

# Rebound of a Coal Tar Creosote Plume following Partial Source Zone Treatment with Permanganate

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# Background

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Management of dissolved phase plumes from coal tar creosote contaminated sites is a technical challenge..

- 100's of different compounds
- origin of the coal
- distilling process

85% aromatic hydrocarbons

10% phenolic compounds

5% N-S-O heterocyclics

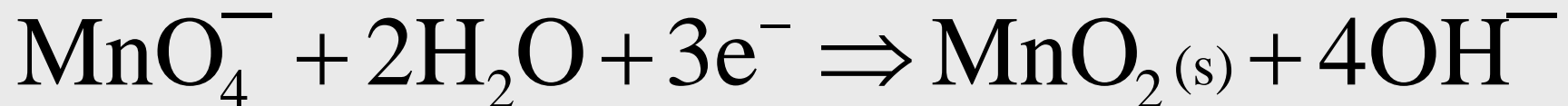
# Potential Remedy

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When contaminant mass removal is not primary remedial goal...

look at source zone stabilization methods

Reduction of permanganate ...



# Manganese Oxides

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- form at the point of reaction
- highly insoluble
- aggregate to form colloids

Precipitation of these solids has been shown to:

- decrease hydraulic conductivity
- cause flow divergence
- reduce post-treatment mass transfer



# Research Objective

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The potential of partial permanganate treatment to reduce the ability of a coal tar creosote source zone to generate a multi-component plume at the pilot-scale...

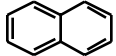
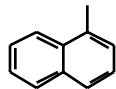
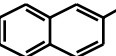
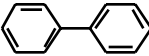

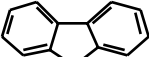
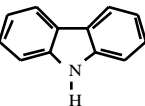
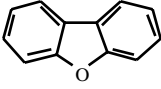
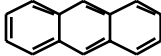
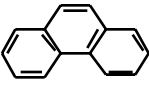
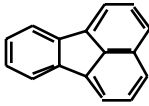
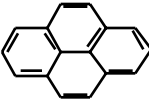
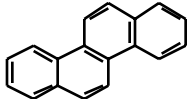
- short-term (weeks to months)
- long-term (years)

# Approach

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- **bench-scale experiments**
  - kinetics
  - post-treatment mass load
- **pilot-scale (10 years plume data)**

# Reactivity Kinetic Data

Compound	Formula	Structure	T <sub>1/2</sub> [min]
naphthalene	C <sub>10</sub> H <sub>8</sub>		1000
1-methylnaphthalene	C <sub>11</sub> H <sub>10</sub>		800
2-methylnaphthalene	C <sub>11</sub> H <sub>10</sub>		600
biphenyl	C <sub>12</sub> H <sub>10</sub>		NR
acenaphthene	C <sub>12</sub> H <sub>10</sub>		50
fluorene	C <sub>13</sub> H <sub>10</sub>		25
carbazole	C <sub>12</sub> H <sub>9</sub> N		25
dibenzofuran	C <sub>12</sub> H <sub>8</sub> O		NR
anthracene	C <sub>14</sub> H <sub>10</sub>		<2
phenanthrene	C <sub>14</sub> H <sub>10</sub>		30
fluoranthene	C <sub>16</sub> H <sub>10</sub>		10
pyrene	C <sub>16</sub> H <sub>10</sub>		5
chrysene	C <sub>18</sub> H <sub>12</sub>		900

