Gasco FS Modeling Meeting

September 12, 2023

Preliminary | For Discussion Purposes Only

Agenda

- Site-wide groundwater model update
  - Background
  - Model improvements
  - Recalibration
- Modeling of groundwater restoration time frames
  - Background
  - DNAPL dissolution modeling
  - Model design and setup
  - Simulating remedial options

Site-Wide Groundwater Model

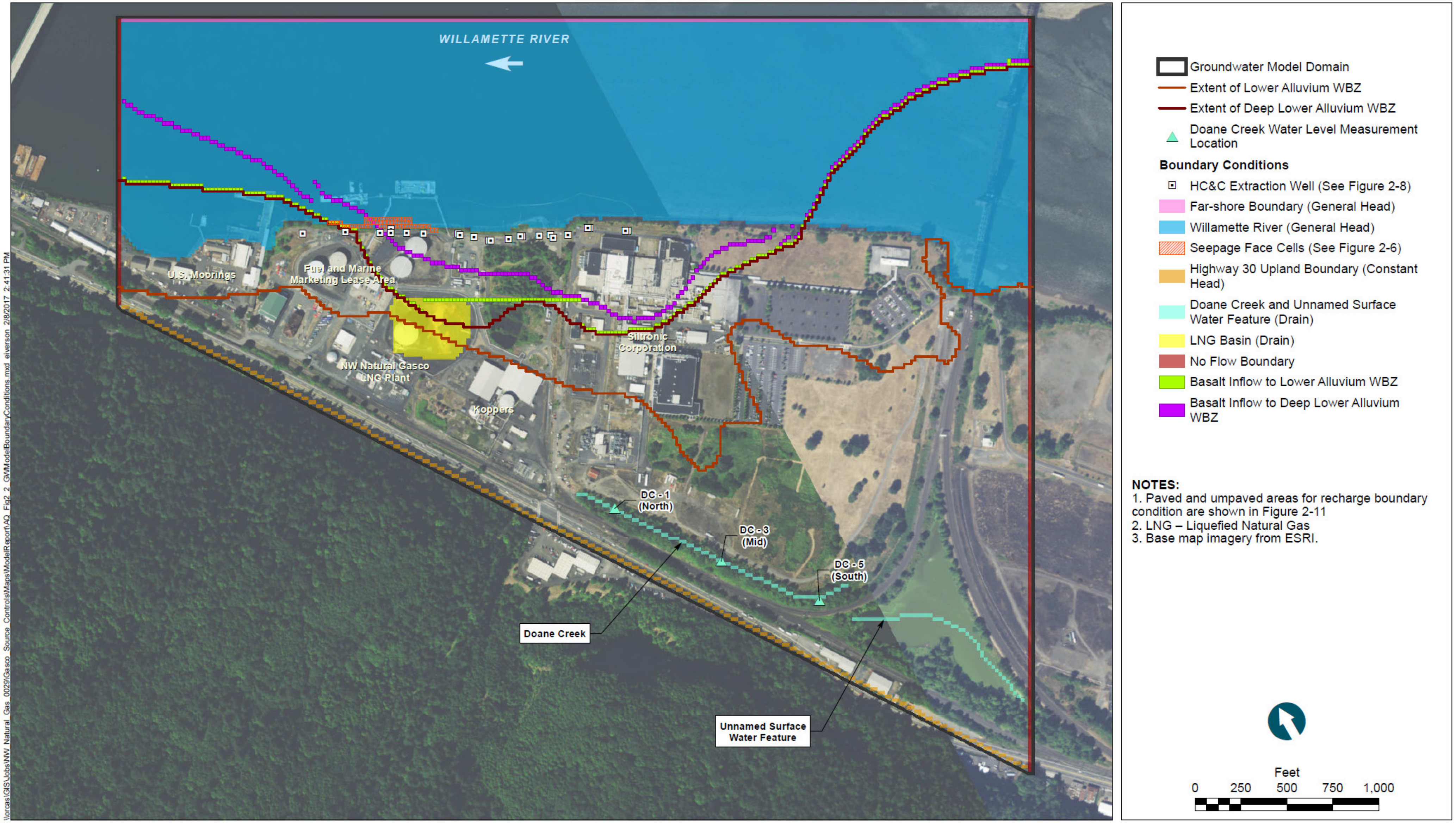
Brief Recap

- 3D MODFLOW model representing entire unconsolidated site stratigraphy
  - Original model developed circa 2008 to 2011, further refined in 2014[1], and calibrated to transient (tidal) and steady-state, seasonal conditions[2]
  - Used for successful HC&C system design
- Steady-state model using long-term average (2014 to 2017) conditions (river stage, HC&C pumping rates, and precipitation → recharge) used to simulate changes with Koppers and LNG improvements[3]
  - Used in 2020 for Fill WBZ trench design simulations

[1] Anchor QEA (Anchor QEA, LLC) 2014. *Revised Final Hydraulic Source Control and Containment System Groundwater Model Update Report, NW Natural Site*. Prepared for NW Natural. August 2014.
[2] Anchor QEA, 2017. *Gasco Groundwater Modeling Report, NW Natural Gasco Site*. Prepared for NW Natural. February 17, 2017.
[3] Anchor QEA, 2018. Memorandum to: D. Bayuk and H. Larsen, Oregon Department of Environmental Quality. Regarding: Revised Liquified Natural Gas Basin and Koppers Lease Area Groundwater Evaluation NW Natural Gasco Site, Portland, Oregon, ECSI No. 84.

