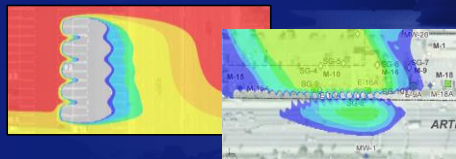


Reactive Transport Modeling: A New Paradigm in the Design of In Situ Treatment Systems

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 2. Manhattan College
 3. Columbia University



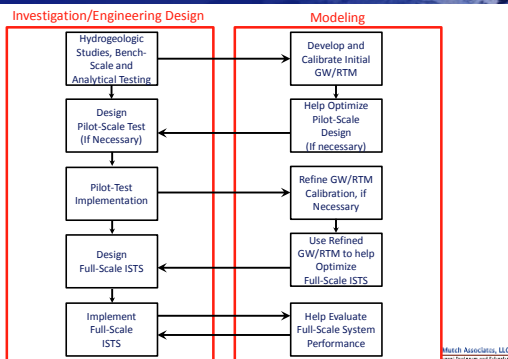
Presented at the 2017 NGWA Groundwater Summit
 Nashville, TN
 December 4, 2017



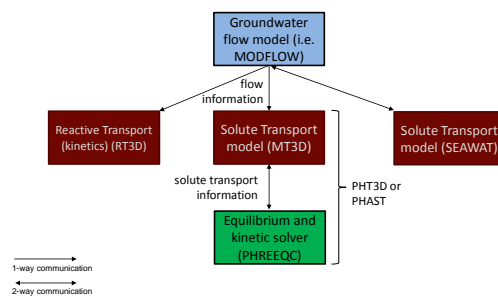
Reactive Transport Modeling

- Provides 3-D insights into what is going on in the subsurface
- Allows designs to be carefully tailored to a site's unique hydrogeologic and geochemical conditions and the specific physical, chemical and biological characteristics of the IST technology
- Helps avoid ISTs falling short of expectations or failing altogether
- Saves time and money

Optimum Process Flow Diagram



Model Hierarchy



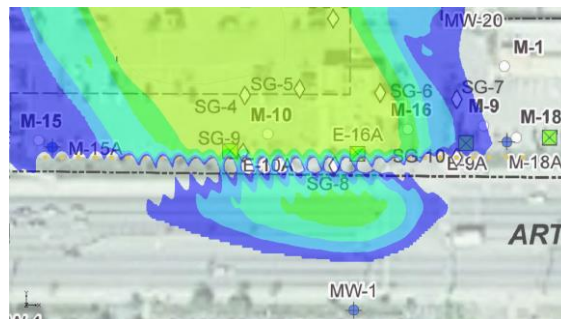
Reactive Transport Libraries

Reactive transport libraries for modeling in-situ treatment:

- Reduction of Cr(VI) by calcium polysulfide (CaS₂)
- ISCO of chlorinated solvents by CHP
- ISCO of chlorinated ethylenes by KMnO₄
- ISCO of chlorinated solvents and 1,4-dioxane by activated persulfate
- Enhanced reductive dechlorination using emulsified vegetable oil
- pH adjustment of aquifers via addition of acids and bases
- Numerous reductive dechlorination/MNA packages
 - PCE→TCE→DCE→VC→ethene
 - CTET→chloroform→methylene chloride→chloromethane



Enhanced Reductive Dechlorination Using Emulsified Vegetable Oil



Modeling PRB Spacing & Effectiveness

Mobile oil:
$$\frac{\partial C_m}{\partial t} = \frac{\partial}{\partial x} \left(D \frac{\partial C_m}{\partial x} \right) + \frac{\partial}{\partial x} (v C_m) - K_A C_m$$

Immobile oil:
$$\frac{\partial C_{im}}{\partial t} = K_A C_m \frac{\phi}{p_b}$$

Attachment rate:
$$K_A = \frac{3v}{2} \left(\frac{1-\phi}{d_c} \right) \alpha \left(\frac{C_m^{max} - C_m}{C_m^{max}} \right) \eta$$

Labels: dispersion, advection, attachment, attachment, Empty bed collector efficiency, Maximum oil concentration, Single collector efficiency

From Borden and co-workers:



Modeling PRB Spacing & Effectiveness

PCE, TCE etc. degradation is modeled as a second order reaction (first order with respect to immobile oil concentration):

$$\left(\frac{\partial C_{PCE}}{\partial t} \right)_{/non} = -k_{PCE} C_m C_{PCE}$$

$$\left(\frac{\partial C_{TCE}}{\partial t} \right)_{/non} = -k_{TCE} C_m C_{TCE} + k_{PCE} Y_{TCE/PCE} C_m C_{TCE}$$

$$\left(\frac{\partial C_{DCE}}{\partial t} \right)_{/non} = -k_{DCE} C_m C_{DCE} + k_{TCE} Y_{DCE/TCE} C_m C_{DCE}$$

$$\left(\frac{\partial C_{VC}}{\partial t} \right)_{/non} = -k_{VC} C_m C_{VC} + k_{DCE} Y_{VC/DCE} C_m C_{VC}$$

Rates of PCE, TCE dechlorination assumed dependent upon the concentration of immobile oil

(from Borden and co-workers)



Injection Parameters (from Work Plan)

Parameter	Value
Number of injection wells	30
Wells injected simultaneously	10
Spacing	15 ft
Flow rate:	2 gpm (385 ft ³ /d)
Injection duration:	1.15 d per well
Volume of water/oil injection:	100,000 gal (375,000 L)
Concentration of oil injected	41,000 mg/L
Total mass of oil delivered	32,000 lb (14,500 kg)



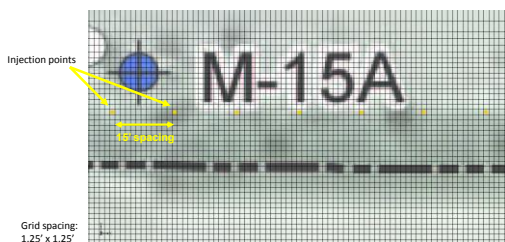
Reaction Module Parameters

Parameter	Value
Effective porosity	0.10
C _{oil,max}	1,600 mg/kg
Empty bed collector efficiency, α	0.000025
Single collector efficiency, η	0.56
Collector diameter, d _c	0.0001 m
Pore velocity, v	0.094 m/d
Bulk density	1800 kg/m ³
PCE degradation rate constant	0.00014 kg soil/mg oil-d

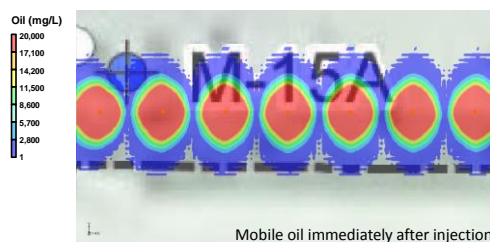
In the absence of site-specific parameters, typical values were assumed from the literature



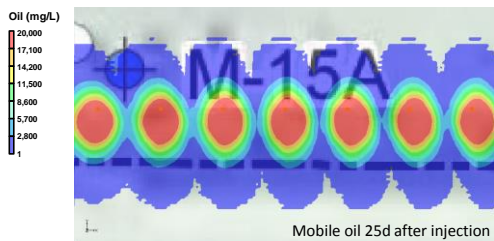
Modeling PRB Spacing & Effectiveness



Run 3: Modeling PRB Spacing & Effectiveness

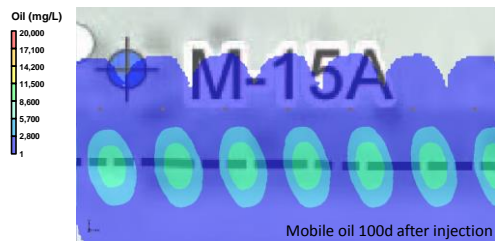


Run 3: Modeling PRB Spacing & Effectiveness



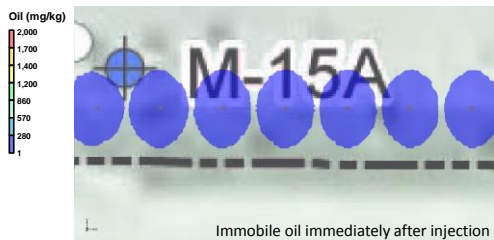
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Professional Engineers and Geologists

Run 3: Modeling PRB Spacing & Effectiveness



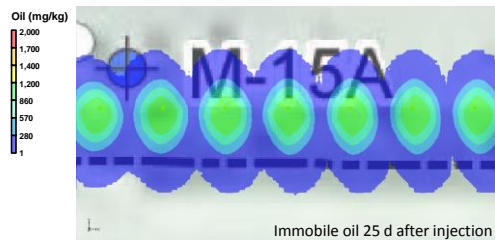
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Modeling PRB Spacing & Effectiveness



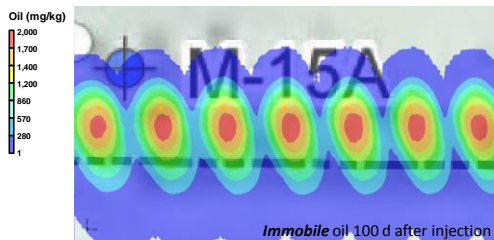
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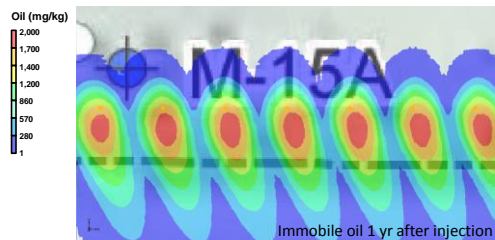
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Run 3: Modeling PRB Spacing & Effectiveness



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Run 3: Modeling PRB Spacing & Effectiveness



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Run 3: Mobile Oil



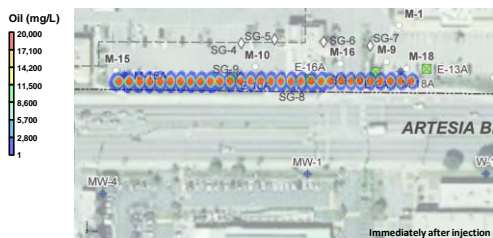
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Run 3: Mobile Oil



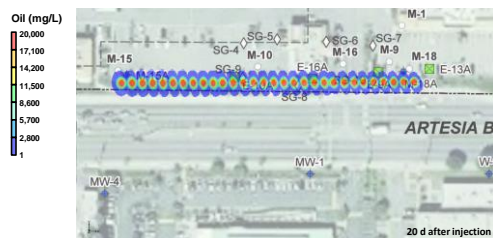
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Run 3: Mobile Oil



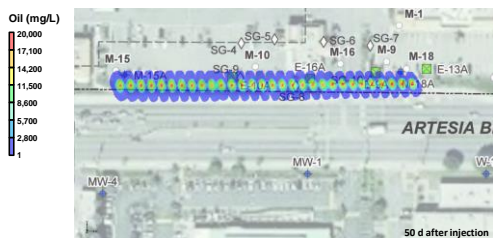
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Run 3: Mobile Oil



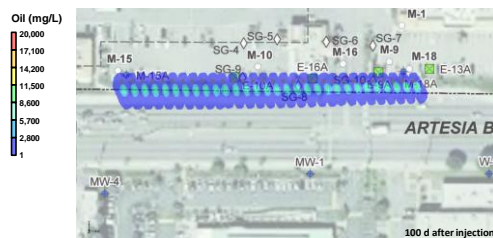
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Run 3: Mobile Oil



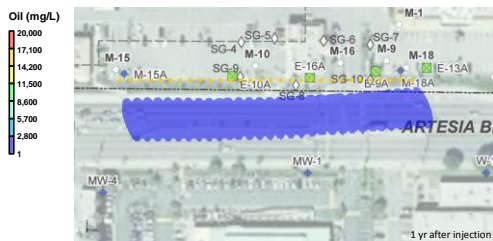
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Run 3: Mobile Oil



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Run 3: Mobile Oil



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Run 3: Immobile Oil



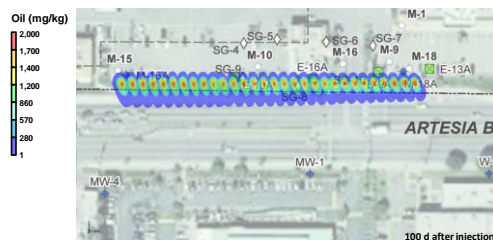
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Run 3: Immobile Oil



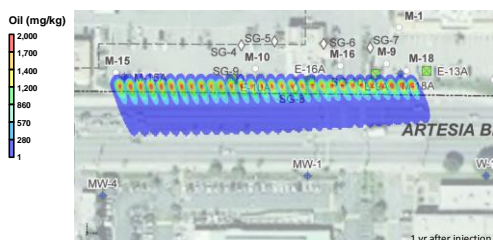
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Run 3: Immobile Oil



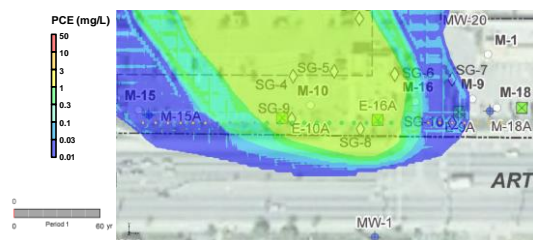
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Run 3: Immobile Oil



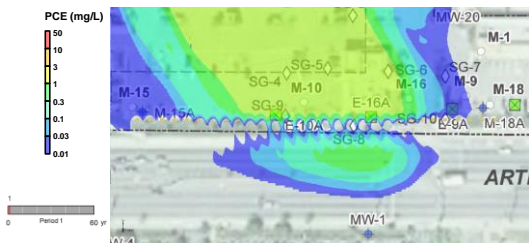
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Run 3: Downgradient PCE



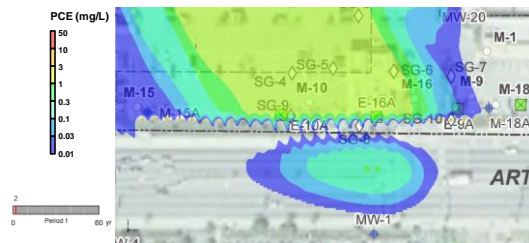
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Run 3: Downgradient PCE



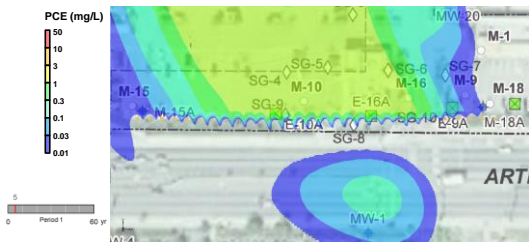
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Environmental, Technical and Scientific

Run 3: Downgradient PCE



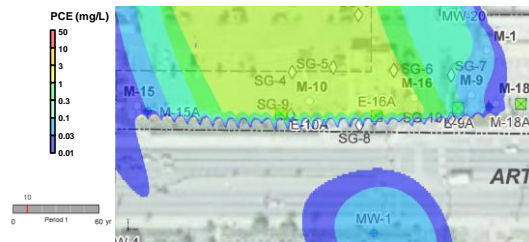
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Environmental, Technical and Scientific

Run 3: Downgradient PCE



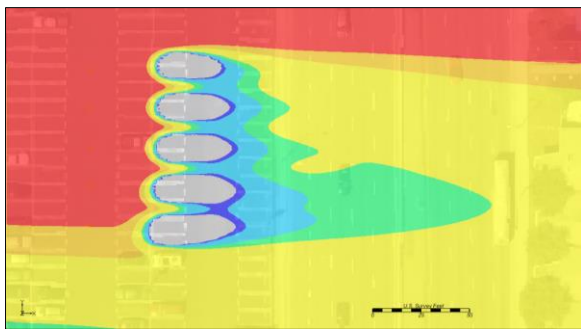
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Run 3: Downgradient PCE



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Persulfate ISCO Case Study



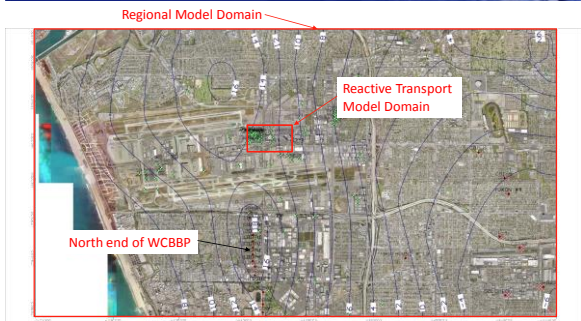
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Project Objectives

- Develop an IRM to reduce migration of chlorinated ethenes and 1,4-dioxane from the property
- IRM to operate while source control measures are implemented
- Evaluate whether an ISCO PRB was feasible in this hydrogeologic regime and could be cost-competitive with groundwater pump & treat
- Working collaboratively with AMEC FW

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Regional and Reactive Transport Model Domains and Model-Predicted Potentiometric Contours in Gage Aquifer



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Modeling Objectives

- Model injection of activated persulfate to treat plume containing 1,4-dioxane and 1,1-DCE
 - Estimate barrier replenishment frequency (i.e. reinjection recurrence period)
 - Estimate mass flux reduction
 - Provide estimates of downgradient sulfate and chromate plumes

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Reactive Transport Model Development

- Current version of model has the following state variables:
 - Persulfate
 - 1,4-Dioxane
 - 1,1-DCE
 - Tracer
 - NOD (immobile)
 - Sulfate
 - Chromate
- Starting concentrations of 1,4-dioxane and DCE are from recent plume mapping

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Persulfate & NOD Modeling

Persulfate persistence modeled as a second order reaction with soil natural oxidant demand (NOD) and first-order auto-degradation rate:

$$\frac{dC_{per}}{dt} = -k_1 C_{per} NOD - k_{auto} C_{per}$$

$$\frac{dNOD}{dt} = -k_1 C_{per} NOD$$

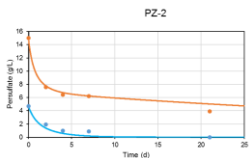
Model parameters/unknowns:

- NOD for PZ-1 soil
- NOD for PZ-2 soil
- k_1
- k_{auto}

Coupled differential equations - no analytical solution
Equations solved numerically (explicit Euler)

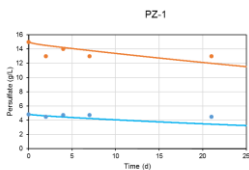
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Persulfate & NOD Modeling



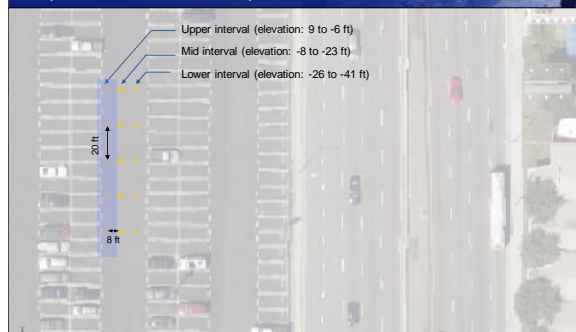
Data from all 4 experiments fit simultaneously:

- $k_{auto} = 0.015 / d$ (half-life = 46 d)
- $k_1 = 0.1 L/g/d$
- PZ-1 NOD = 0.1 g/L
- PZ-2 NOD = 8.0 g/L