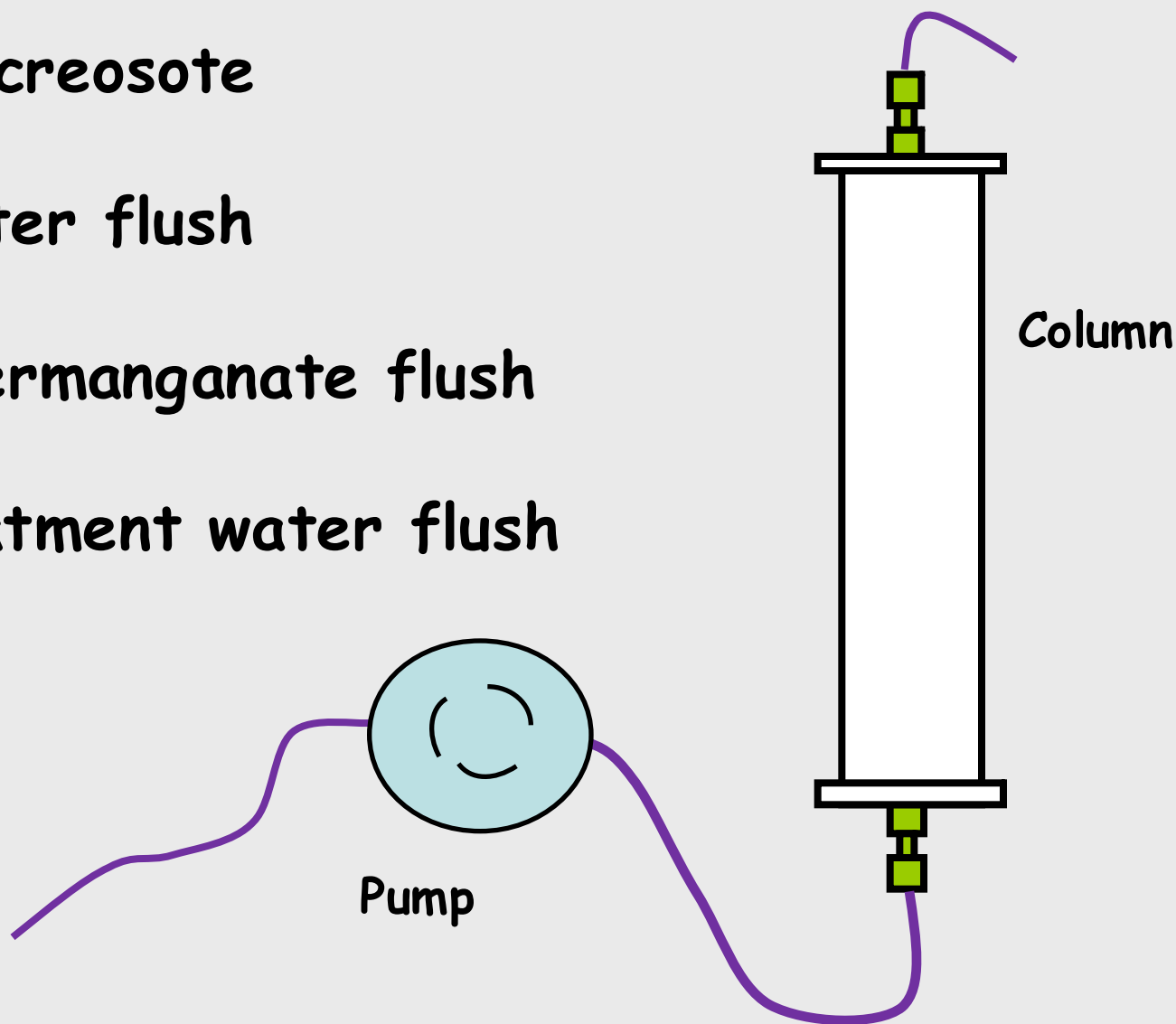


not reactive

fast

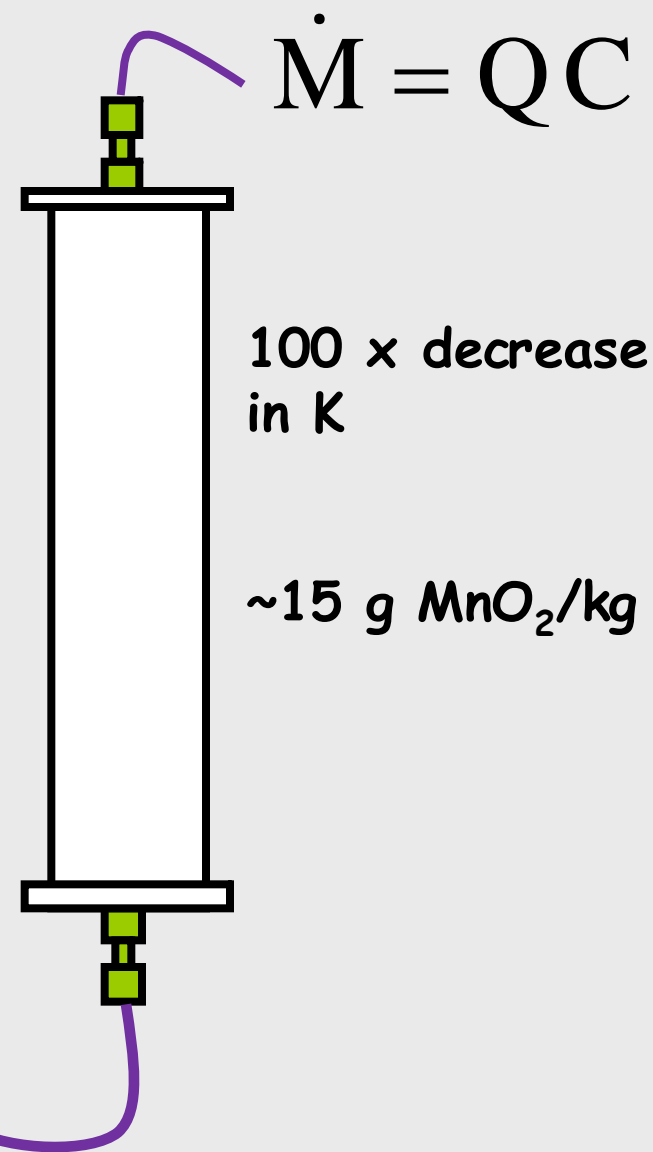
# Bench-Scale Effort

- 3% (v/v) creosote
- initial water flush
- 7 days permanganate flush
- post-treatment water flush

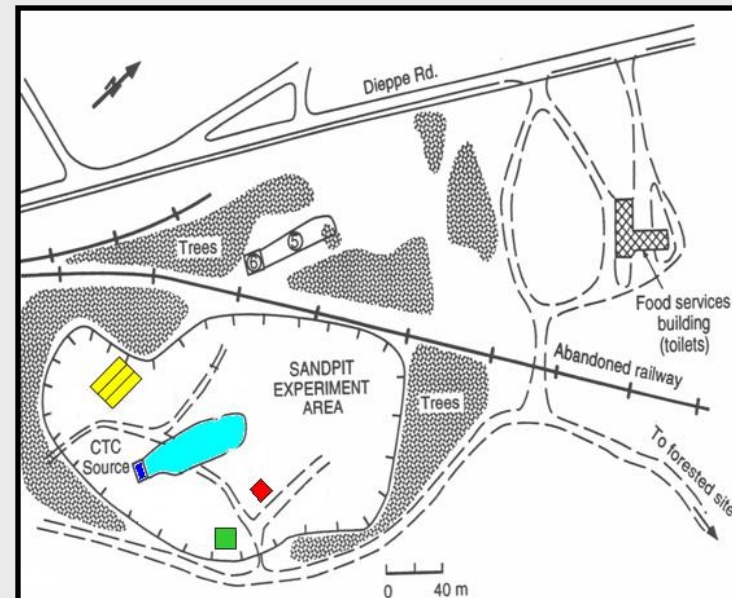
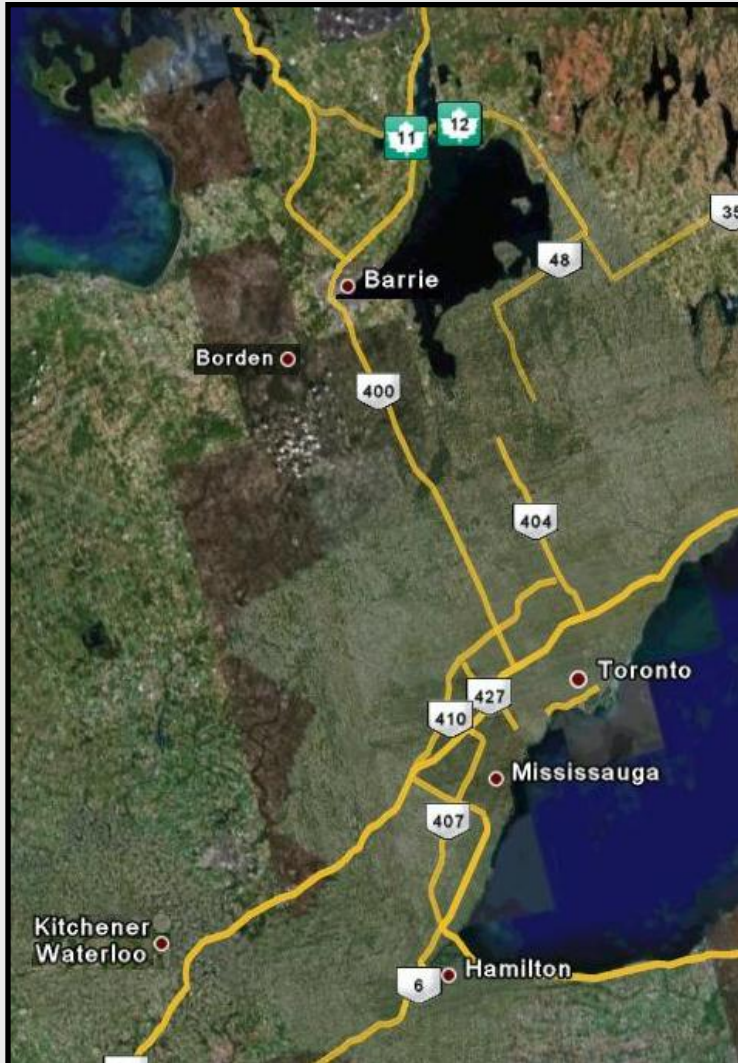


# Bench-Scale Effort

Compound	MW [g/mol]	Aqueous Solubility [mg/L]	Mass Fraction [%]	Percent Change
naphthalene	128.2	31.7	8.1	-14
indole+2-methylnaphthalene	142.2	24.4	3.9	-26
1-methylnaphthalene	142.2	28.5	1.8	-29
acenaphthylene	152.2	-	0.2	-76
biphenyl	154.2	7.5	1.5	92
acenaphthene	154.2	3.9	6.0	-55
fluorene	166.2	2	4.7	-65
carbazole	167.2	1	0.87	-97
dibenzofuran	168.2	10	4.0	44
phenanthrene	178.2	1.3	10.4	-52
anthracene	178.2	0.07	1.1	-60
fluoranthene	202.3	0.26	5.2	41
pyrene	202.3	0.14	4.0	-81
Total:			51.8	-25