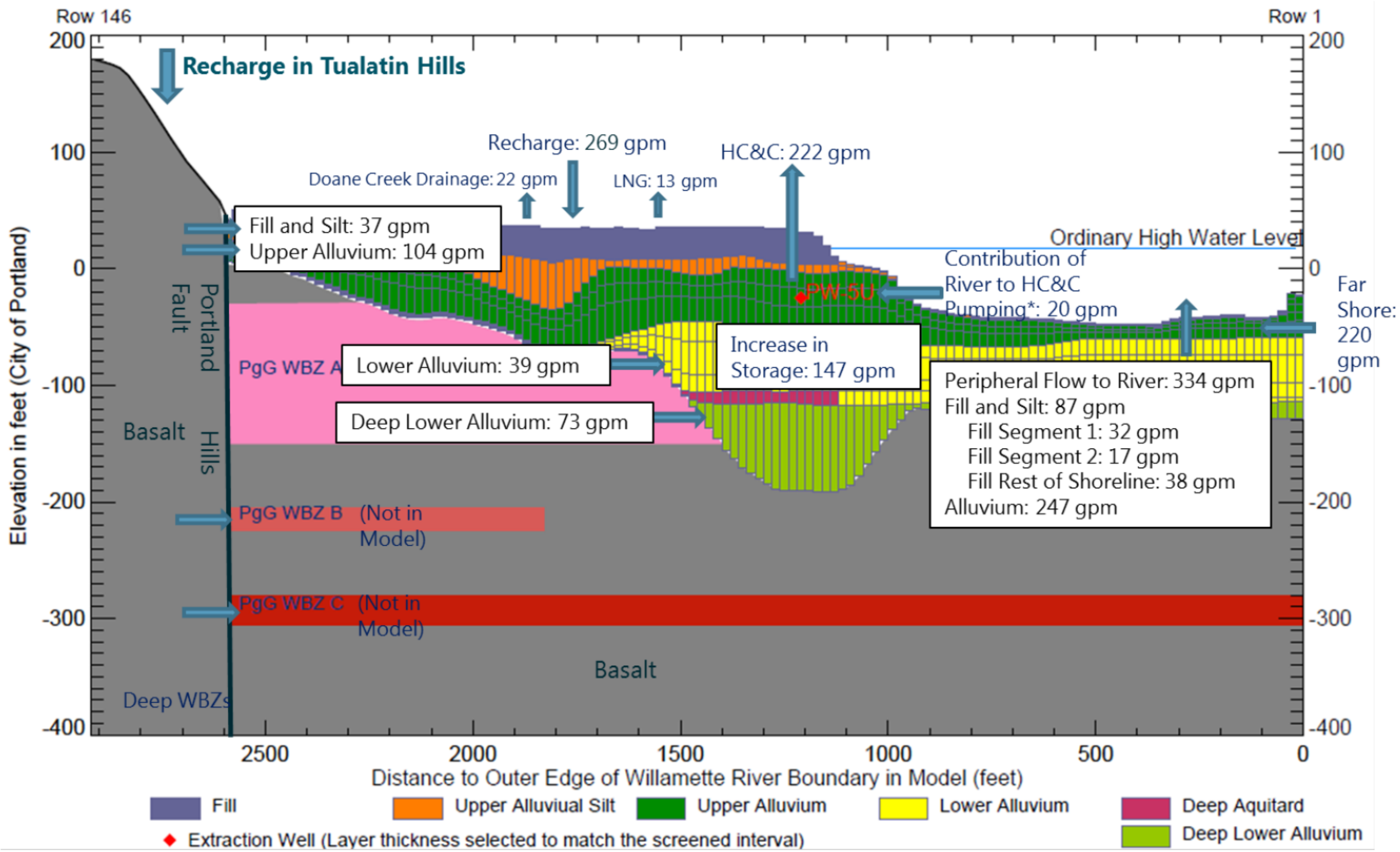
New Modifications

- Upgradient specified head and specified flux boundaries converted to general head boundaries (GHBs)
  - GHBs allow simulated hydraulic heads and inflow rates at model boundary to fluctuate, as appropriate, in response to on-site hydraulic changes (extraction, barriers, and ISS zones)
- Increased hydraulic conductivity (*K*) of Upper and Lower Silt Units-based estimates from Data Gaps Investigation grain-size data (horizontal *K*) and lab measurements (vertical *K*)
- Added local discontinuities in Lower Silt Unit (Layer 9) based on gaps seen on cross sections—in those areas, changed silt *K* to match *K* in Deep Lower Alluvium WBZ



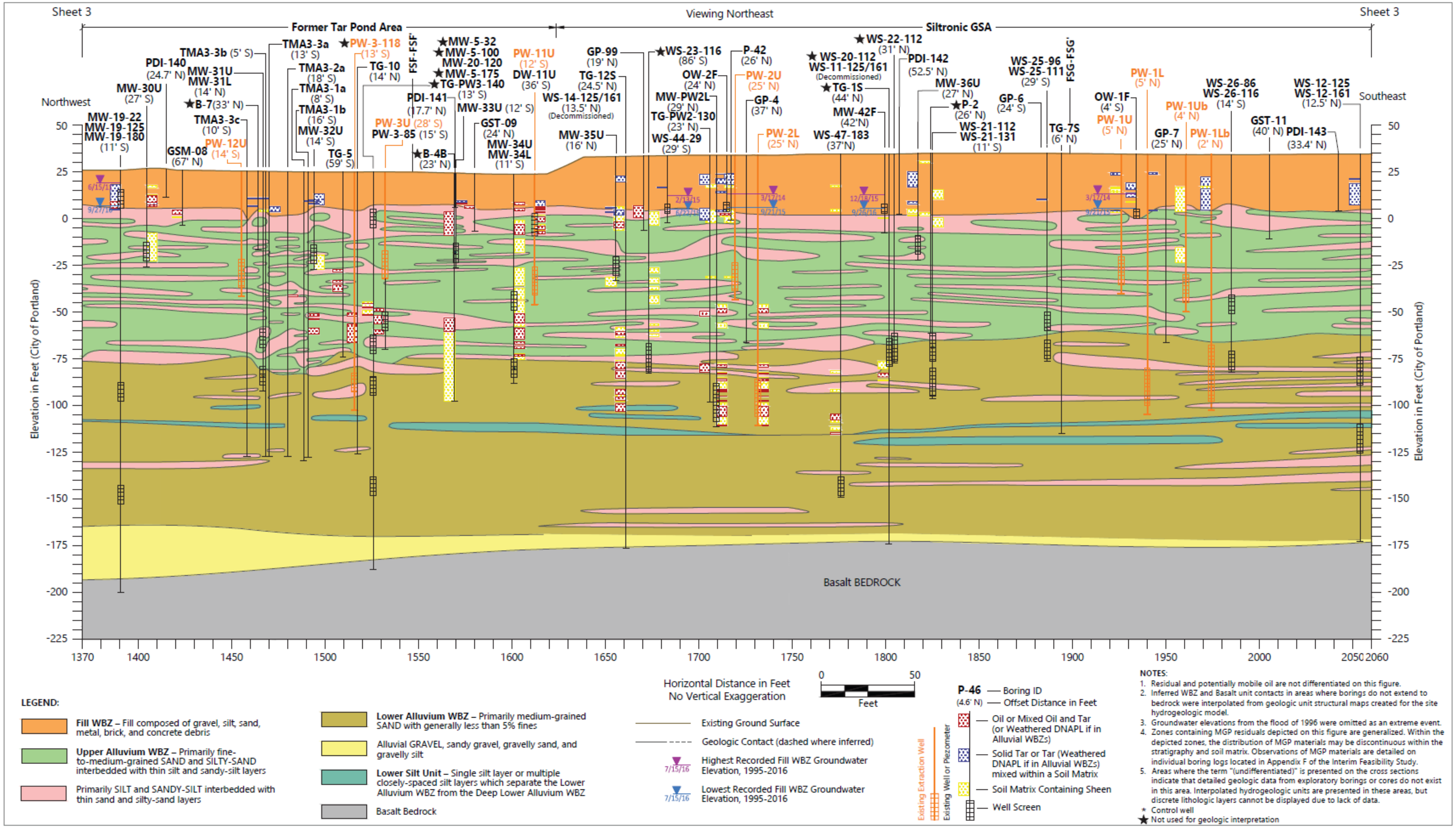
NOTES:
1. Paved and unpaved areas for recharge boundary condition are shown in Figure 2-11
2. LNG – Liquefied Natural Gas
3. Base map imagery from ESRI.

Source: Anchor QEA, 2017. *Gasco Groundwater Modeling Report, NW Natural Gasco Site*. Prepared for NW Natural. February 17, 2017.



*Contribution of river to HC&C pumping was estimated from a tracer transport simulation that used steady-state flow model run using average of boundary conditions from the Phase 1, Step 6 transient simulation

Source: Anchor QEA, 2017. *Gasco Groundwater Modeling Report, NW Natural Gasco Site*. Prepared for NW Natural. February 17, 2017.



LEGEND:

- **Fill WBZ** – Fill composed of gravel, silt, sand, metal, brick, and concrete debris
- **Upper Alluvium WBZ** – Primarily fine-to-medium-grained SAND and SILTY-SAND interbedded with thin silt and sandy-silt layers
- Primarily SILT and SANDY-SILT interbedded with thin sand and silty-sand layers
- **Lower Alluvium WBZ** – Primarily medium-grained SAND with generally less than 5% fines
- Alluvial GRAVEL, sandy gravel, gravelly sand, and gravelly silt
- **Lower Silt Unit** – Single silt layer or multiple closely-spaced silt layers which separate the Lower Alluvium WBZ from the Deep Lower Alluvium WBZ
- Basalt Bedrock
- Existing Ground Surface
- Geologic Contact (dashed where inferred)
- 7/15/16 Highest Recorded Fill WBZ Groundwater Elevation, 1995-2016
- 7/15/16 Lowest Recorded Fill WBZ Groundwater Elevation, 1995-2016
- **P-46** — Boring ID
- (4.6' N) — Offset Distance in Feet
- Oil or Mixed Oil and Tar (or Weathered DNAPL if in Alluvial WBZs)
- Solid Tar or Tar (Weathered DNAPL if in Alluvial WBZs) mixed within a Soil Matrix
- Soil Matrix Containing Sheen
- Well Screen

NOTES:

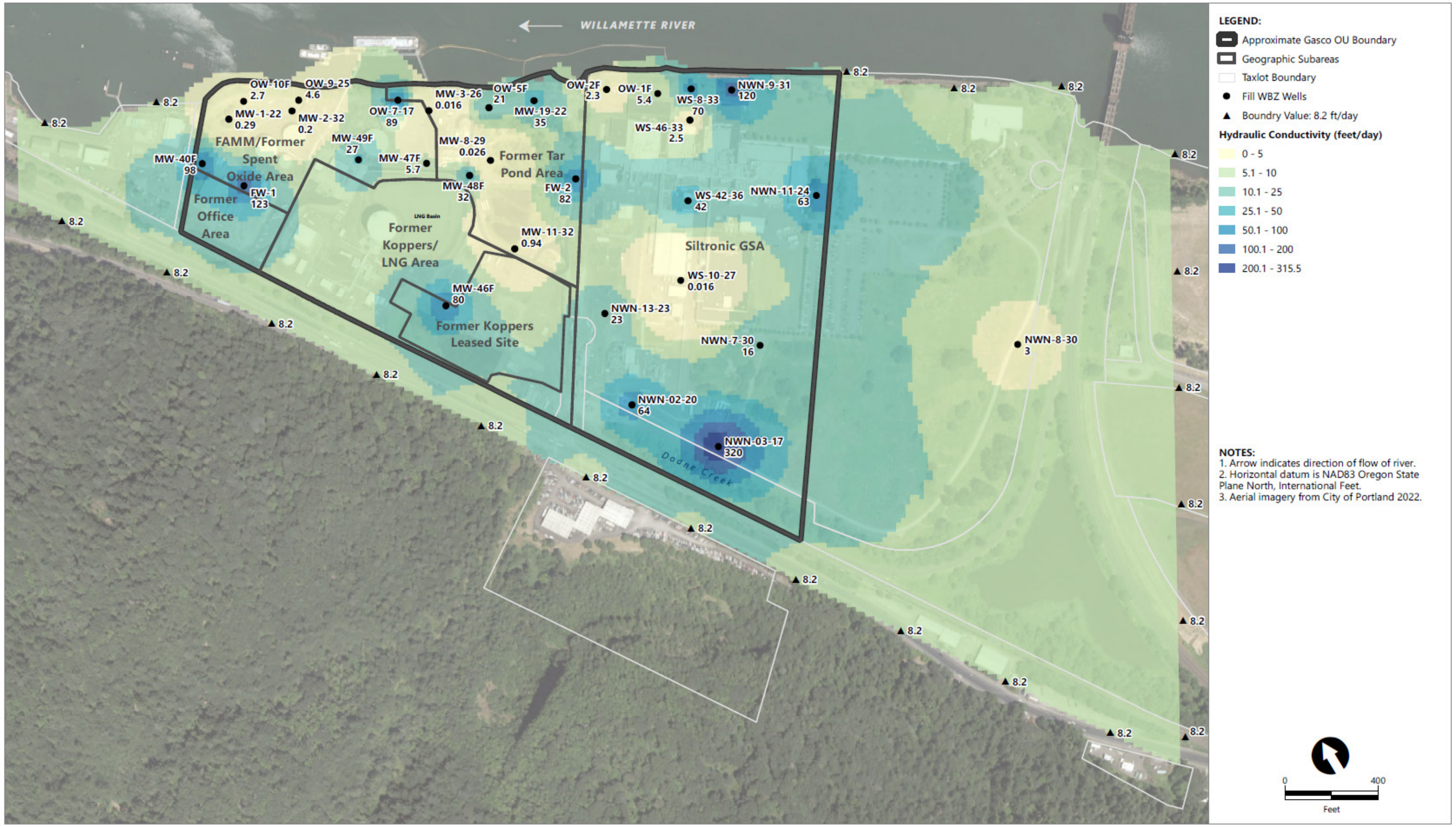
1. Residual and potentially mobile oil are not differentiated on this figure.
2. Inferred WBZ and Basalt unit contacts in areas where borings do not extend to bedrock were interpolated from geologic unit structural maps created for the site hydrogeologic model.
3. Groundwater elevations from the flood of 1996 were omitted as an extreme event.
4. Zones containing MGP residuals depicted on this figure are generalized. Within the depicted zones, the distribution of MGP materials may be discontinuous within the stratigraphy and soil matrix. Observations of MGP materials are detailed on individual boring logs located in Appendix F of the Interim Feasibility Study.
5. Areas where the term "(undifferentiated)" is presented on the cross sections indicate that detailed geologic data from exploratory borings or cores do not exist in this area. Interpolated hydrogeologic units are presented in these areas, but discrete lithologic layers cannot be displayed due to lack of data.

* Control well
★ Not used for geologic interpretation

New Modifications (cont.)

- Increased model depth at PZ7-150 and PZ9-150 to include them as targets
- Created a new Layer 11 at bottom of Deep Lower Alluvium WBZ to improve simulation of potential leakage under barrier wall, if needed
- *K* in Fill WBZ refined based on Data Gaps Investigation field hydraulic tests—contoured and imported *K* data into Layer 1

Fill WBZ Hydraulic Conductivity Contours



NOTES:
1. Arrow indicates direction of flow of river.
2. Horizontal datum is NAD83 Oregon State Plane North, International Feet.
3. Aerial imagery from City of Portland 2022.

Recalibration

- Basic approach
  - Steady-state calibration—FS predictive simulations to be conducted in steady state
  - Recharge rates calibrated to match heads measured in Fill WBZ using same recharge zones discussed in Anchor QEA 2018[4]
  - Upgradient GHB heads and conductance values calibrated to match heads in alluvium layers

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[4] Anchor QEA, 2018.

Recalibration – Additional Details

- 12-month calibration period: September 2021 to August 2022 inclusive
  - Relatively steady pumping at HC&C system and Fill WBZ trenches
    - HC&C pumping rates (195 gpm total)—includes entire volume pumped by a pair of wells where a well was replaced by a new one (PW-11Ub replaced PW-11U; PW-1Uc replaced PW-1U)
    - Fill WBZ trench pumping rates (24 gpm total from two trenches)
  - River level (8.62 feet COP)

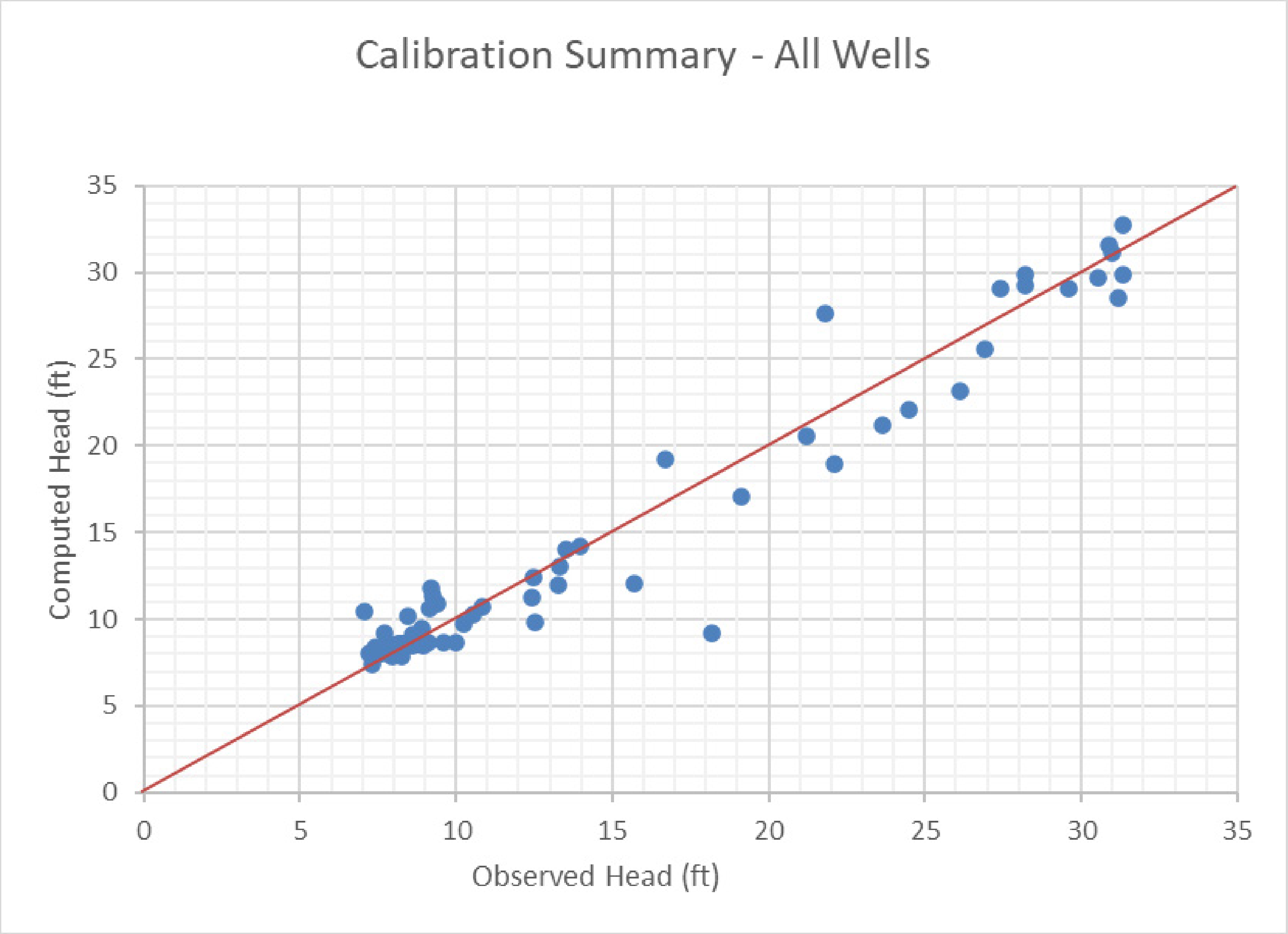
Recalibration – Calibration Targets

- Hydraulic heads at non-pumped monitoring wells and piezometers
  - 101 with transducers (minimum of 48 out of 52 weeks)
  - 11 monitoring wells not equipped with transducers but with multiple manual water level data available for averaging
    - Weekly (1)
    - Quarterly (3)
    - Semiannually in 4Q 2021 and 2Q 2022 (Fill WBZ unit only—minimal tidal influence; 7)
- 112 calibration targets total
- Used PEST parameter optimization software

