Preliminary Analysis of Self-Cleaning Capacity of Lake Pontchartrain using Fugacity Analysis

MESL RESEARCH GROUP

S. Kilic, K. Nam and M. Aral

Hurricane Katrina

A Devastated City

Short Term Solutions to Drain The City of New Orleans

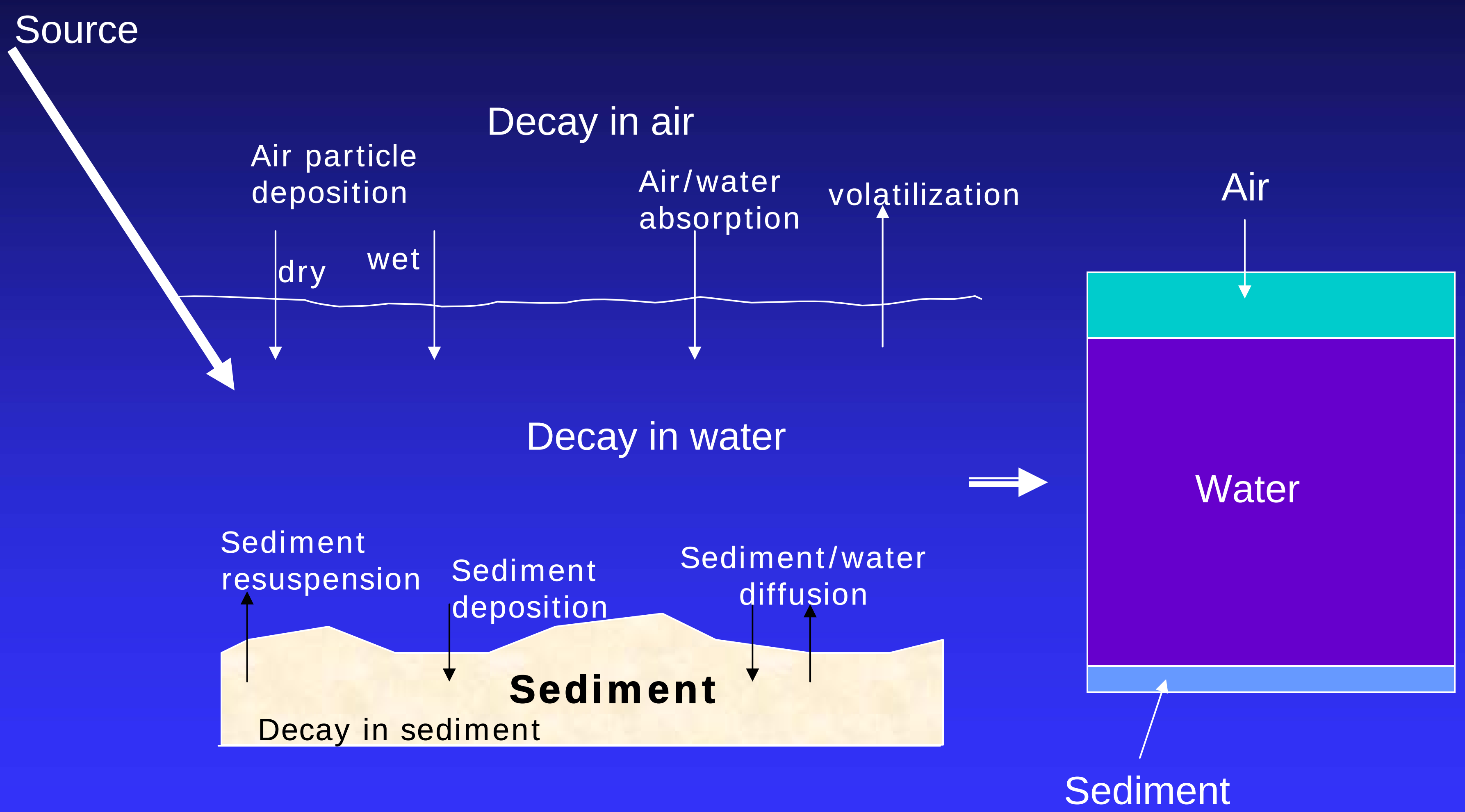
Is Dilution Really the Solution?

How Long will it take Lake Pontchartrain to replenish itself?

Objective

- How long will it take Lake Pontchartrain to be "clean" again?
- The mechanisms involved
  - Dilution
  - Decay
  - Volatilization – removal by winds
  - Deposition
  - Removal with outflow

Natural Processes in the Lake



Natural Processes in the Lake

- **In the water:**
  - **Source**
  - **Deposition from air**
  - **Resuspension from sediment**
  - **First order decay**
  - **Outflow from lake**
- **In the air:**
  - **Volatilization from water**
  - **First order decay**
  - **Wind induced air flow out of the lake system**
- **In the sediment:**
  - **Deposition from water**
  - **Diffusion between water**
  - **First order decay**

Mathematical Model

$$V_w Z_{bw} \frac{dF_W}{dt} = E_w + (K_{aw} A_w Z_w + Q_{dry} Z_{aerosol} + Q_{wet} Z_{aerosol}) F_A + (Q_{res} Z_s + K_{sw} A_s Z_w) F_S - (k_w V_w Z_w + Q_{dep} Z_p + Q_{out} Z_{bw} + K_{aw} A_w Z_w) F_W$$

Water Phase

$$V_a Z_{aw} \frac{dF_A}{dt} = (K_{aw} A_w Z_w) F_W - (Q_{dry} Z_{aerosol} + k_a V_a Z_a + Q_{wet} Z_{aerosol} + Q_{air} Z_{ba} + K_{aw} A_w Z_w) F_A$$

Air Phase

$$V_s Z_{bs} \frac{dF_S}{dt} = (Q_{dep} Z_p + K_{sw} A_s Z_w) F_W - (k_s V_s Z_s + Q_{res} Z_s + K_{sw} A_s Z_w) F_S$$

Sediment Phase

Parameters Used in the Model

- Fw : water fugacity
- Fa : air fugacity
- Fs : sediment fugacity
- Vw : volume of water
- Va : volume of air
- Vs : volume of sediment
- Aw : water surface area
- As: sediment surface area
- Qout : outgoing water flowrate
- Qair : air flowrate
- Qdep : particle deposition rate
- Qres : sediment resuspension rate
- Qdry : dry air deposition rate
- Qwet : wet air deposition rate
- t : time

- Kaw : water-air mass transfer coefficient
- Ksw : sediment-water mass transfer coefficient
- kw : water decay constant
- ka: air decay constant
- ks : sediment decay constant
- Zw : water fugacity capacity
- Za : air fugacity capacity
- Zs : sediment fugacity capacity
- Zp : wate particle fugacity capacity
- Zaerosol : aerosol fugacity capacity
- Zbw : bulk water fugacity capacity
- Zba :bulk air fugacity capacity
- Zbs : bulk sediment fugacity capacity