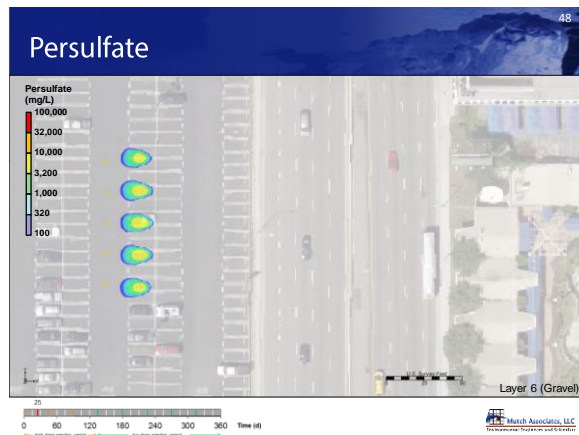
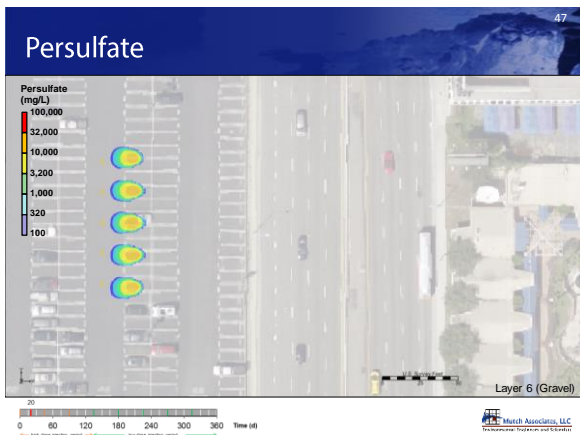
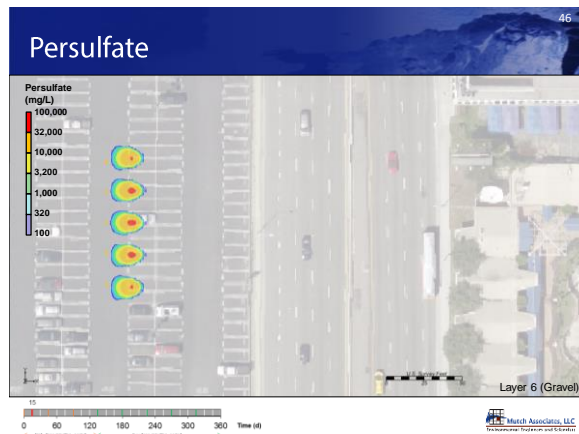
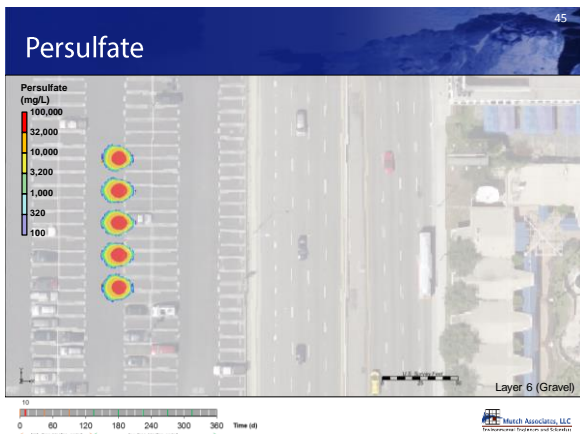
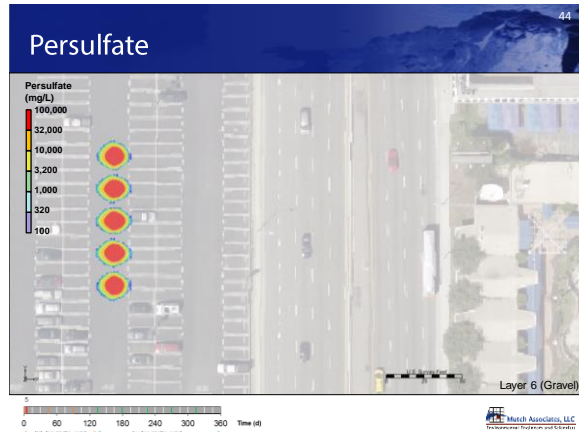
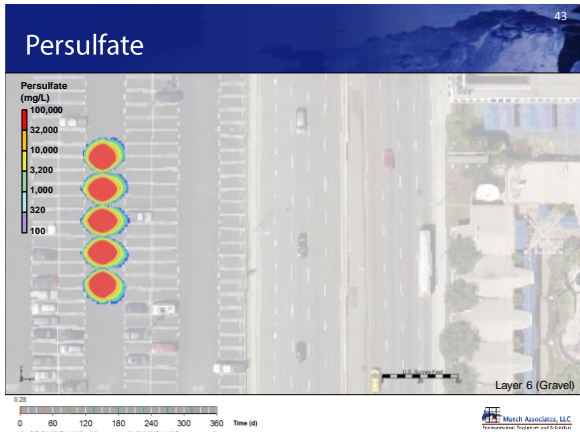


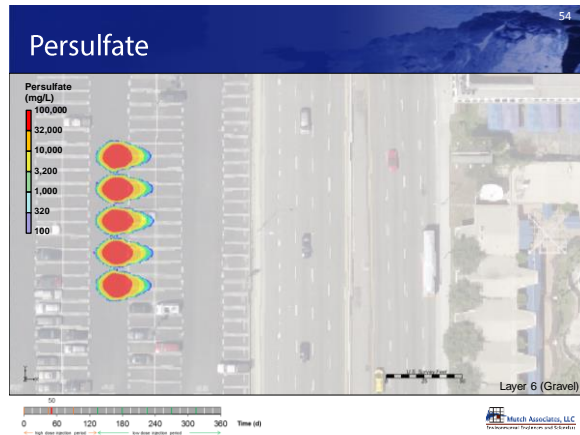
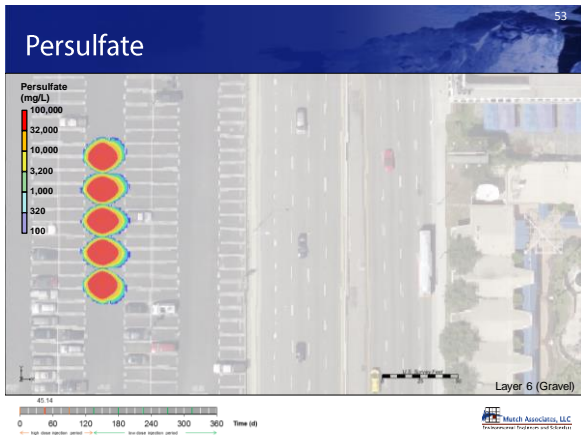
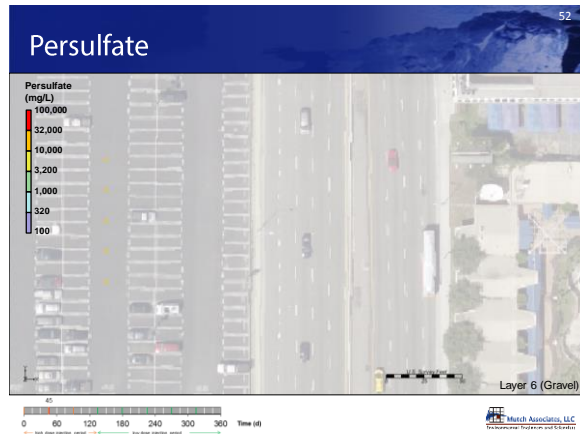
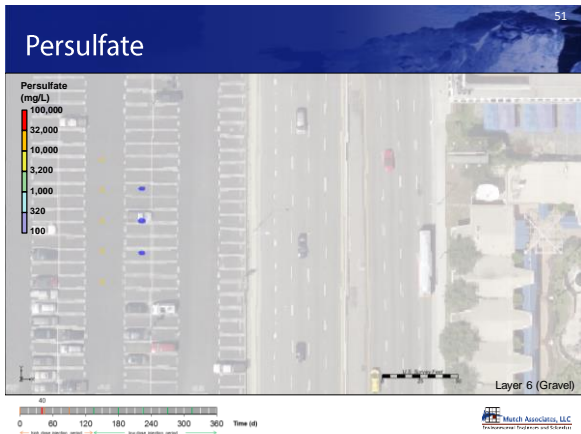
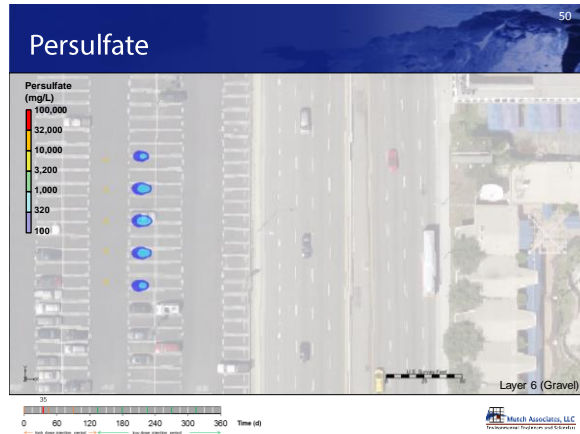
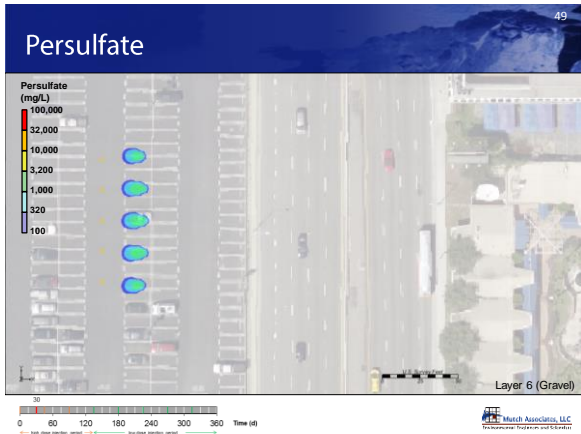
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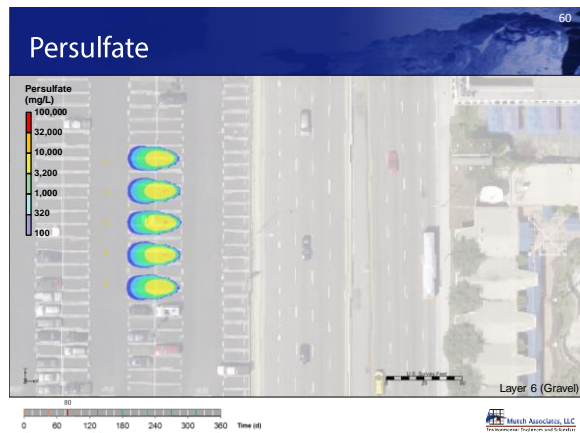
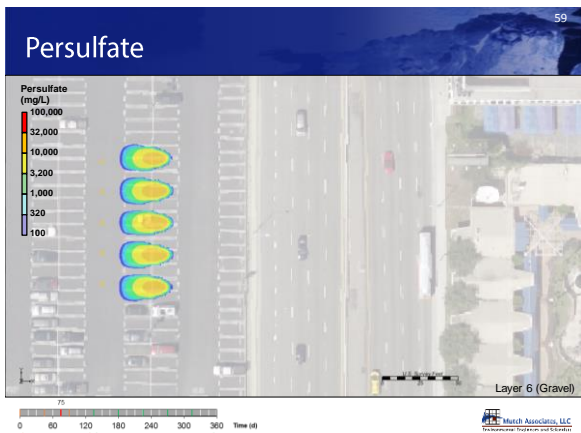
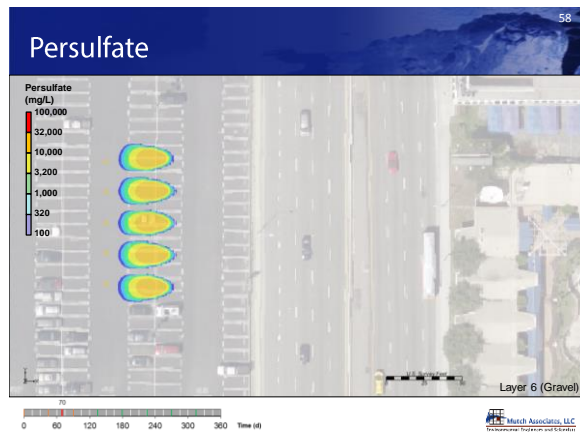
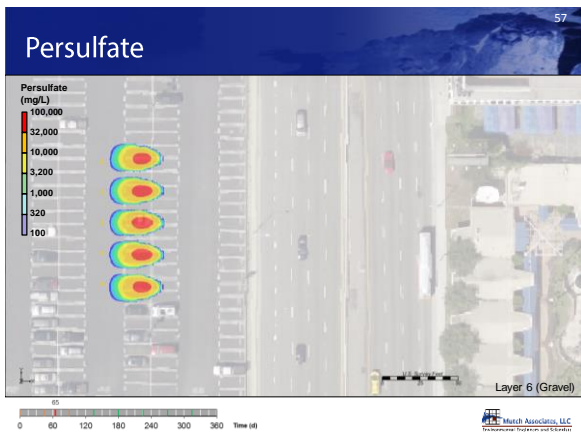
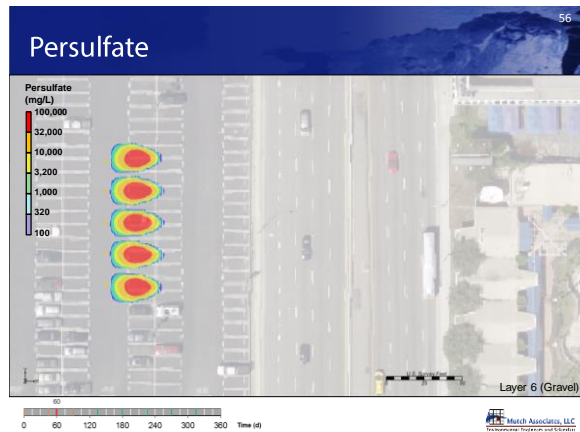
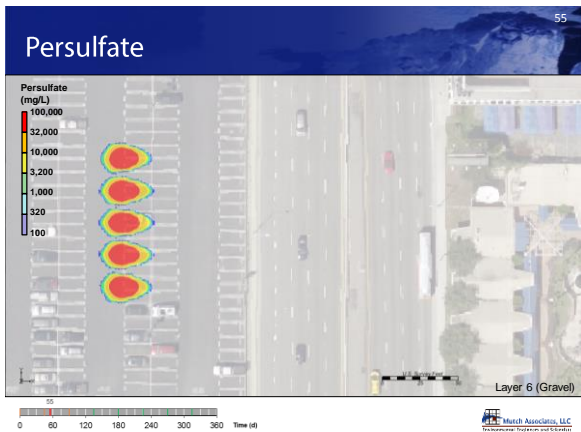
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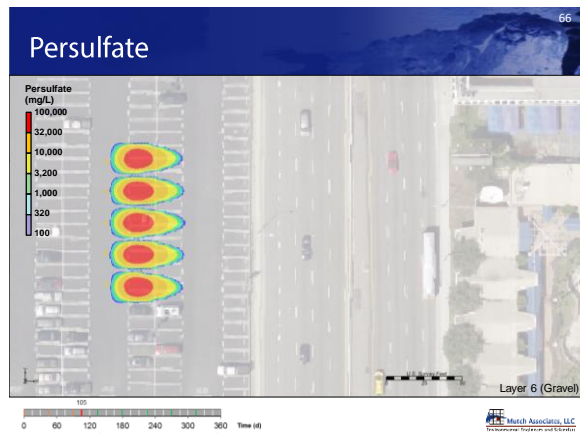
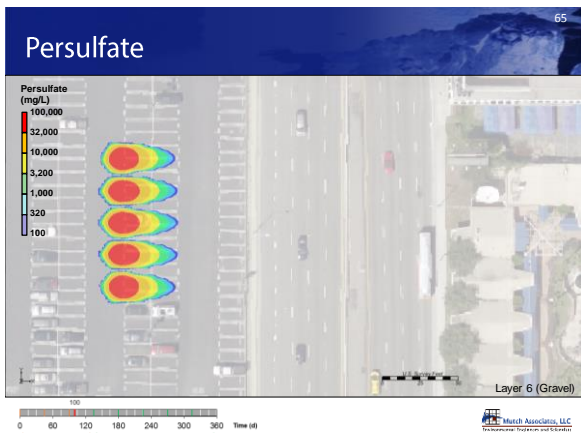
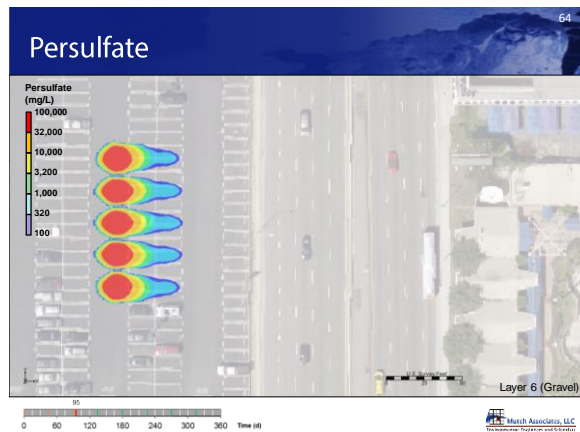
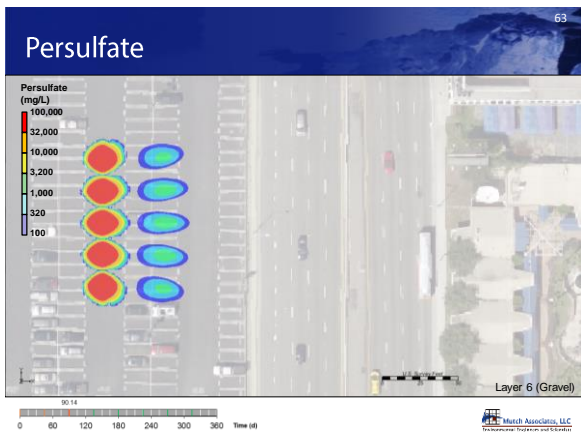
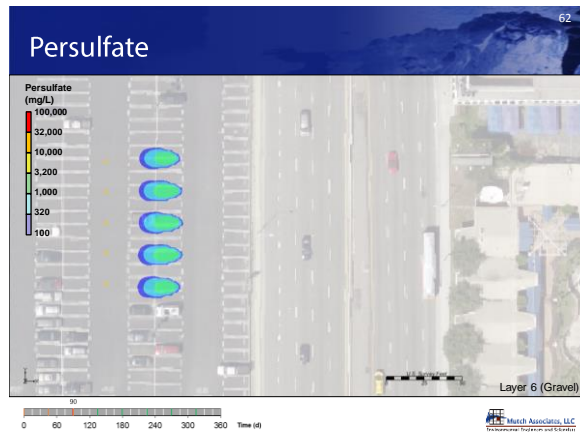
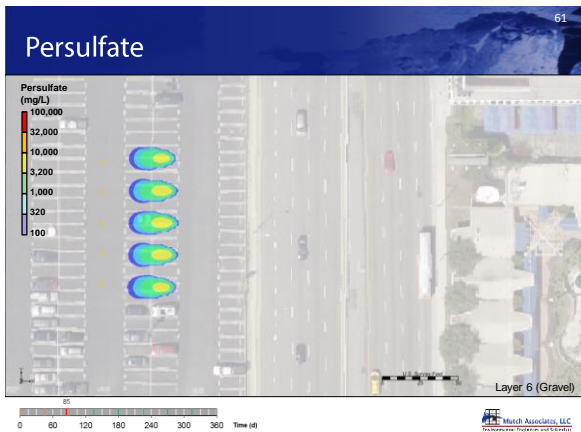


