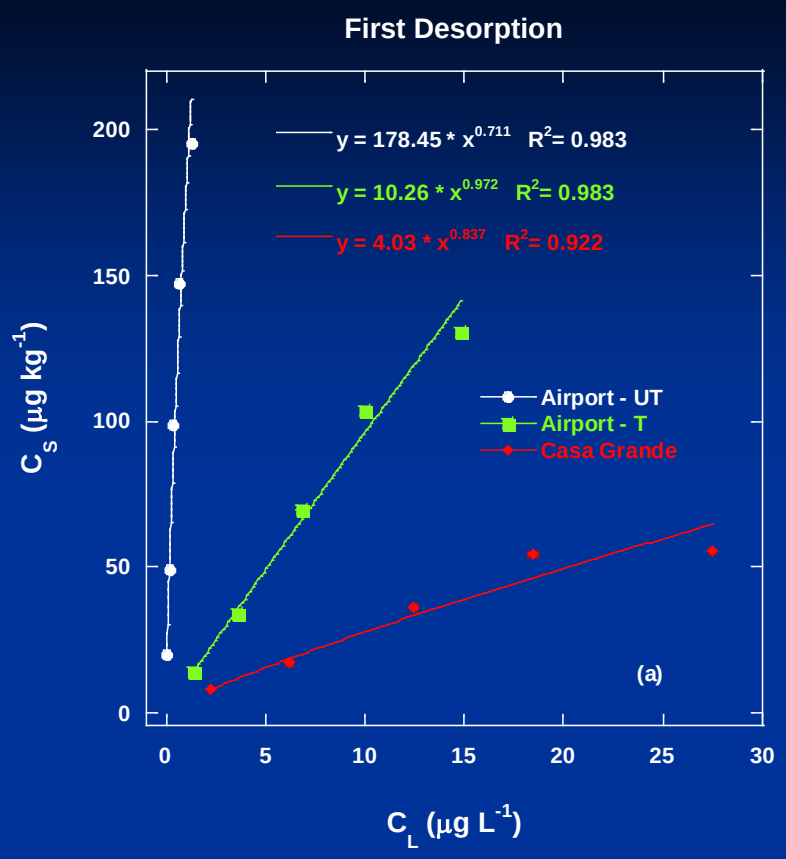


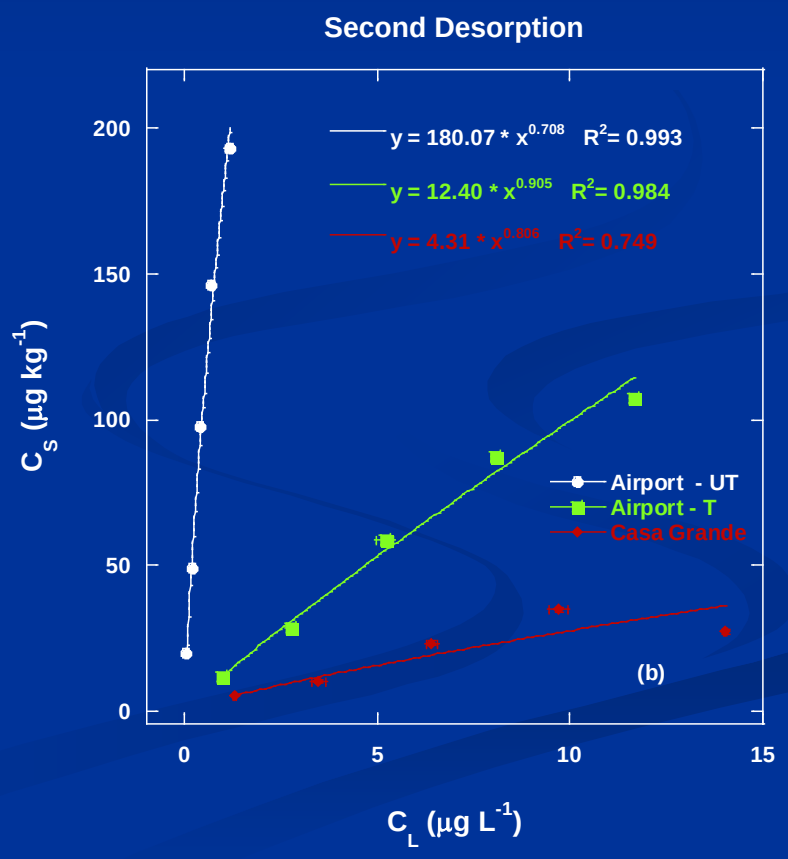
Soil Characteristic	Airport-UT†	Airport-T‡	Casa Grande§
pH¶	7.8	7.3	7.3
EC (dS m^{-1}) ¶	0.49	1.48	2.5
% Sand	43	39	63
% Silt	32.5	32	14.5
% Clay	24.5	29	22.5
% Organic Carbon	1.42	1.58	0.29
CEC (cmol(+)/100g)	12.3	13.1	11.4

† Airport silt loam.
‡ Airport silt loam with biosolids added at rate of 137 Mg ha^{-1} y^{-1}.
§ Casa Grande clay loam.
¶ Determined from saturated paste extract.

Adsorption

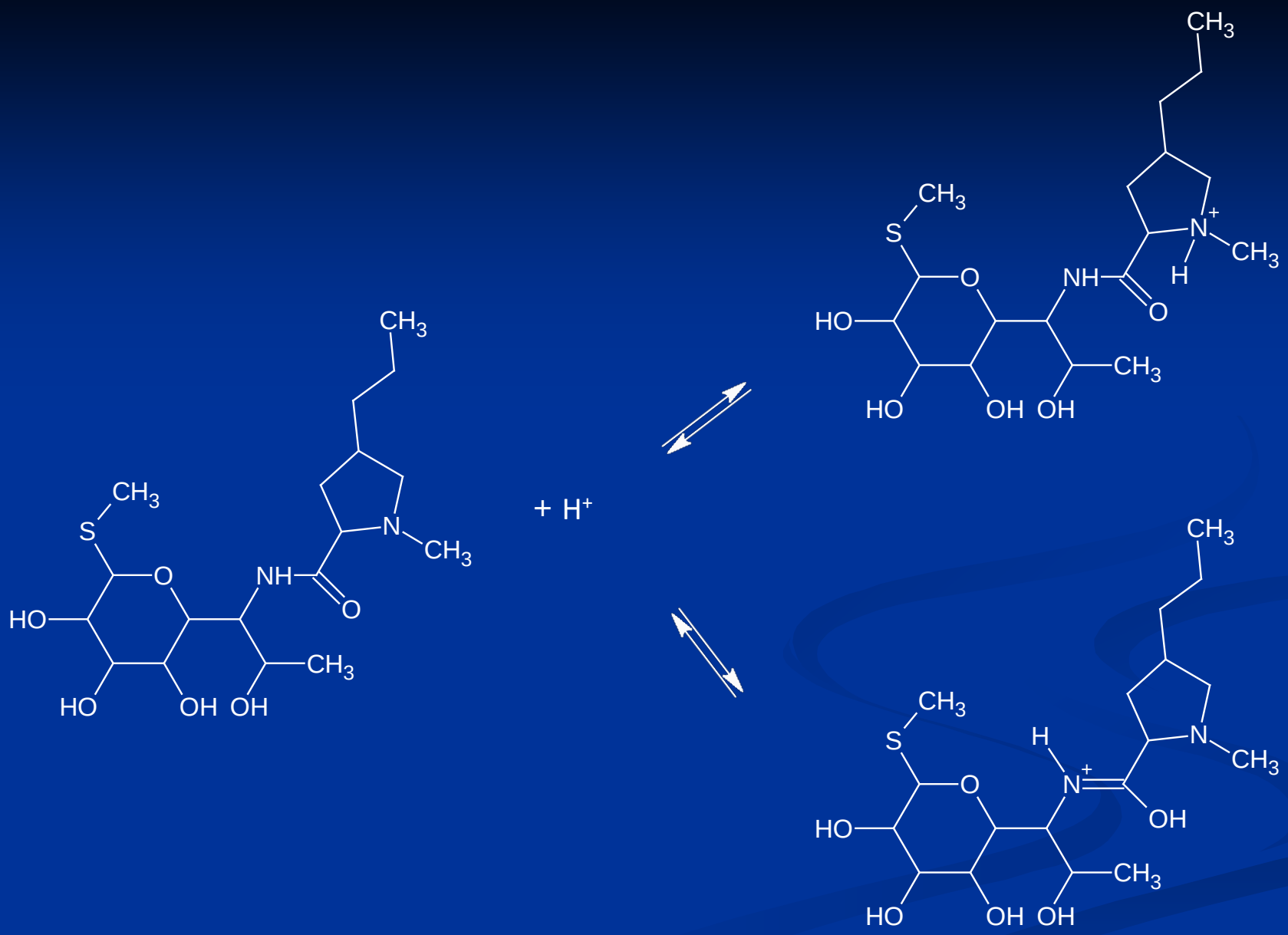

200
150
100
50
0
0
10
20
30
40
50
C_S (µg kg^{-1})
C_L (µg L^{-1})
Airport - UT
Airport - T
Casa Grande
$y = 210.15 * x^{0.759}$ $R^2 = 0.982$
$y = 11.98 * x^{0.948}$ $R^2 = 0.992$
$y = 5.09 * x^{0.959}$ $R^2 = 0.988$