Information Required to Solve the Governing Equations

- Information about the lake
  - Volume of lake, sediments, and air parcel
  - Surface area
  - Flow rate of outgoing tributaries
  - Air flow rate
  - Sediment deposition rate
  - Sediment resuspension rate
  - Dry deposition rate
  - Wet deposition rate
- Information about the content of the flood waters

The Contents of the Flood Waters

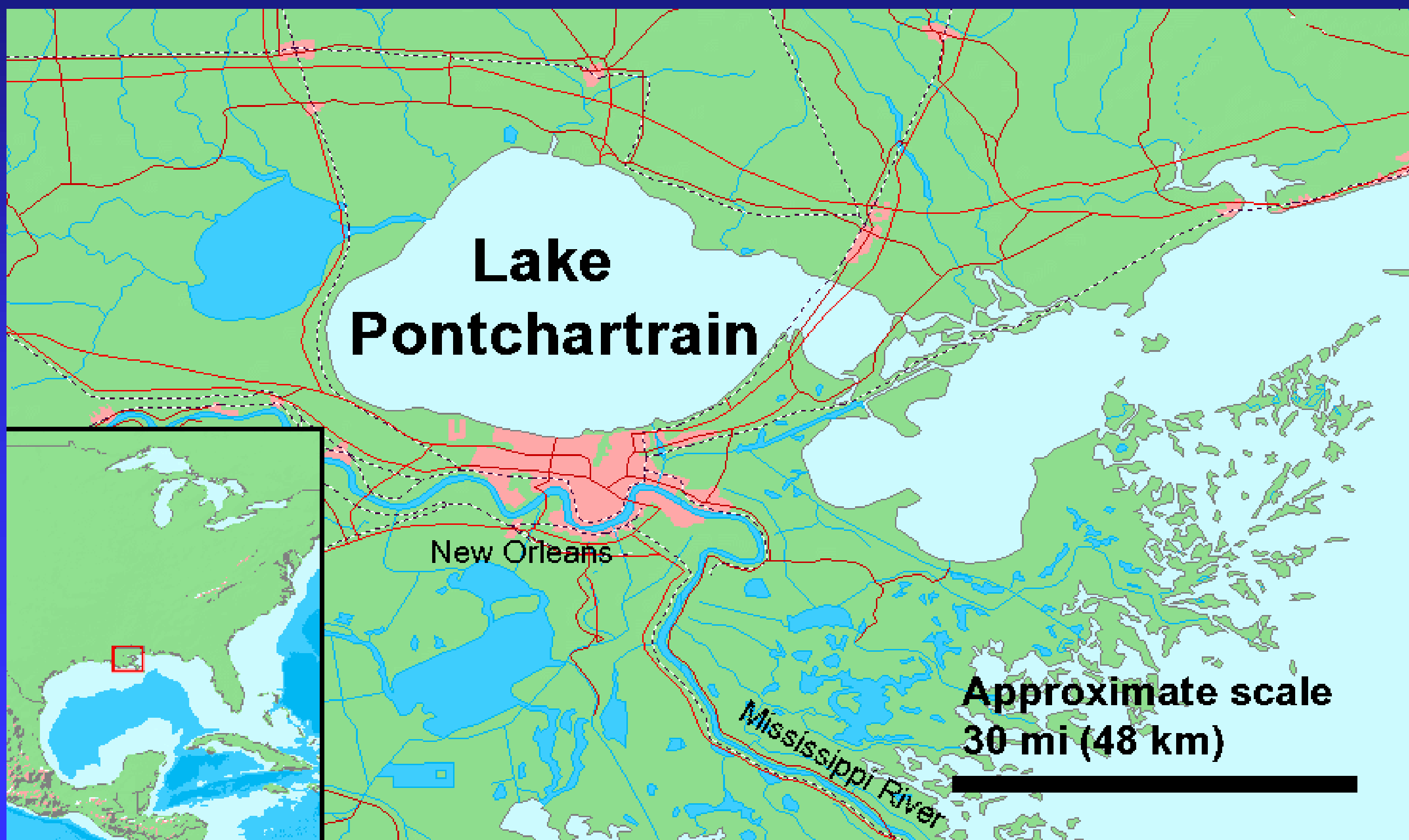
No information

Contaminants Selected for this Study

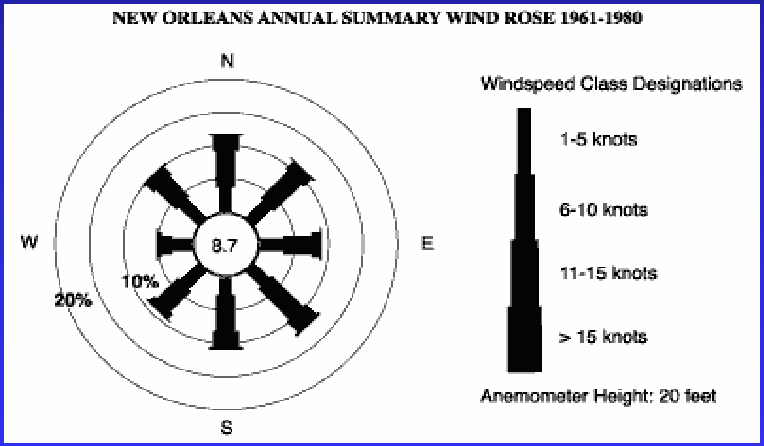
- **Benzene**
  - **Volatile, primary pollutant, commonly used, health issues**
- **Lindane**
  - **Pesticide, used commonly by agricultural practice, health issues**
- **PCBs**
  - **Primary pollutant, recalcitrant, toxic, bioaccumulative**

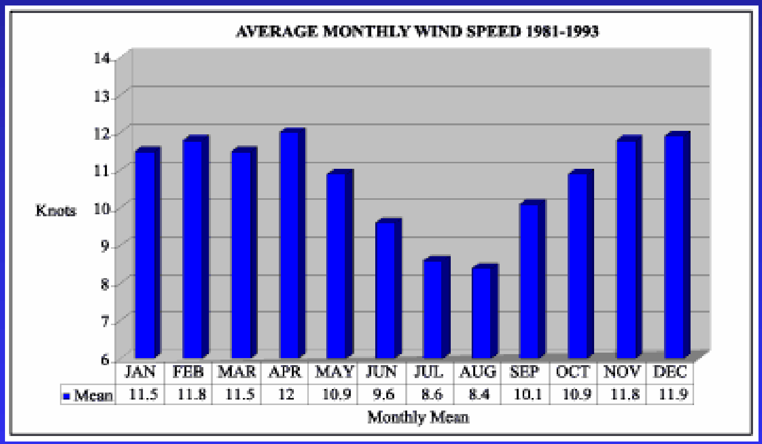
Lake Pontchartrain

Surface Area	: 1632000000 m^2 (630 mi^2)
Average Depth	: 3.65 m (12 ft)
Total water outflow	: 1563352 m^3/h (15336 cfs)
Wind speed on lake	: 10.75 knots (19908.83 m/h)
Depth of air on lake	: 0.5 m
Volume of air	: 816000000 m^3
Depth of sediment	: 0.05 m
Volume of sediment	: 81600000 m^3
Density of sediment	: 2400 kg/m^3