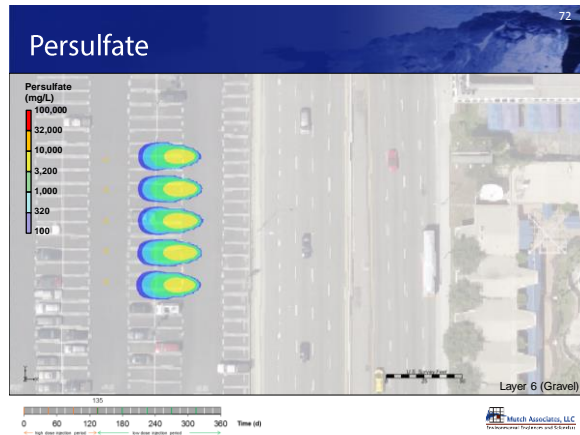
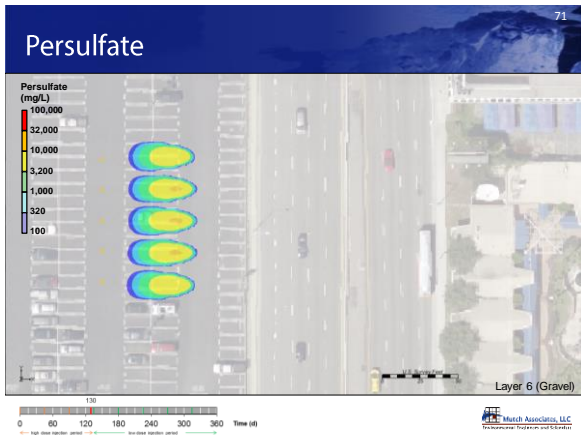
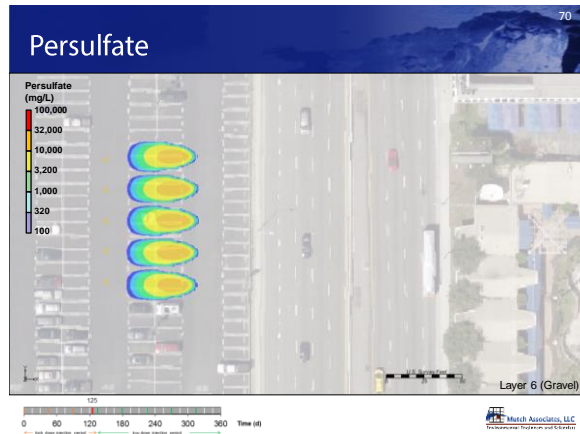
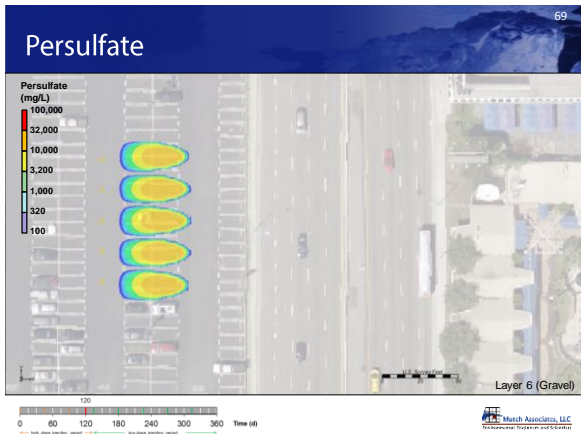
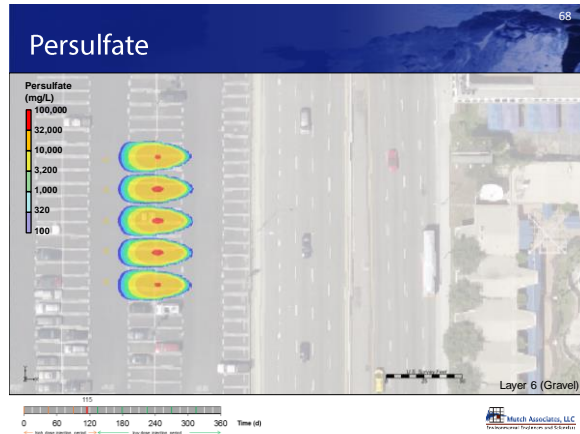
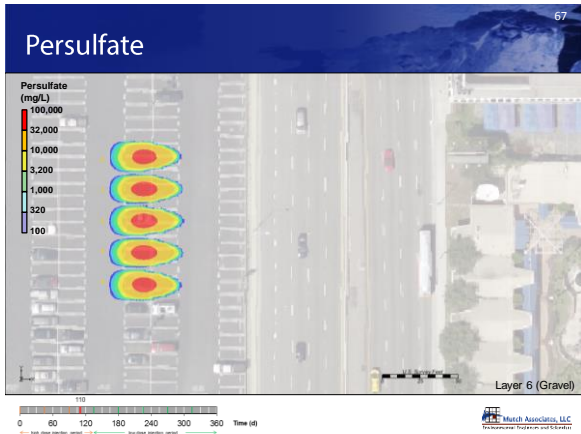
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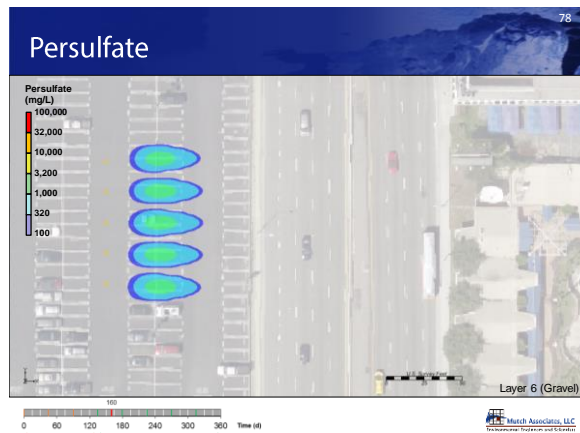
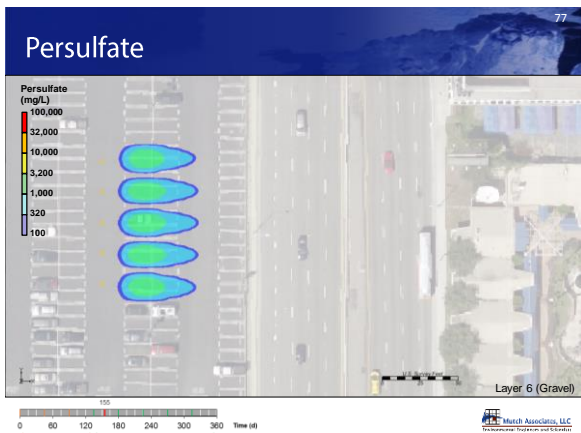
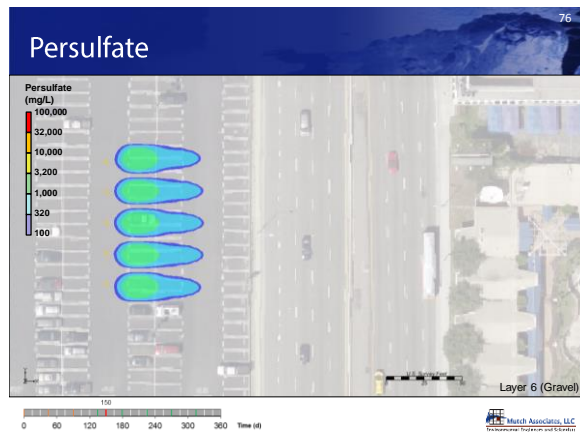
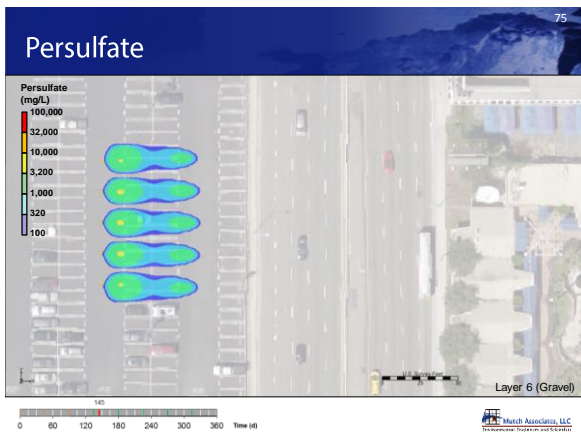
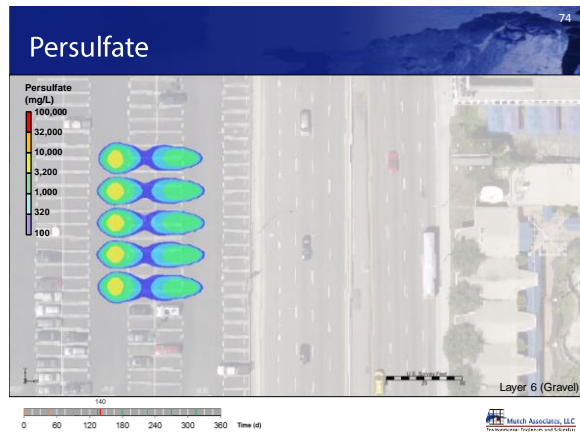
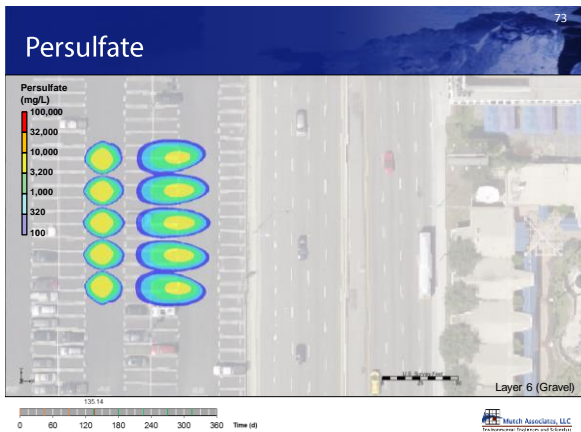


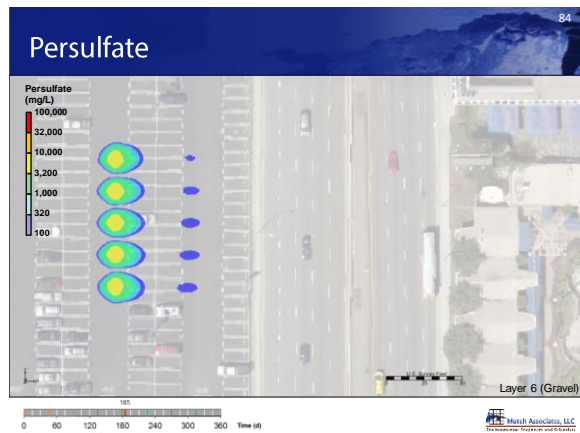
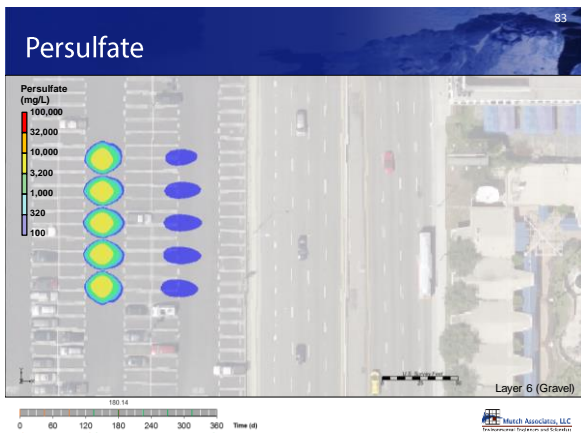
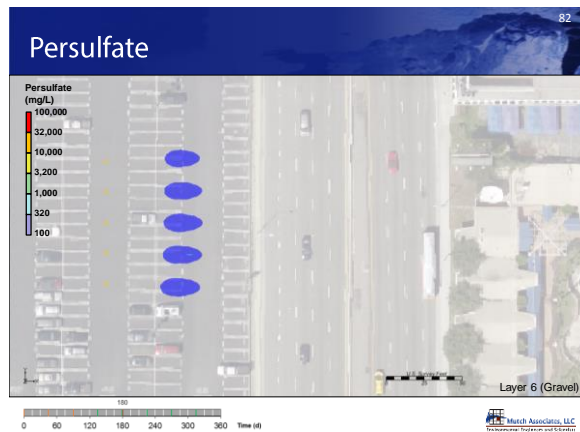
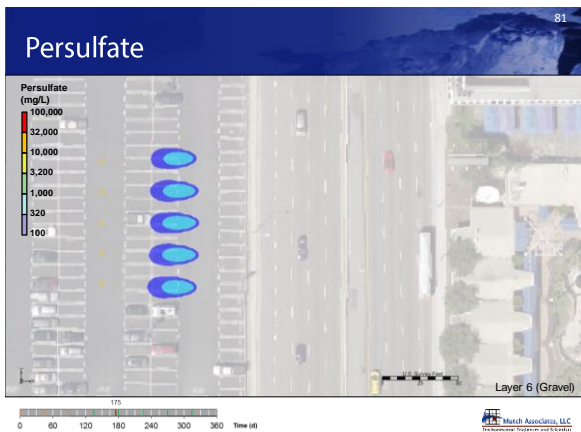
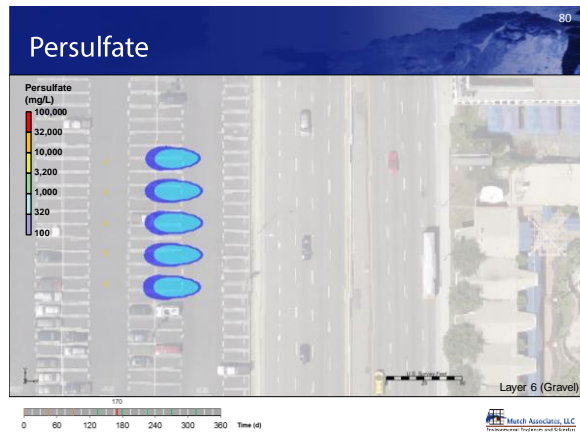
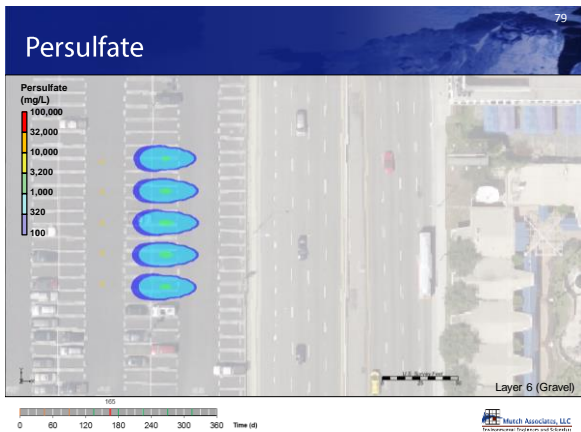


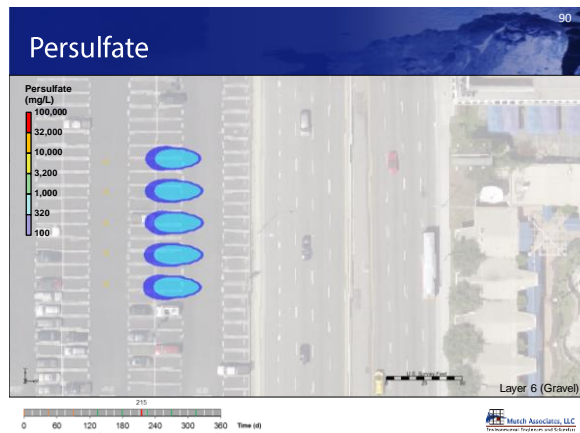
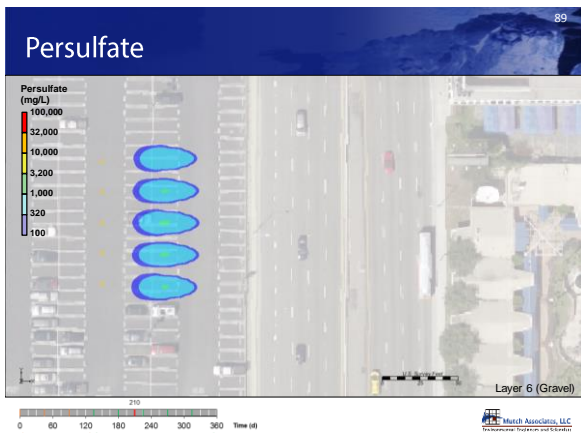
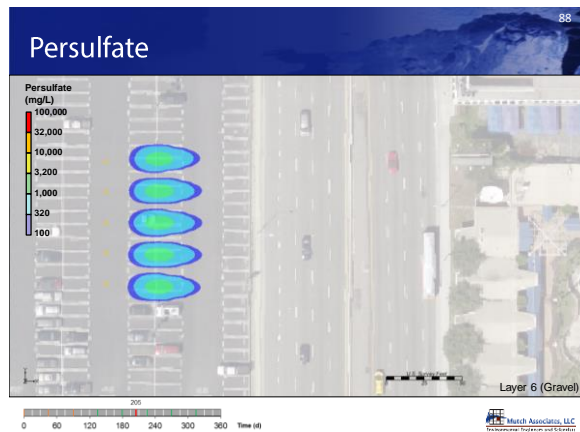
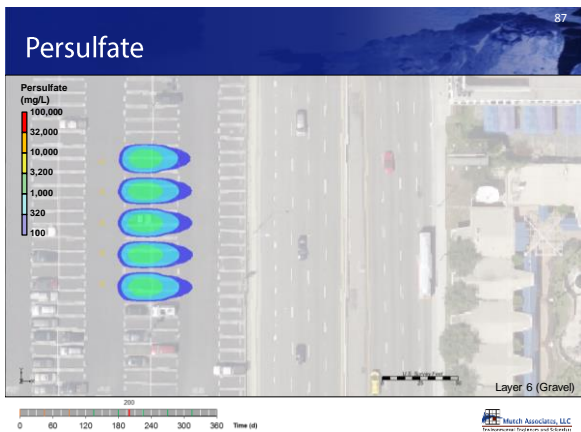
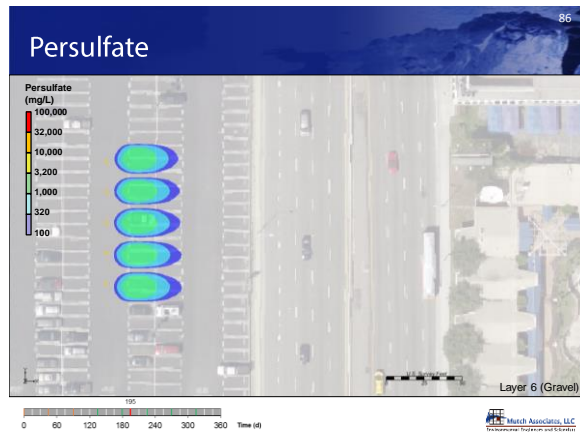
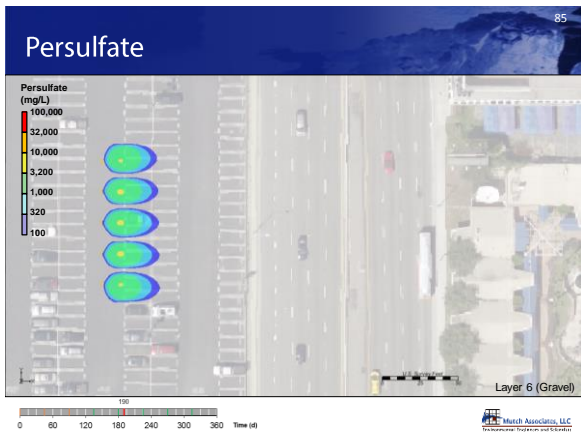


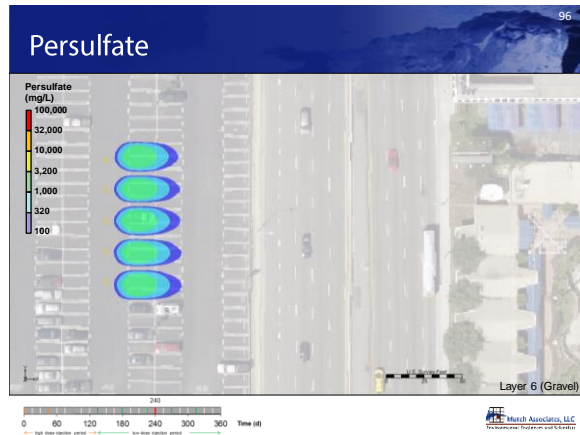
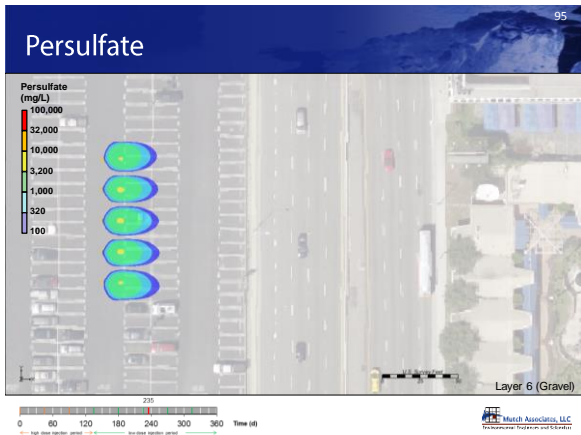
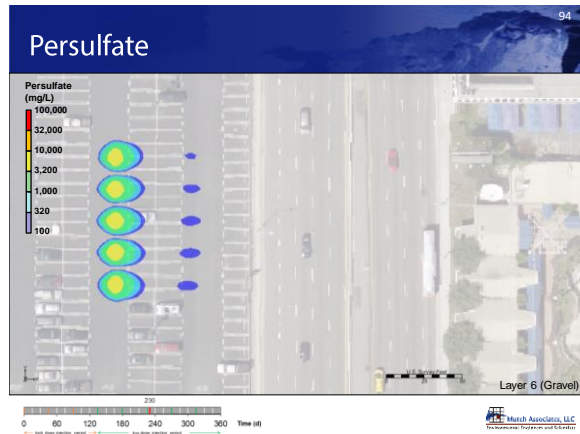
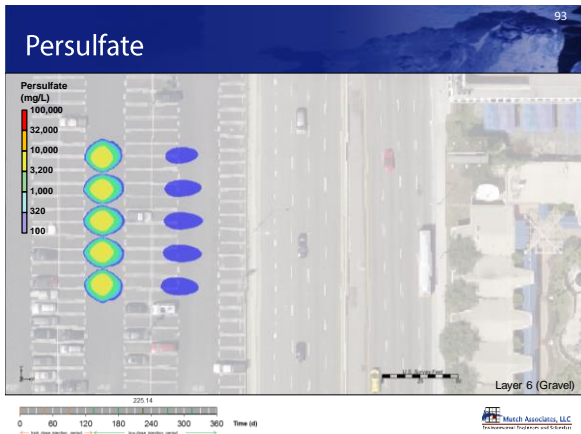
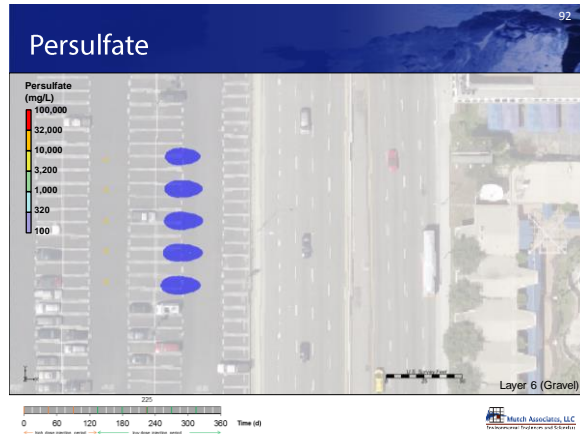
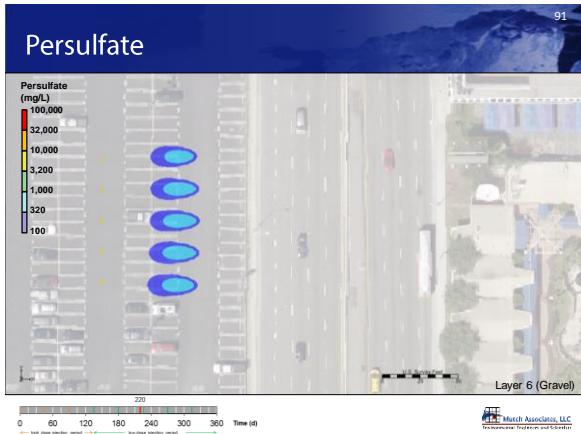