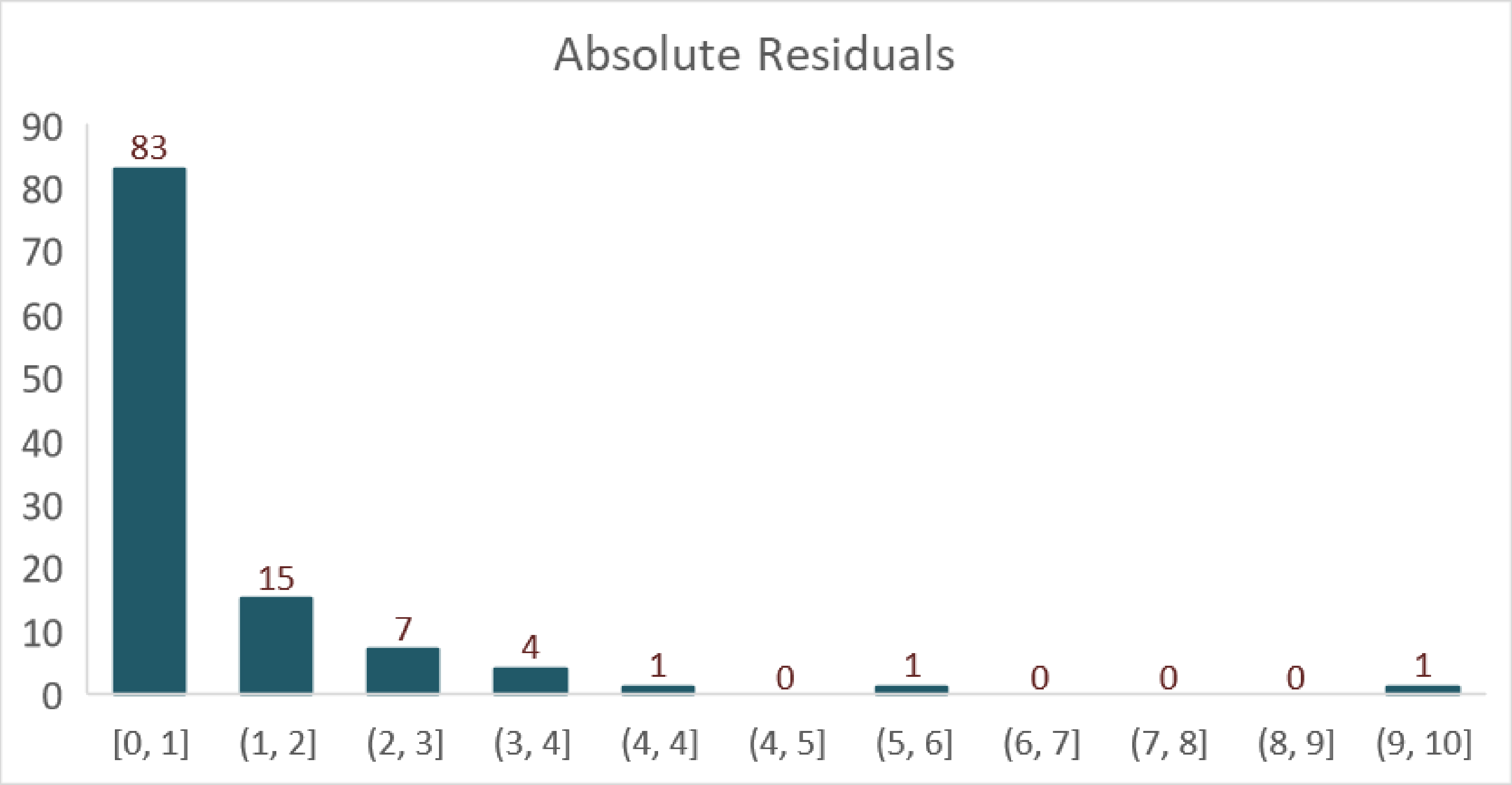
Recalibration – Results

- Residual Mean (foot)
  - Whole model: -0.05
  - Fill WBZ: 0.034
  - Upper Alluvium WBZ: 0.028
  - Lower Alluvium WBZ: -0.289
  - Deep Lower Alluvium WBZ: -0.067
- Scaled Standard Deviation
  - Whole model: 0.061

Recalibration – Results (cont.)



Recalibration – Results (cont.)