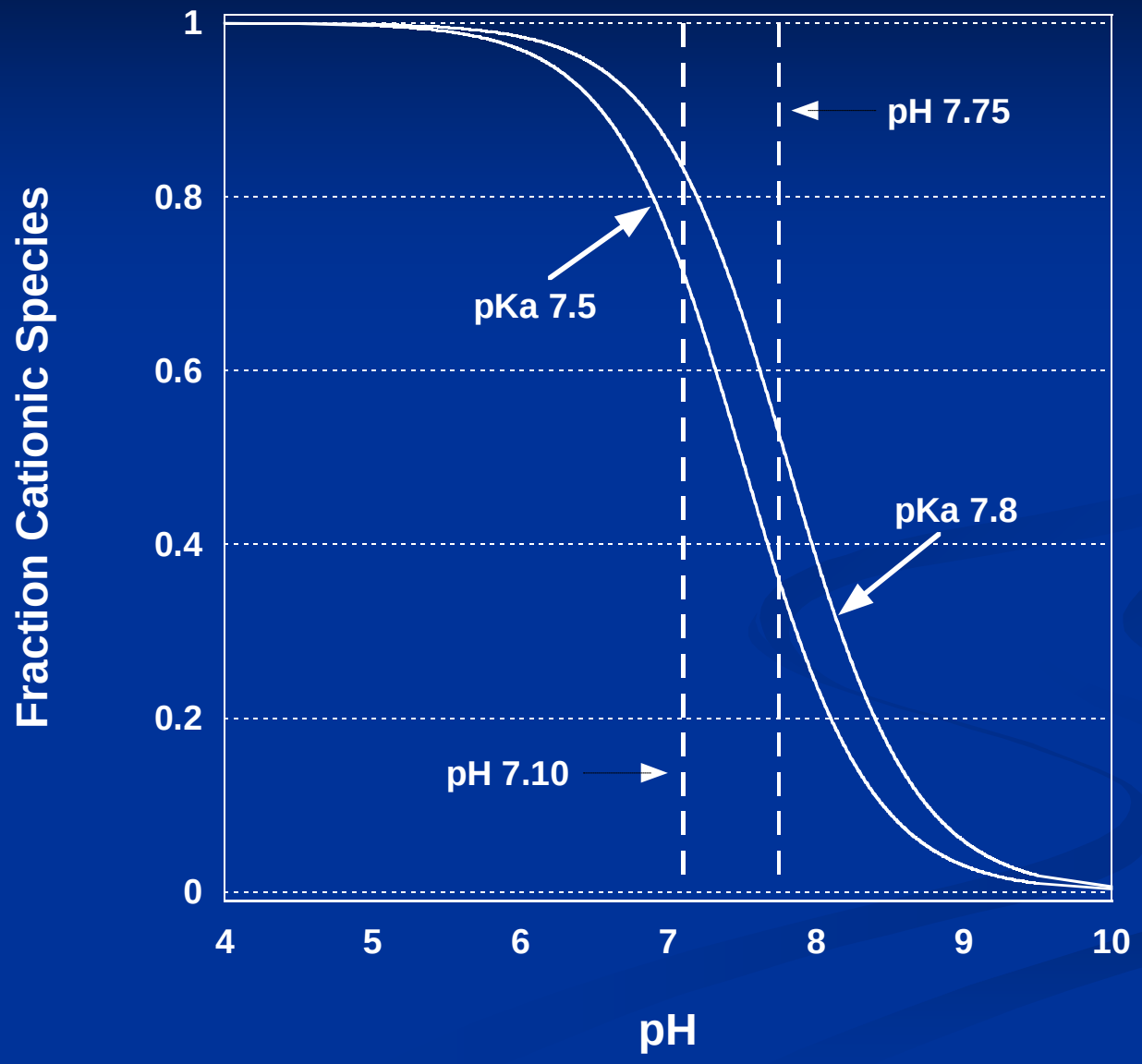

First Desorption
y = 178.45 * x^0.711 R^2= 0.983
y = 10.26 * x^0.972 R^2= 0.983
y = 4.03 * x^0.837 R^2= 0.922
Airport - UT
Airport - T
Casa Grande
(a)
C_S (µg kg^-1)
C_L (µg L^-1)
0
50
100
150
200
0
5
10
15
20
25
30


Second Desorption
y = 180.07 * x^0.708 R^2= 0.993
y = 12.40 * x^0.905 R^2= 0.984
y = 4.31 * x^0.806 R^2= 0.749
Airport - UT
Airport - T
Casa Grande
(b)
C_S (µg kg^-1)
C_L (µg L^-1)
0
50
100
150
200
0
5
10
15

Equilibrium Solution pH

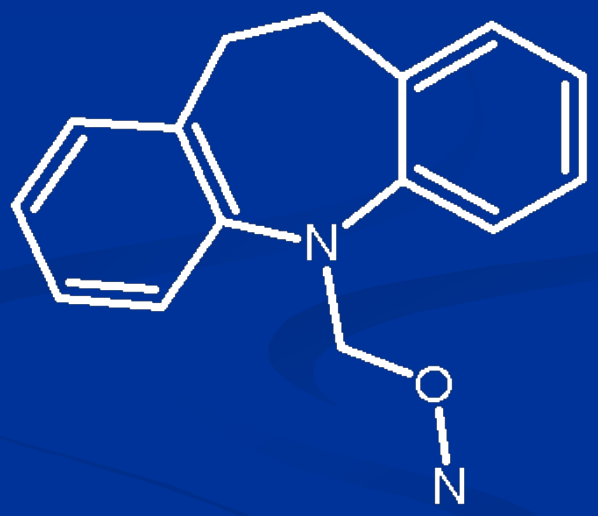
	Airport-UT	Airport-T	Casa Grande
Adsorption	7.75 (0.36 – 0.53)	7.25 (0.64 – 0.78)	7.25 (0.64 – 0.78)
Desorption 1	7.50 (0.50 – 0.67)	7.23 (0.65 – 0.79)	7.21 (0.66 – 0.80)
Desorption 2	7.50 (0.50 – 0.67)	7.10 (0.72 – 0.83)	7.20 (0.67 – 0.80)


CH3
S
O
NH
O
N
CH3
HO
HO
OH
OH
+ H+
H
N+


Fraction Cationic Species
1
0.8
0.6
0.4
0.2
0
4
5
6
7
8
9
10
pH
pH 7.75
pKa 7.5
pKa 7.8
pH 7.10

Sorption of the Human Drug Carbamazepine to Soil

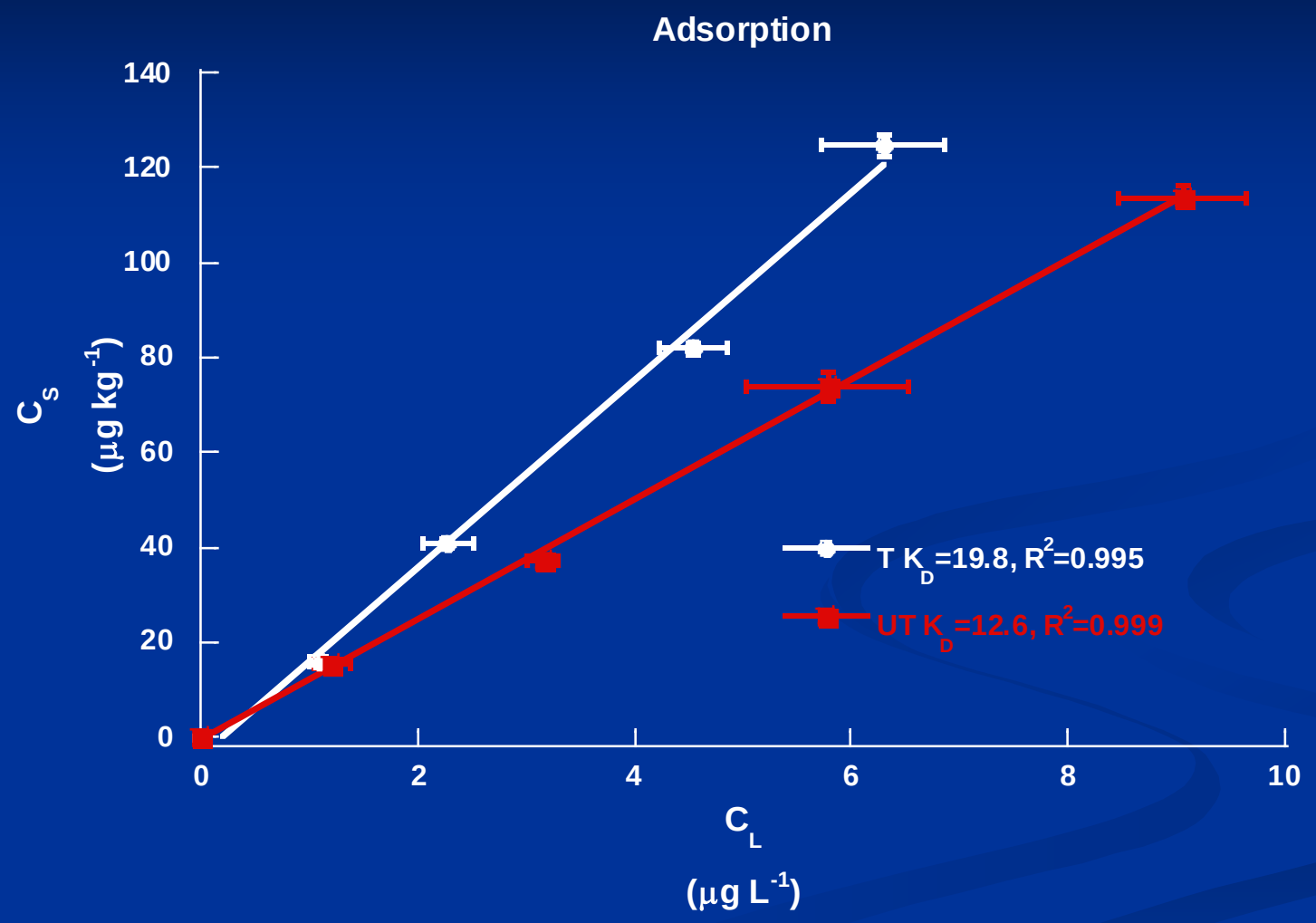
- Two Soils – Airport silt loam
- With biosolids
  - 3 Mg ha^{-1} Biosolids applied over 2 yr period
  - 3 years after application
- Without biosolids
- Alfalfa for 10 years