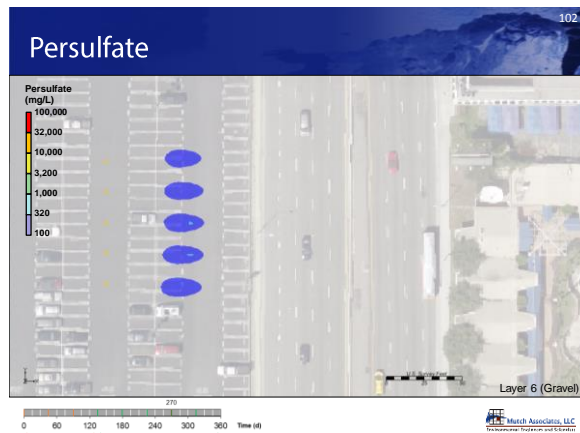
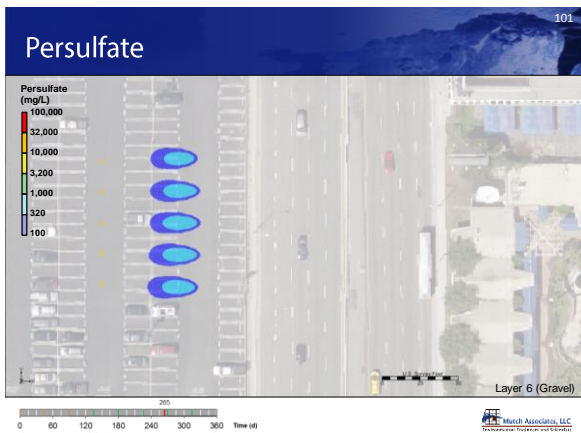
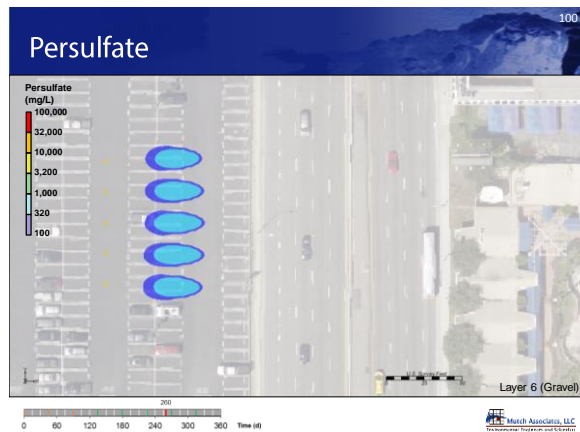
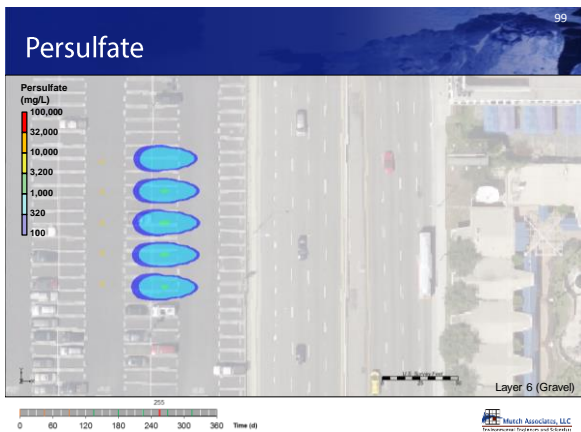
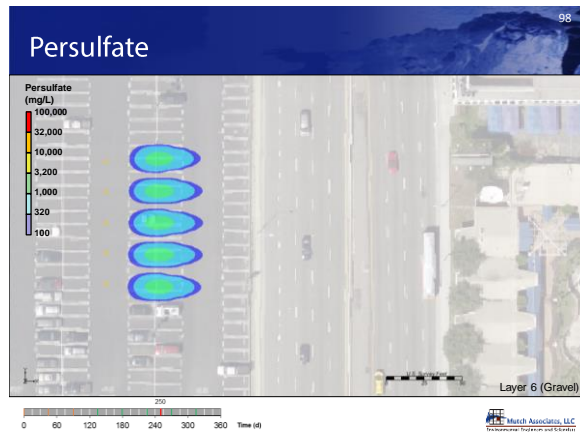
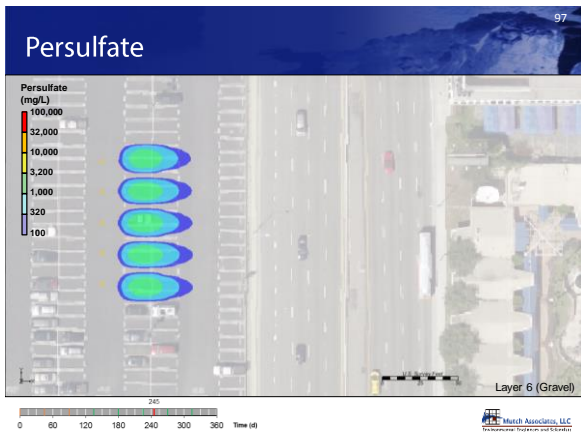


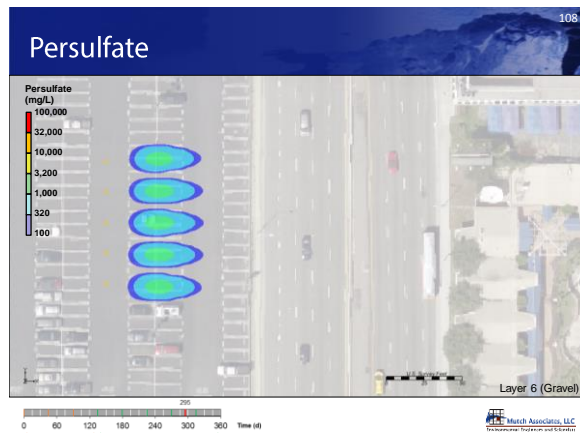
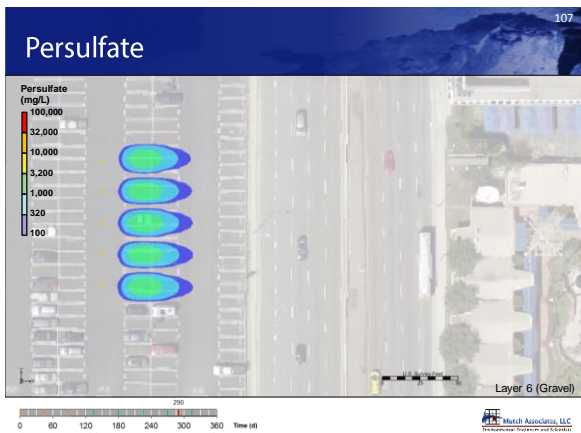
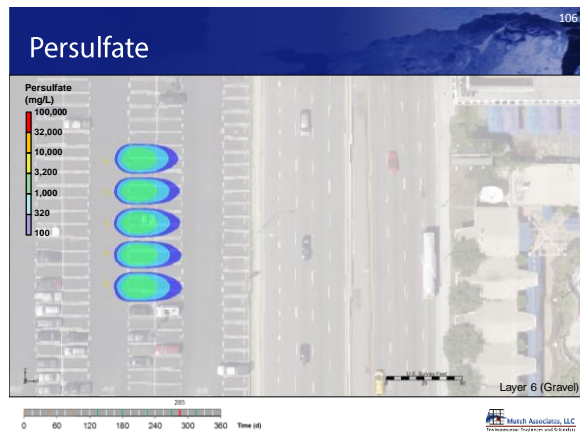
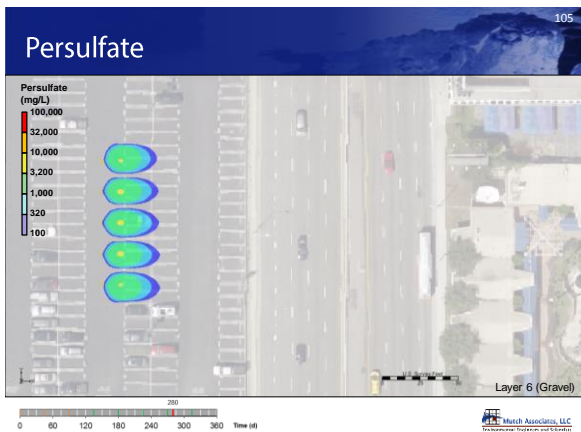
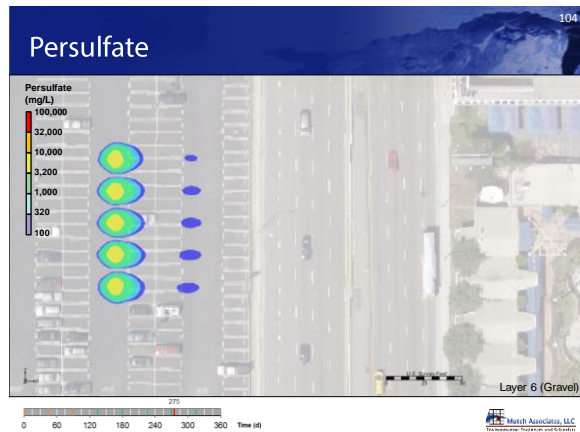
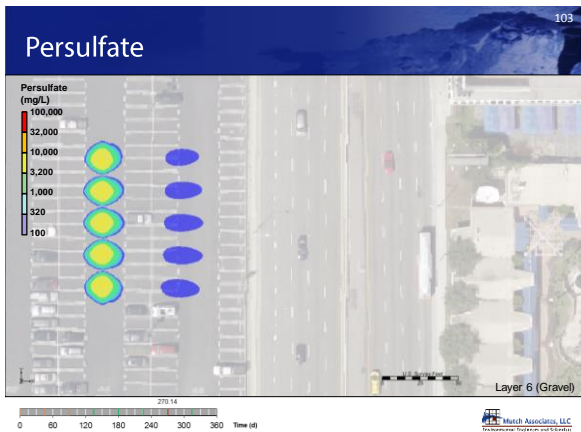


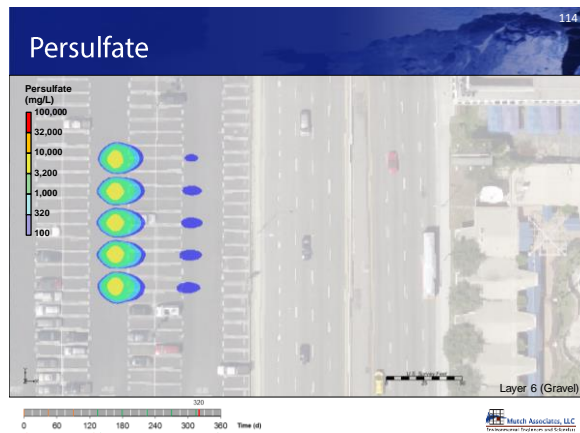
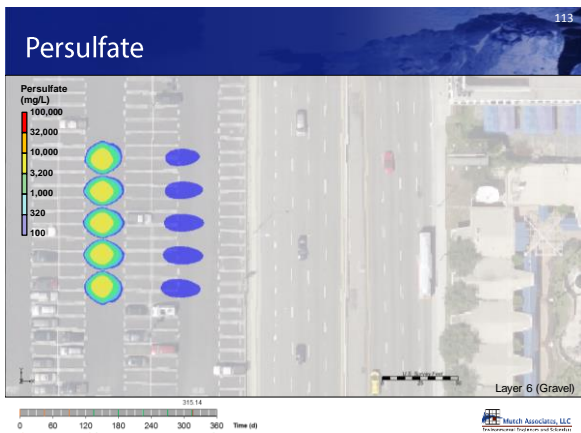
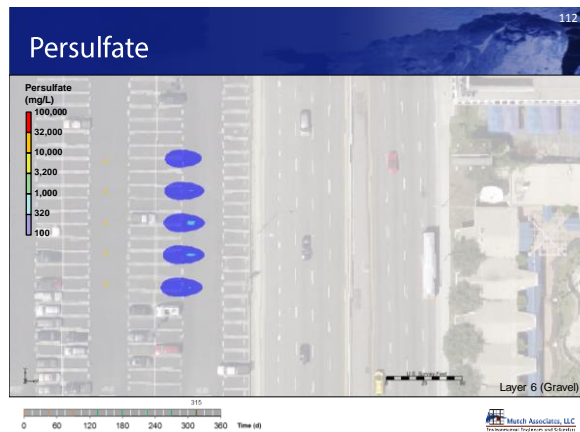
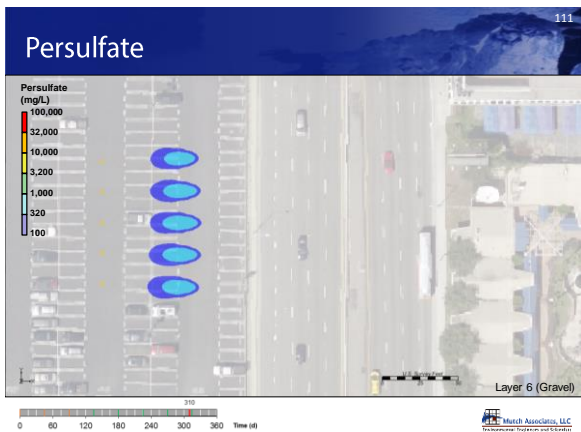
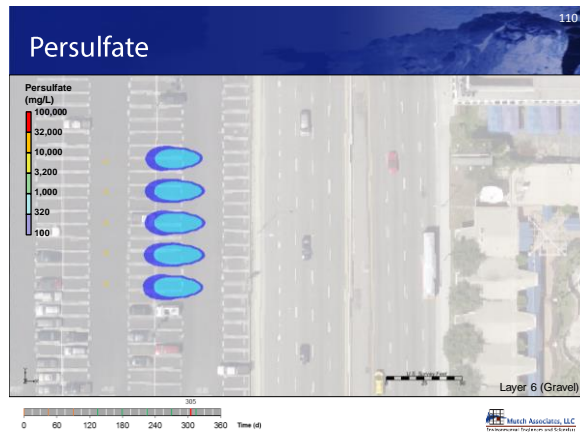
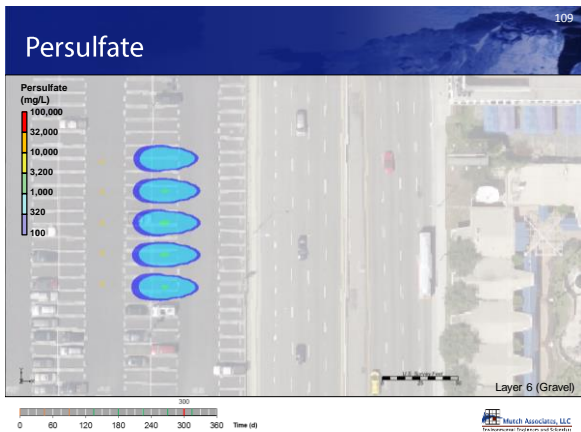


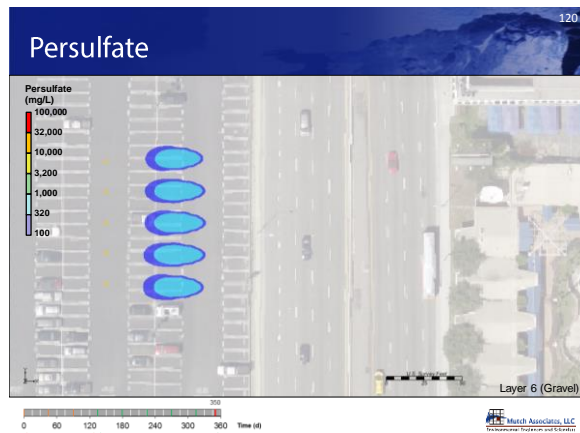
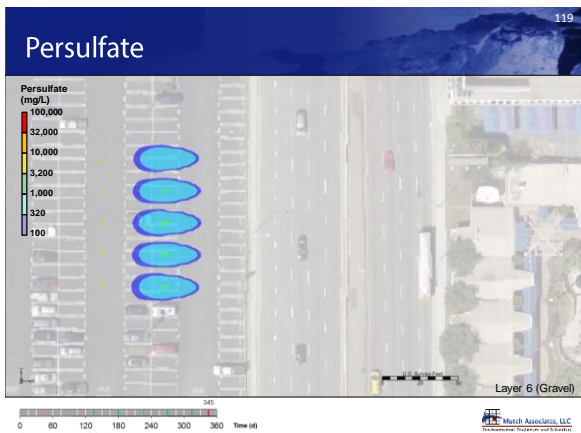
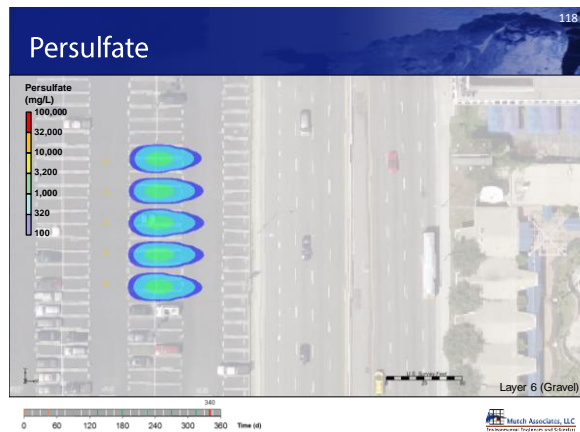
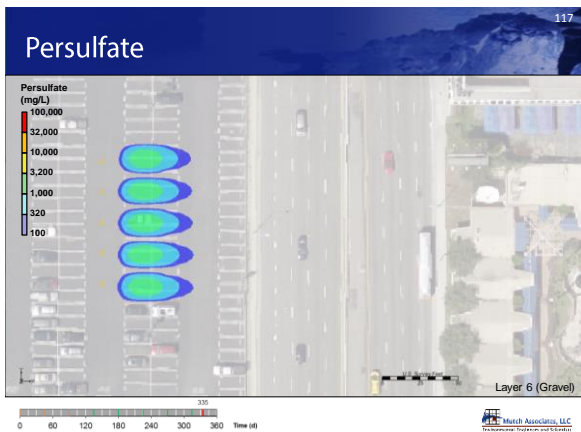
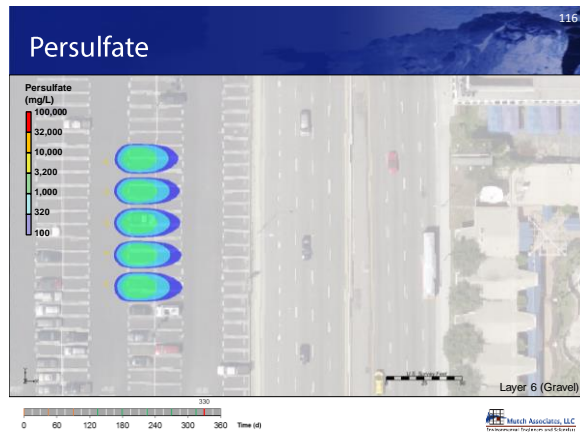
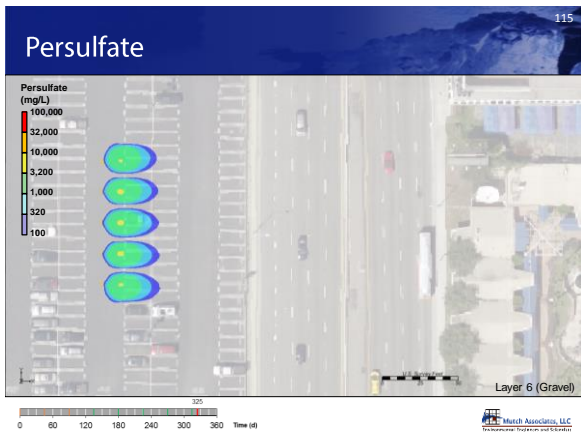