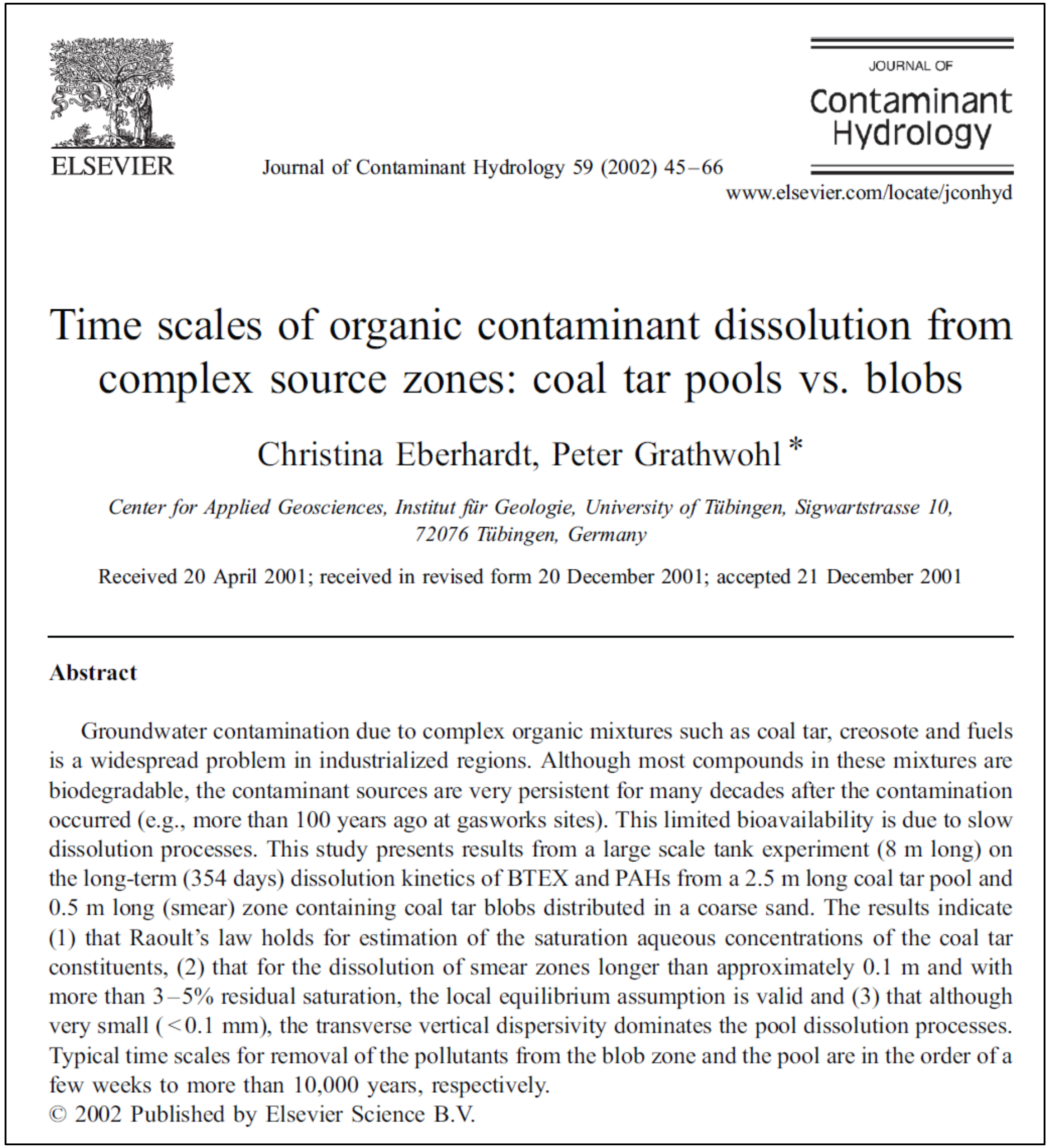


Modeling of Groundwater Restoration Time Frames

Overview

- DEQ regulations require predicting groundwater restoration time
- Predominant constituents of concern (COCs) source in groundwater is DNAPL dissolution, which is slow and gradual and will continue for decades
- General modeling approach: simulate dissolution of select, driver COCs (benzene and naphthalene) from DNAPL to produce order-of-magnitude groundwater restoration times for different remedial options
- New method developed and verified for simulating select-compound dissolution

DNAPL Dissolution from MGP DNAPL



ELSEVIER
Journal of Contaminant Hydrology 59 (2002) 45–66
JOURNAL OF
Contaminant Hydrology
www.elsevier.com/locate/jconhyd

Time scales of organic contaminant dissolution from complex source zones: coal tar pools vs. blobs

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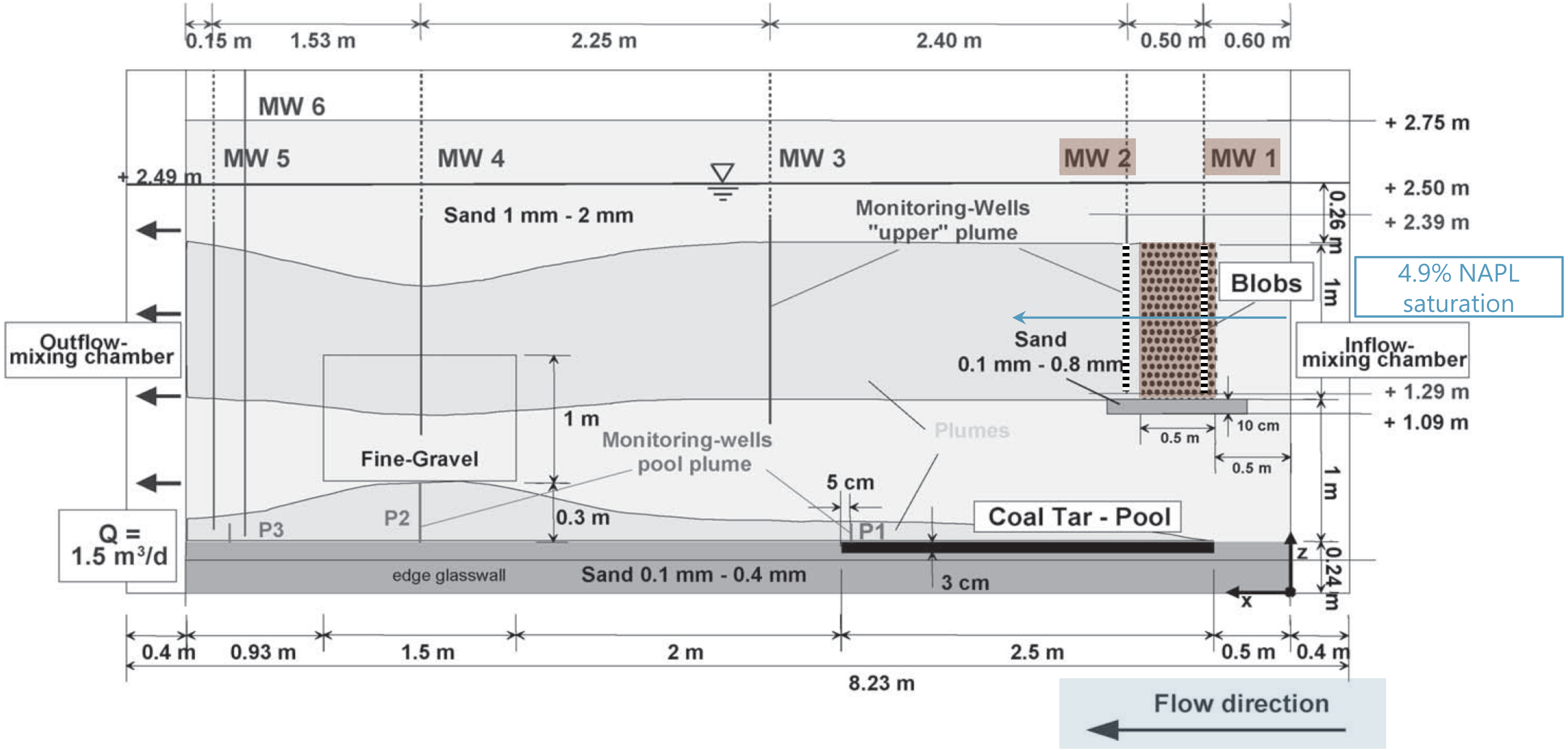
Abstract

Groundwater contamination due to complex organic mixtures such as coal tar, creosote and fuels is a widespread problem in industrialized regions. Although most compounds in these mixtures are biodegradable, the contaminant sources are very persistent for many decades after the contamination occurred (e.g., more than 100 years ago at gasworks sites). This limited bioavailability is due to slow dissolution processes. This study presents results from a large scale tank experiment (8 m long) on the long-term (354 days) dissolution kinetics of BTEX and PAHs from a 2.5 m long coal tar pool and 0.5 m long (smear) zone containing coal tar blobs distributed in a coarse sand. The results indicate (1) that Raoult's law holds for estimation of the saturation aqueous concentrations of the coal tar constituents, (2) that for the dissolution of smear zones longer than approximately 0.1 m and with more than 3–5% residual saturation, the local equilibrium assumption is valid and (3) that although very small ($<$ 0.1 mm), the transverse vertical dispersivity dominates the pool dissolution processes. Typical time scales for removal of the pollutants from the blob zone and the pool are in the order of a few weeks to more than 10,000 years, respectively.

Empirical Sand Tank Experiment with Coal Tar

(Eberhardt and Grathwohl 2002)

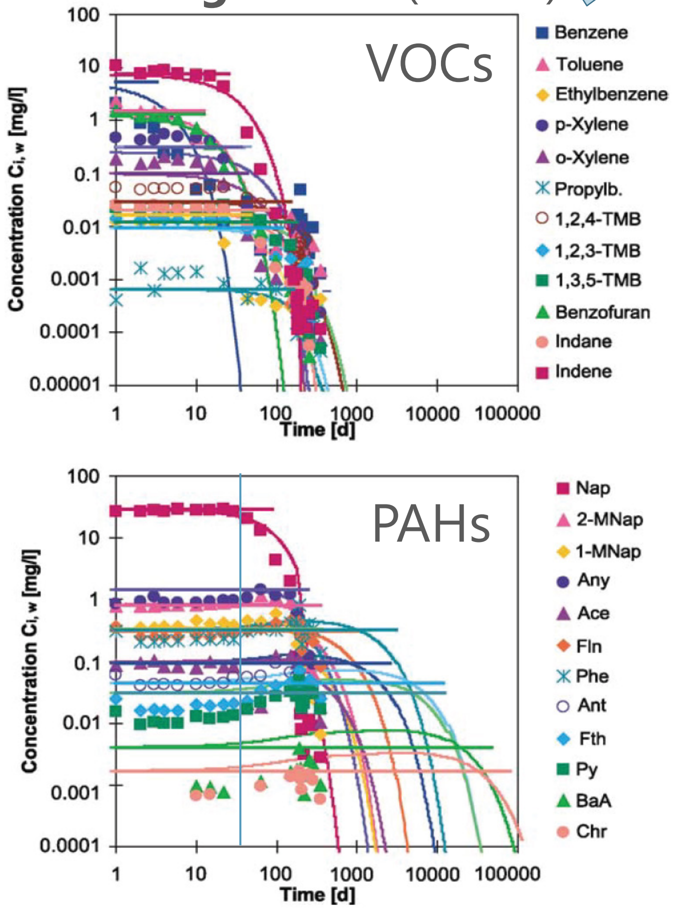


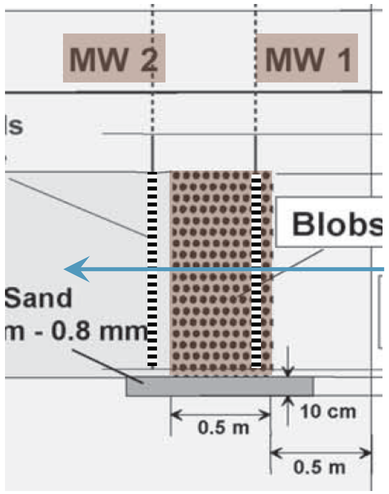
Source: Eberhardt, C., and P. Grathwohl, 2002. “Time Scales of Organic Contaminant Dissolution from Complex Source Zones: Coal Tar Pools vs. Blobs.” *Journal of Contaminant Hydrology* 59:45–66.