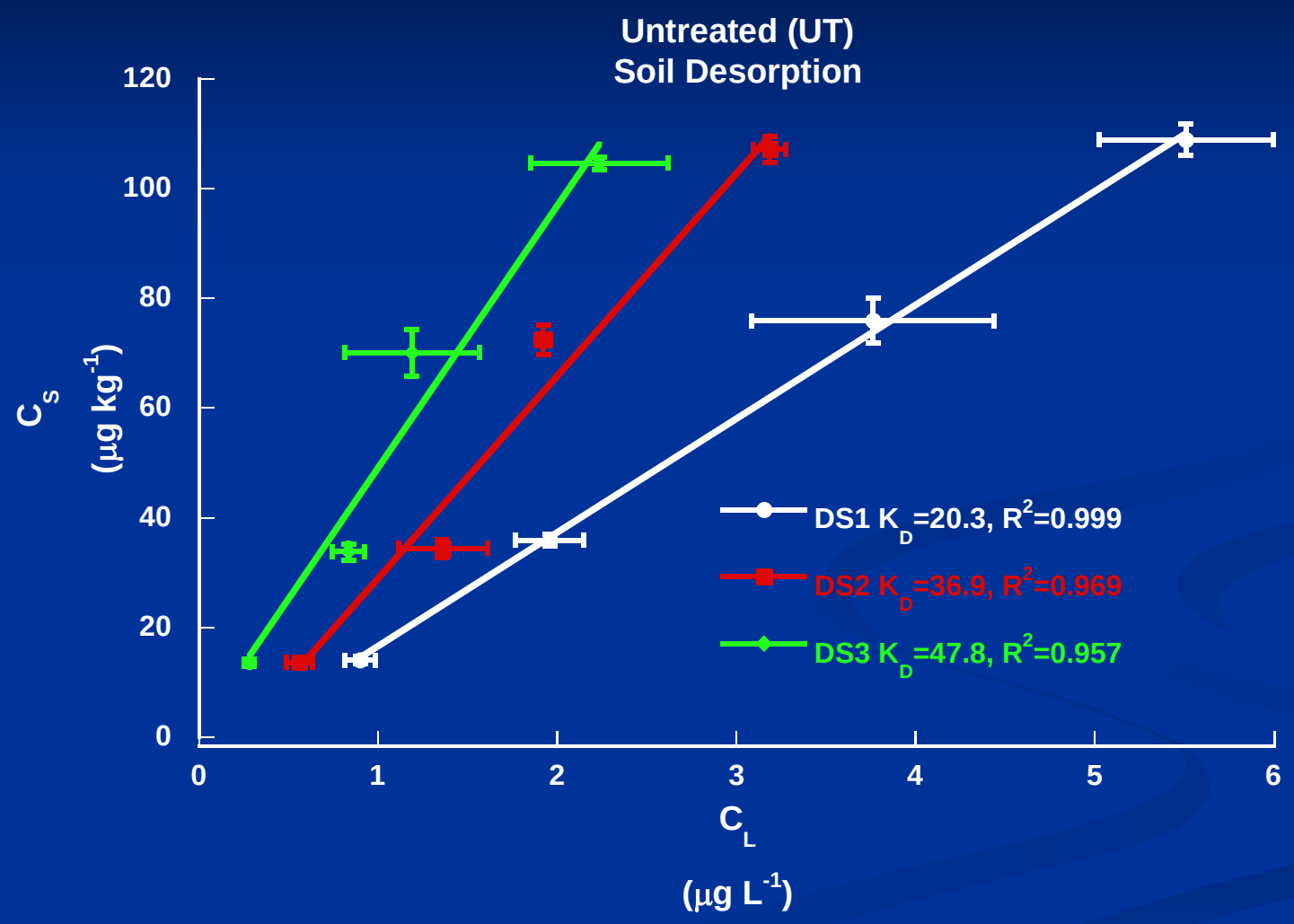


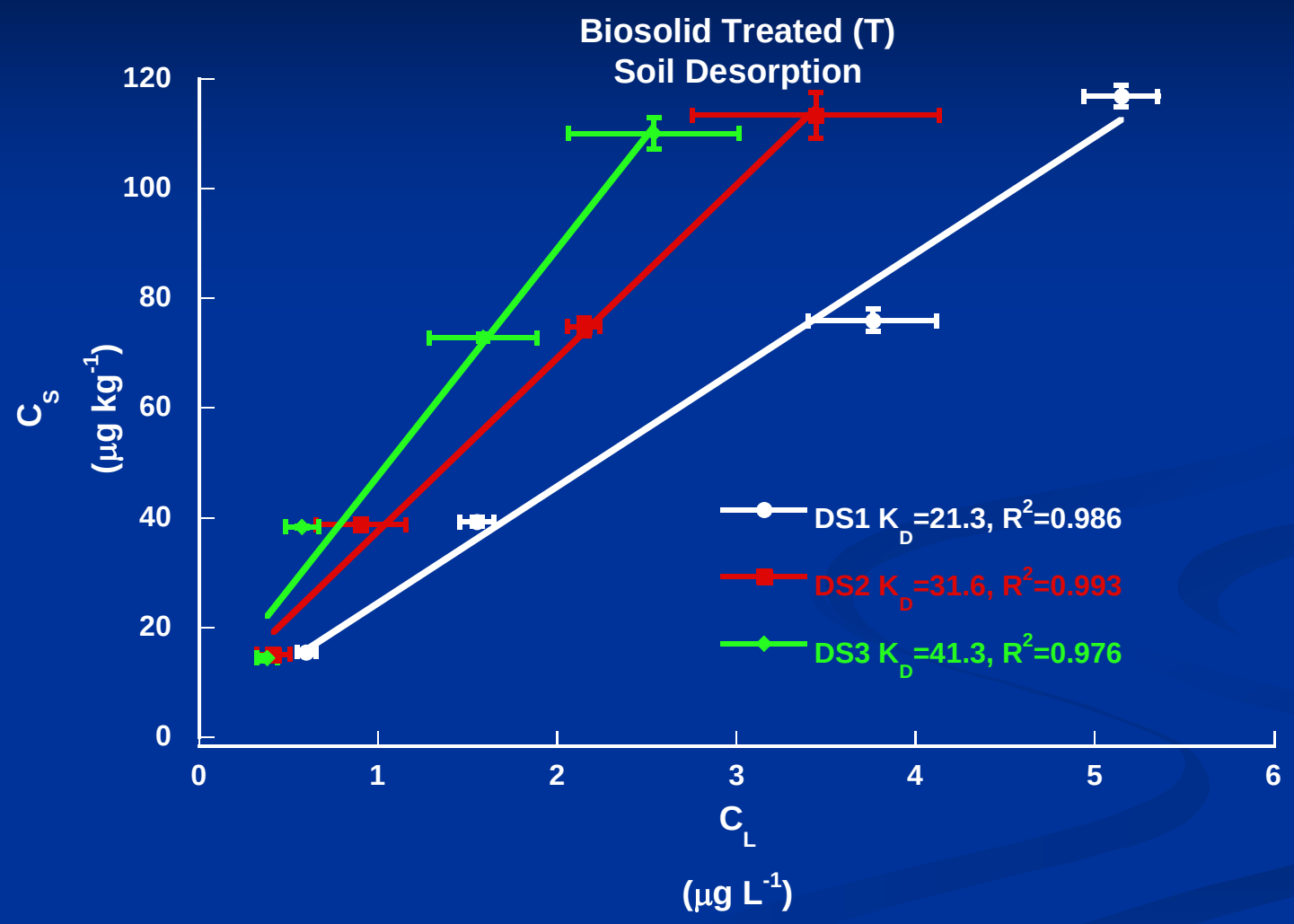
Soil Characteristics

		Soil Characteristic				
Soil	pH	E.C. (dS m^{-1})	Sand %	Silt %	Clay %	O.C %
Without Biosolids	7.0	0.4	45	32	23	1.42
With Biosolids	7.6	1.4	38	32	30	1.58