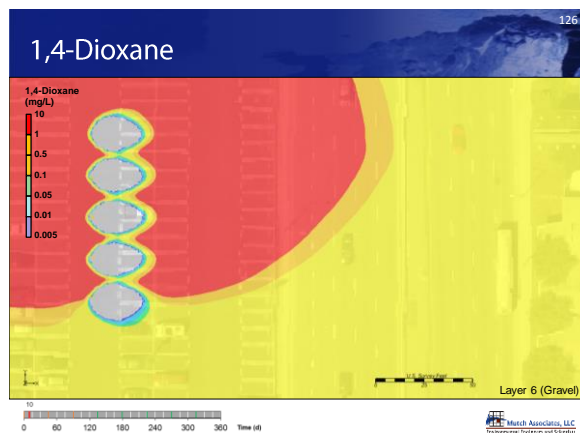
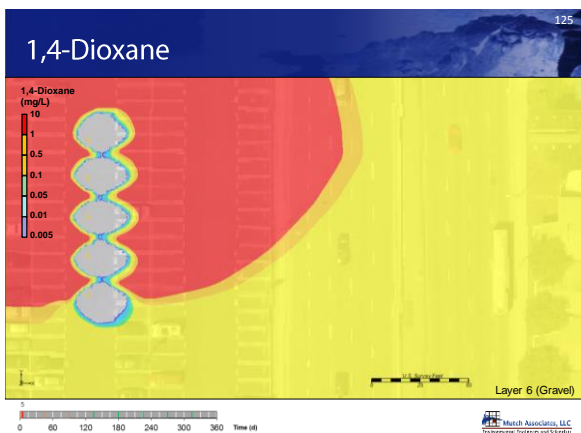
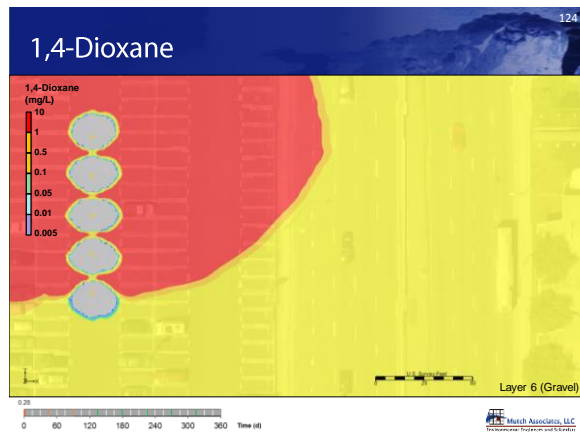
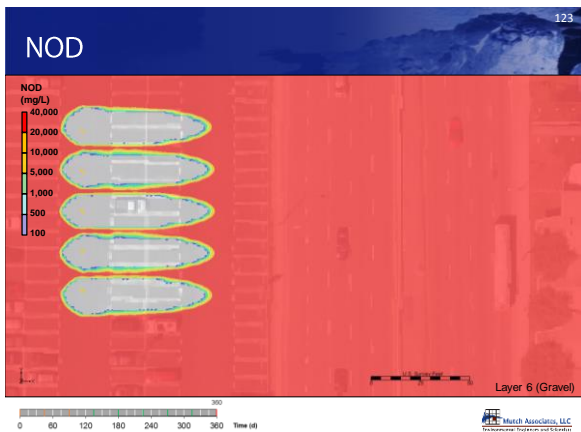
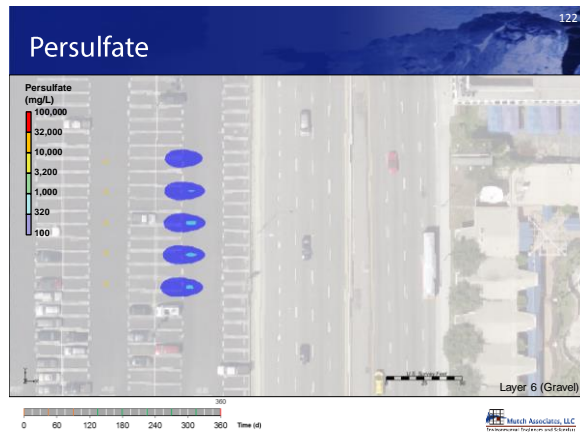
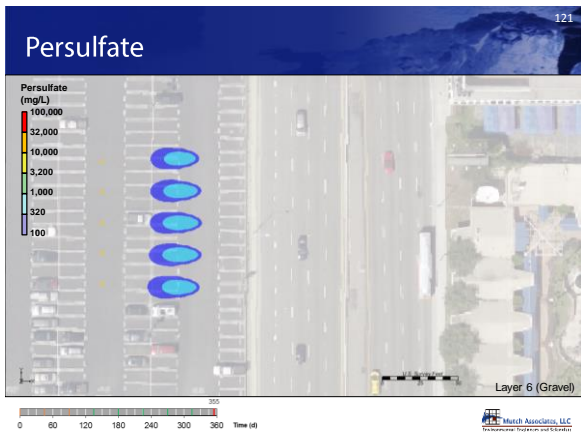


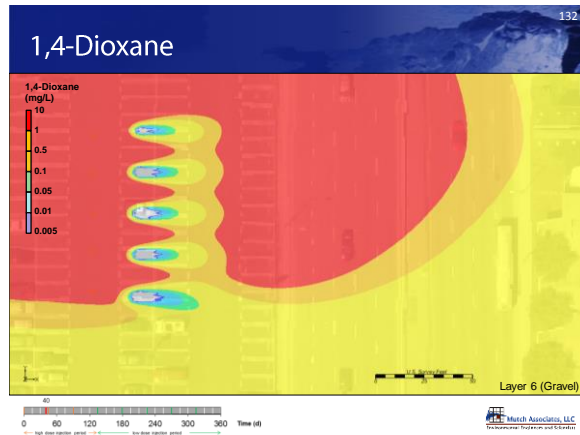
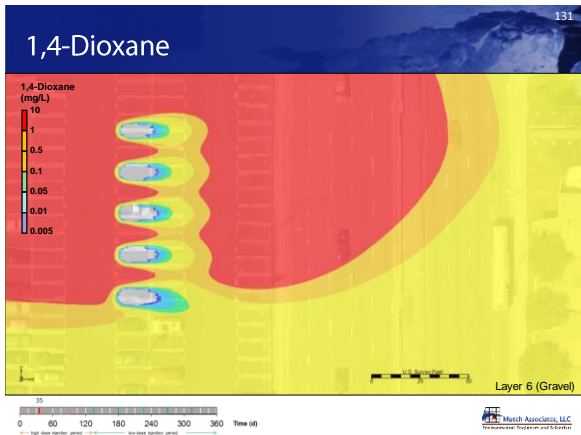
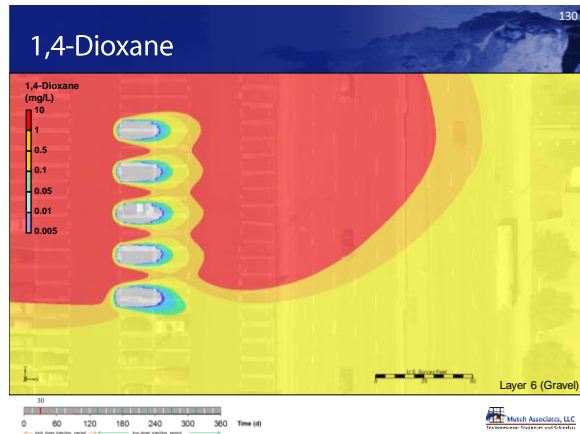
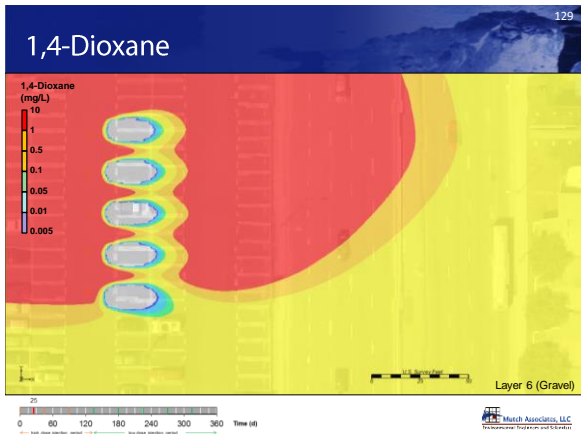
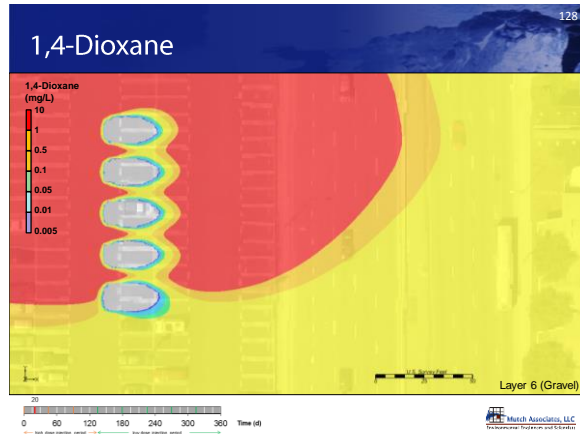
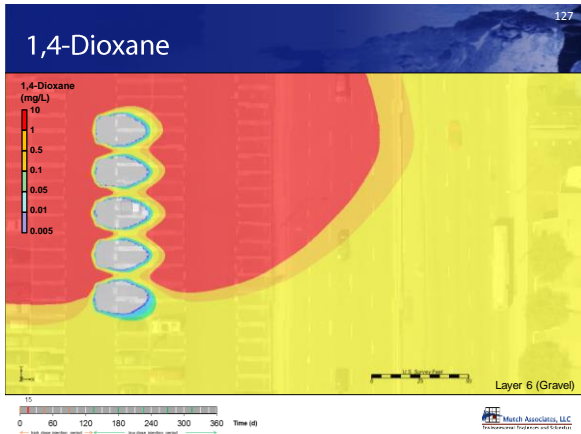


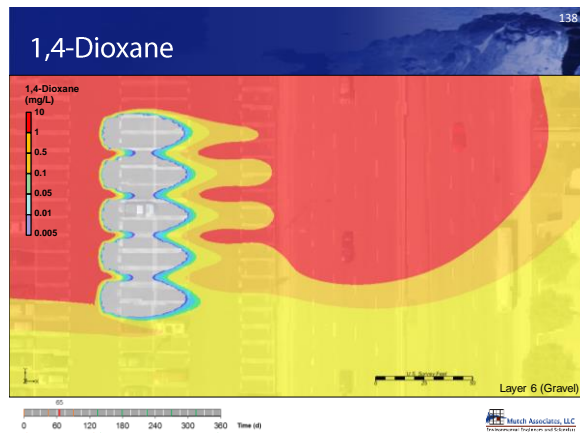
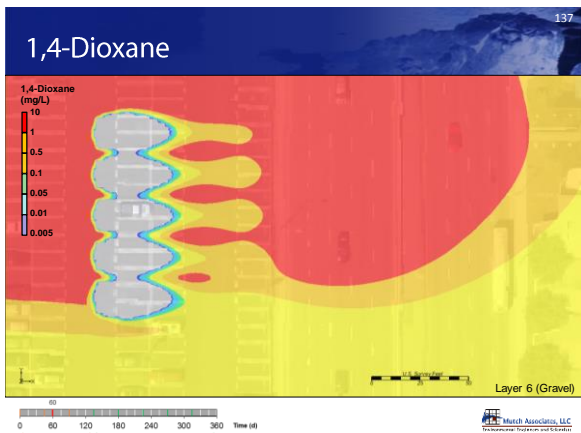
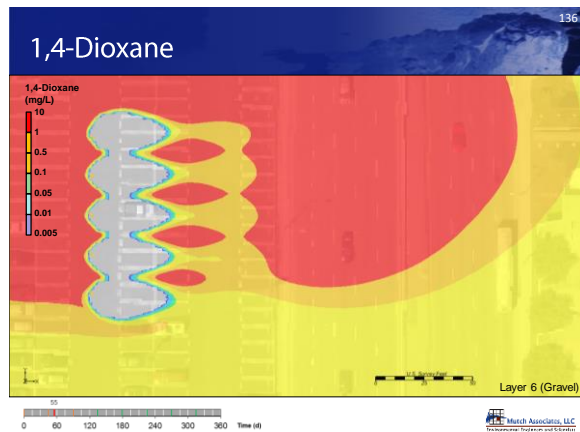
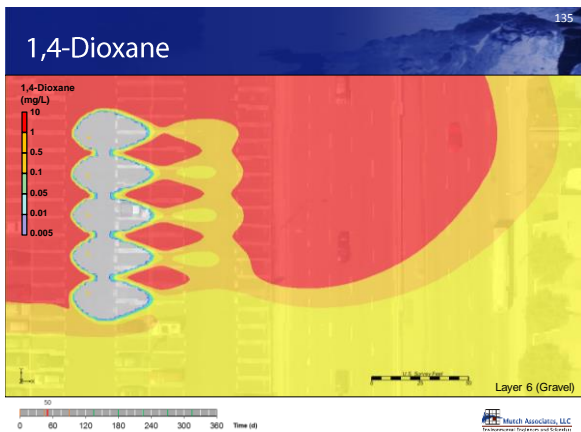
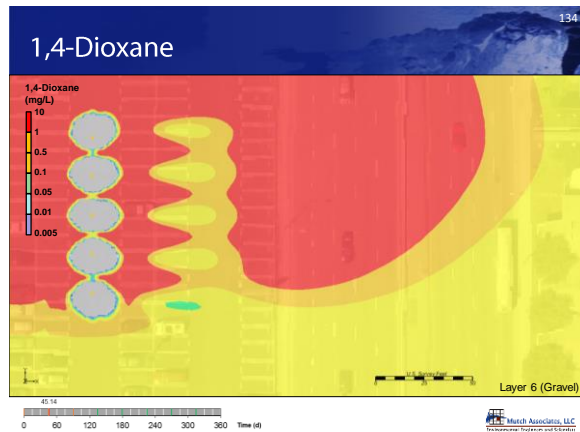
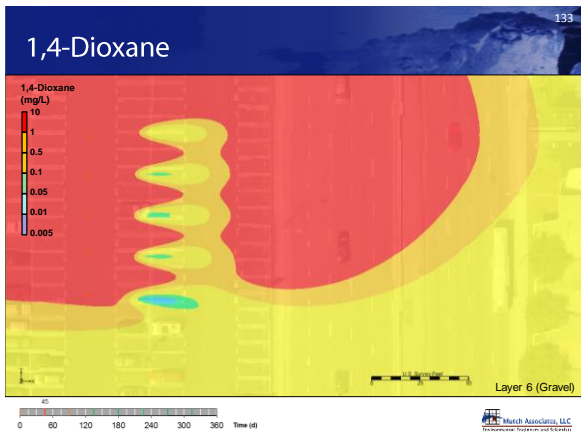


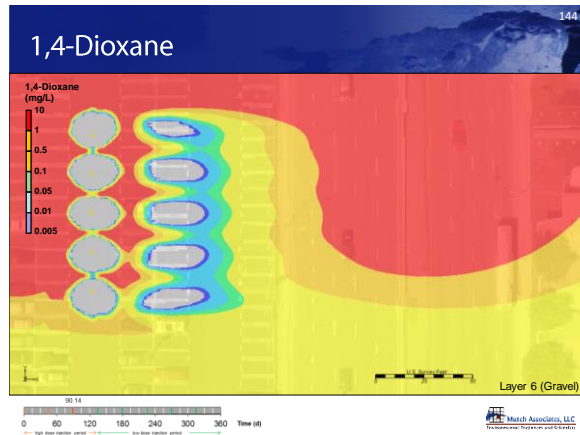
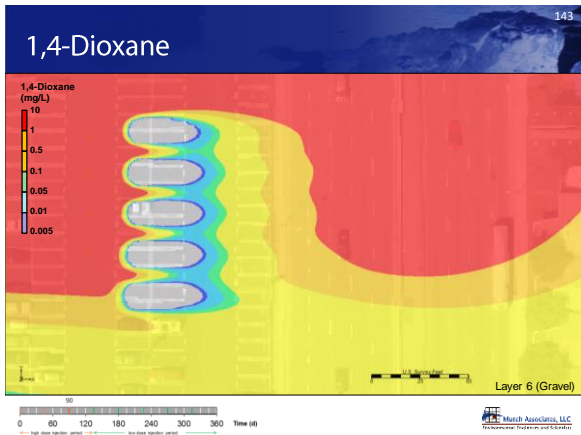
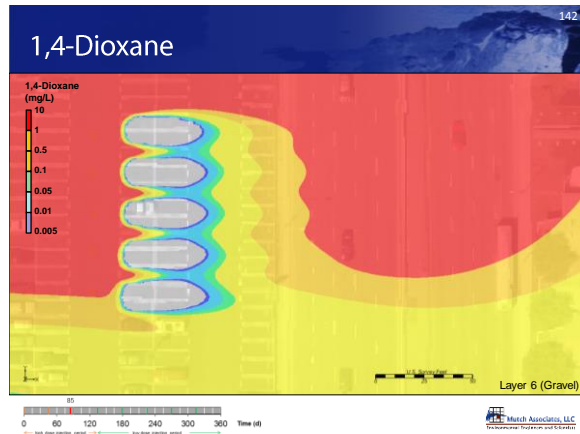
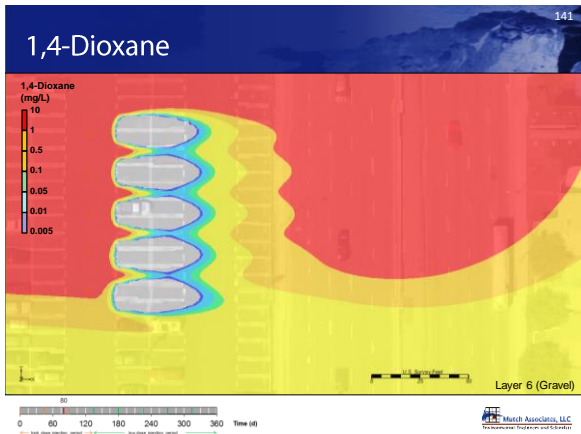
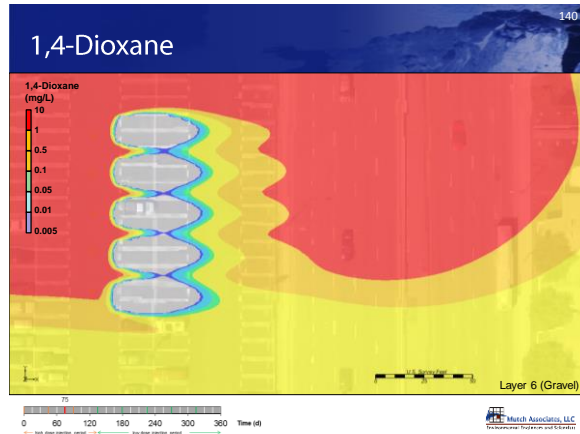
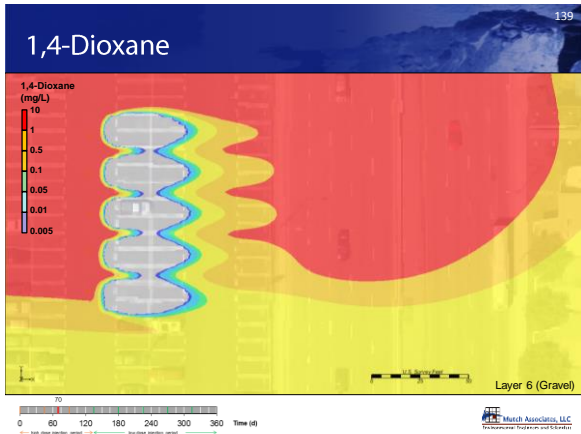