Wind induced advection above Lake Pontchartrain





Qair = 32000000 m^3/hour

Deposition and Resuspension Rates

- Adopted from a Steady-State Fugacity model development in Trent University:
  - $U_{deposition}$ = 0.0000005 m/h
  - $U_{resuspension}$ = 0.0000002 m/h
  - $Q_{dry\ air\ deposition}$ = 2.76 m/hour
  - $Q_{wet\ air\ deposition}$ = 7.34 m/hour

(http://www.trentu.ca/cemc/models)

Mass Transfer Coefficients

- Two-film theory to calculate for each contaminant
- Overall water-air mass transfer coefficient:

$$\frac{1}{K_{aw}} = \frac{1}{k_{water}} + \frac{1}{k_{air} H}$$

K_{aw} = 0.0034 m/hour for PCBs
K_{aw} = 0.00002 m/hour for Lindane
K_{aw} = 0.00958 m/hour for Benzene

Physicochemical Properties Required for Contaminants

- Water Solubility
- Vapor Pressure
- Octanol-Water Partition Coefficient
- Density
- Molecular Weight
- Half lives in each media

$$Z_{air} = \frac{1}{RT}$$

$$Z_{water} = \frac{1}{H} = \frac{C^{s}}{P_{s}}$$

$$Z_{sediment} = \frac{K_{sw}\rho_{s}}{H} = K_{sw}\rho_{s}(Z_{water})$$

$$k_{reaction} = \frac{Ln2}{\tau_{1/2}}$$

Source Rate

- The pumping lasted about one week
- About 10% of lake volume was pumped into the lake
- 3420000 m^3/hour source rate
- 10 % of the dumped water is contaminant by volume.
- Convert to mass rate for each contaminant
  - 2200000000 moles/hour Lindane
  - 3840000000 moles/hour Benzene
  - 1470000000 moles/hour PCB

Solution Technique of the System of Equations

- The nonlinear model yields three equations with three unknowns.
- Finite Difference Method is used to solve the governing equations.
- A matrix solution algorithm is developed for simultaneous solution.

Final Values Used in the Model

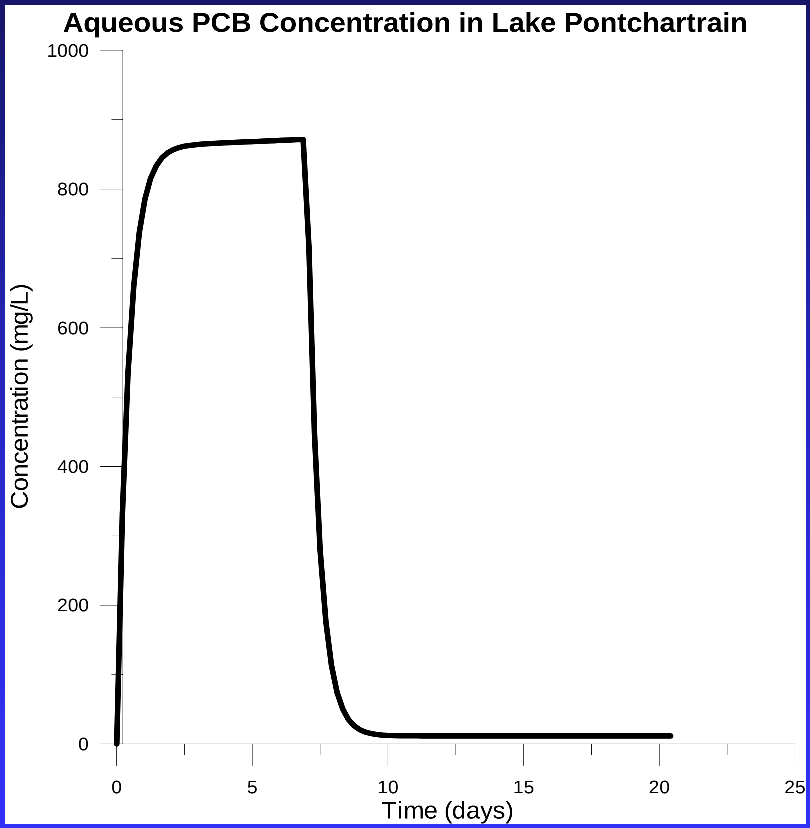
Deposition Rate	816 m^3/h		
Resuspension Rate	326 m^3/h		
Dry air deposition rate	2.76 m^3/h		
Wet air deposition rate	7.34 m^3/h		
	PCB	LINDANE	BENZENE
Air-water MTC (m/h)	0.0034	0.0002	0.00958
Sediment-water MTC (m/h)	0.0001	0.0004	0.0006
Water decay rate (1/h)	5×10^{-6}	4.08×10^{-5}	4.08×10^{-2}
Air decay rate (1/h)	0.0001	4.08×10^{-3}	4.08×10^{-3}
Sediment decay rate (1/h)	2×10^{-6}	1.26×10^{-5}	4.08×10^{-4}