Carbamazepine was not detected in either soil

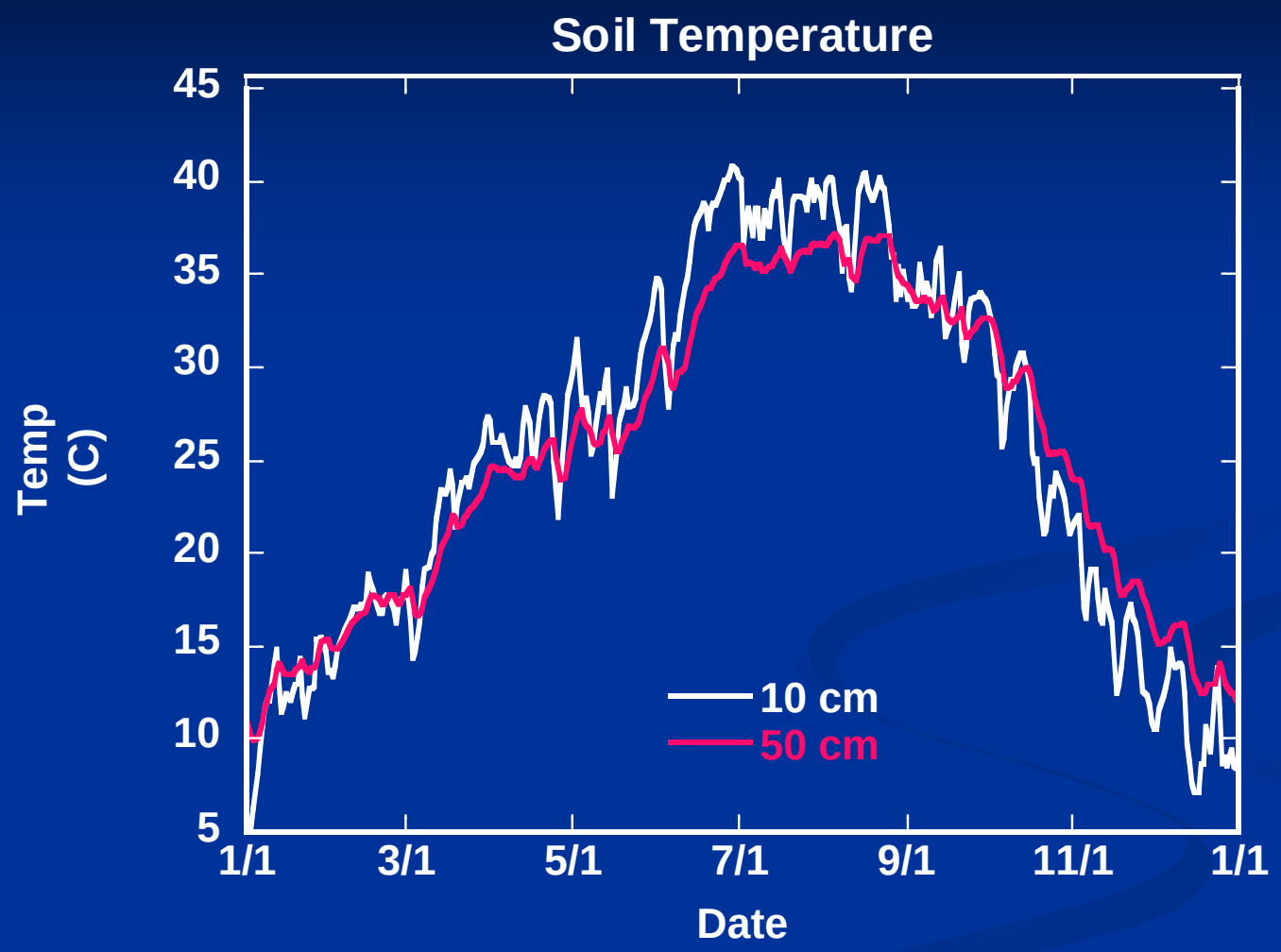

Adsorption
140
120
100
80
60
40
20
0
C_S
($\mu g\ kg^{-1}$)
0
2
4
6
8
10
C_L
($\mu g\ L^{-1}$)
T K_D=19.8, R^2=0.995
UT K_D=12.6, R^2=0.999

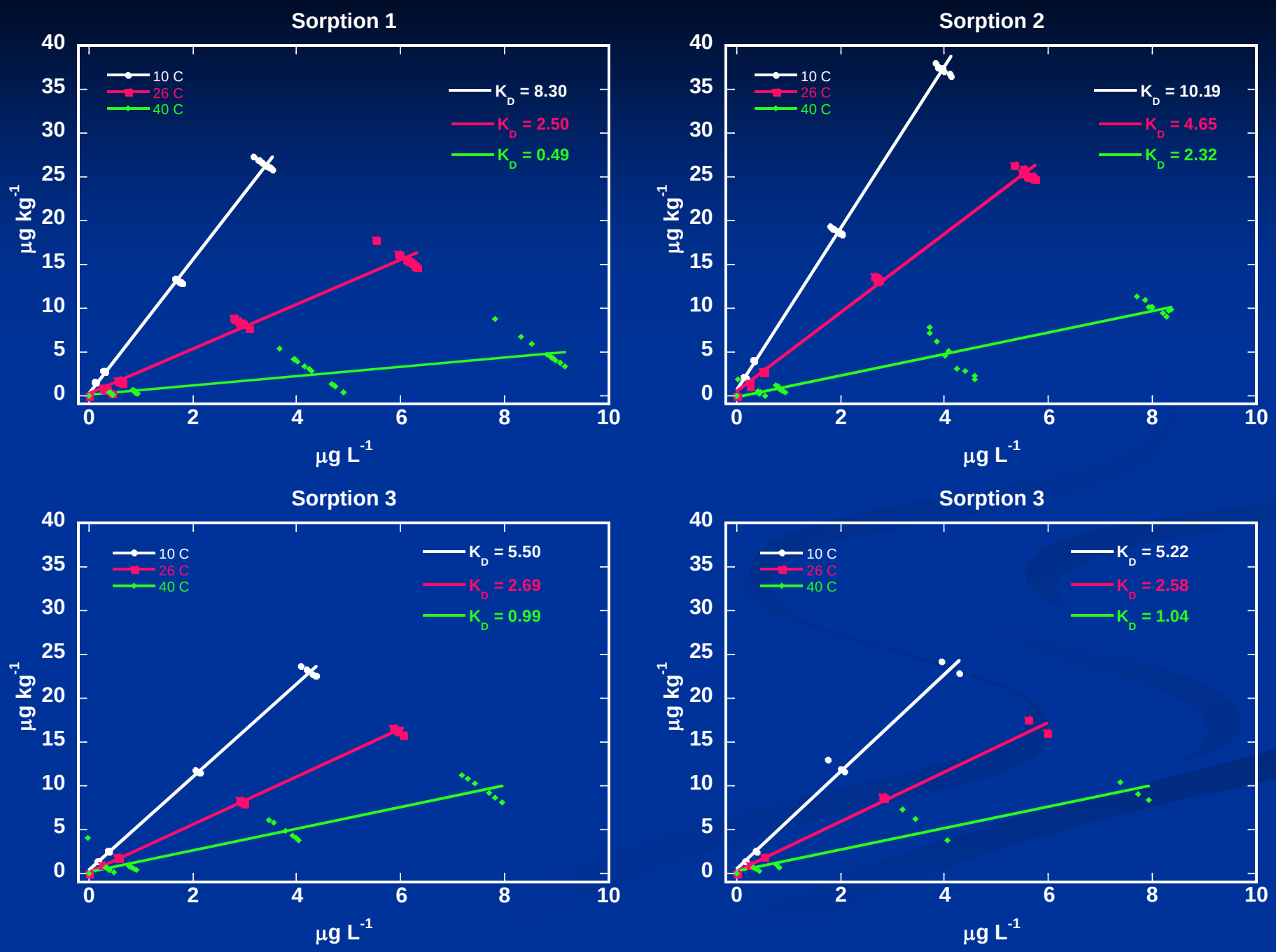

Untreated (UT)
Soil Desorption
120
100
80
60
40
20
0
C_S
($\mu g\ kg^{-1}$)
0
1
2
3
4
5
6
C_L
($\mu g\ L^{-1}$)
DS1 K_D=20.3, R^2=0.999
DS2 K_D=36.9, R^2=0.969
DS3 K_D=47.8, R^2=0.957