# Pilot-Scale

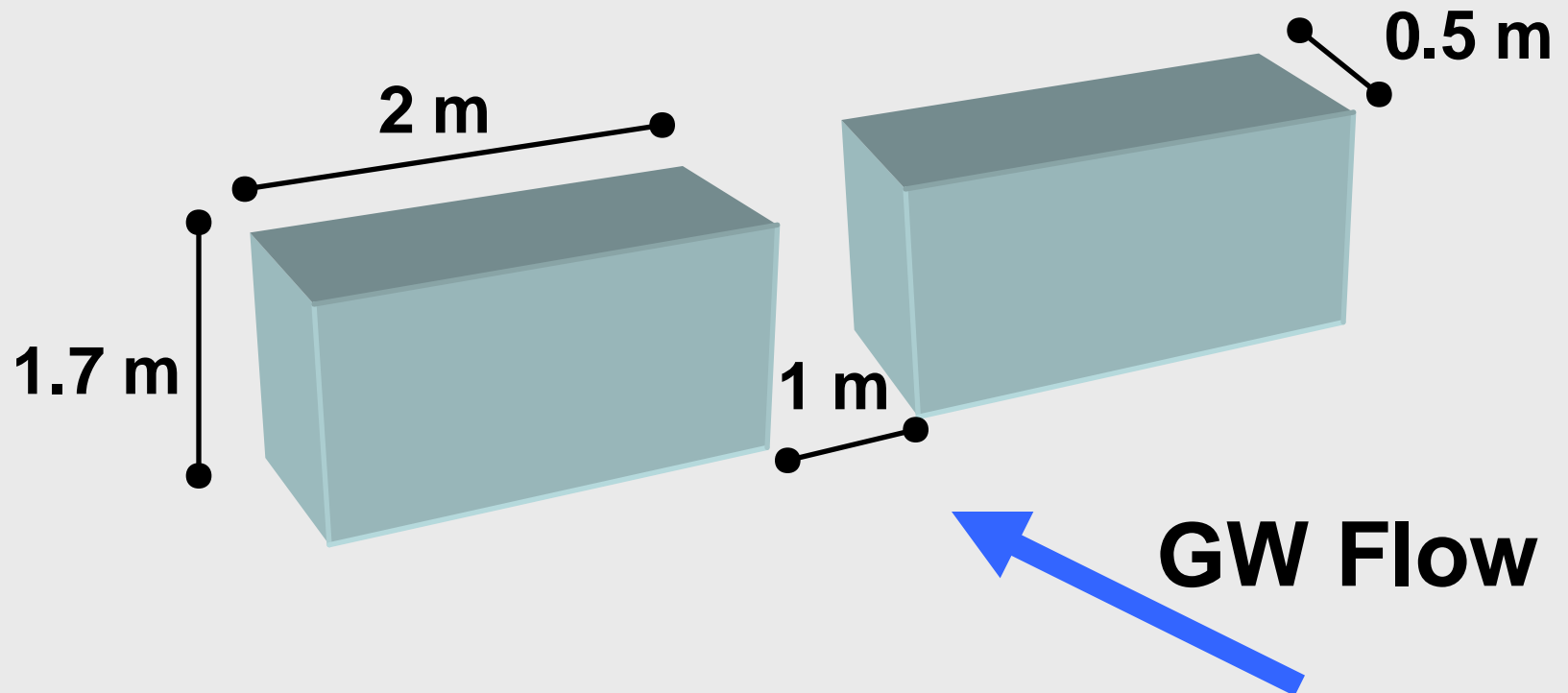


Porosity:	0.33
Bulk Density:	1.81 g/cm <sup>3</sup>
Hydraulic Conductivity:	7x10 <sup>-5</sup> m/s
Depth to Water Table:	varies, 0 - 1.5 mbgs
Hydraulic Gradient:	mean 0.0039
Groundwater Velocity:	0.091 m/day

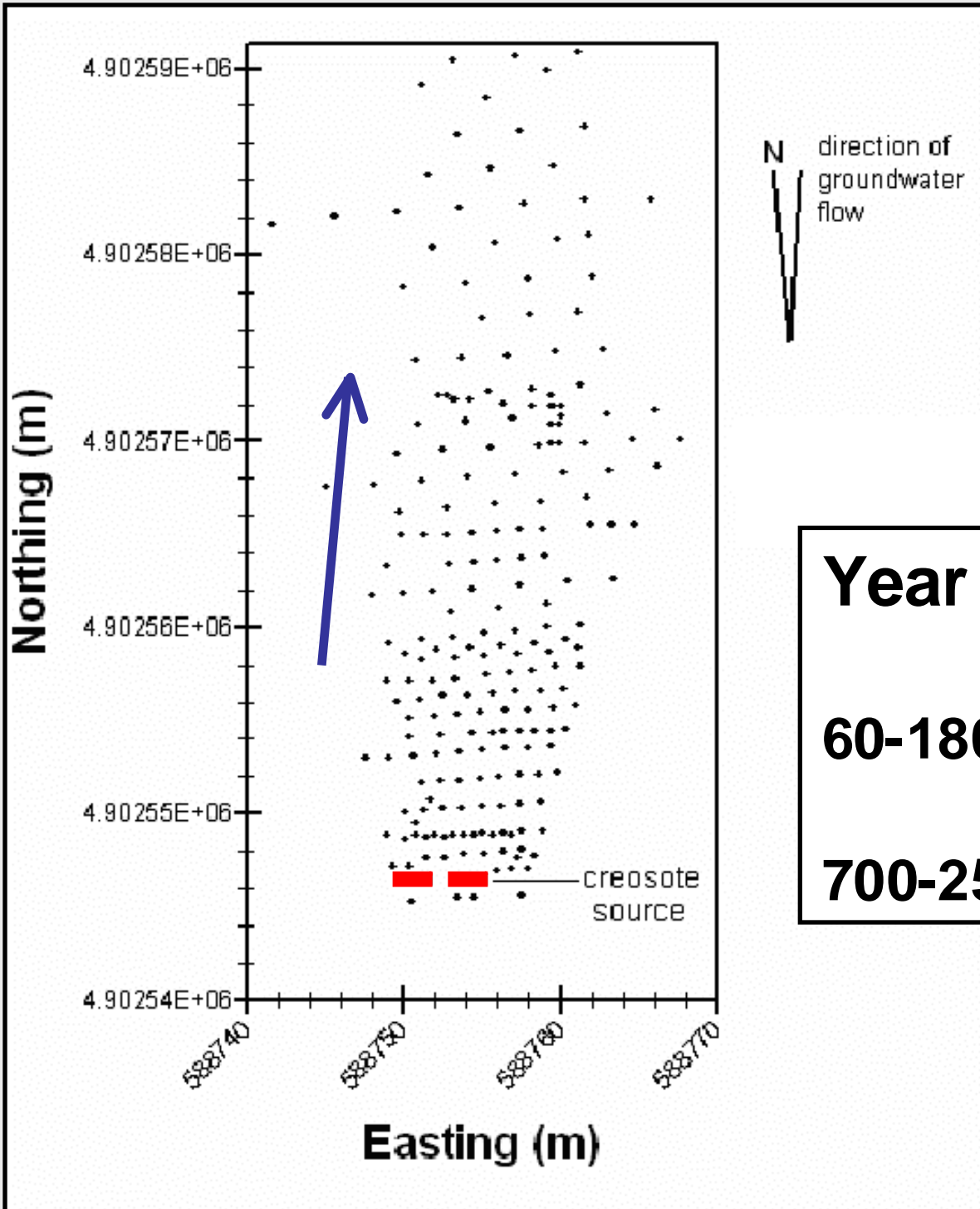
# Pilot-Scale

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74 kg of coal tar creosote was  
emplaced below the water table in  
August 1991 (Year 0)