Results

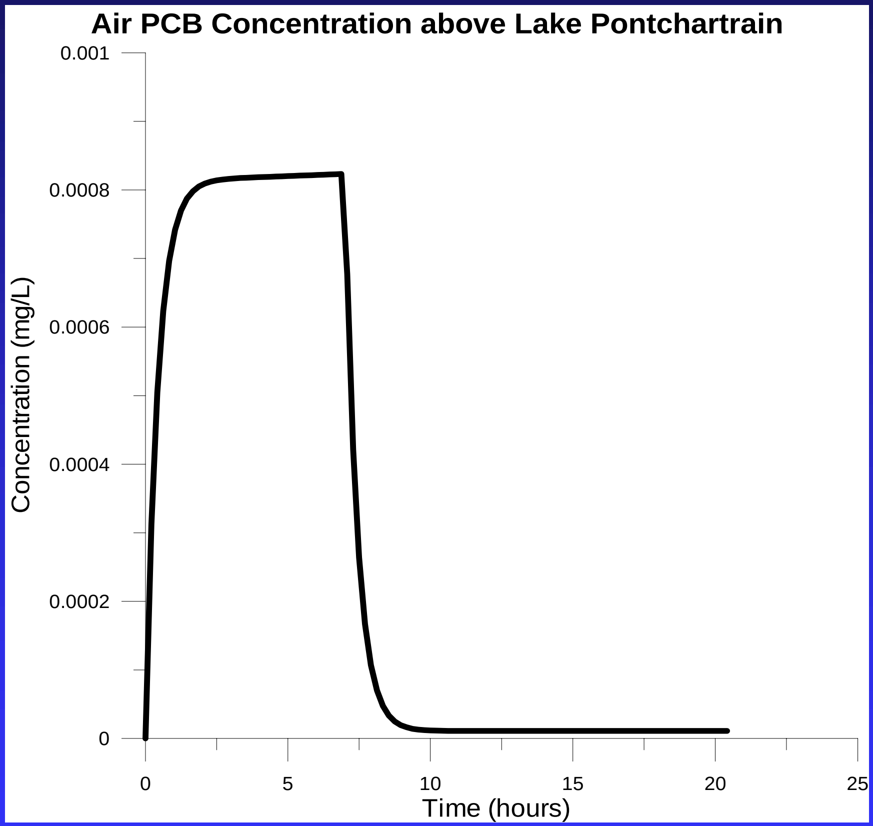
- It will take Lake Pontchartrain:
  - 1 year to recover from Benzene pollution.
  - 13.5 years to recover from Lindane pollution.
  - 81 years to recover from PCB pollution.

- Regulated standard values by EPA in water:
  - Benzene 0.005 mg/L.
  - Lindane 0.0002 mg/L.
  - Total PCBs 0.0005 mg/L.

PCB Results

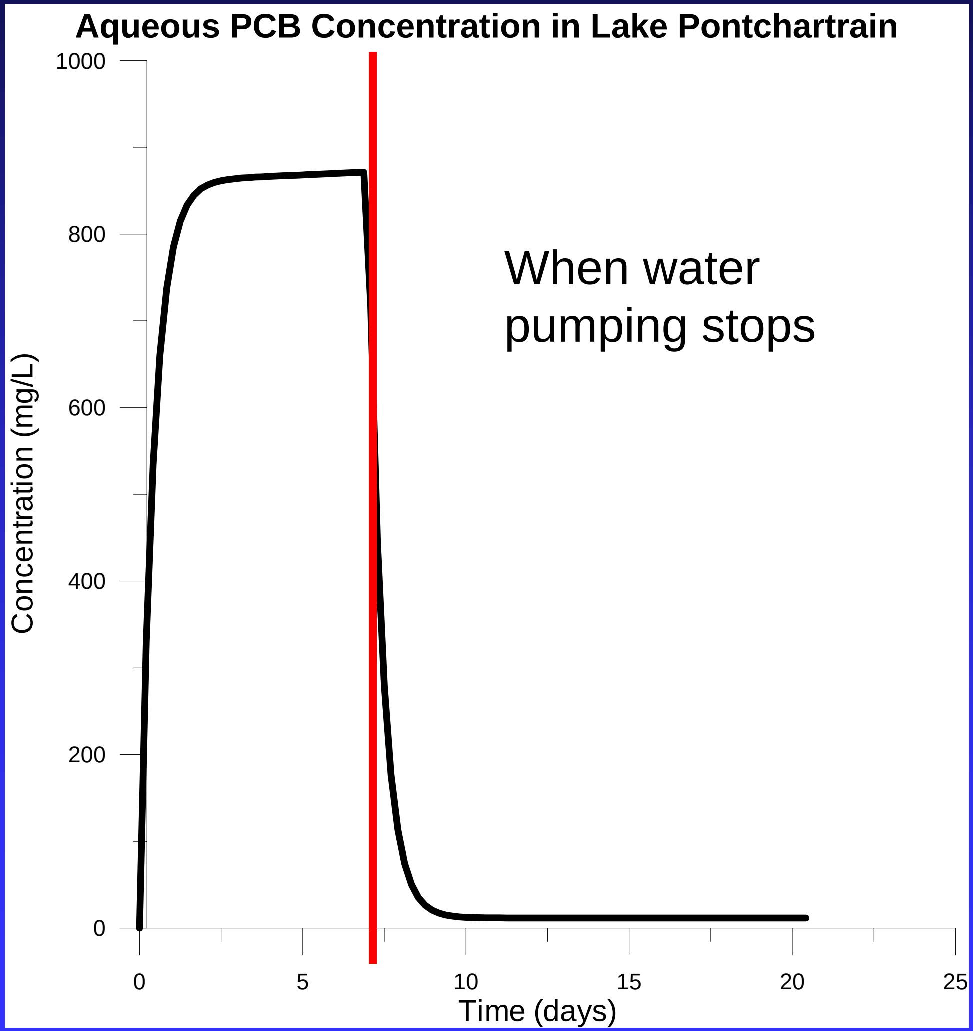


Aqueous PCB Concentration in Lake Pontchartrain
Concentration (mg/L)
1000
800
600
400
200
0
0
5
10
15
20
25
Time (days)

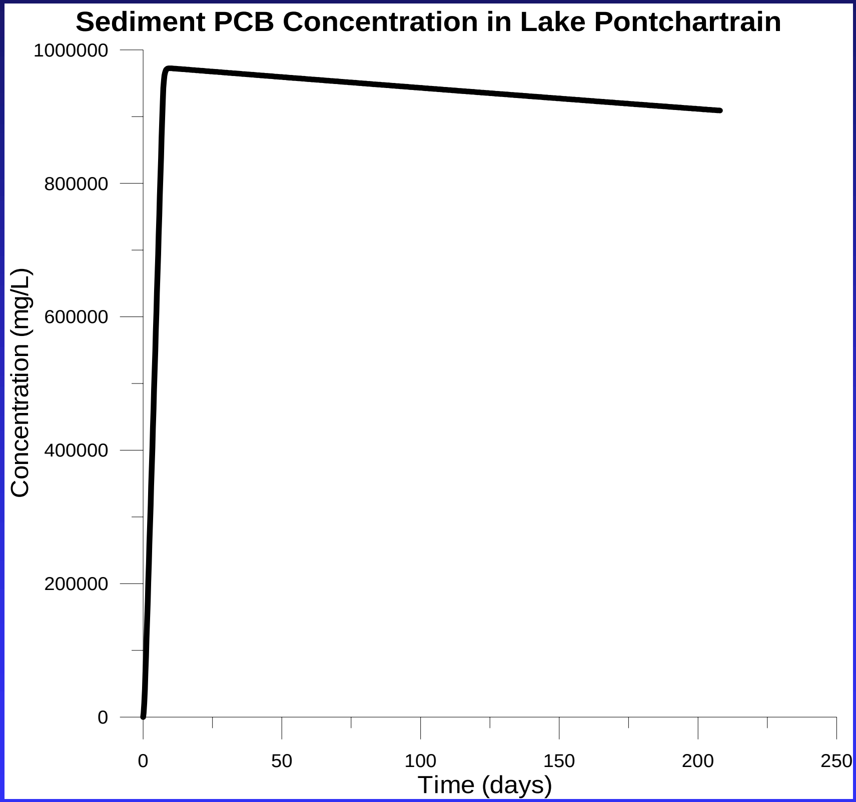


Air PCB Concentration above Lake Pontchartrain
Concentration (mg/L)
0.001
0.0008
0.0006
0.0004
0.0002
0
0
5
10
15
20
25
Time (hours)