Biosolid Treated (T)
Soil Desorption
120
100
80
60
40
20
0
C_S
(µg kg^{-1})
0
1
2
3
4
5
6
C_L
(µg L^{-1})
DS1 K_D=21.3, R^2=0.986
DS2 K_D=31.6, R^2=0.993
DS3 K_D=41.3, R^2=0.976

Event	Biosolid treated soil (T)			Untreated soil (UT)		
	K_D (L kg^{-1})	Intercept# (µg kg^{-1})	R^{2}††	K_D (L kg^{-1})	Intercept# (µg kg^{-1})	R^{2}††
AD†	19.8	-3.51	0.995	12.6	-0.53	0.999
DS1‡	21.3	3.07	0.986	20.3	-4.25	0.999
DS2§	31.6	5.88	0.993	36.9	-8.12	0.969
DS3¶	41.3	6.29	0.976	47.8	1.20	0.957

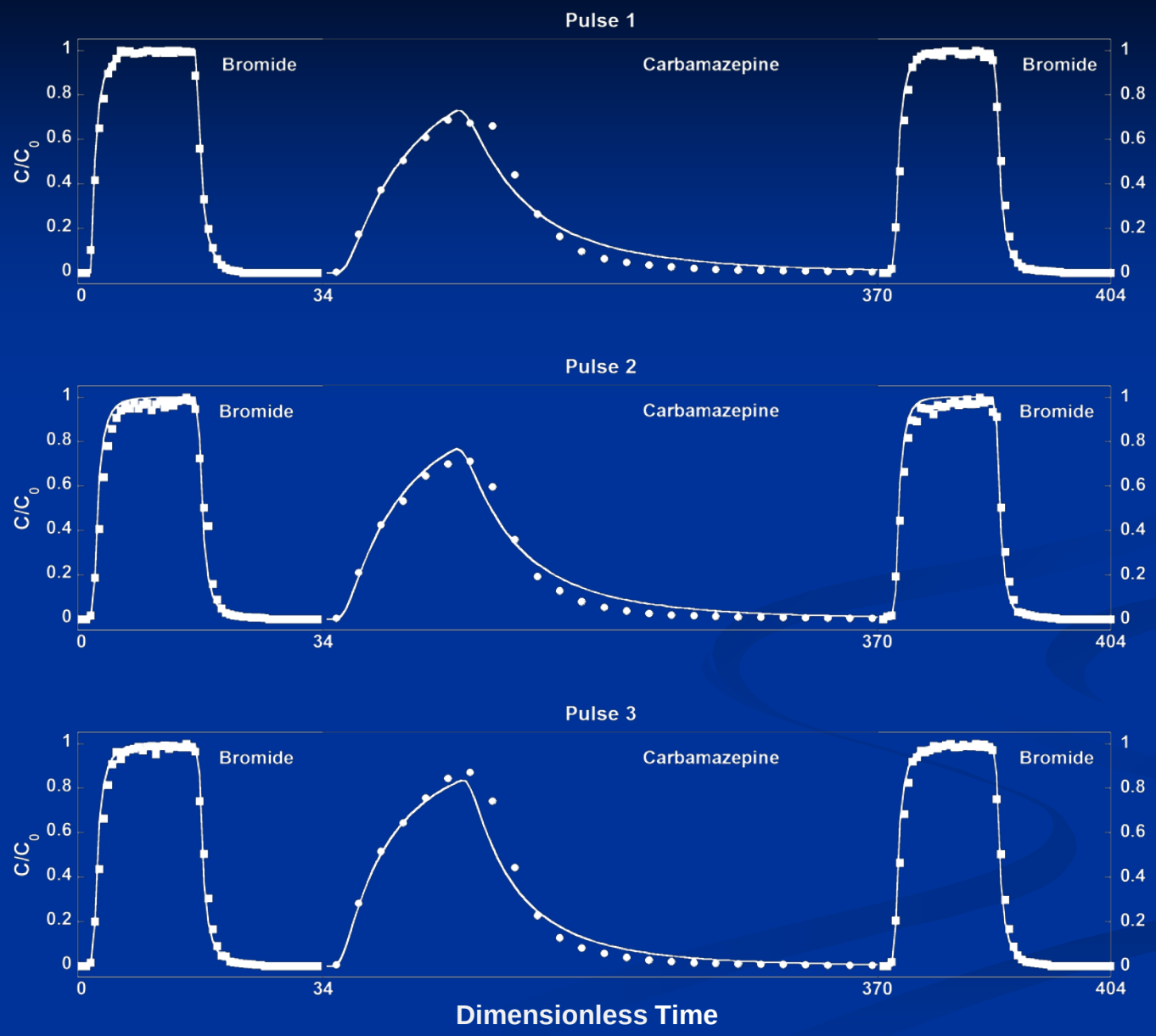
†AD Adsorption carbamazepine distribution coefficient.
‡DS1 Desorption distribution coefficient for the first desorption event.
§DS2 Desorption distribution coefficient for the second desorption event.
¶DS3 Desorption distribution coefficient for the third desorption event.
#Linear regression intercept.
††Linear coefficient of determination.

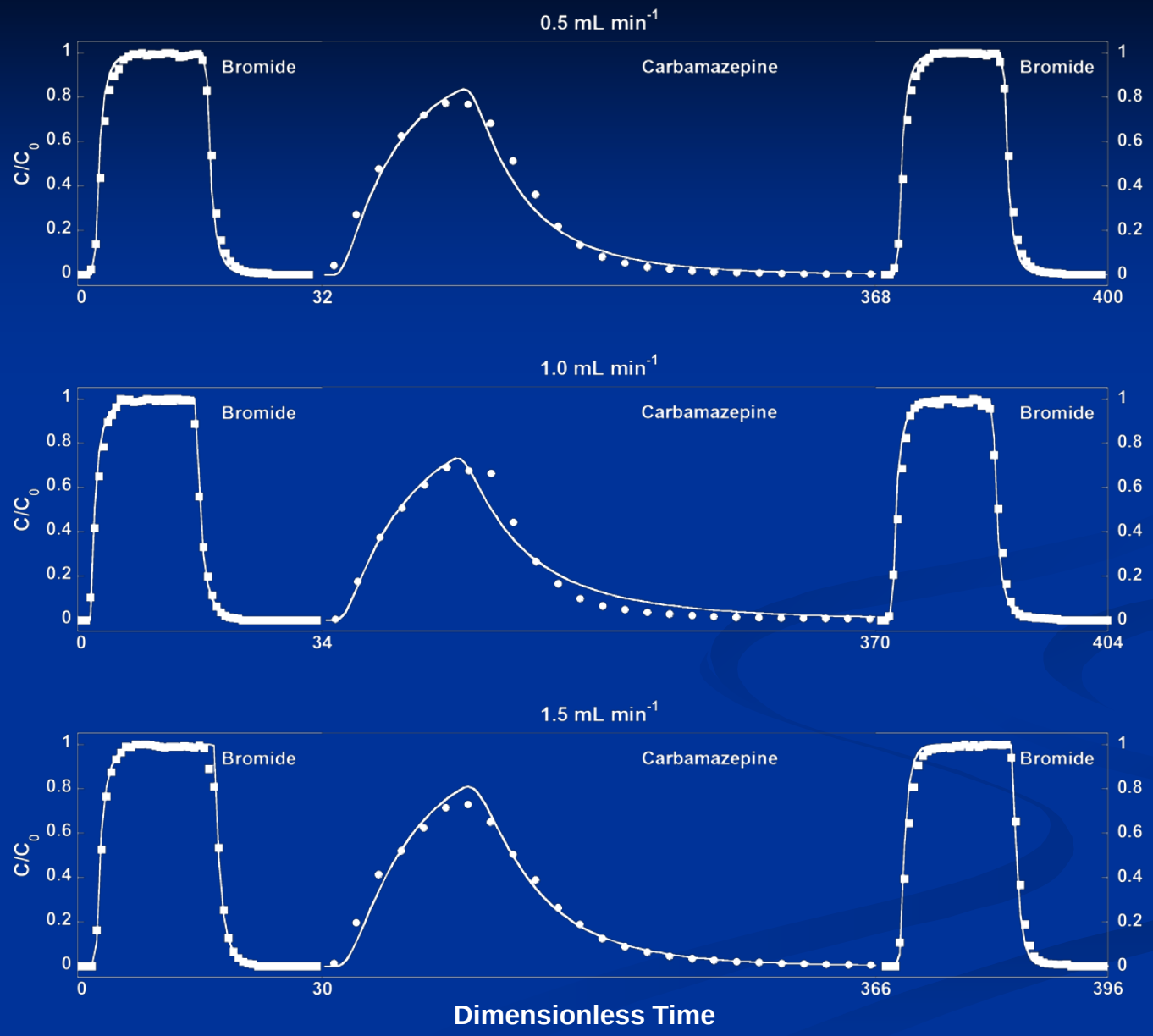

Soil Temperature
45
40
35
30
25
20
15
10
5
Temp
(C)
1/1
3/1
5/1
7/1
9/1
11/1
1/1
Date
10 cm
50 cm