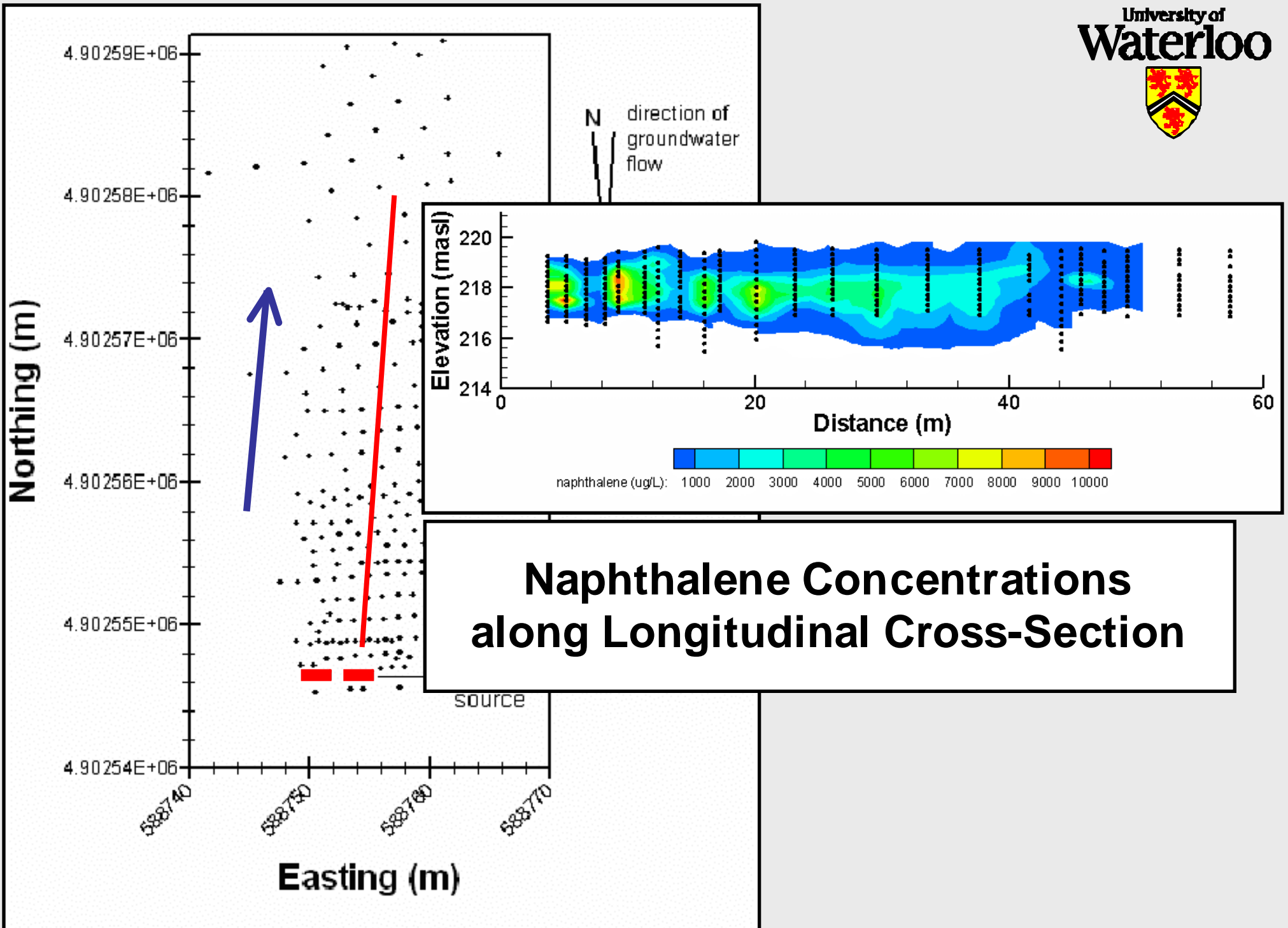
# Initial Plume Monitoring

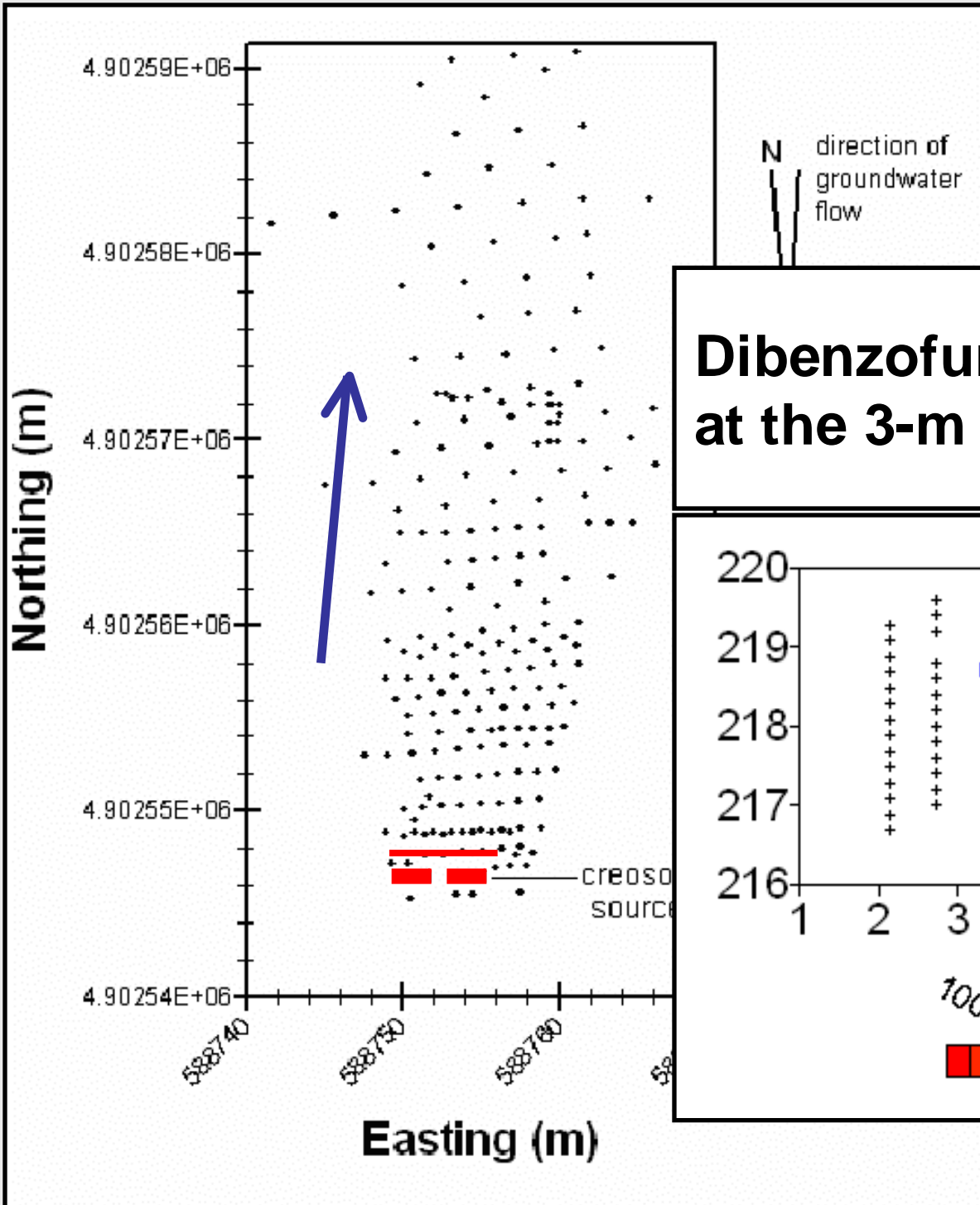


**Year 1, 2, 4, 10**

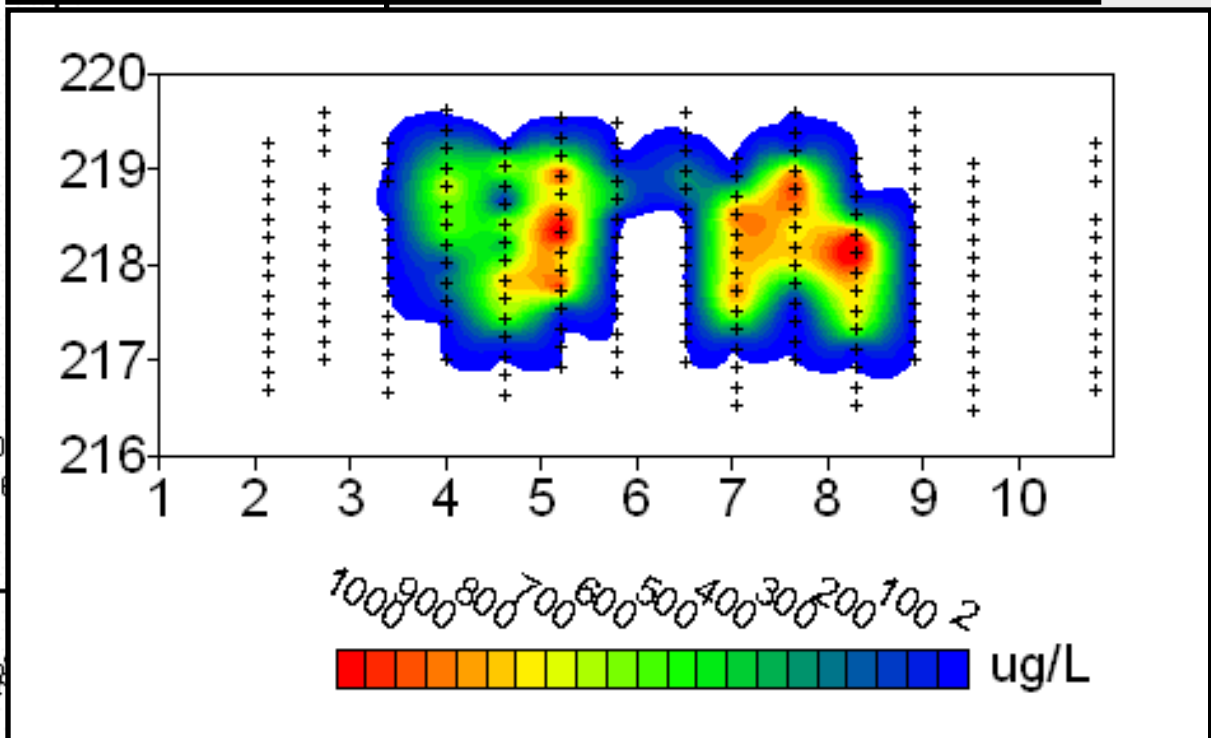
**60-180 multilevel wells**

**700-2500 samples/episode**





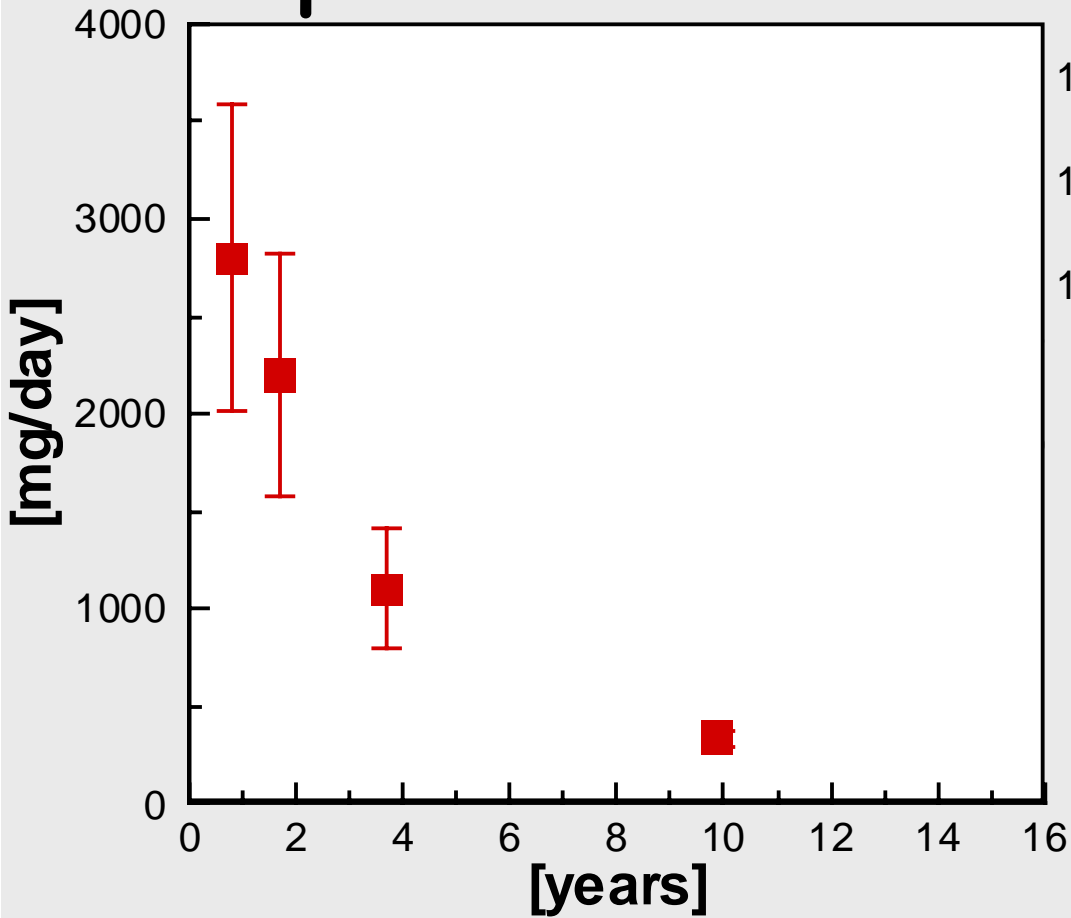
## Dibenzofuran Concentrations at the 3-m Fence line