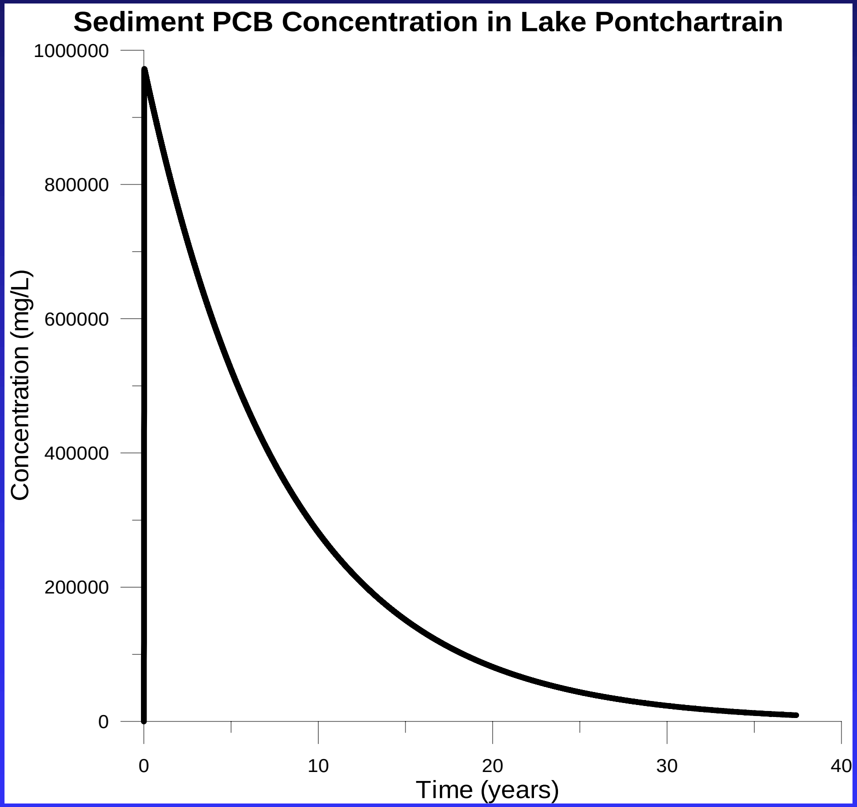
How Lake Pontchartrain Reacts to Contaminant Dumping Water



PCB Results

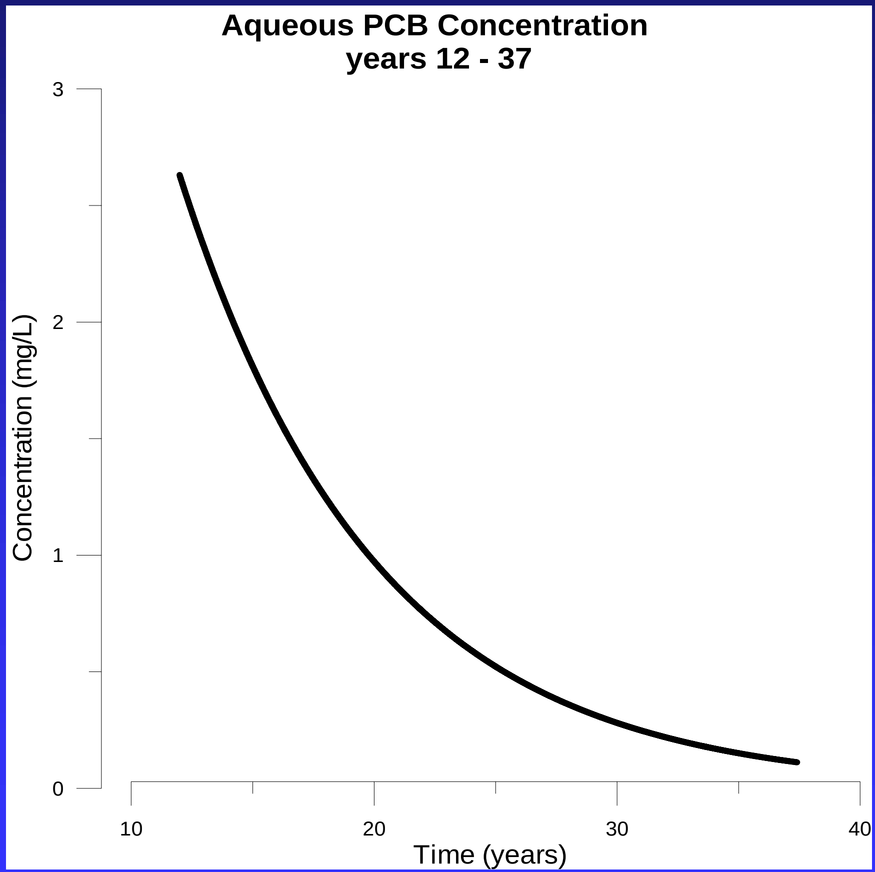


Sediment PCB Concentration in Lake Pontchartrain
Concentration (mg/L)
1000000
800000
600000
400000
200000
0
0
50
100
150
200
250
Time (days)