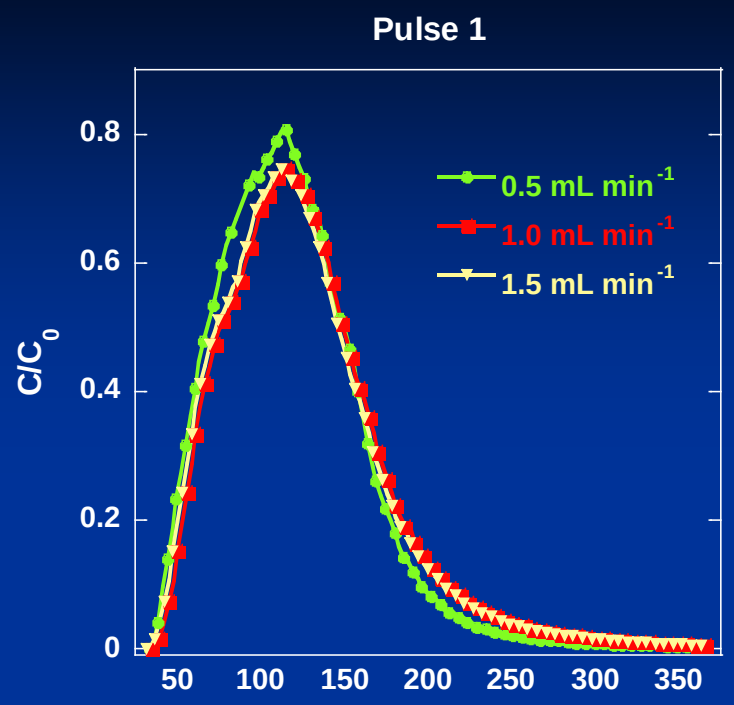

Sorption 1
10 C
26 C
40 C
K_D = 8.30
K_D = 2.50
K_D = 0.49
µg kg-1
µg L-1
Sorption 2
10 C
26 C
40 C
K_D = 10.19
K_D = 4.65
K_D = 2.32
µg kg-1
µg L-1
Sorption 3
10 C
26 C
40 C
K_D = 5.50
K_D = 2.69
K_D = 0.99
µg kg-1
µg L-1
Sorption 3
10 C
26 C
40 C
K_D = 5.22
K_D = 2.58
K_D = 1.04
µg kg-1
µg L-1

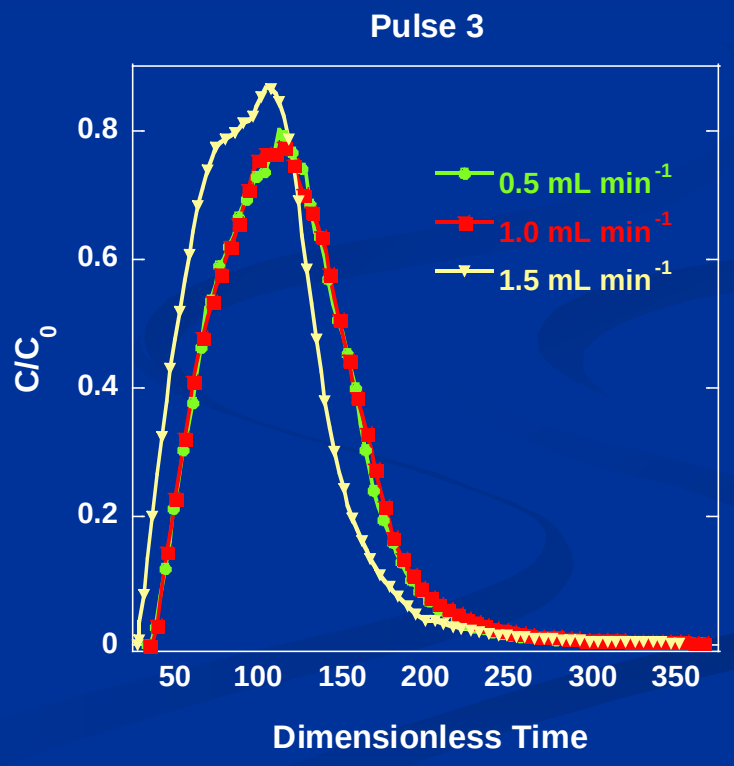
	Adsorption				Desorption		
Temp	1	2	3	4	1	2	3
10	8.30	10.19	5.50	5.22	15.21	21.54	27.66
26	2.50	4.65	2.69	2.58	5.22	9.54	12.05
40	0.49	2.32	0.99	1.04	2.61	2.96	3.55

MODEL 2360 GRADIENT PROGRAMMER
ISCO
Waters
515 HPLC Pump
RETRIEVER II


Pulse 1
Bromide
Carbamazepine
Bromide
C/C0
0
0.2
0.4
0.6
0.8
1
0
34
370
404
Pulse 2
Bromide
Carbamazepine
Bromide
C/C0
0
0.2
0.4
0.6
0.8
1
0
34
370
404
Pulse 3
Bromide
Carbamazepine
Bromide
C/C0
0
0.2
0.4
0.6
0.8
1
0
34
370
404
Dimensionless Time


0.5 mL min-1
Bromide
Carbamazepine
Bromide
C/C0
0
0.2
0.4
0.6
0.8
1
0
32
368
400
1.0 mL min-1
Bromide
Carbamazepine
Bromide
C/C0
0
34
370
404
1.5 mL min-1
Bromide
Carbamazepine
Bromide
C/C0
0
30
366
396
Dimensionless Time


Pulse 1
0.8
0.6
0.4
0.2
0
C/C0
50
100
150
200
250
300
350
0.5 mL min-1
1.0 mL min-1
1.5 mL min-1


Pulse 3
0.8
0.6
0.4
0.2
0
C/C0
50
100
150
200
250
300
350
Dimensionless Time
0.5 mL min-1
1.0 mL min-1
1.5 mL min-1

	K_D (L kg^{-1})				
Linear Velocity (cm hr^{-1})	Pulse 1	Pulse 2	Pulse 3	Batch	
1.8	23.0 (0.4)	20.3 (0.2)	17.4 (0.3)	Ad	12.6
3.5	20.5 (1.2)	18.0 (0.9)	16.1 (0.2)	Des 1	20.3
5.3	19.1 (1.2)	15.9 (0.3)	14.7 (0.1)	Des 2	36.9

Soil Persistence and Fate of Pharmaceuticals at a recharge facility

- 67.2 ac recharge area
- Permitted for 8 mgd
- Depth to groundwater
  - 168 ft prior to recharge
  - 145 ft now
- Recharge began Dec 1998
- To date 40,000 acre-feet recharged