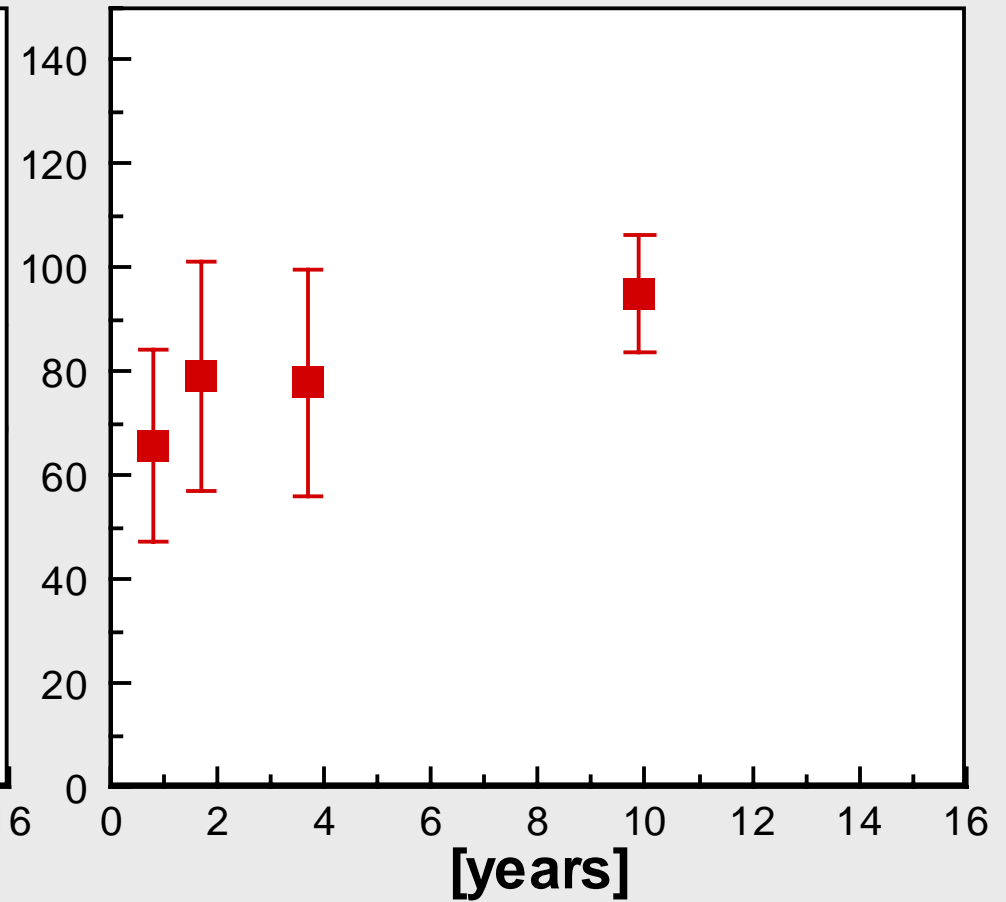
# Mass Loading

$$\dot{M} = \int q C dA$$

## Naphthalene



## Dibenzofuran

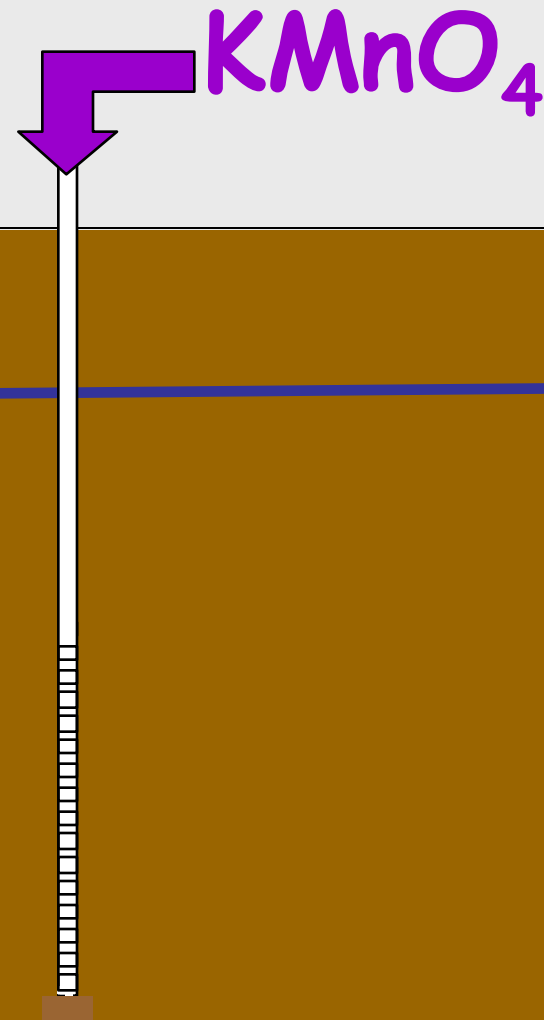


# Source Zone Treatment

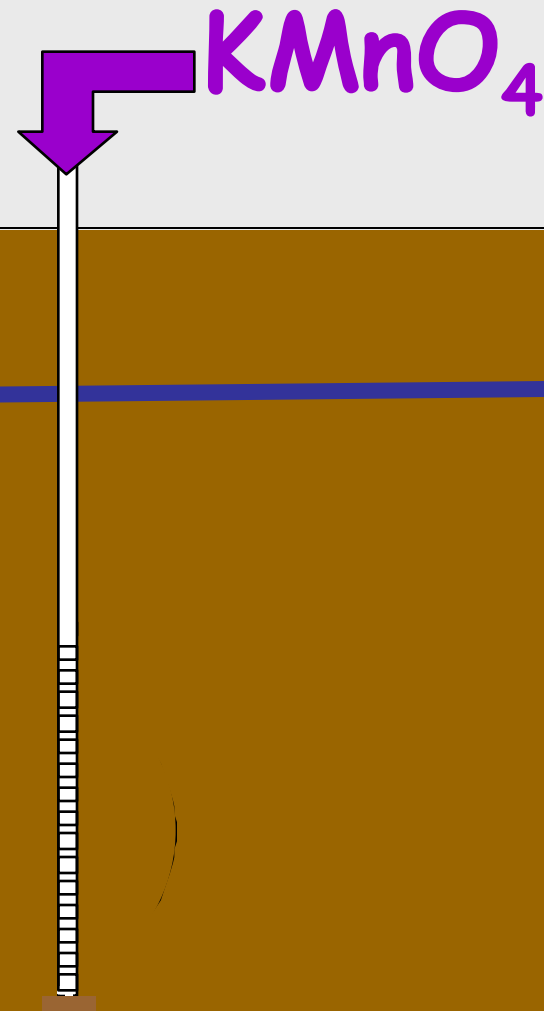
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- semi-passive pulse injection system

# Semi-Passive Pulse Injection Concept



# Semi-Passive Pulse Injection Concept



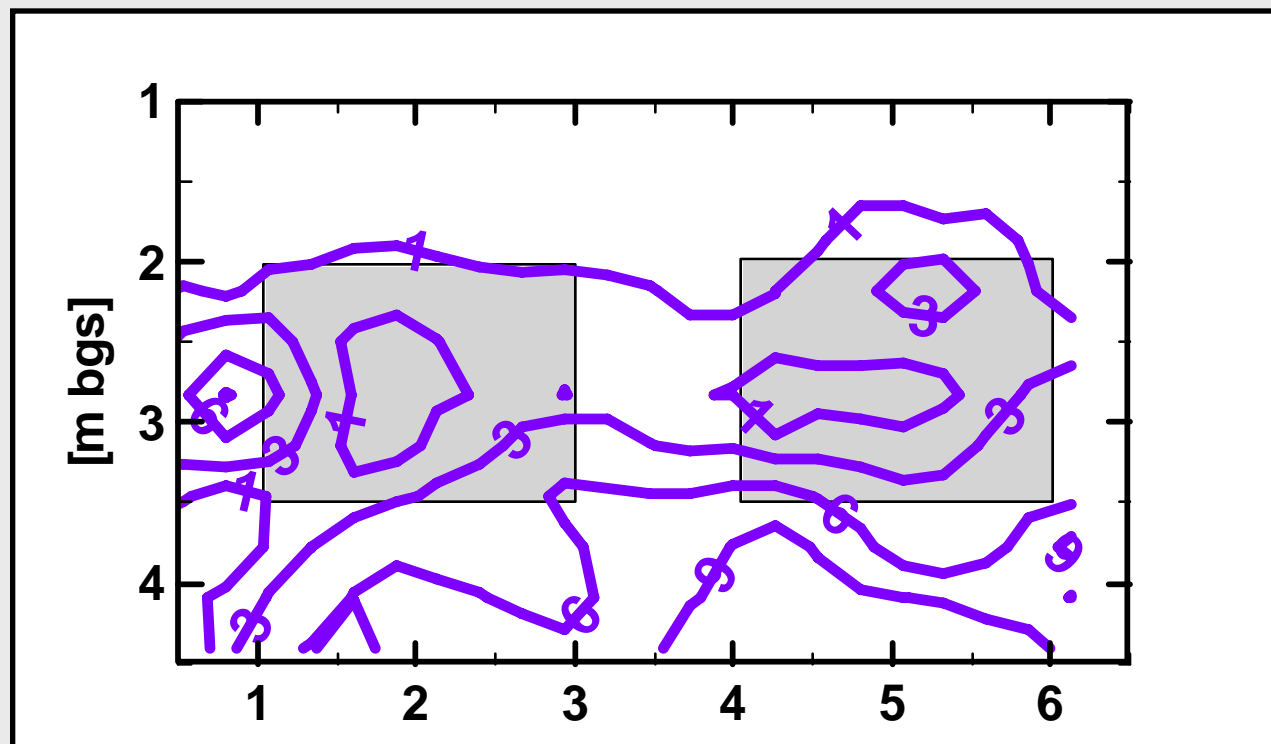