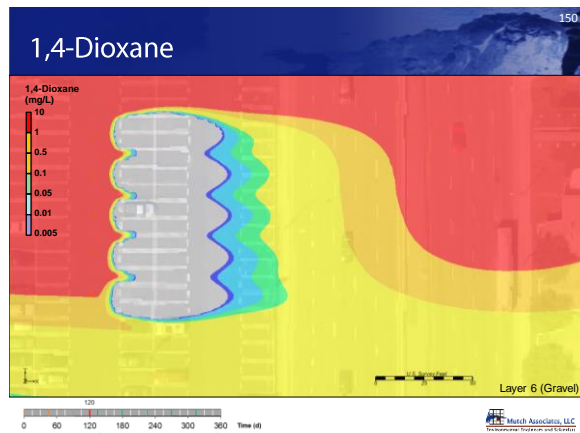
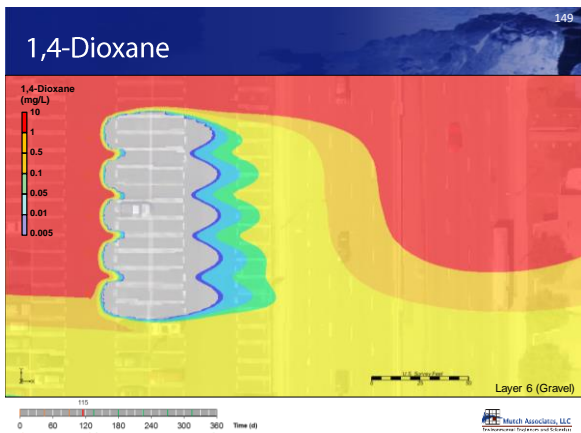
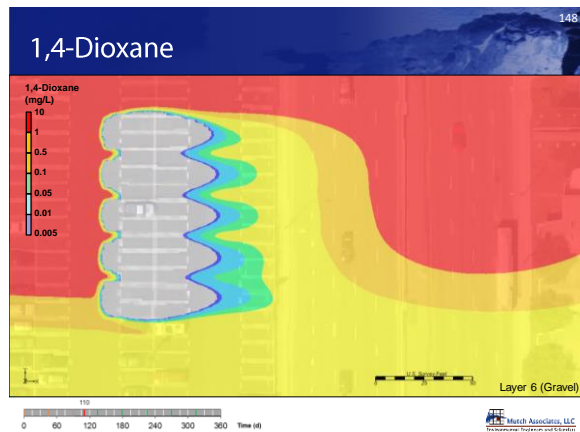
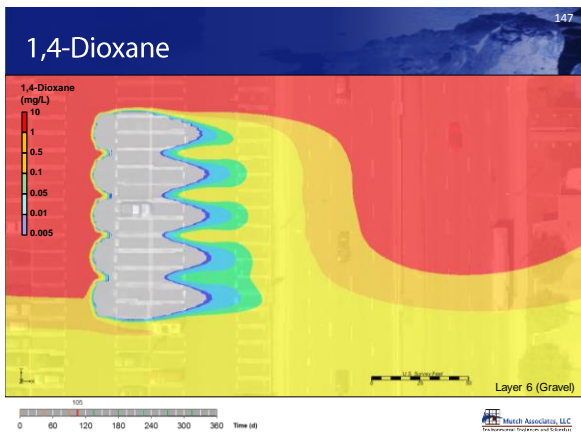
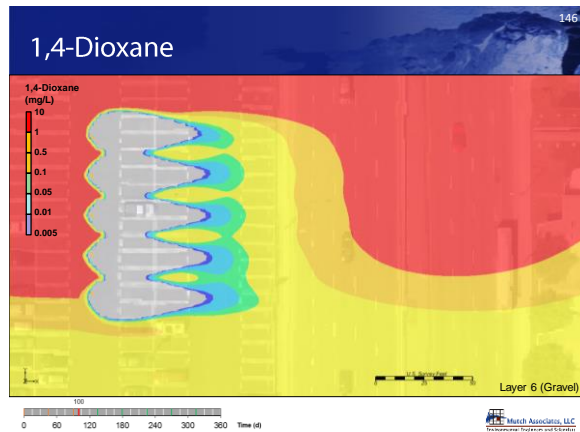
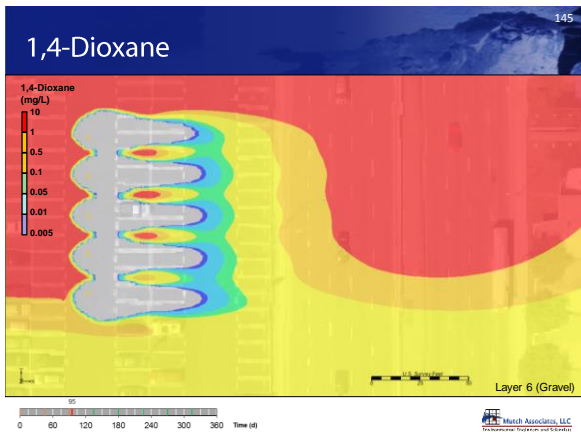


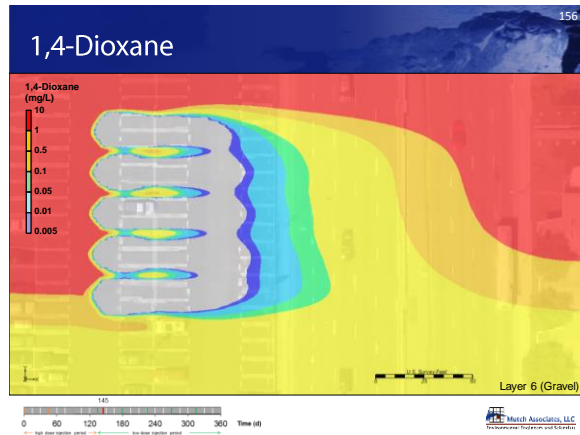
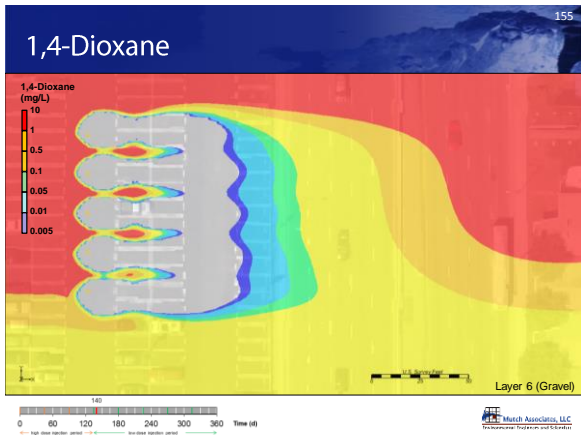
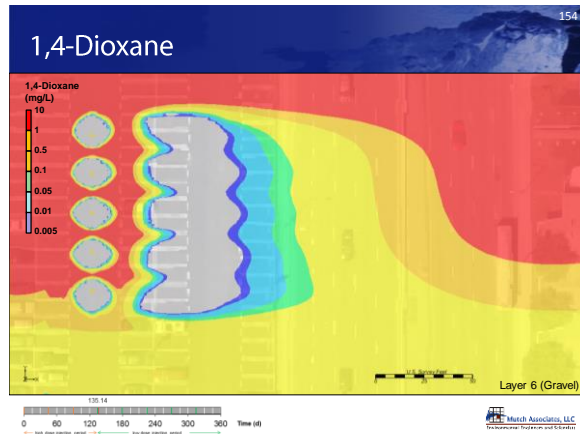
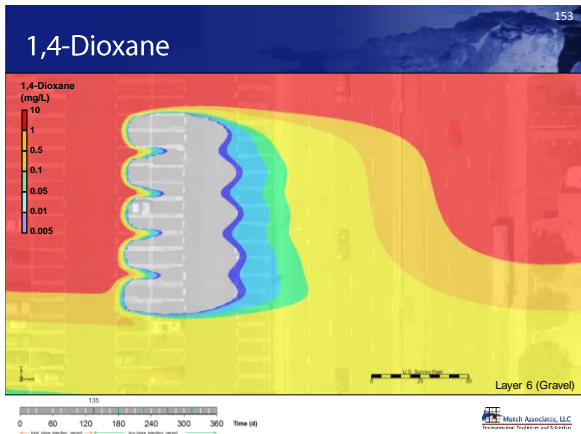
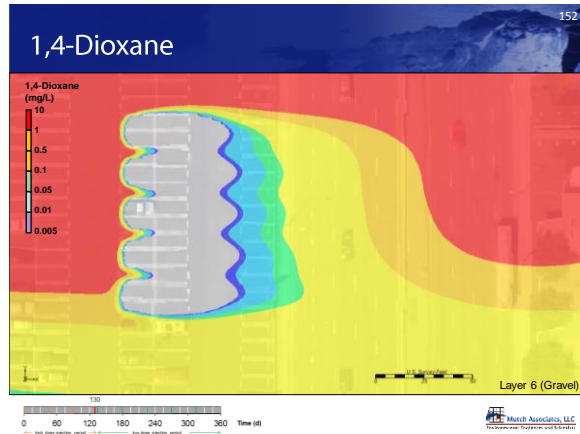
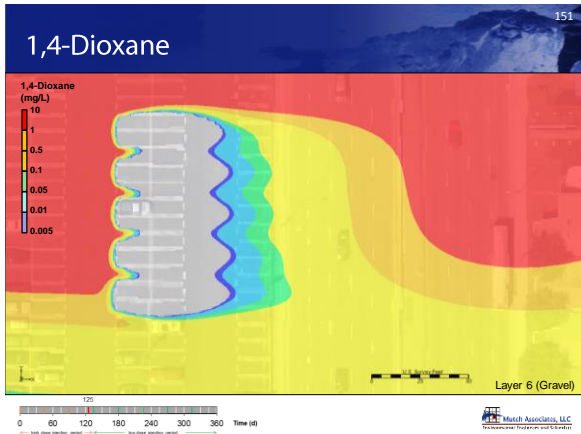


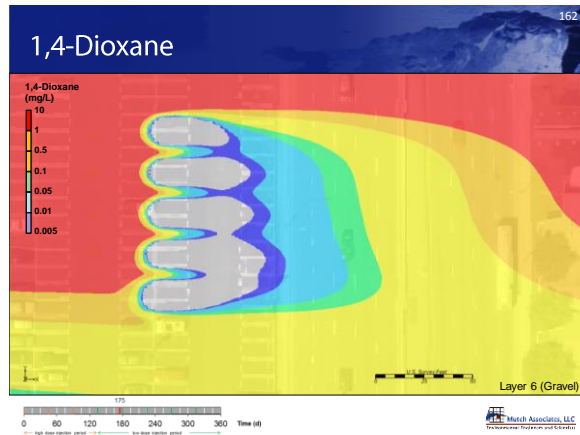
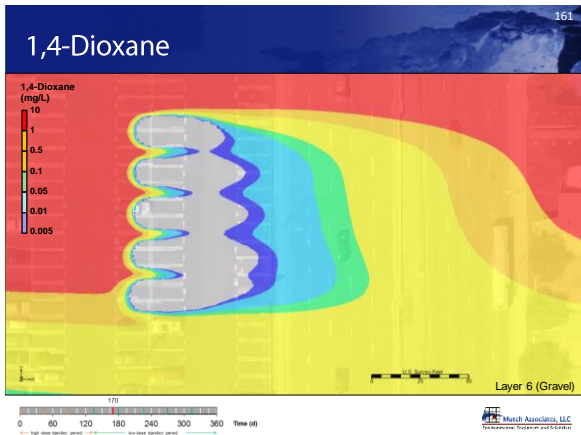
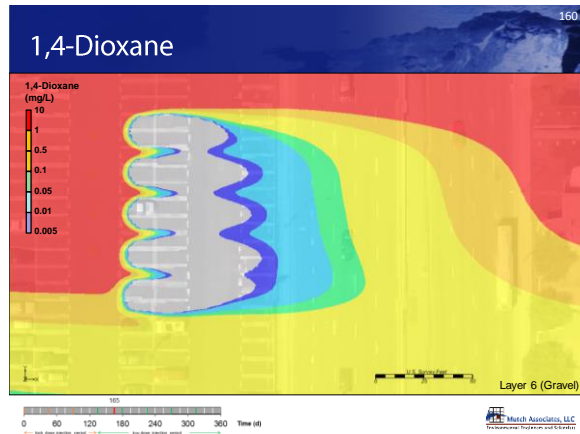
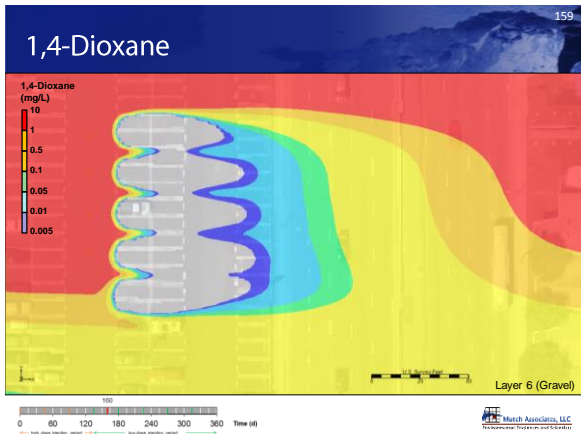
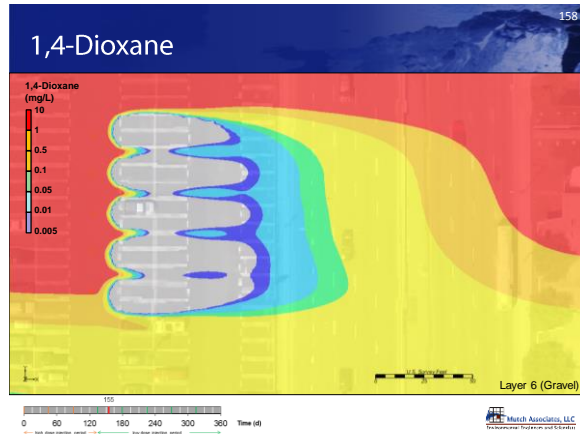
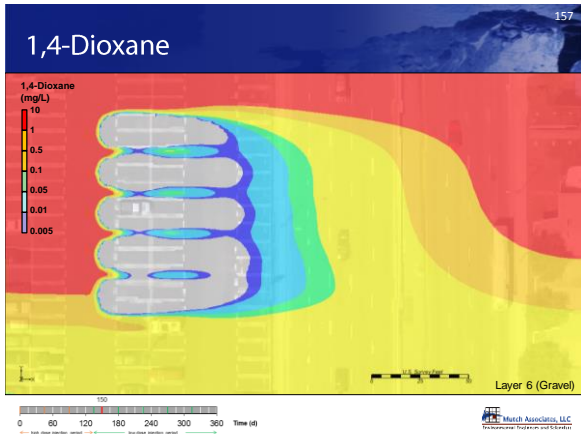


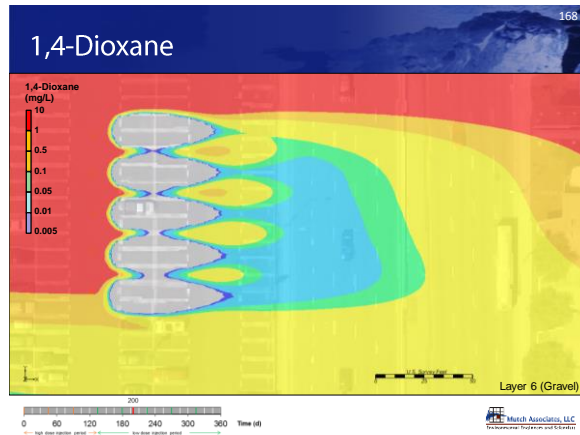
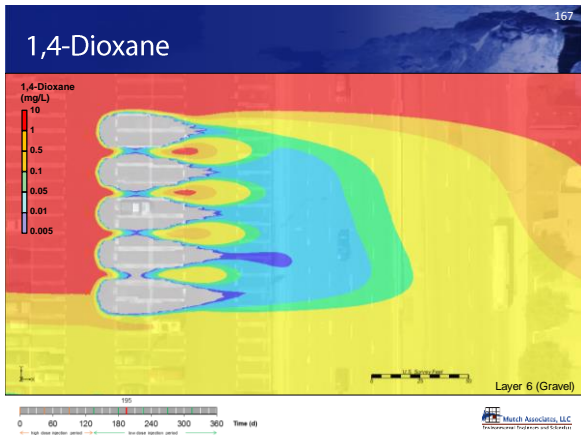
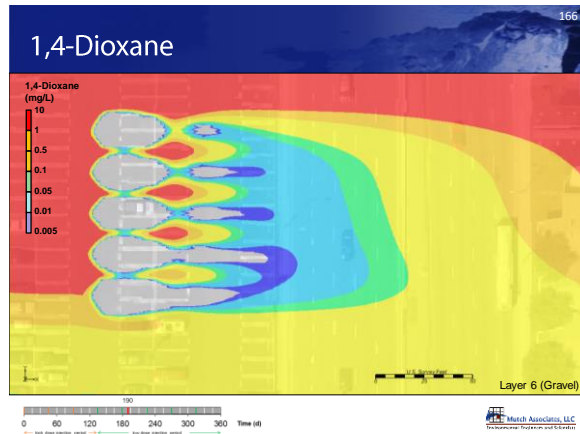
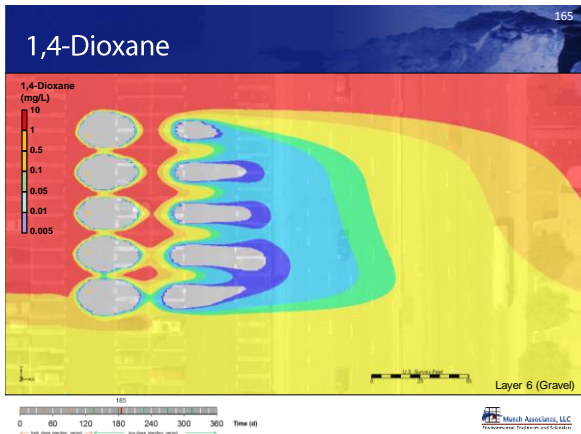
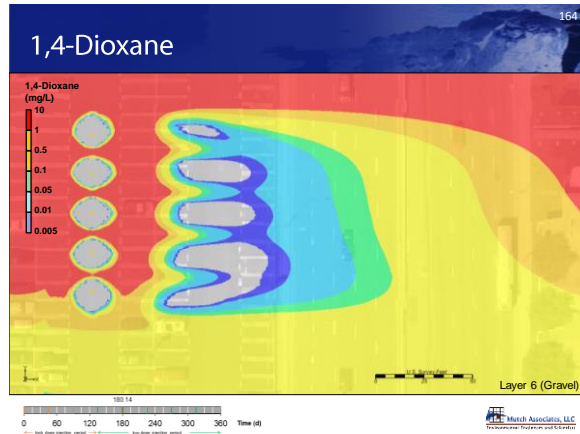
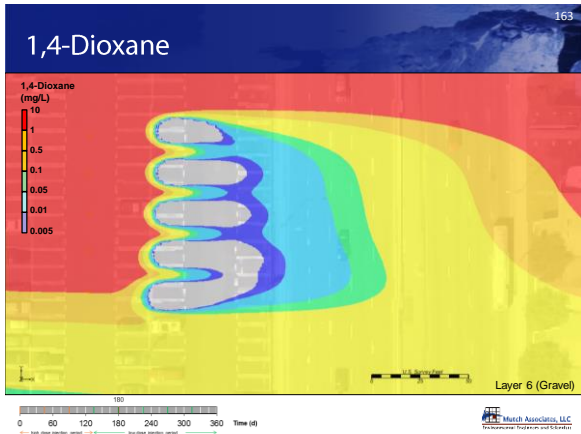


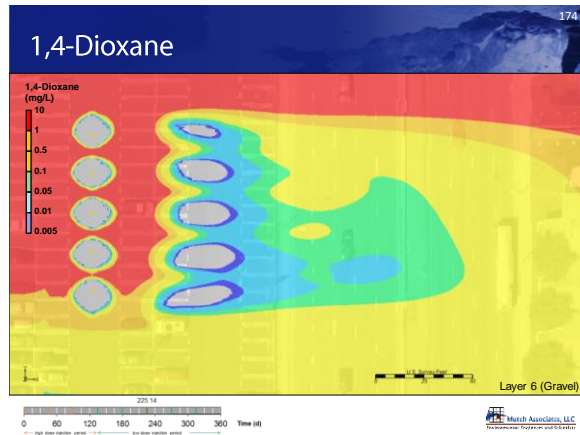
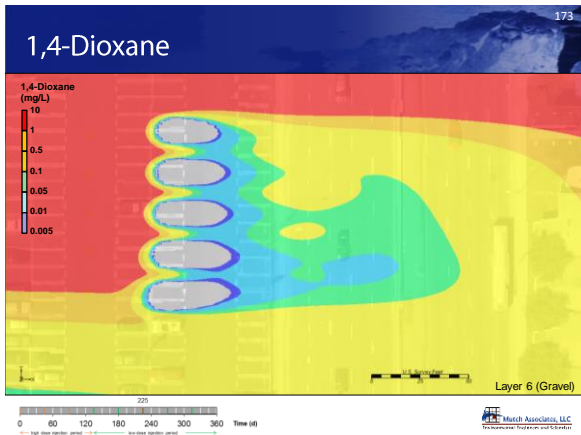
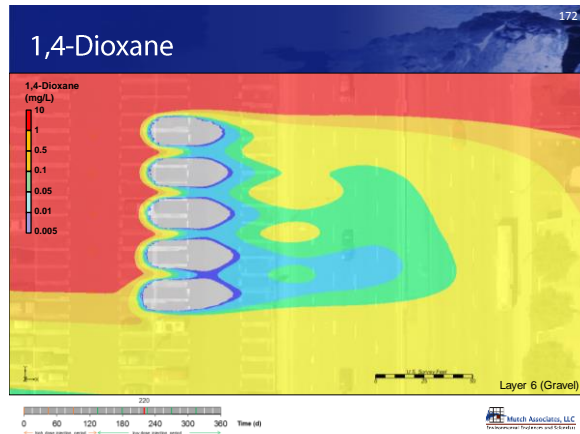
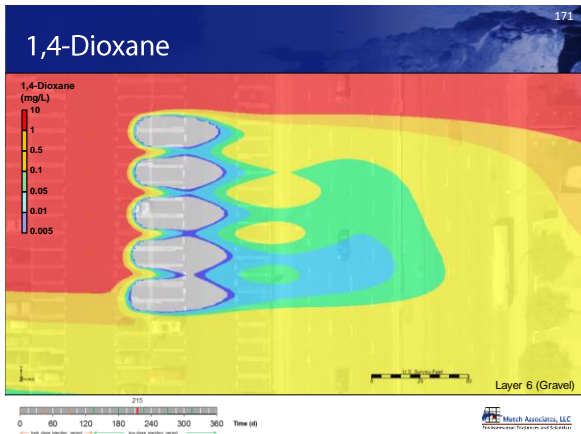
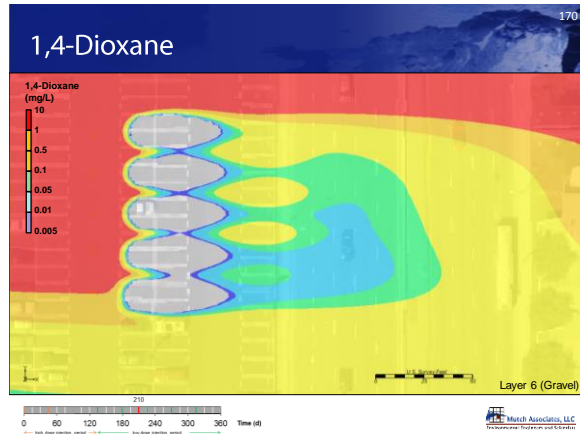
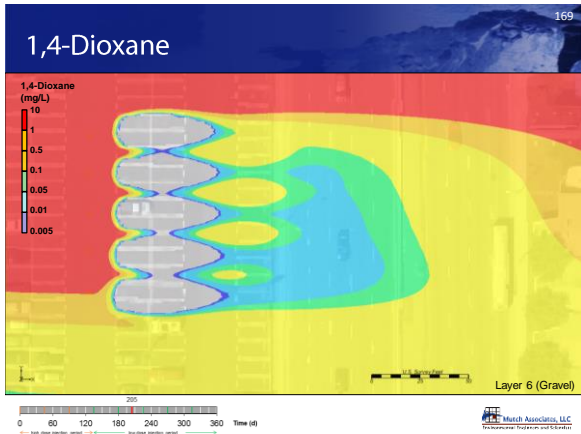