JOHN DEERE
425

425

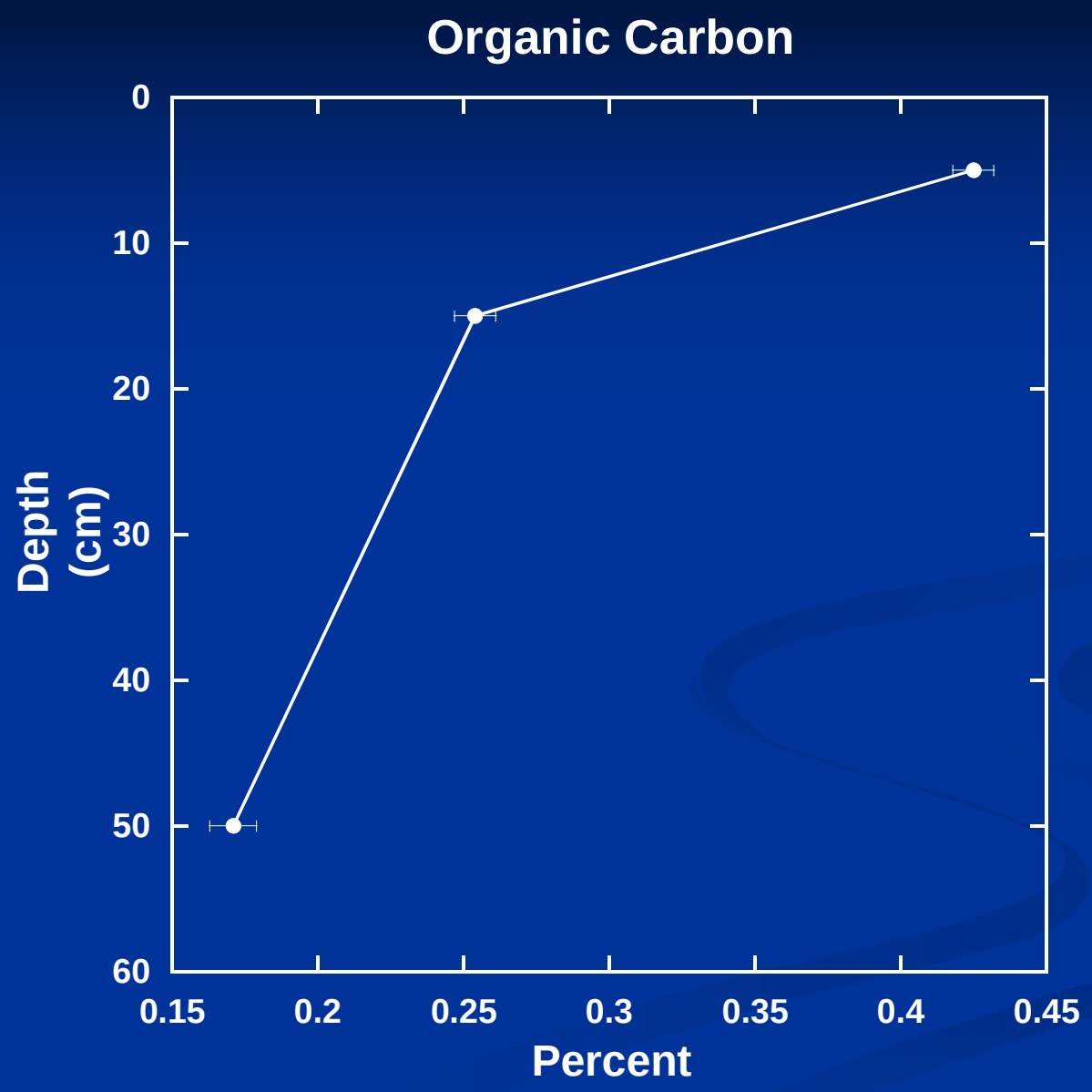
12/22/2007

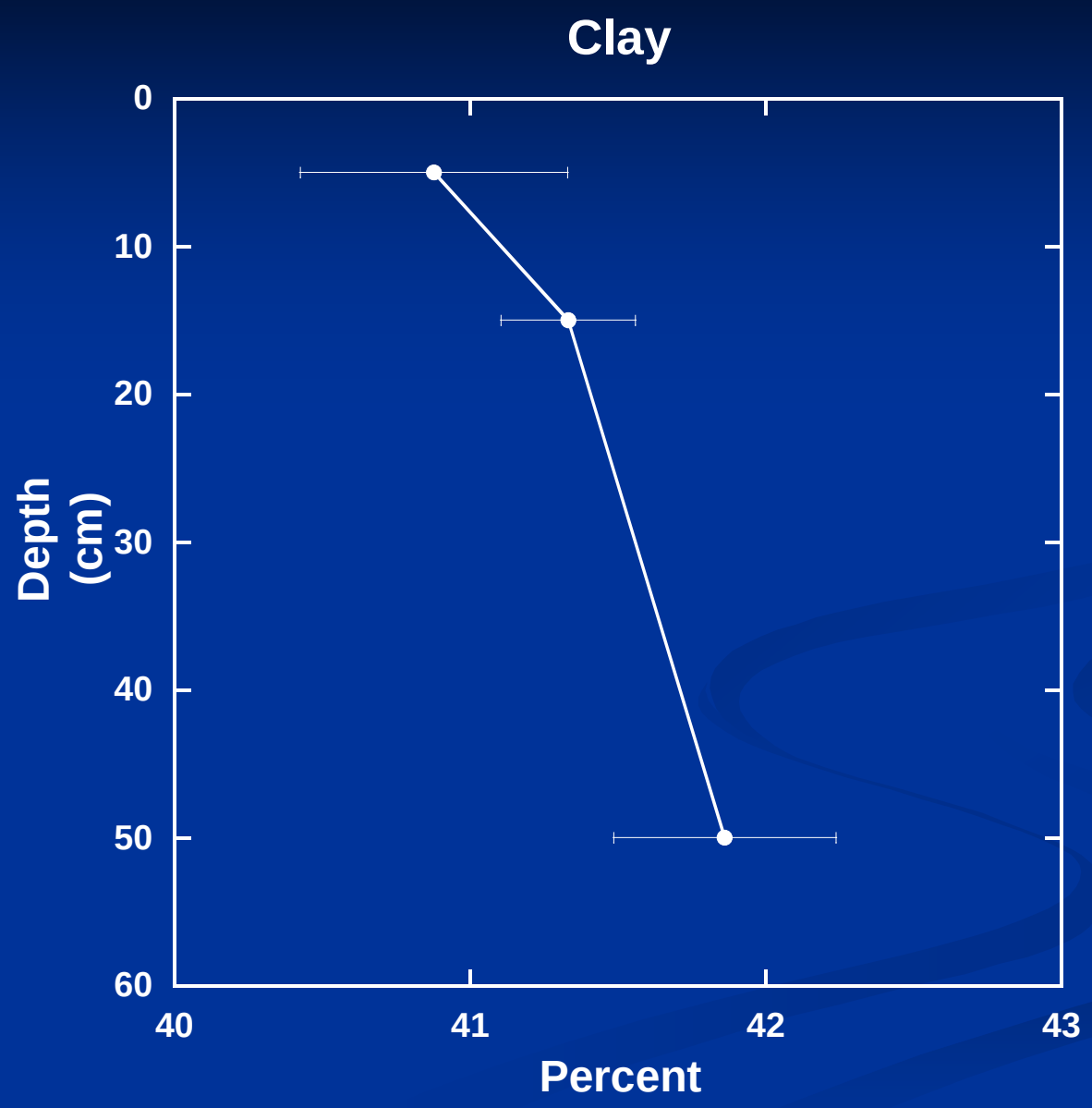
ubbermaid
GOTT
NKING WATER
20- 3 1/8" x 48"