# Source Zone Treatment

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- semi-passive pulse injection system
- 3200 L of 15 g/L per episode
- 7-day intervals
- monitored hydraulics and permanganate breakthrough down gradient
- 6 episodes / 125 kg
- ~ 20 pore volumes
- ~35% of estimated reactive compounds

# Source Zone Treatment

## Permanganate



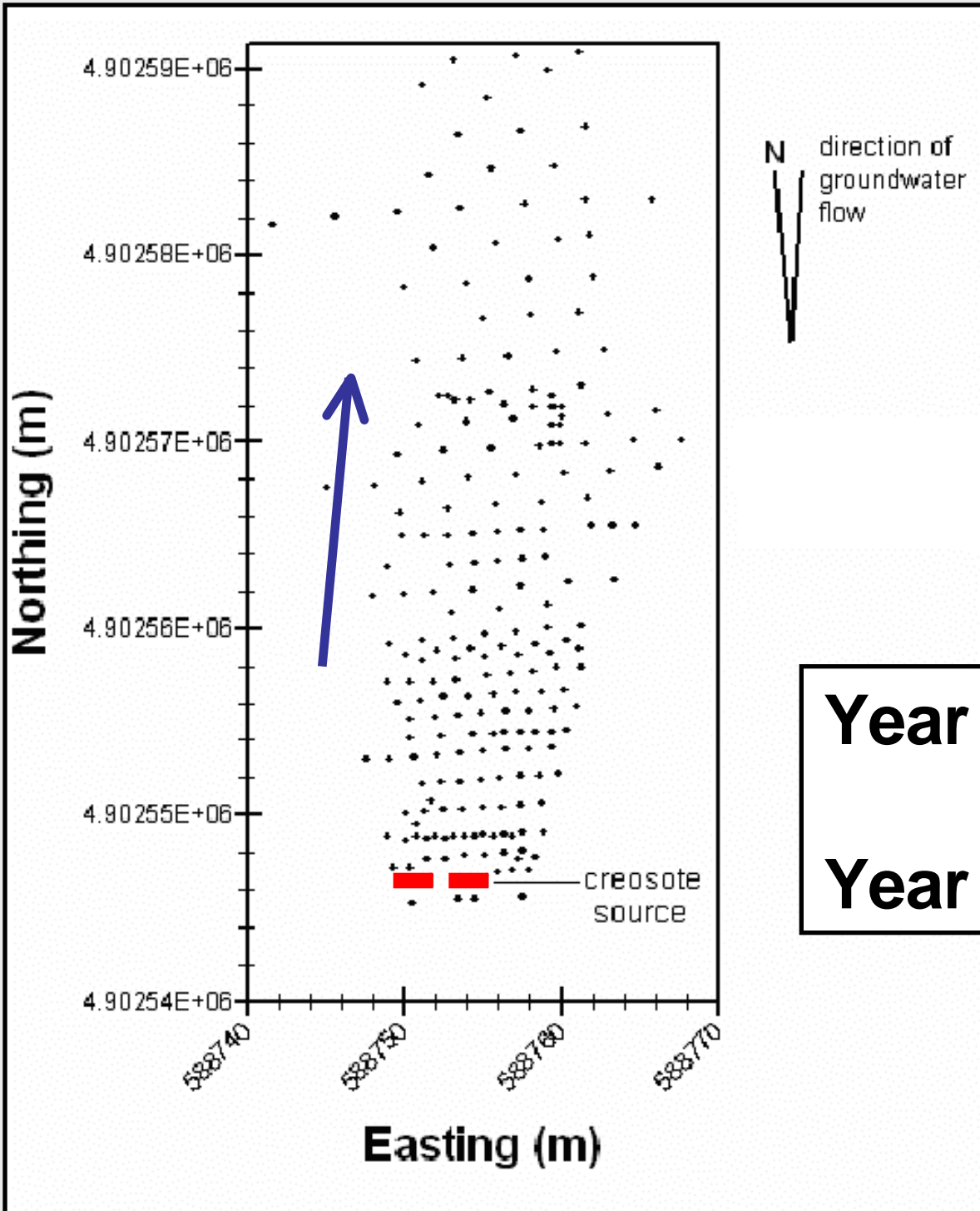
(7 days after 3<sup>rd</sup> injection)