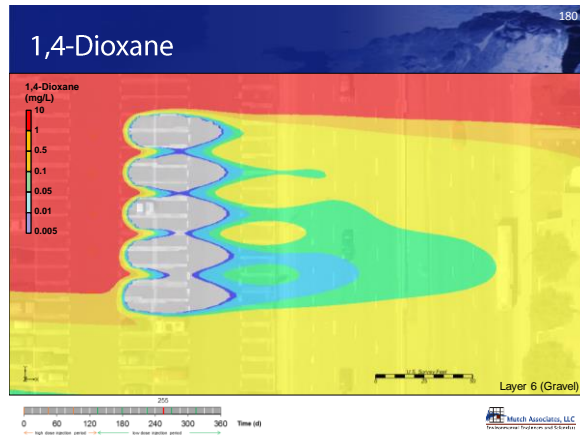
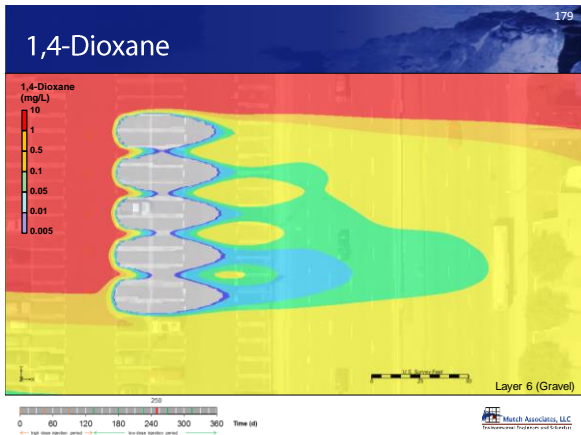
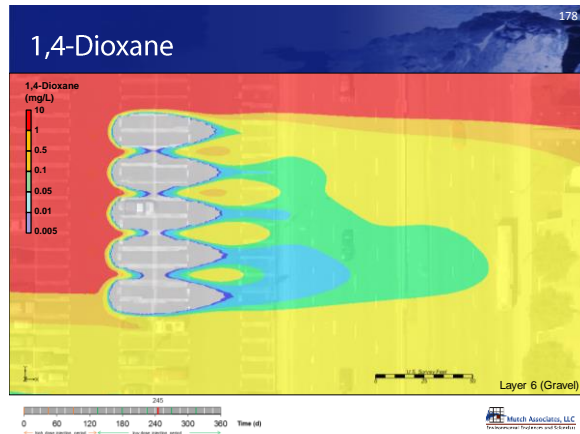
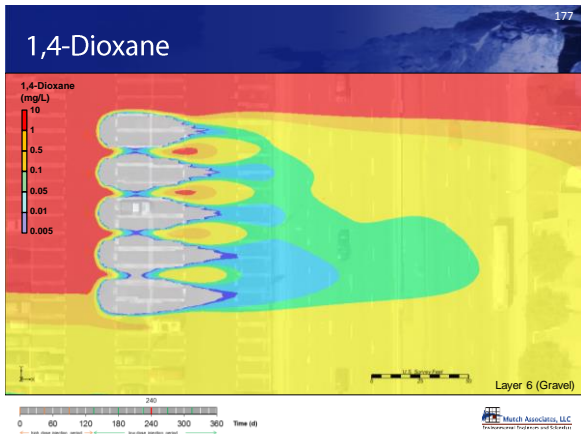
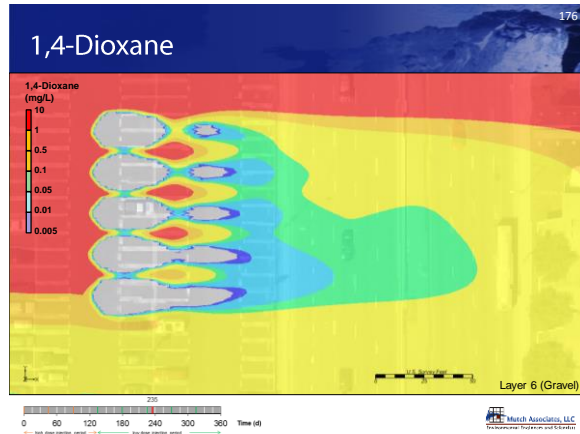
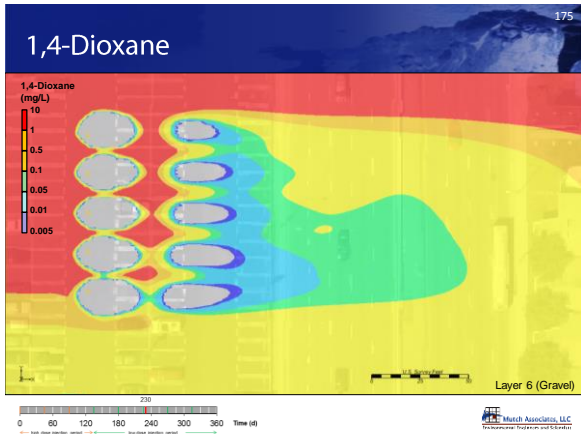


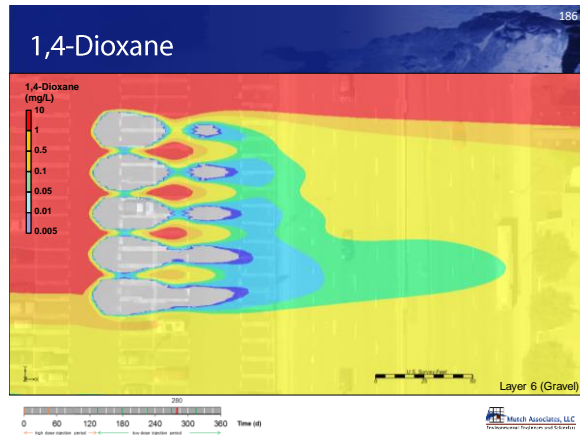
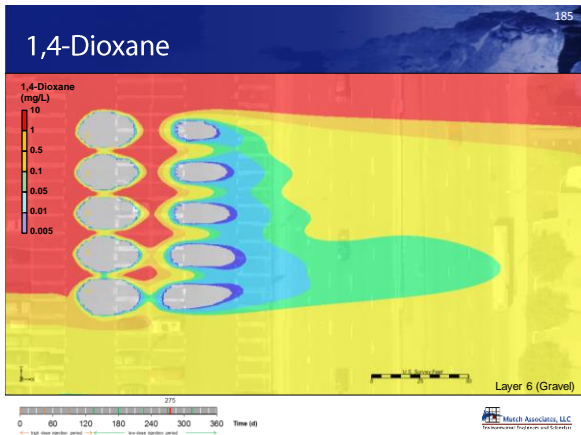
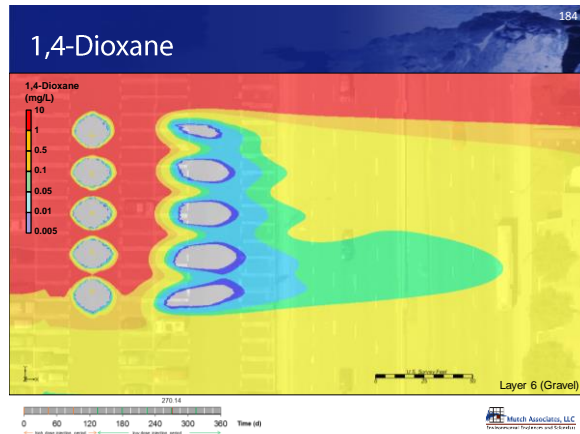
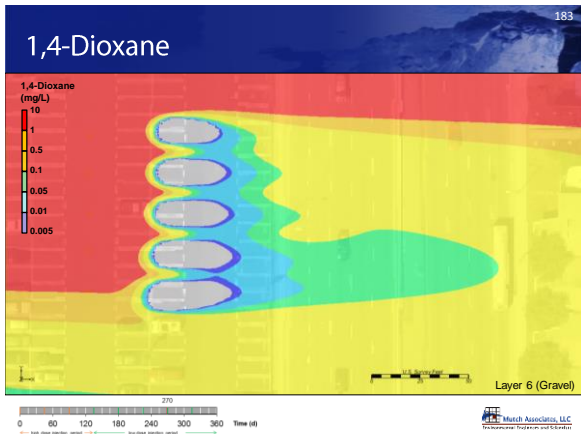
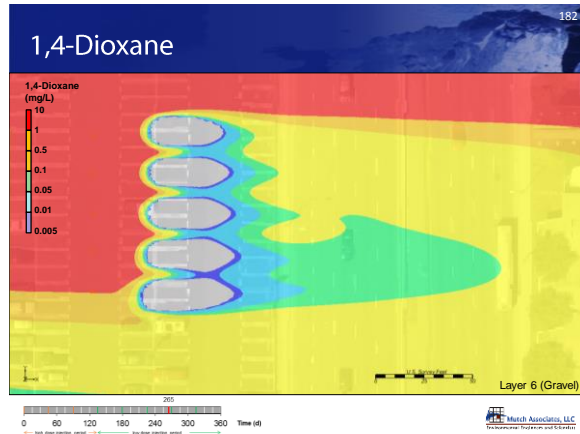
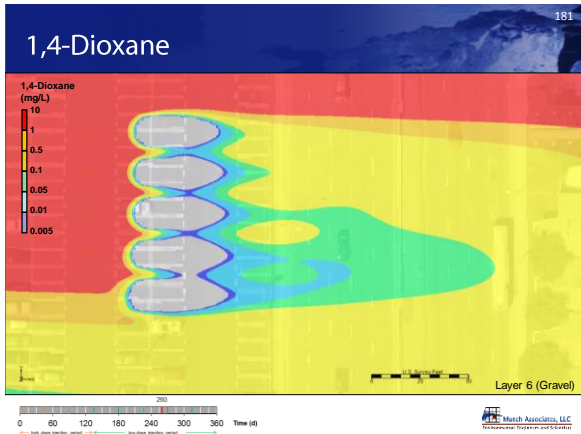


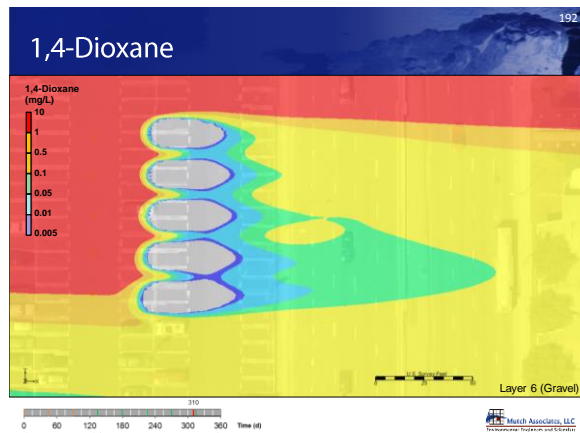
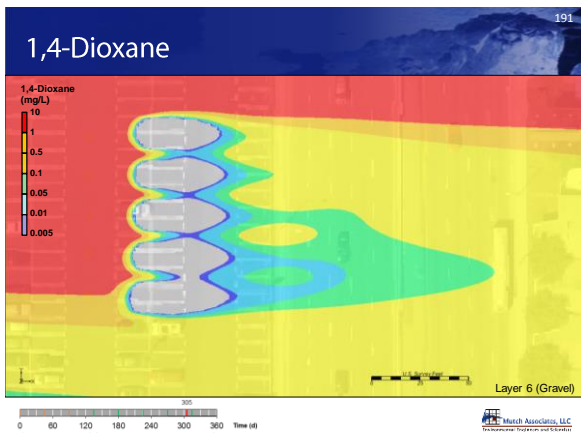
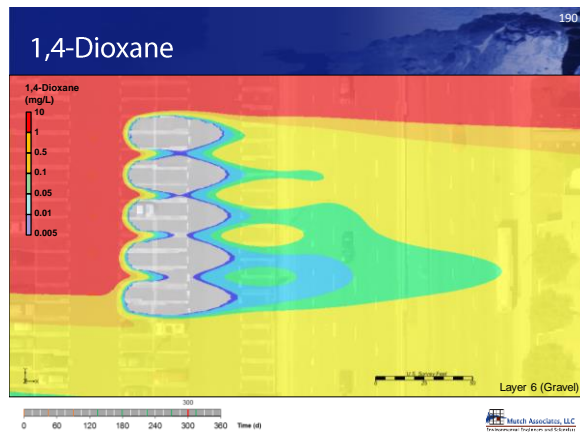
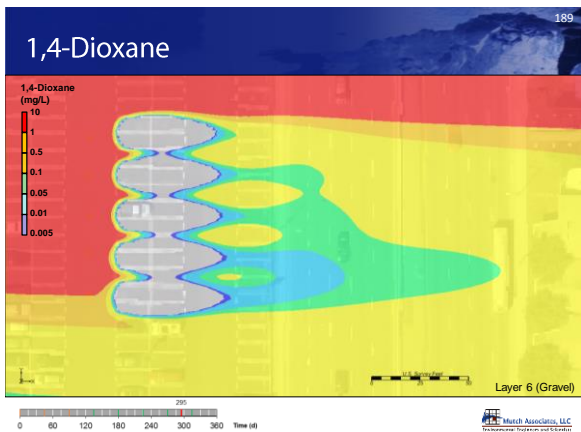
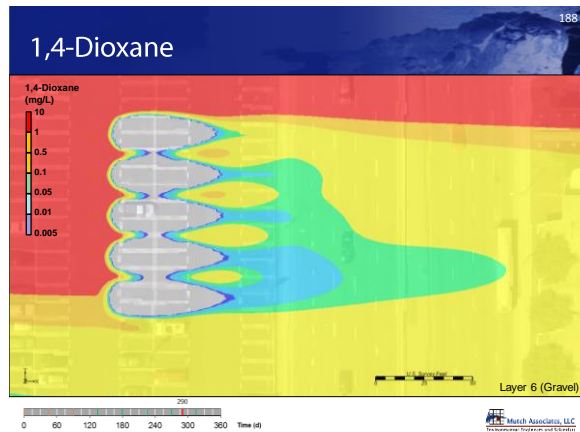
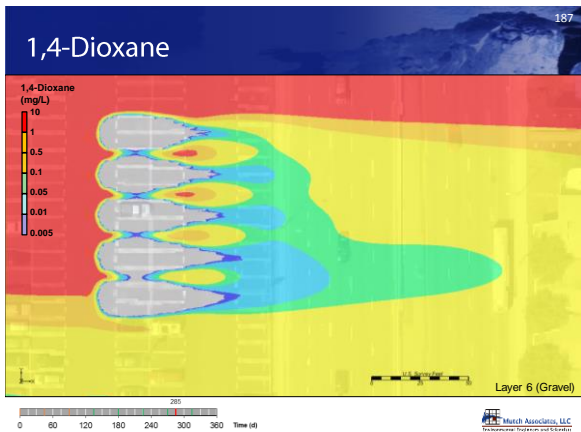


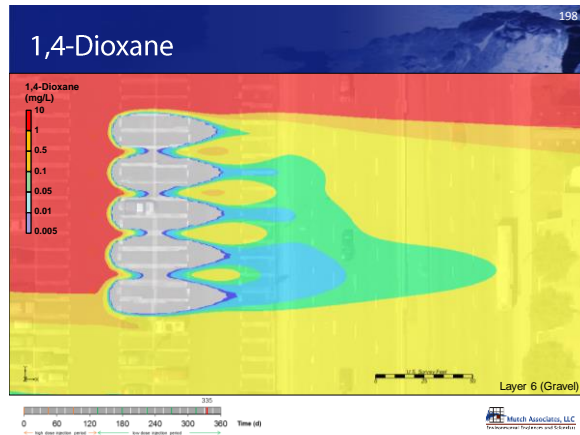
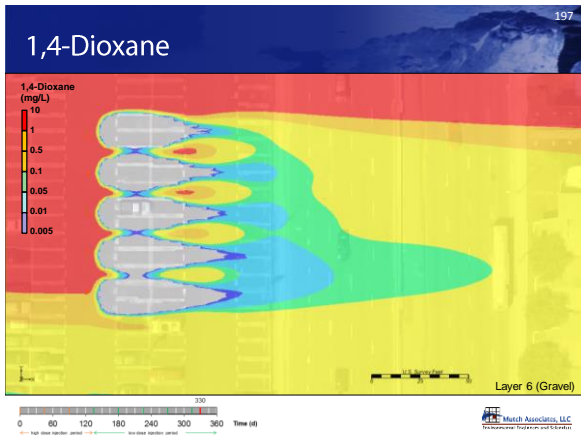
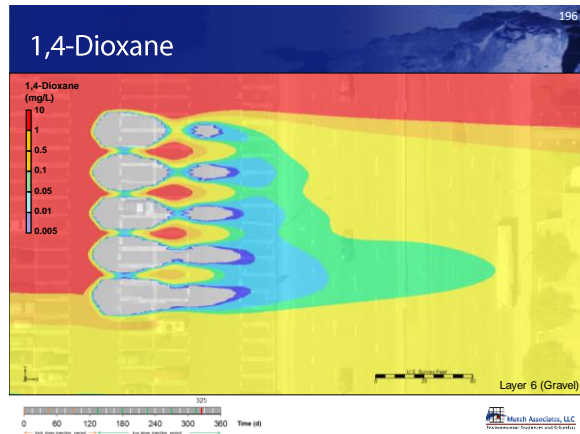
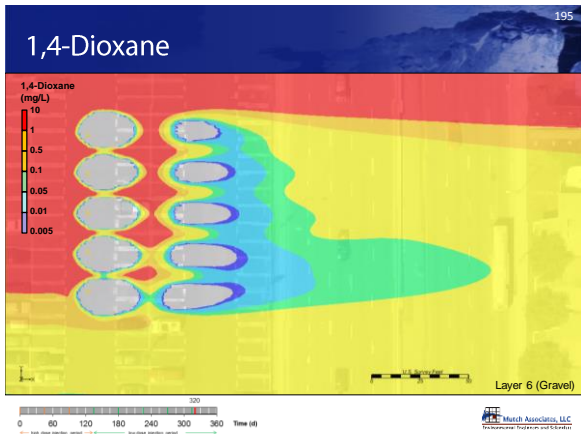
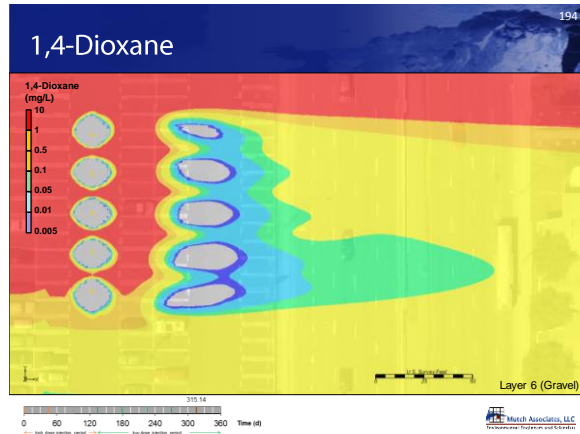
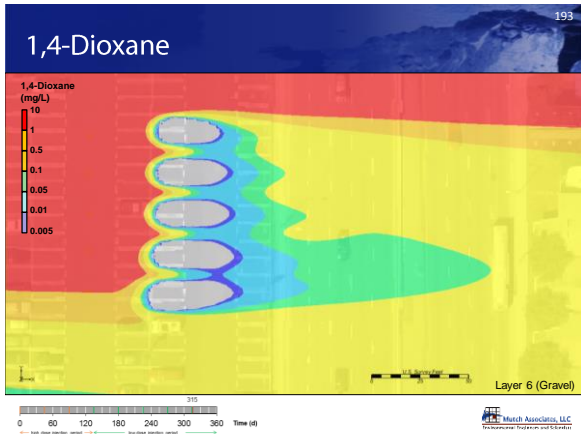