Dissolved Concentrations Versus Time

(Eberhardt and Grathwohl 2002)

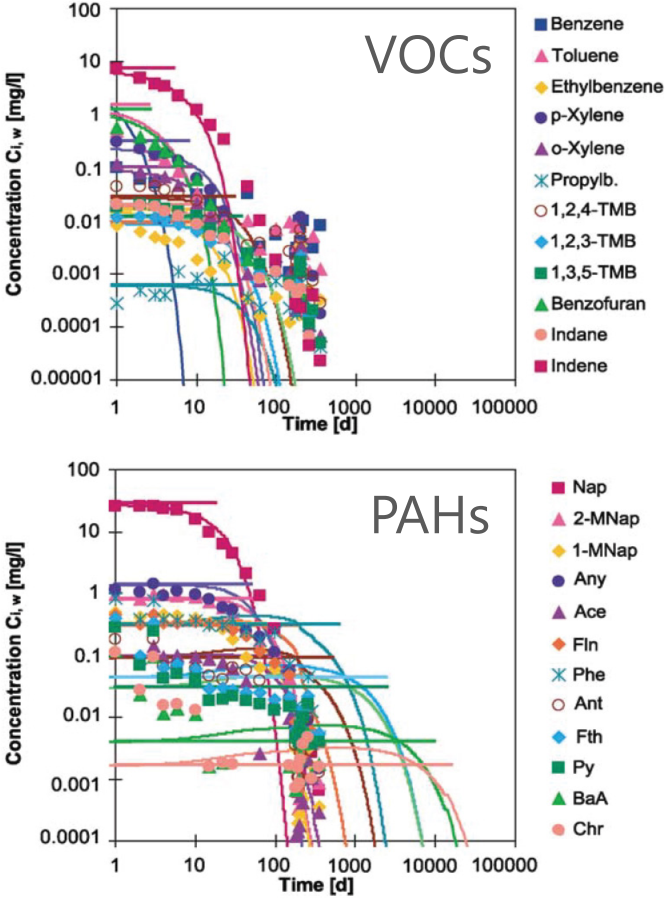
Downgradient (MW 2)





Water travel time through NAPL zone **≤8 hours**

In NAPL Zone (MW 1)



Dissolution Front Retardation

- **120 pore volume exchanges** before naphthalene concentration decreased downgradient of NAPL zone
- Retardation of dissolution front relative to porewater flow[5]

Equation 1: $R = 1 + (\rho_0 f_{i,o} n S^0) / (C_{i,sat} n_c)$

where:

ρ_0 = NAPL density

$f_{i,o}$ = mass fraction of compound *i* in NAPL

n = total porosity in NAPL zone

S^0 = NAPL saturation

$C_{i,sat}$ = effective solubility for compound *i*

n_c = effective (water-filled) porosity in the NAPL zone

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[5] Eberhardt, C. and P. Grathwohl, 2002. "Time Scales of Organic Contaminant Dissolution from Complex Source Zones: Coal Tar Pools vs. Blobs." *Journal of Contaminant Hydrology* 59:45–66.

Equilibrium Partitioning Method

- Standard retardation equation for clean-water front during desorption (standard solute-transport modeling)

Equation 2: $R = 1 + (\rho_b/n)\,K_d$

where:
ρ_b = bulk density
n = total porosity
K_d = distribution coefficient

- Equating (1) and (2)

Equation 3: $K_d = (\rho_0\, f_{i,o}\, n^2\, S^0) / (\rho_b\, C_{i,sat}\, n_c)$

- Hypothesis: Dissolution of a select compound from multicomponent NAPL can be approximated as desorption, with an effective K_d value that can be readily calculated

Verification Model Setup

- 1D MT3D model through NAPL zone (1-m long)
- 100 cells parallel to flow
- Initial dissolved concentration in NAPL zone = $C_{i,sat}$
- K_d value used in NAPL zone; zero elsewhere (equilibrium partitioning)
- Initial sorbed concentration calculated by model
- Other parameters from Eberhardt and Grathwohl 2002

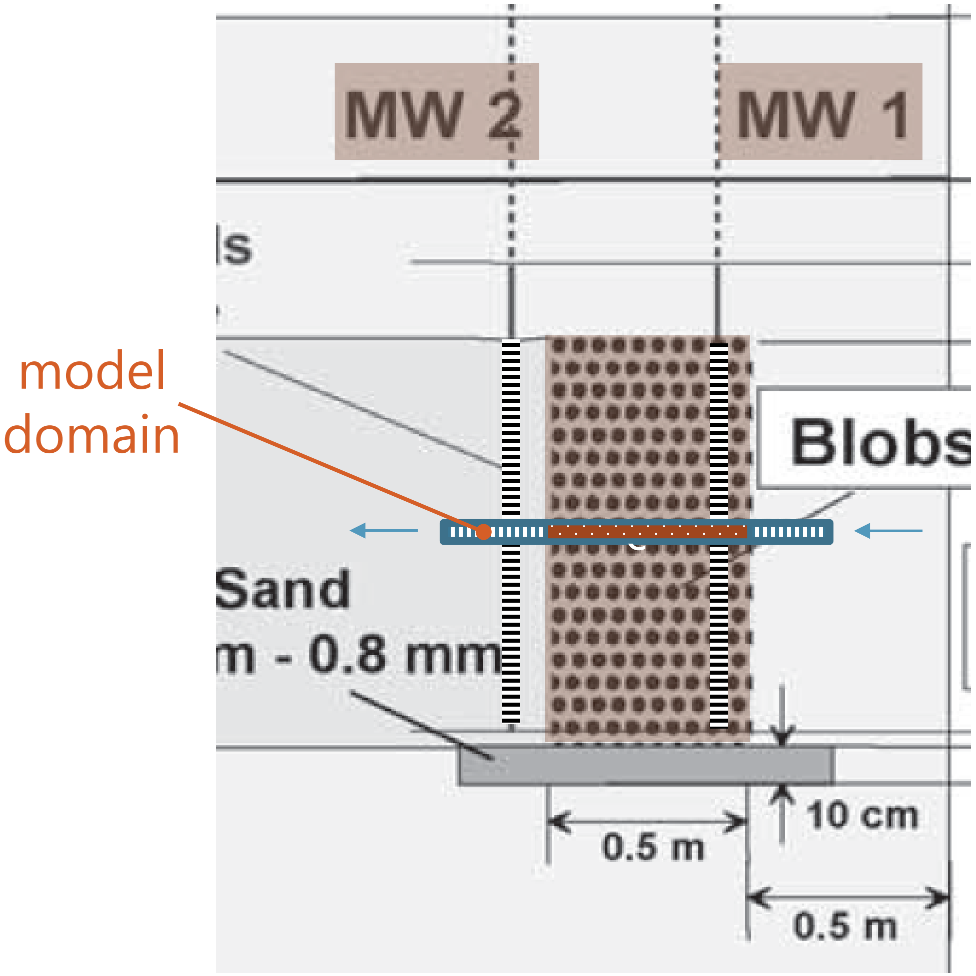

Figure source: Eberhardt, C. and P. Grathwohl, 2002. "Time Scales of Organic Contaminant Dissolution from Complex Source Zones: Coal Tar Pools vs. Blobs." *Journal of Contaminant Hydrology* 59:45–66.