# Short-Term Monitoring

Compound	Pre [mg/day]	Post [mg/day]	Percent Change
naphthalene	750	310	-59
1-methylnaphthalene	200	120	-40
acenaphthylene	15	6	-58
biphenyl	84	71	-15
acenaphthene	430	200	-53
fluorene	110	51	-54
carbazole	61	18	-70
dibenzofuran	250	210	-16
phenanthrene	96	60	-37
anthracene	31	14	-55
fluoranthene	13	11	-11
pyrene	9	3	-63
<b>Total</b>	<b>2048</b>	<b>1075</b>	<b>-47</b>

Changes in  
mass load  
at fence line  
150 days  
after  
treatment

$$\dot{M} = \int q C dA$$



# Post-Treatment Plume Monitoring

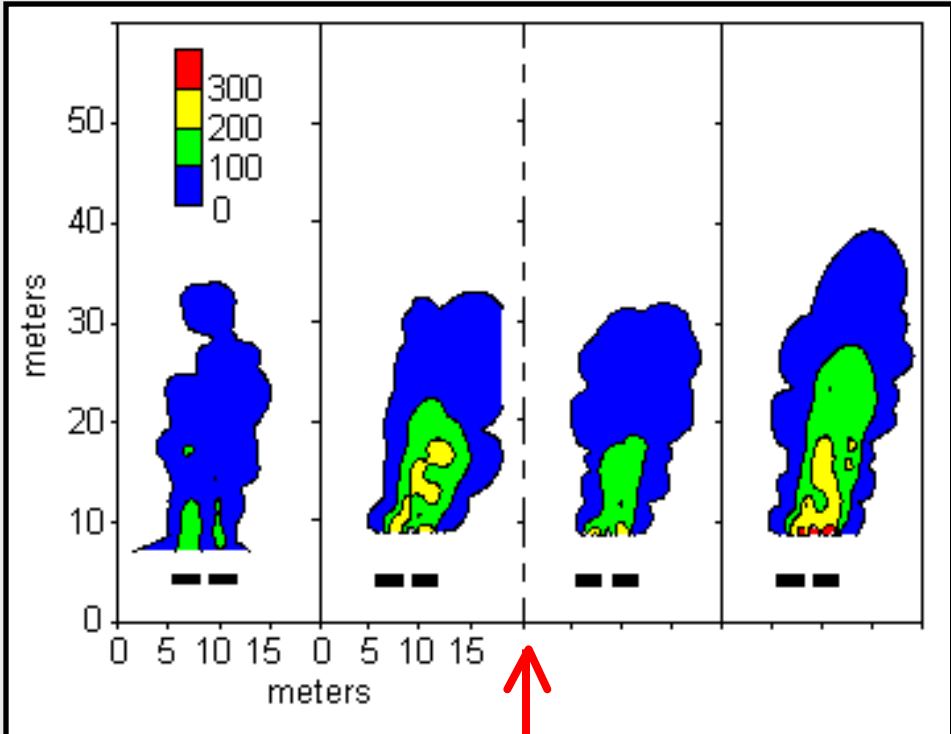
**Year 1, 2, 4, 10 (pre)**

**Year 11, 12, 14 (post)**

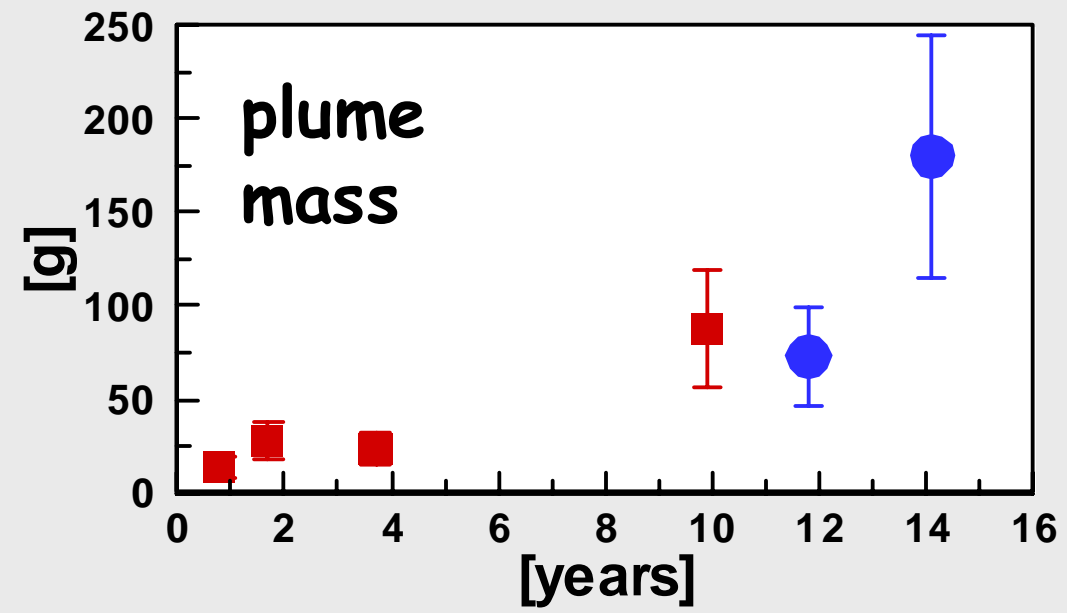
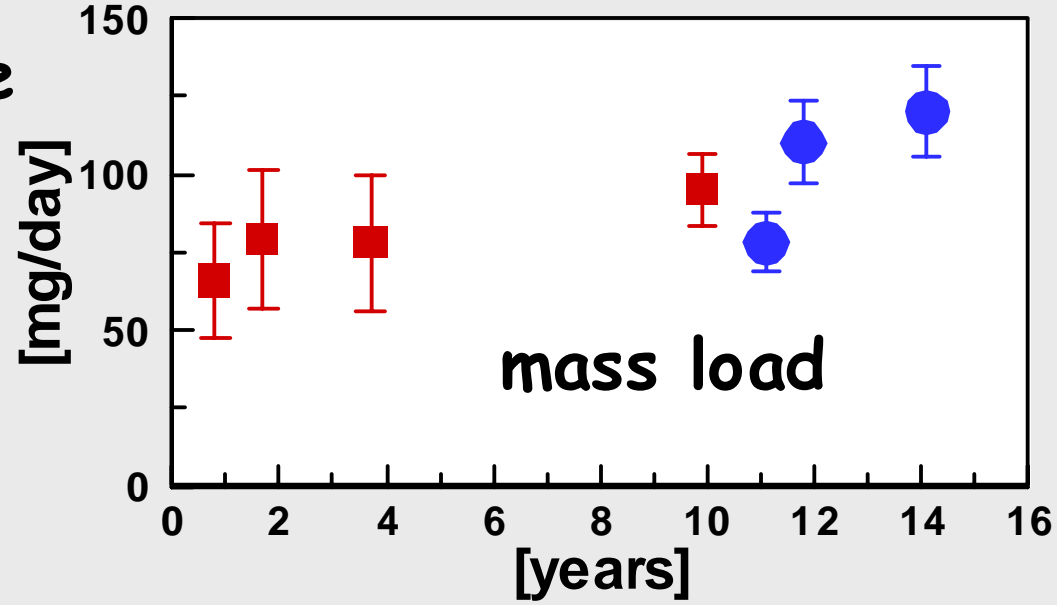
# Long-Term Monitoring