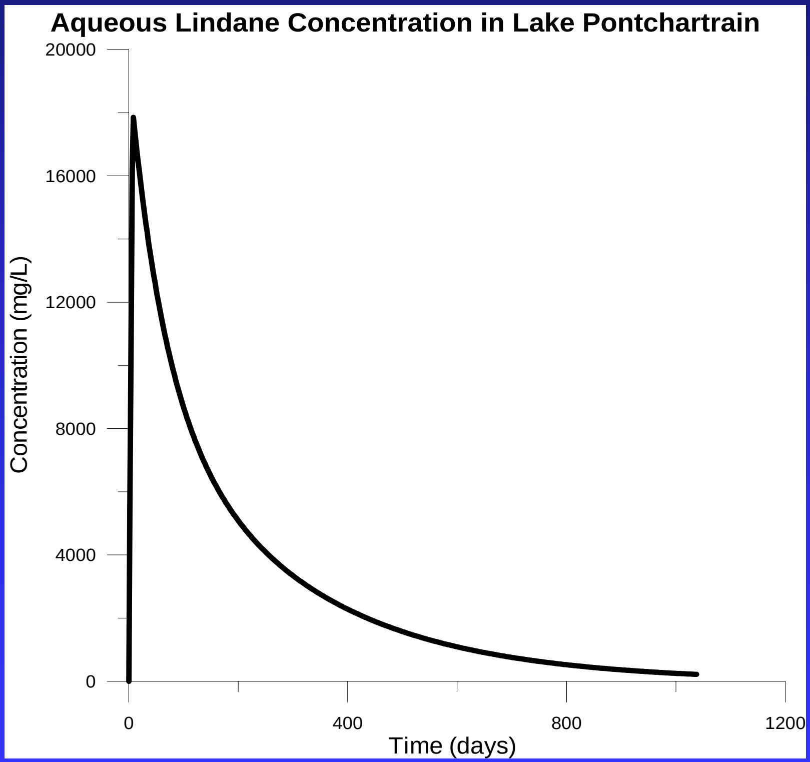
Sediment PCB Concentration in Lake Pontchartrain
Concentration (mg/L)
1000000
800000
600000
400000
200000
0
0
10
20
30
40
Time (years)

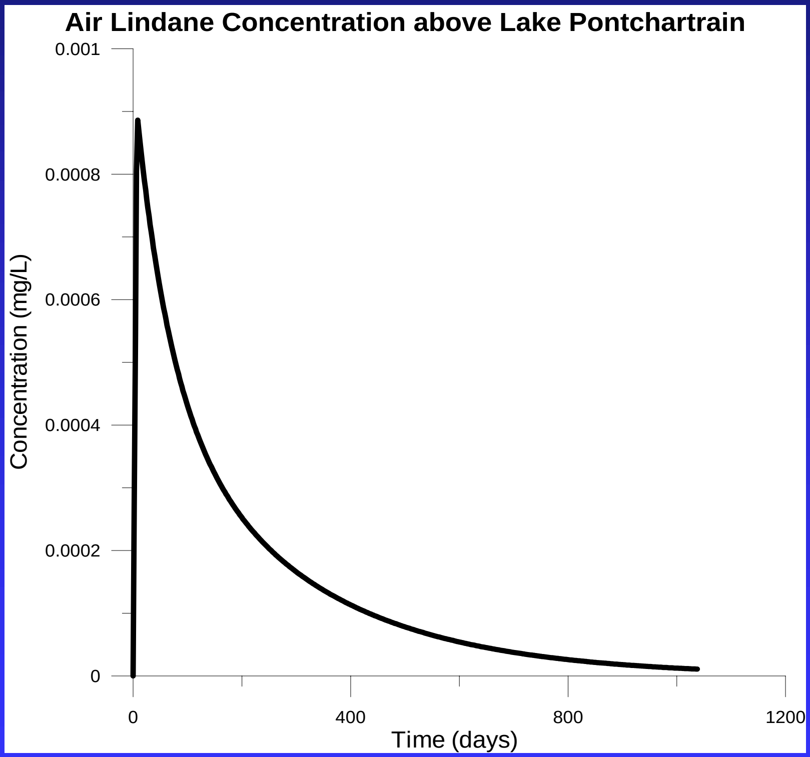
PCB Results



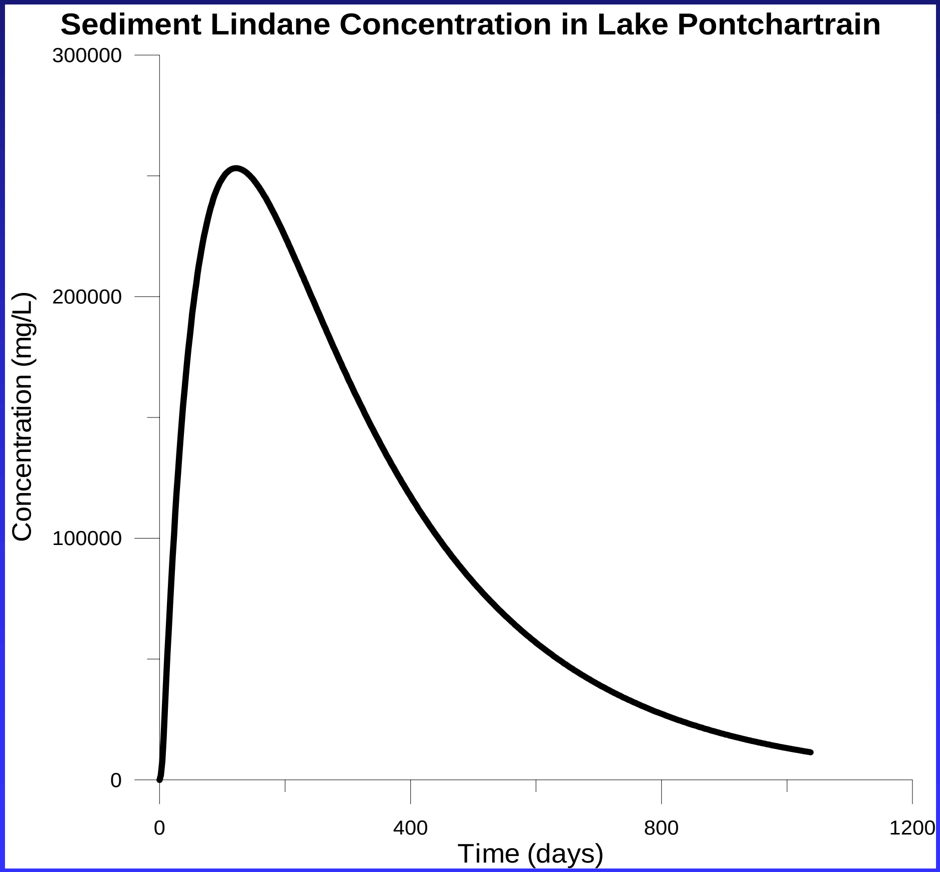
Aqueous PCB Concentration
years 12 - 37
Concentration (mg/L)
0
1
2
3
10
20
30
40
Time (years)