Example of Verification Modeling Results: MW 2

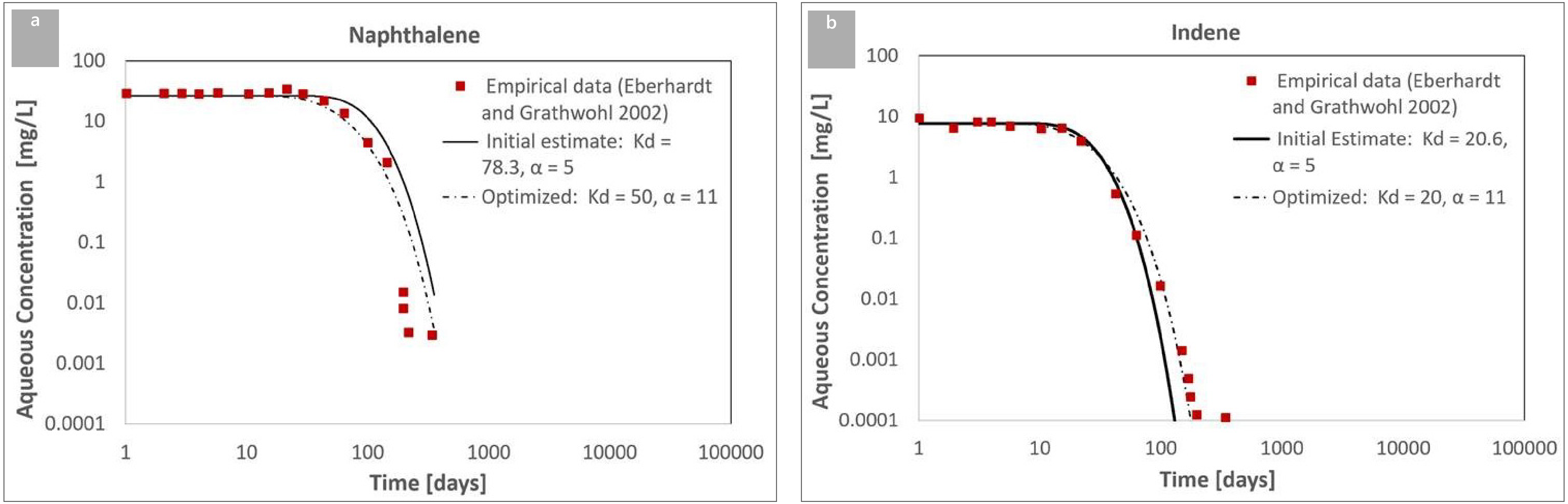

Figure 2 – MT3D model results (black solid and dashed lines) and empirical concentrations (red squares) for naphthalene (a) and indene (b) downgradient of coal tar NAPL zone. Solid line is model result with the initial K_d value calculated using Equation 1. Dashed line is model result with K_d and α optimized to match both datasets.

Source: Gefell, M.J, and D. Gurung, 2023. "Simulating Dissolution of the Most Soluble Compounds from Complex NAPLs Using Equilibrium Partitioning." *Applied NAPL Science Review* 11(2).

Verification Model Results

- Simulation results closely matched timing of dissolution front observed in empirical model[6]
- Predicted times to achieve a three-order-of-magnitude concentration decrease downgradient of NAPL zone matched within a factor of approximately 2
- Calibrated Kd values were within a factor of approximately 2 of the initial K_d estimates calculated using Equation 3
- Minor differences between model results and empirical data may relate to non-uniform NAPL composition and saturation in the empirical sand tank model

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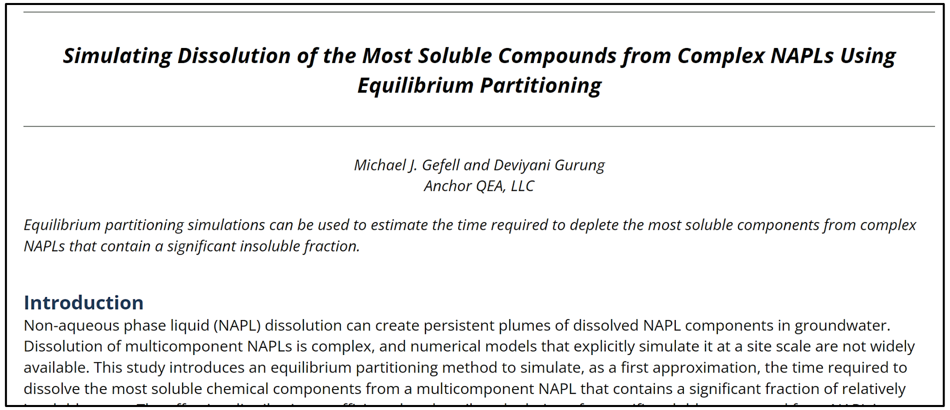
[6] Eberhardt, C., and P. Grathwohl, 2002.

Publications Regarding New Modeling Method

Simulating Dissolution of the Most Soluble Compounds from Complex NAPLs Using Equilibrium Partitioning
Volume 11, Issue 2 | April 2023

Applied NAPL Science Review
Simulating Dissolution of the Most Soluble Compounds from Complex NAPLs Using Equilibrium Partitioning

Editor: Lisa Reyenga, PE



Simulating Dissolution of the Most Soluble Compounds from Complex NAPLs Using Equilibrium Partitioning

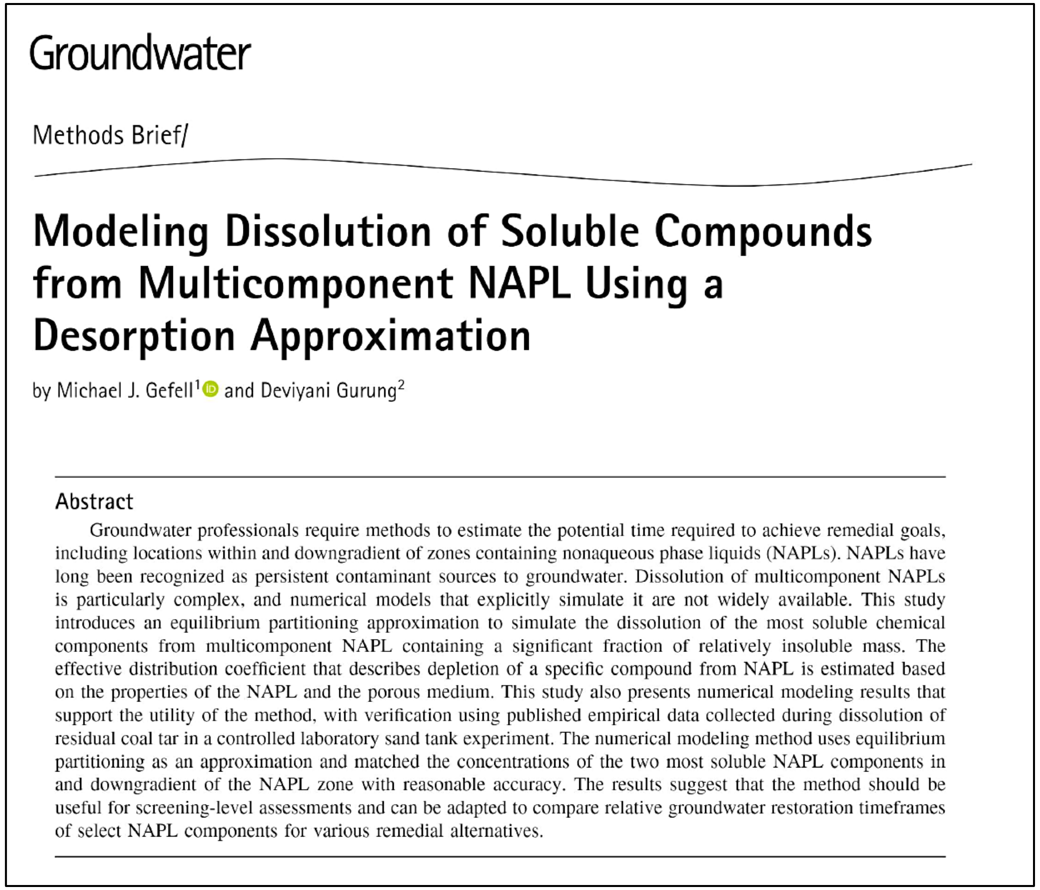
Michael J. Gefell and Deviyani Gurung
Anchor QEA, LLC

Equilibrium partitioning simulations can be used to estimate the time required to deplete the most soluble components from complex NAPLs that contain a significant insoluble fraction.