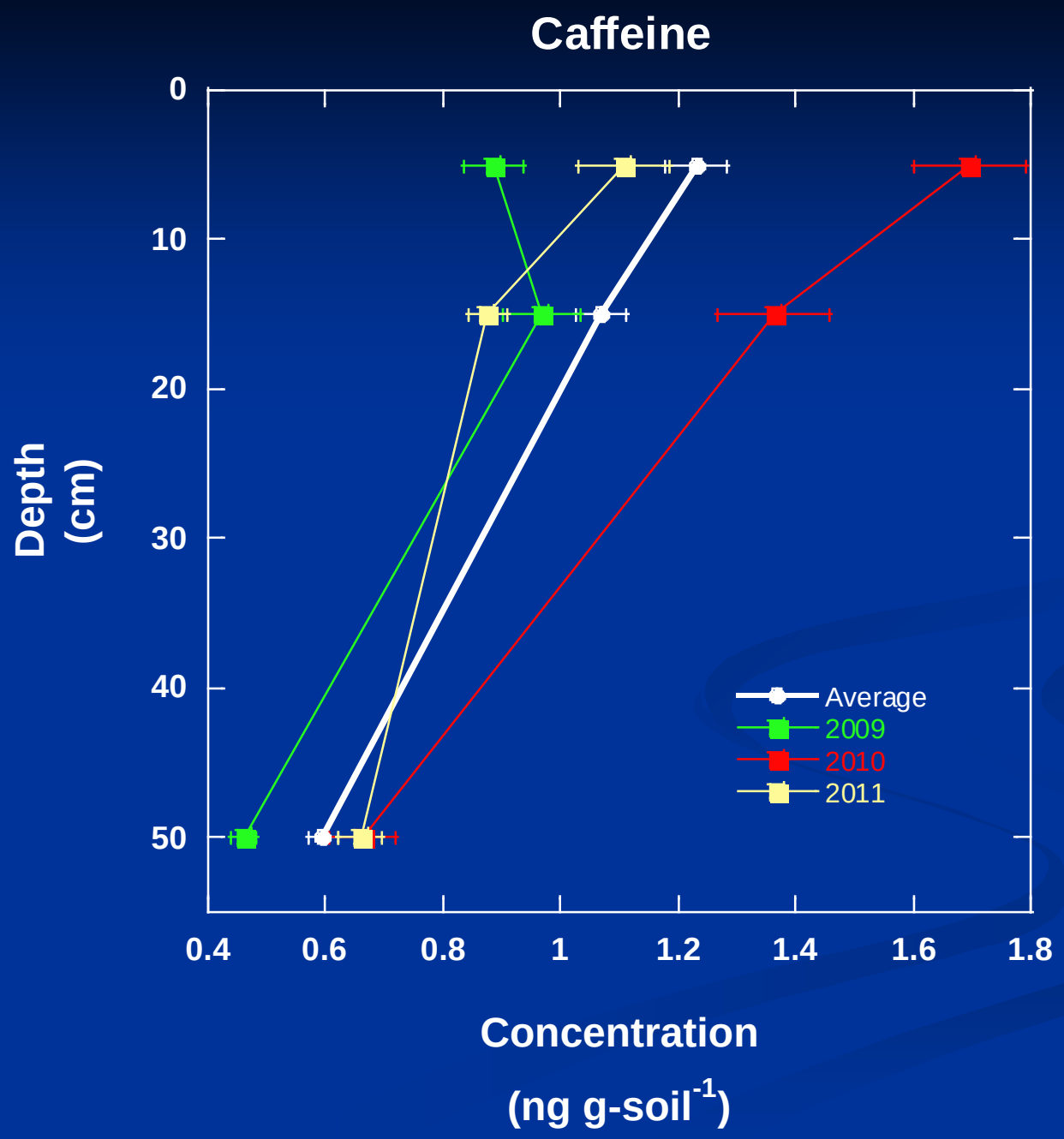
PARAFILM

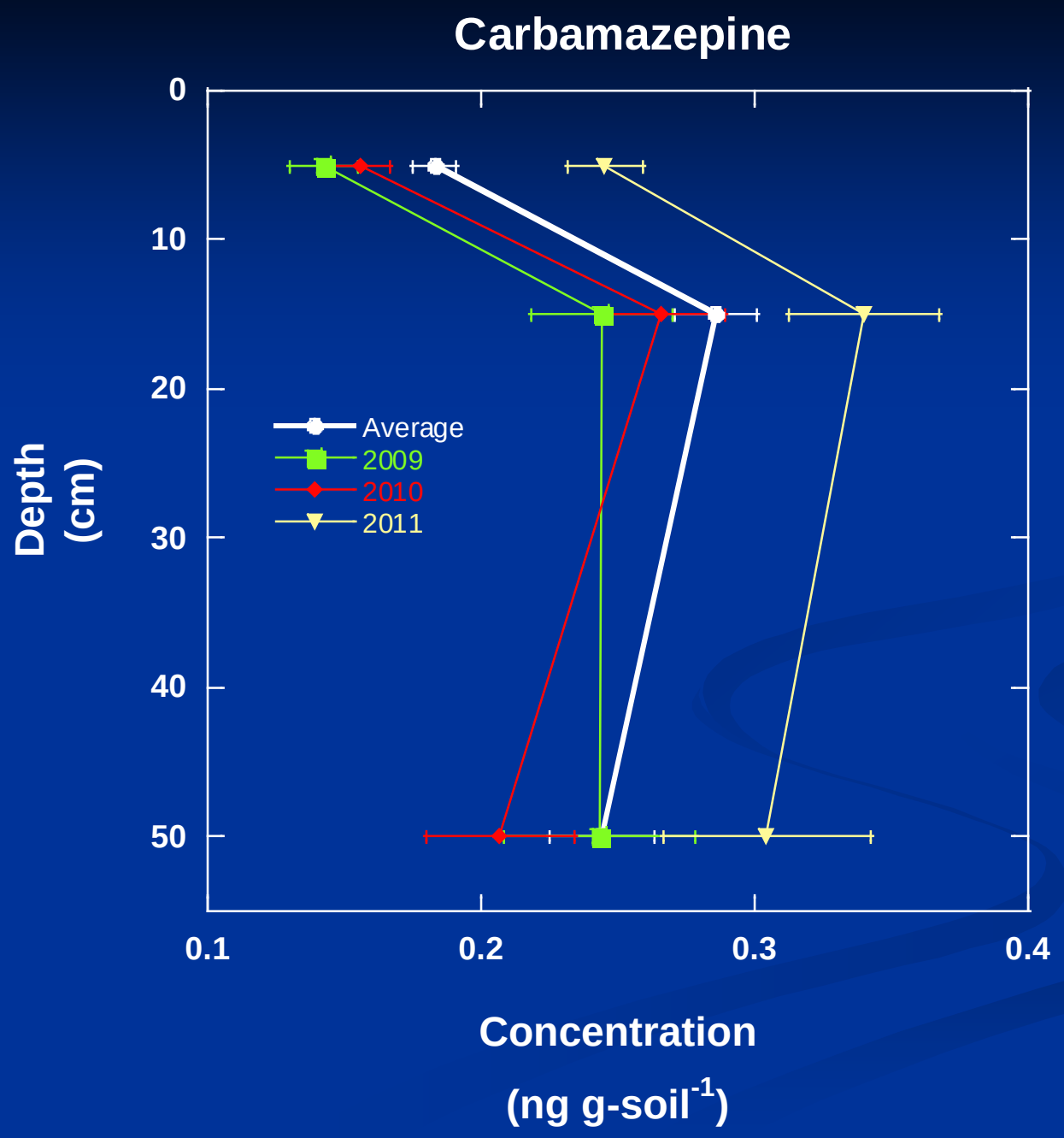
Extraction Procedure

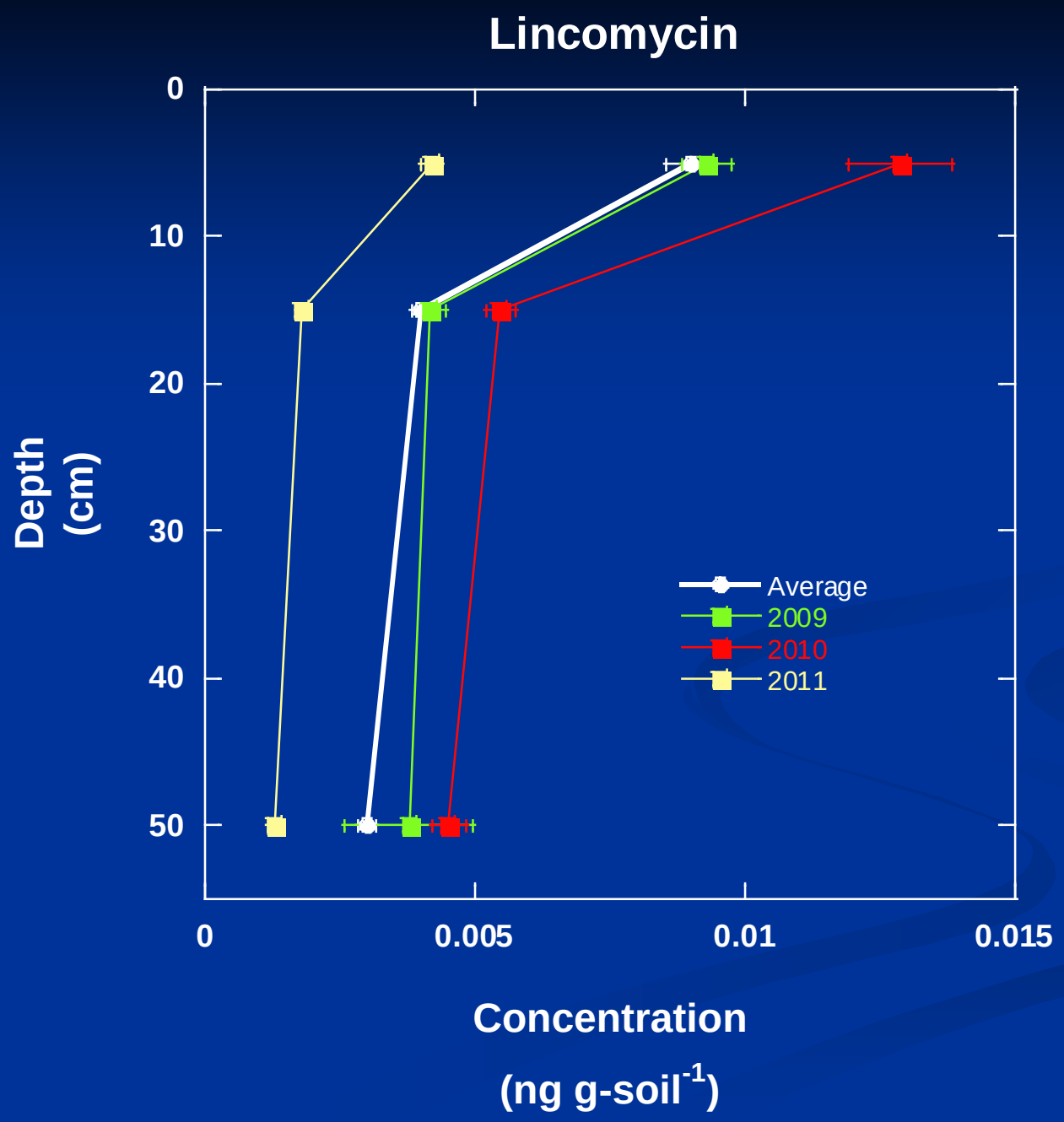
- Static 5 min
- Flush 60%
- 3 cycles with MeOH:Water 25:75
- Purge 100 sec
- Pressure 1500 psi
- 100 C


Organic Carbon
Depth (cm)
0
10
20
30
40
50
60
0.15
0.2
0.25
0.3
0.35
0.4
0.45
Percent


Clay
0
10
20
30
40
50
60
Depth (cm)
40
41
42
43
Percent


Caffeine
Depth (cm)
0
10
20
30
40
50
0.4
0.6
0.8
1
1.2
1.4
1.6
1.8
Concentration
(ng g-soil-1)
Average
2009
2010
2011


Carbamazepine
0
10
20
30
40
50
Depth (cm)
Average
2009
2010
2011
0.1
0.2
0.3
0.4
Concentration
(ng g-soil-1)


Lincomycin
Depth (cm)
0
10
20
30
40
50
0
0.005
0.01
0.015
Concentration
(ng g-soil-1)
Average
2009
2010
2011

Conclusions

- Caffeine concentration is increasing year to year
- Carbamazepine concentration is increasing year to year
  - Carbamzepine concentration in the surface shows signs of degradation
- Lincomycin is not accumulating
- No Ibuprofen was detected in any sample due to low solubility

Collaborators

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Shad Nelson – Texas A&M, Kingsville
Lonnie Frost – Town of Gilbert
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Technical Help

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PSU Farm Services

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