Dibenzofuran - non reactive

4      10      12      14

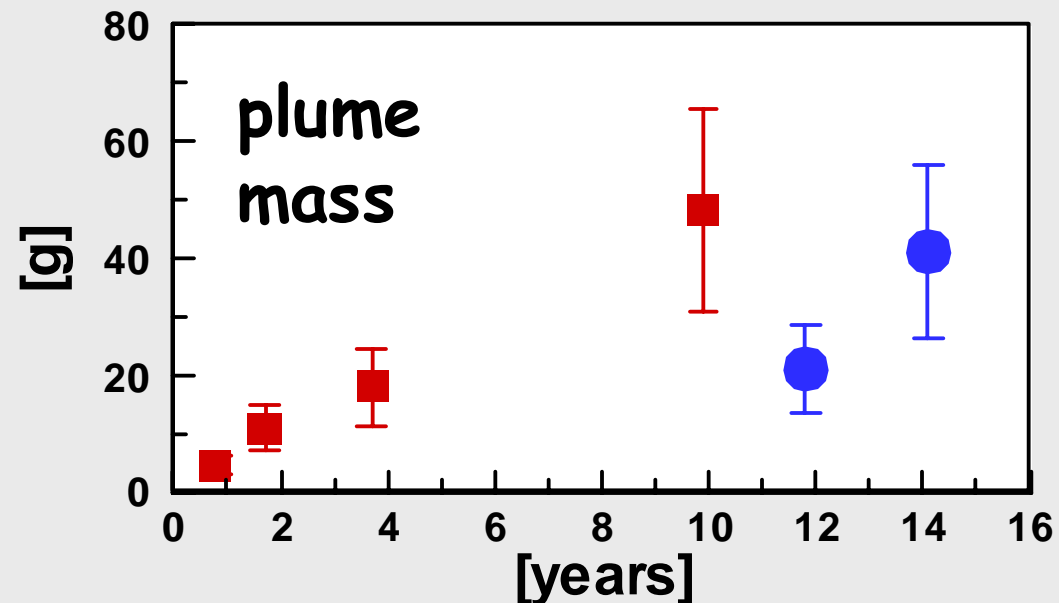
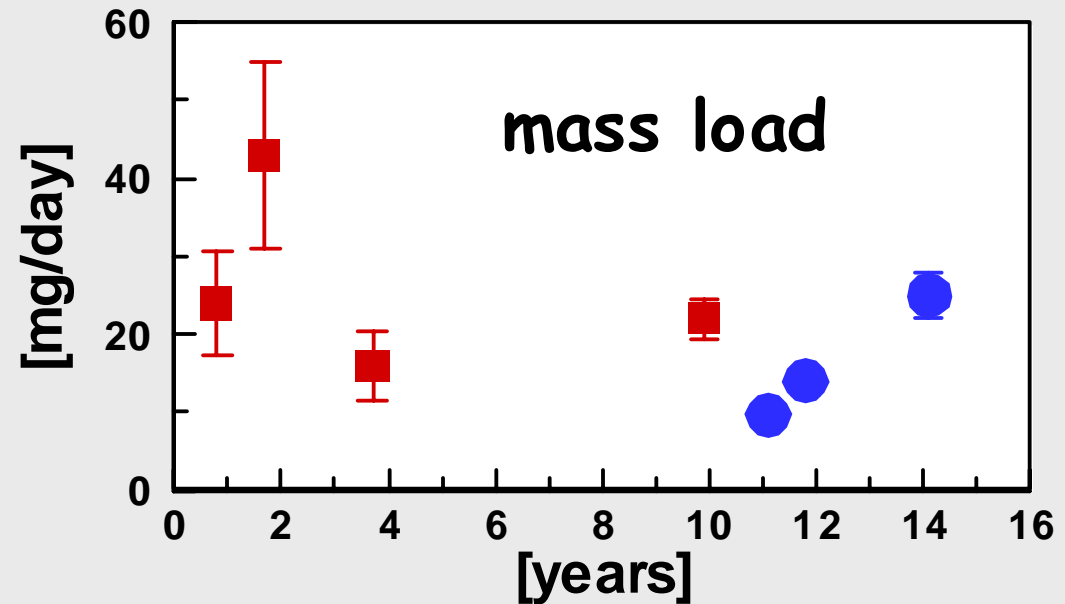
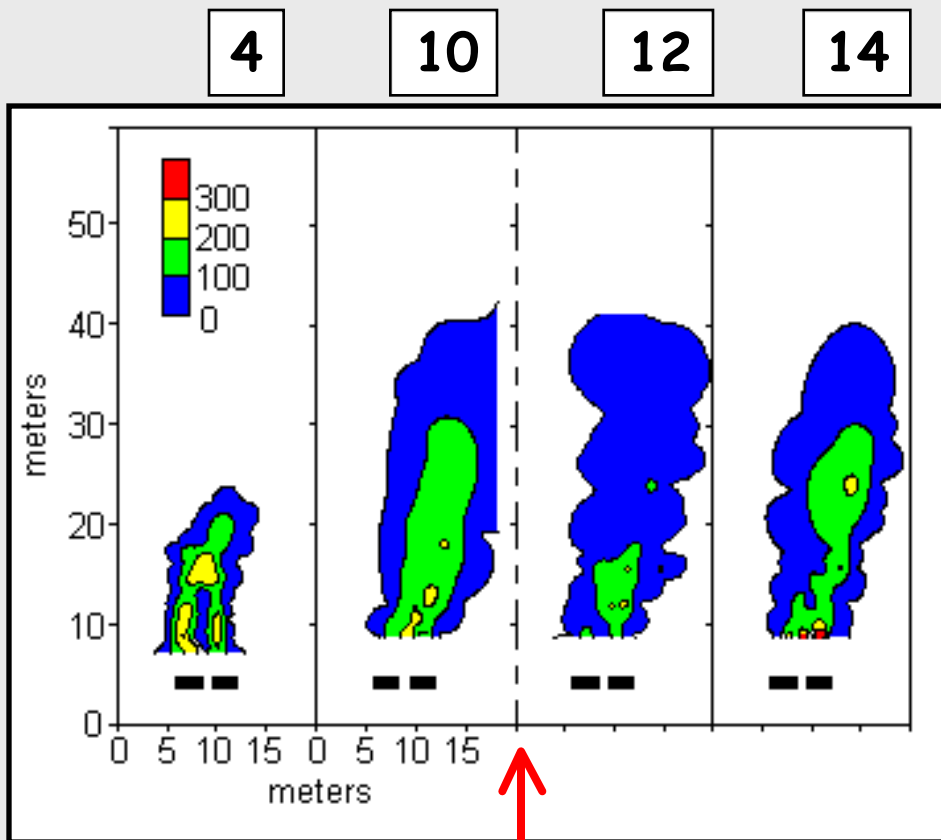


treatment



# Long-Term Monitoring

Carbazole - reactive



# Summary

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- >35% reduction in mass load after 150 days for all reactive compounds
- Decrease in mass load and/or plume mass for all monitored compounds after 1 and 2 years
- Rebound in both mass load and plume mass for all monitored compounds to pre-treatment or higher levels by 4 years
- Anthracene only compound that shows continual decrease (highly sorbing;  $R \approx 20$ )

**Long-term monitoring required!!!**

# Thanks

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- **Funding:**
    - American Petroleum Institute
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    - Paul Johnson
    - Mark Sobon
    - Bruce Stickney
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