Lindane Results

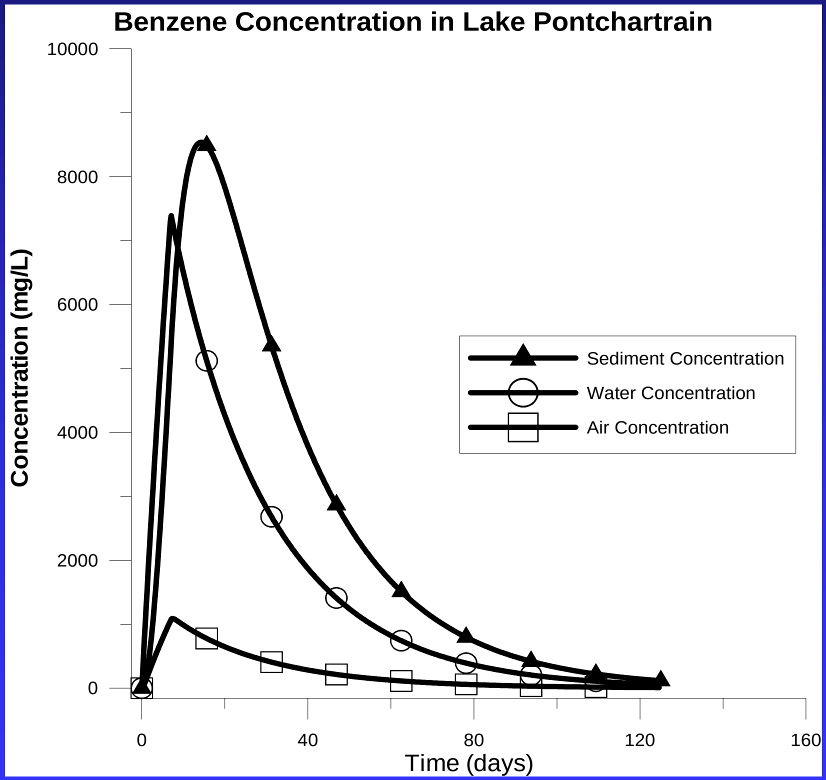


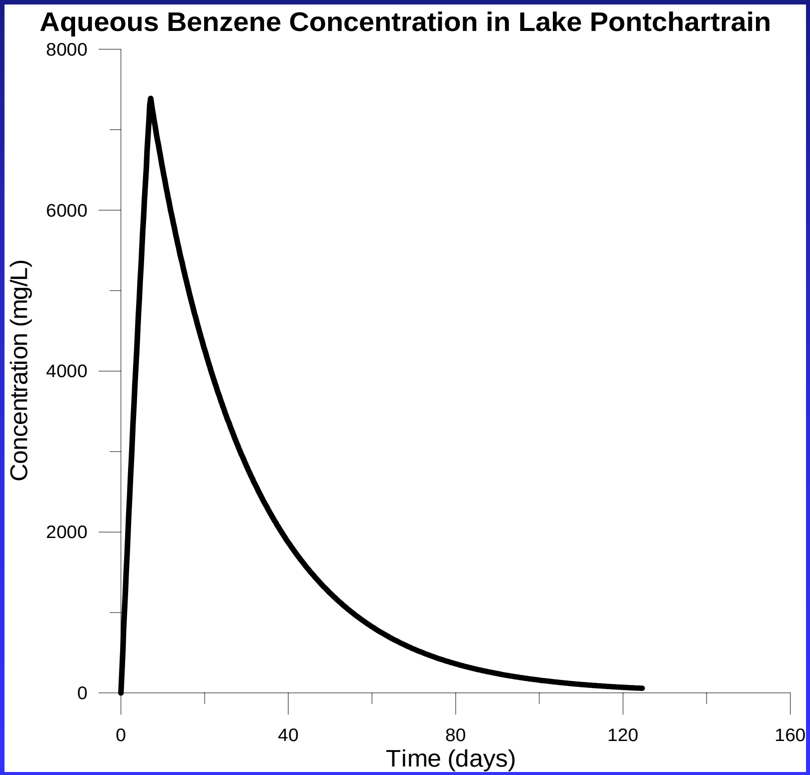


Lindane Results

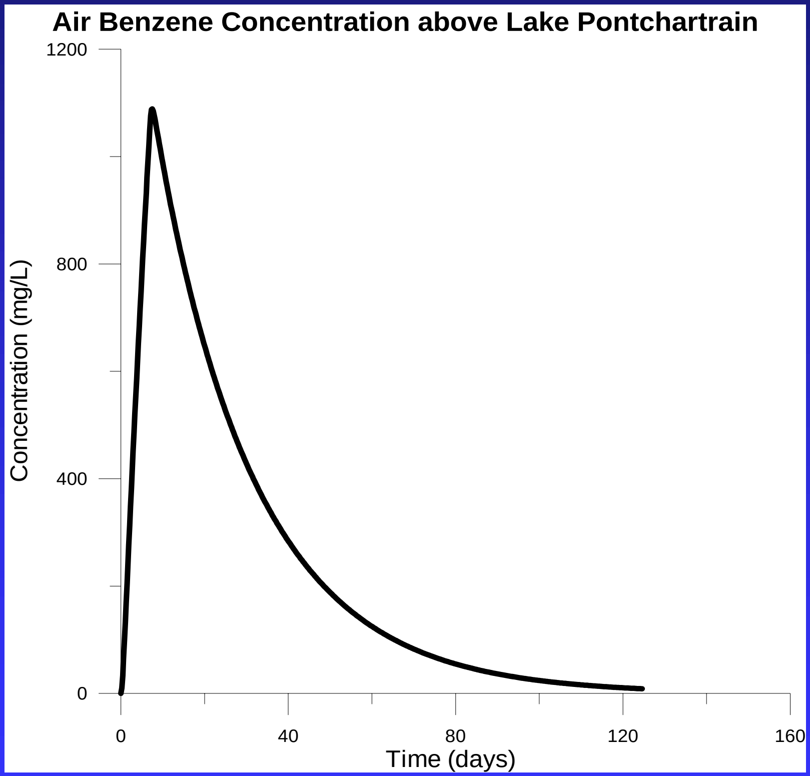


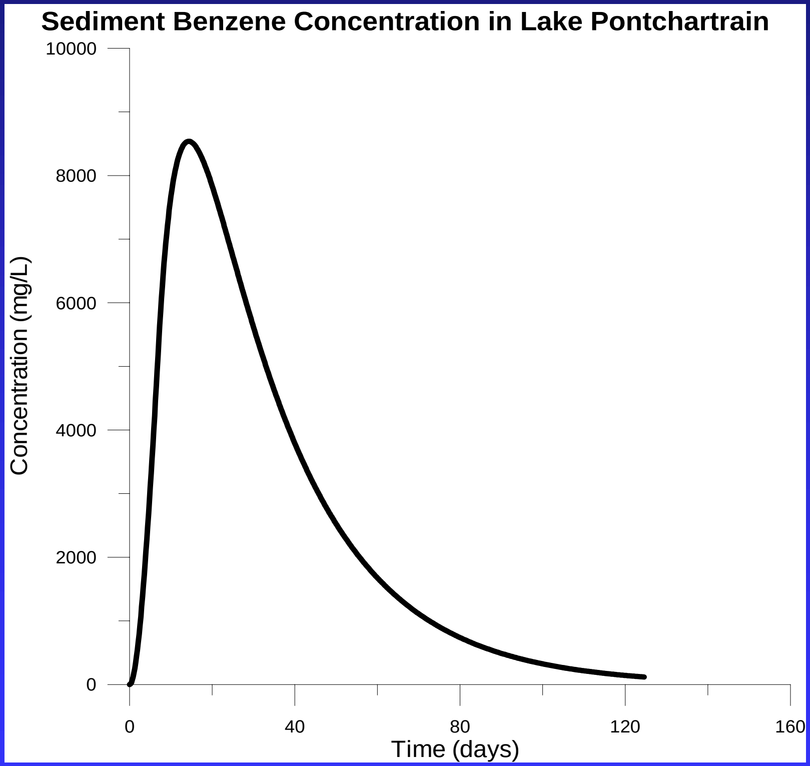
Benzene Results





Benzene Results





Some Observations

- Air Phase recover quickest for all three contaminants
- As Benzene is more volatile, it partitions into air sooner and removed from the system – about 1 year
- PCB stays longest – 81 years
- All three chemicals stay longest in the sediments
- Benzene partitions more proportionally among three phases

Sensitivity Analysis - PCB

Parameter	Change	Time	Percent Change	Parameter	Change	Time	Percent Change
Kaw	10%	80.902	0.00405	ka	10%	81.307	0
	-10%	81.718	-0.00411		-10%	81.307	0
	20%	80.502	0.00805		20%	81.307	0
	-20%	82.135	-0.00828		-20%	81.307	0
Ksw	10%	81.359	-0.00052	Qres	10%	81.598	-0.00291
	-10%	81.256	0.00051		-10%	80.936	0.00371
	20%	81.41	-0.00103		20%	81.815	-0.00508
	-20%	81.21	0.00097		-20%	80.457	0.0085
kw	10%	81.307	0	Qdep	10%	80.982	0.00325
	-10%	81.313	-6E-05		-10%	81.621	-0.00314
	20%	80.301	0.01006		20%	80.64	0.00667
	-20%	81.315	-8E-05		-20%	81.895	-0.00588
ks	10%	74.321	0.06986	Qair	10%	81.307	0
	-10%	89.743	-0.08436		-10%	81.307	0
	20%	68.442	0.12865		20%	81.307	0
	-20%	100.137	-0.1883		-20%	81.307	0

Sensitivity Analysis - Lindane

Parameter	Change	Time	Percent Change	Parameter	Change	Time	Percent Change
Kaw	10%	13.234	0.00025	ka	10%	13.259	0
	-10%	13.285	-0.00026		-10%	13.259	0
	20%	13.207	0.00052		20%	13.259	0
	-20%	13.311	-0.00052		-20%	13.259	0
Ksw	10%	13.746	-0.00487	Qres	10%	13.302	-0.00043
	-10%	12.844	0.00415		-10%	13.318	-0.00059
	20%	14.309	-0.0105		20%	13.147	0.00112
	-20%	12.498	0.00761		-20%	13.38	-0.00121
kw	10%	13.067	0.00192	Qdep	10%	13.348	-0.00089
	-10%	13.438	-0.00179		-10%	13.164	0.00095
	20%	12.892	0.00367		20%	13.424	-0.00165
	-20%	13.633	-0.00374		-20%	13.076	0.00183
ks	10%	12.905	0.00354	Qair	10%	13.259	0
	-10%	13.698	-0.00439		-10%	13.259	0
	20%	12.667	0.00592		20%	13.259	0
	-20%	13.993	-0.00734		-20%	13.259	0

Sensitivity Analysis - Benzene

Parameter	Change	Time	Percent Change	Parameter	Change	Time	Percent Change
Kaw	10%	1.012557	0.0001484	ka	10%	1.0245	2.897E-05
	-10%	1.04509	-0.00017693		-10%	1.03025	-2.853E-05