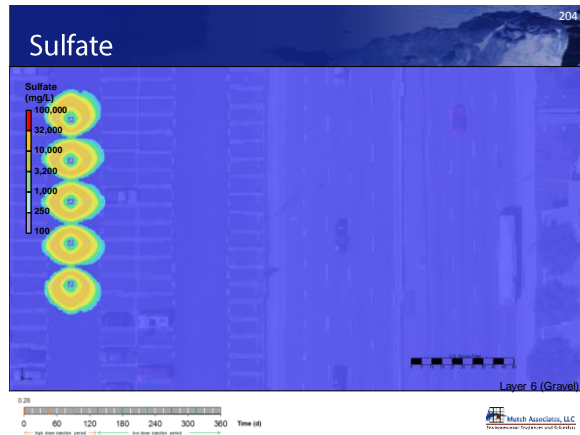
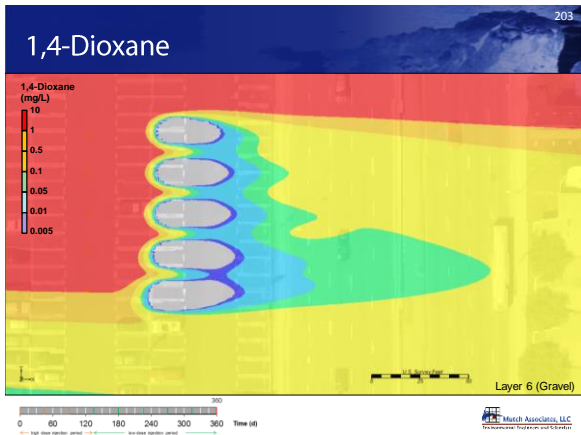
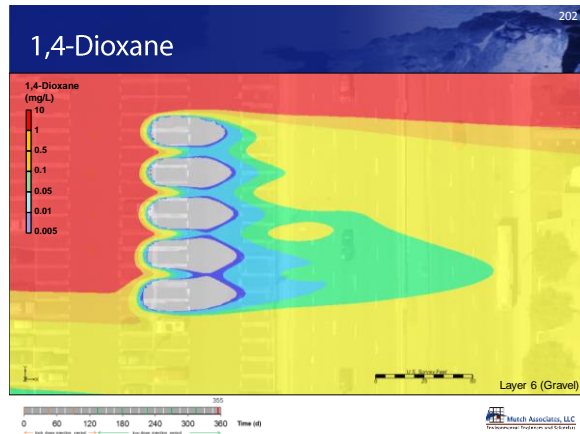
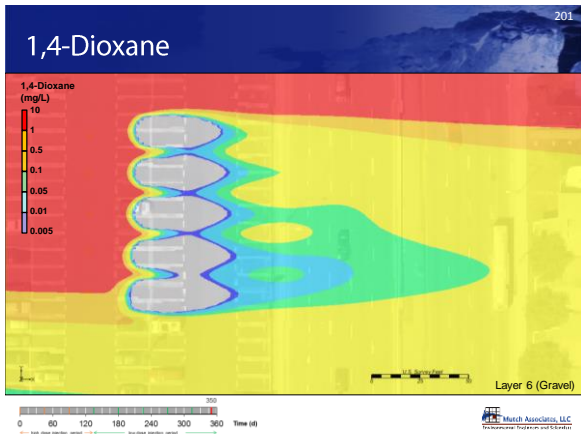
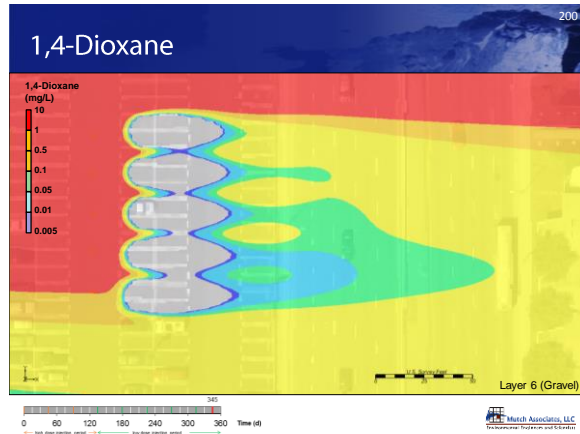
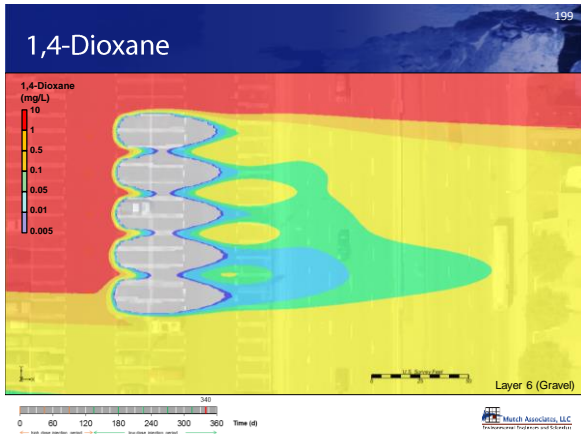


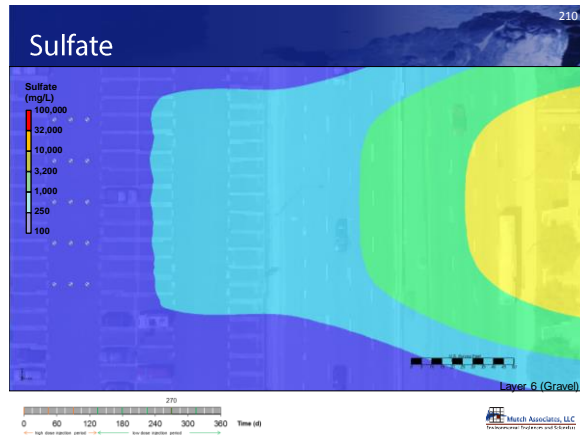
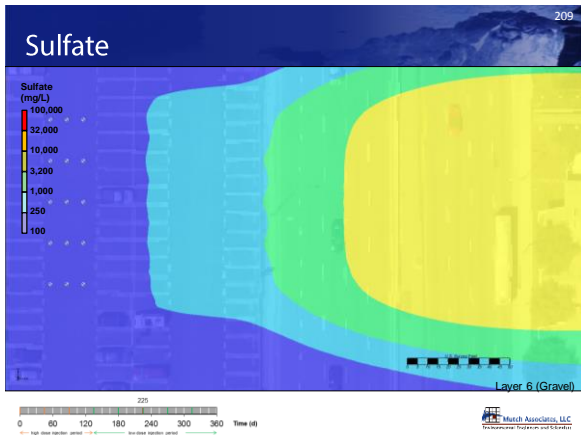
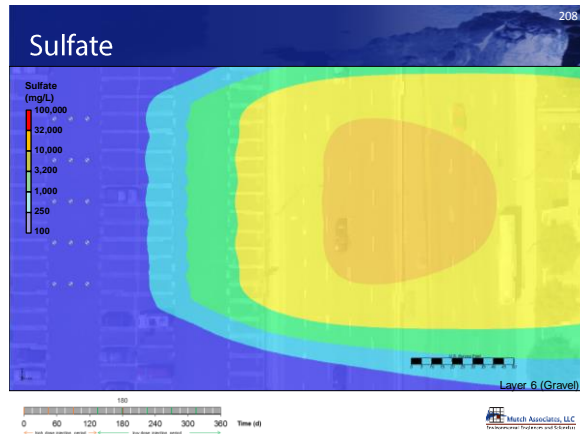
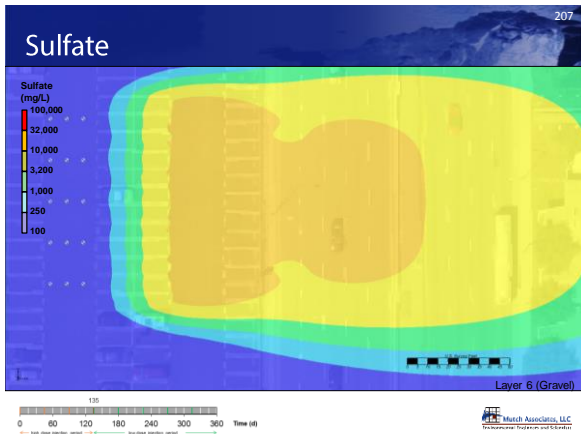
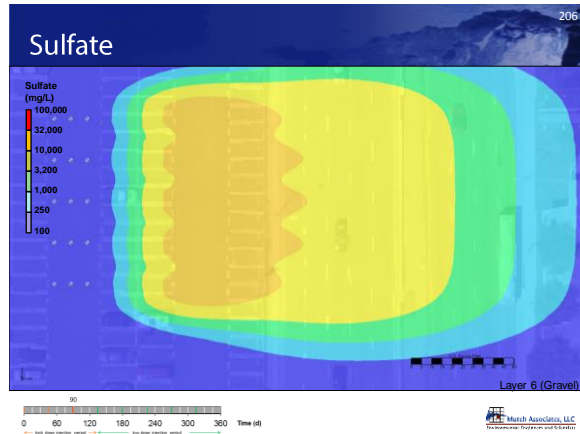
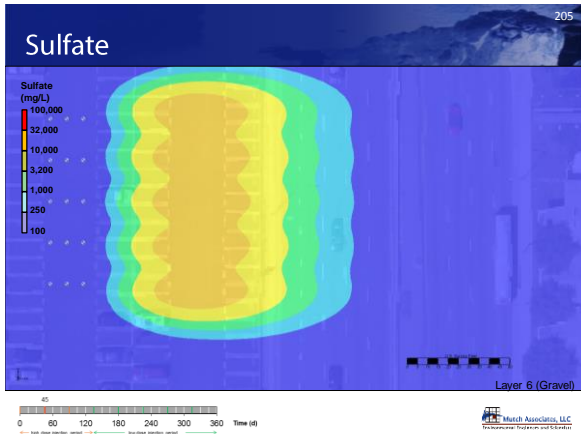


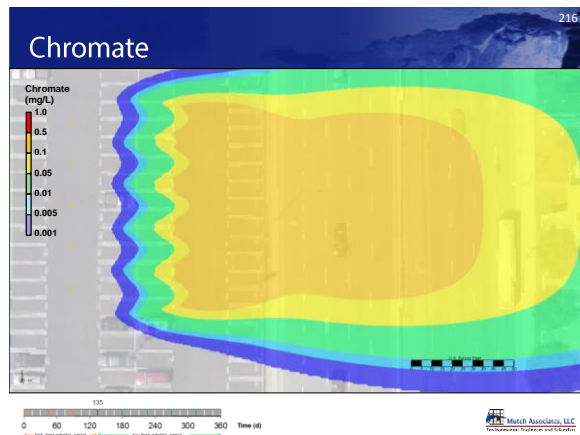
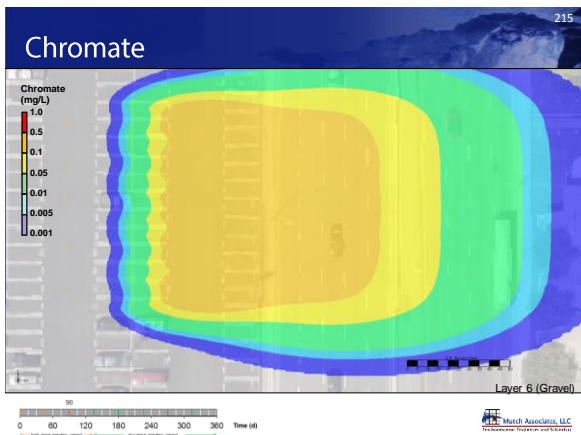
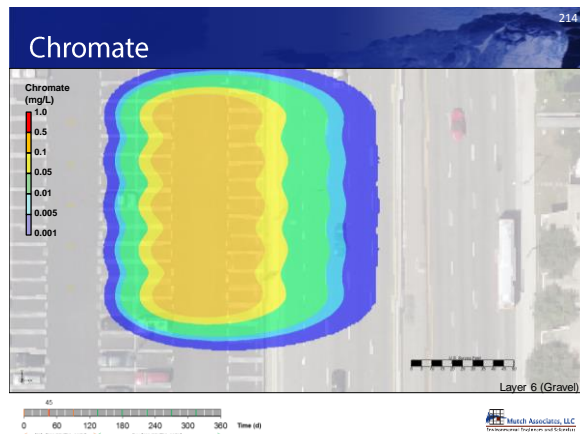
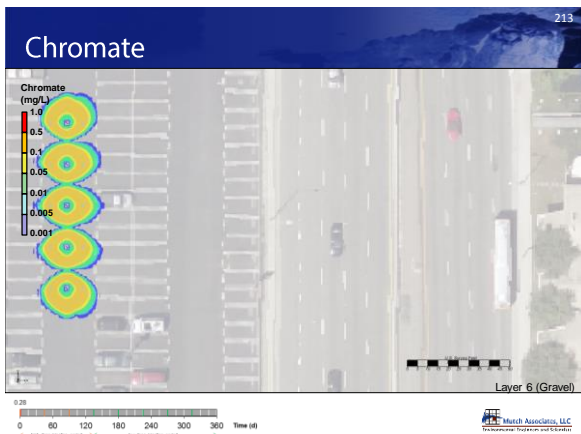
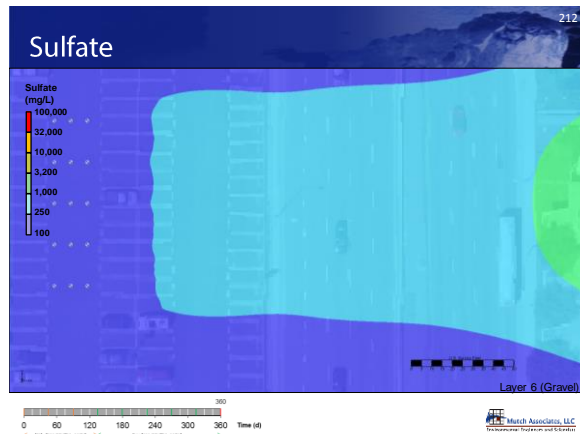
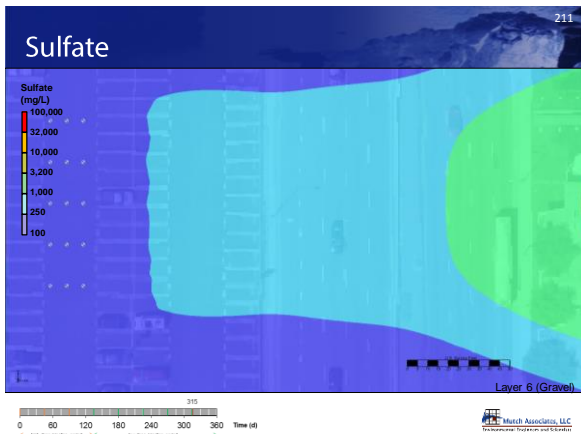


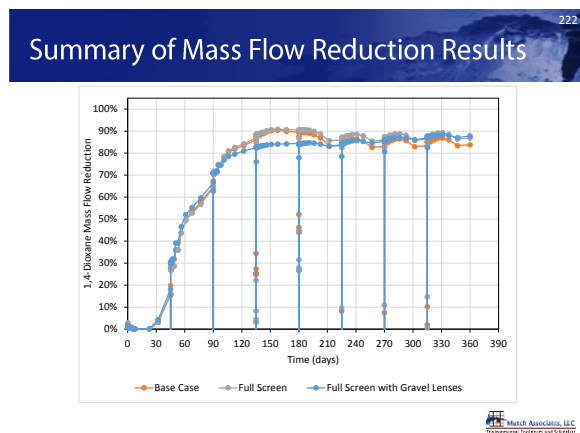
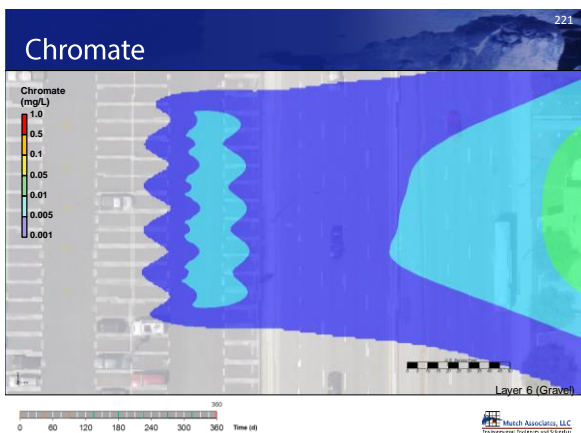
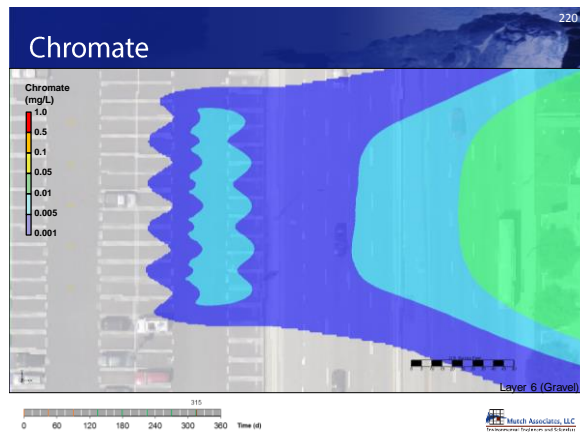
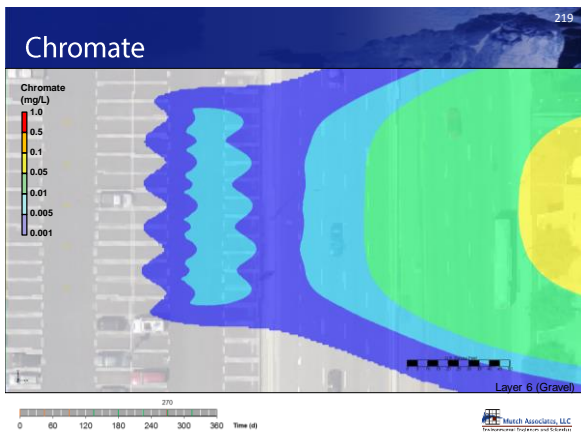
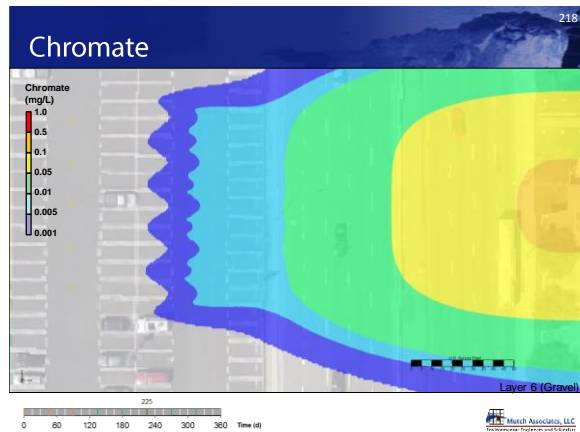
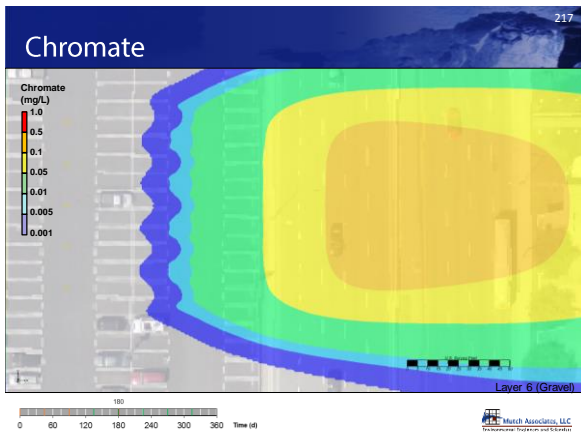












Summary and Conclusions

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- 3-D reactive transport modeling is revolutionizing the design of in situ treatment systems
 - Offers unparalleled insights into what is happening in the subsurface
 - Helps avoid ISTs falling short of performance objectives or failing altogether
 - Saves time and money
 - Applicable to most permutations of ISCO, ISCR, and in situ bioremediation