	20%	1.577626	-0.00550229		20%	1.02226	5.137E-05
	-20%	1.066781	-0.00039384		-20%	1.0331	-5.703E-05
Ksw	10%	1.0371	-9.703E-05	Qres	10%	1.027397	0
	-10%	1.018265	9.132E-05		-10%	1.027397	0
	20%	1.046233	-0.00018836		20%	1.027397	0
	-20%	1.009703	0.00017694		-20%	1.027397	0
kw	10%	0.985731	0.00041666	Qdep	10%	1.027397	0
	-10%	1.073059	-0.00045662		-10%	1.027397	0
	20%	0.946918	0.00080479		20%	1.027397	0
	-20%	1.123288	-0.00095891		-20%	1.027397	0
ks	10%	1.026826	5.71E-06	Qair	10%	0.998858	0.00028539
	-10%	1.027968	-5.71E-06		-10%	1.059361	-0.00031964
	20%	1.026256	1.141E-05		20%	0.973174	0.00054223
	-20%	1.028539	-1.142E-05		-20%	1.09589	-0.00068493

Observations about Sensitivity Analysis (1)

- The most important parameter is sediment reaction rate constant (ks) – derived from half lives
- The higher the half life in sediment, longer it takes the lake to recover
- The second most effective parameter is sediment-water mass transfer rate (Ksw). When the contaminant passes to sediment, it takes it longer to get out of the system.
- On the other hand, air-water mass transfer rate (Kaw) has the inverse effect. As the contaminant passes into air, it is removed from the system quicker, due to faster decay and air outflow

Observations about Sensitivity Analysis (2)

- Benzene is more sensitive for parameter changes.
- Benzene is more volatile, thus when air-water mass transfer coefficient is higher, removal of benzene from the system is quicker

Conclusion

- Hydrophobicity. Higher the octanol-water partition coefficient, longer it will take a lake to replenish (PCB – 6.6; Benzene – 2.13; Lindane – 3.70)
- Volatile compounds will be removed faster, however will create air pollution problems in the immediate vicinity
- During the first couple of weeks following the dumping of the flood waters, some living organisms must have been harmed as the contaminants reach very high concentrations in the lake

Ongoing Work:

- Inclusion of bioaccumulation module to this model.
- Consider speciation.
- Develop a dynamic model, which also has a spatial variability.
- Uncertainty analysis.

For additional information or questions, you may contact:

M. M. Aral: ***maral@ce.gatech.edu***

Or visit MESL web page at

http://www.ce.gatech.edu/research/MESL/