Introduction

Non-aqueous phase liquid (NAPL) dissolution can create persistent plumes of dissolved NAPL components in groundwater. Dissolution of multicomponent NAPLs is complex, and numerical models that explicitly simulate it at a site scale are not widely available. This study introduces an equilibrium partitioning method to simulate, as a first approximation, the time required to dissolve the most soluble chemical components from a multicomponent NAPL that contains a significant fraction of relatively

Source: http://naplansr.com/simulating-dissolution-of-the-most-soluble-compounds-from-complex-napls-using-equilibrium-partitioning/



Methods Brief/

Modeling Dissolution of Soluble Compounds from Multicomponent NAPL Using a Desorption Approximation

by Michael J. Gefell[1] and Deviyani Gurung[2]

Abstract

Groundwater professionals require methods to estimate the potential time required to achieve remedial goals, including locations within and downgradient of zones containing nonaqueous phase liquids (NAPLs). NAPLs have long been recognized as persistent contaminant sources to groundwater. Dissolution of multicomponent NAPLs is particularly complex, and numerical models that explicitly simulate it are not widely available. This study introduces an equilibrium partitioning approximation to simulate the dissolution of the most soluble chemical components from multicomponent NAPL containing a significant fraction of relatively insoluble mass. The effective distribution coefficient that describes depletion of a specific compound from NAPL is estimated based on the properties of the NAPL and the porous medium. This study also presents numerical modeling results that support the utility of the method, with verification using published empirical data collected during dissolution of residual coal tar in a controlled laboratory sand tank experiment. The numerical modeling method uses equilibrium partitioning as an approximation and matched the concentrations of the two most soluble NAPL components in and downgradient of the NAPL zone with reasonable accuracy. The results suggest that the method should be useful for screening-level assessments and can be adapted to compare relative groundwater restoration timeframes of select NAPL components for various remedial alternatives.

Source: Gefell, M.J., and D. Gurung, *in press*. "Modeling Dissolution of Soluble Compounds from Multi-Component NAPL Using a Desorption Approximation." Accepted for Publication in *Groundwater*.

Implications

- Dissolution of a relatively soluble compound from a complex NAPL can be simulated equivalent to desorption using a calculated K_d value
  - Timing of dissolution front
  - Concentration decrease over time
- Equilibrium partitioning numerical models widely available and versatile
  - Heterogeneous porous medium properties
  - Various NAPL properties (composition, saturation, etc.)
  - Hydraulic gradient changes (tides, pump and treat, etc.)
  - Degradation in aqueous phase
- Can compare cleanup time frames for various remedial alternatives

Method Applicability

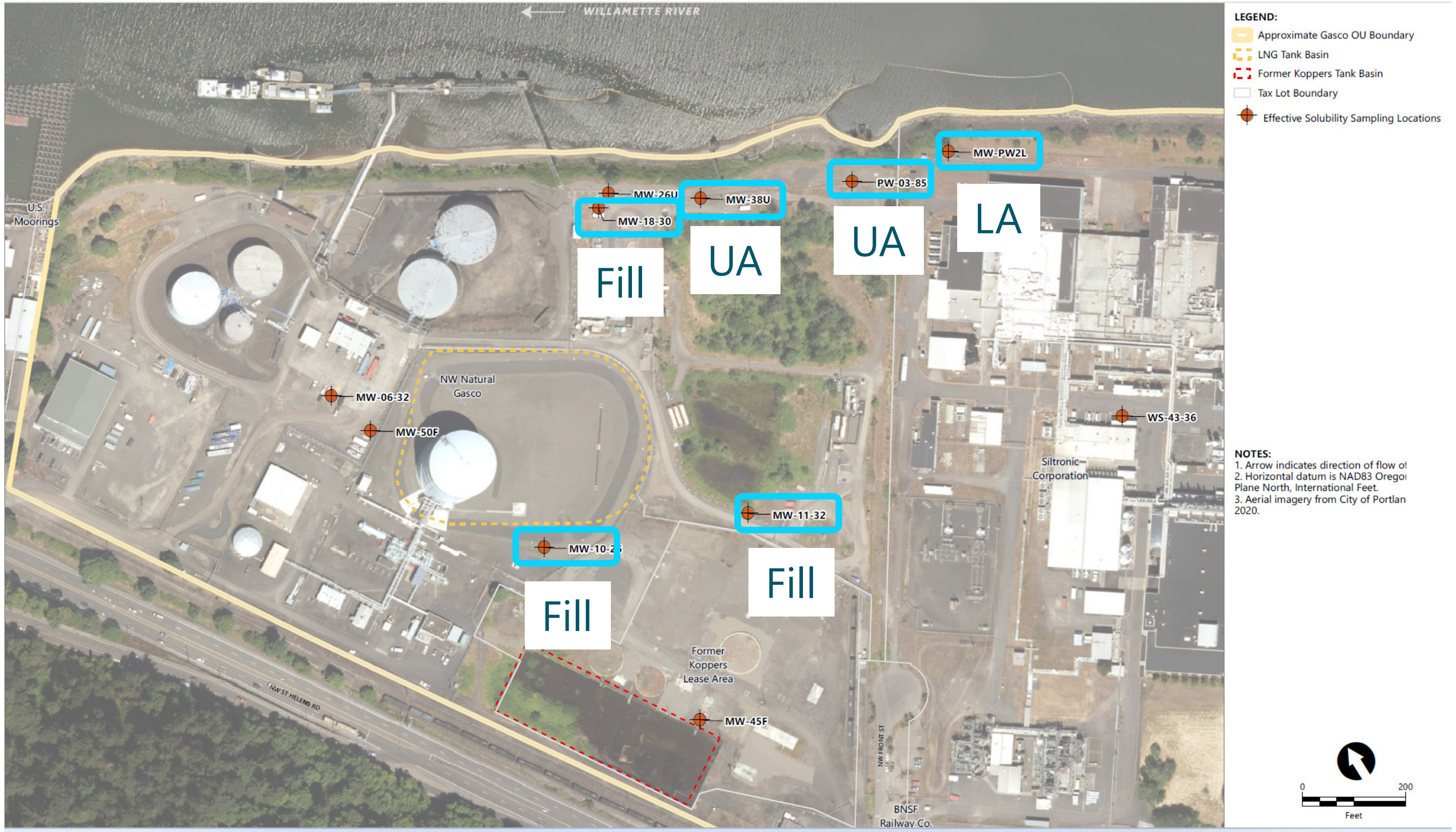
- Assumption: Other than dissolution of selected compounds, DNAPL undergoes no other changes in composition or volume
  - Method should only be used for the most soluble DNAPL components
    - Eberhardt and Grathwohl 2002 (naphthalene and indene = 76% of the total effective solubility of all of the compounds identified in DNAPL)
    - Gasco OU effective solubility groundwater samples (naphthalene and benzene ≥ 75% at 6 wells out of 11 sampled in March to April 2023)
  - Method assumes the selected compounds compose a relatively small fraction of total DNAPL mass
    - Eberhardt and Grathwohl 2002 (naphthalene and indene = 14% of DNAPL mass)
    - Gasco OU DNAPL samples (naphthalene and benzene ≤15% of DNAPL mass at 9 out of 11 wells sampled in March to April 2023)

Effective Solubility and DNAPL Composition Sampling (March to April 2023)

Well	Water Bearing Zone	TarGOST Composite Waveform Color	GSA
MW-10-25 *	Fill	Orange	Former Koppers/LNG Area
MW-11-32 *	Fill	Orange	Former Tar Pond Area
MW-26U	Upper Alluvium	Yellow	Former Tar Pond Area
MW-18-30 *	Fill	Orange	Former Tar Pond Area
MW-38U *	Upper Alluvium	Orange	Former Tar Pond Area
MW-50F	Fill	Yellow	Former Koppers/LNG Area
MW-06-32	Fill	Blue-Green	Former Koppers/LNG Area
MW-PW-2L *	Lower Alluvium	Orange	Siltronic GSA
MW-45F	Fill	Blue-Green	Former Koppers/LNG Area
PW-3-85 *	Upper Alluvium	Orange	Former Tar Pond Area
WS-43-36	Fill	Orange	Siltronic GSA

Note:
* Best wells for DNAPL dissolution modeling for benzene and naphthalene

Effective Solubility and DNAPL Composition Sampling

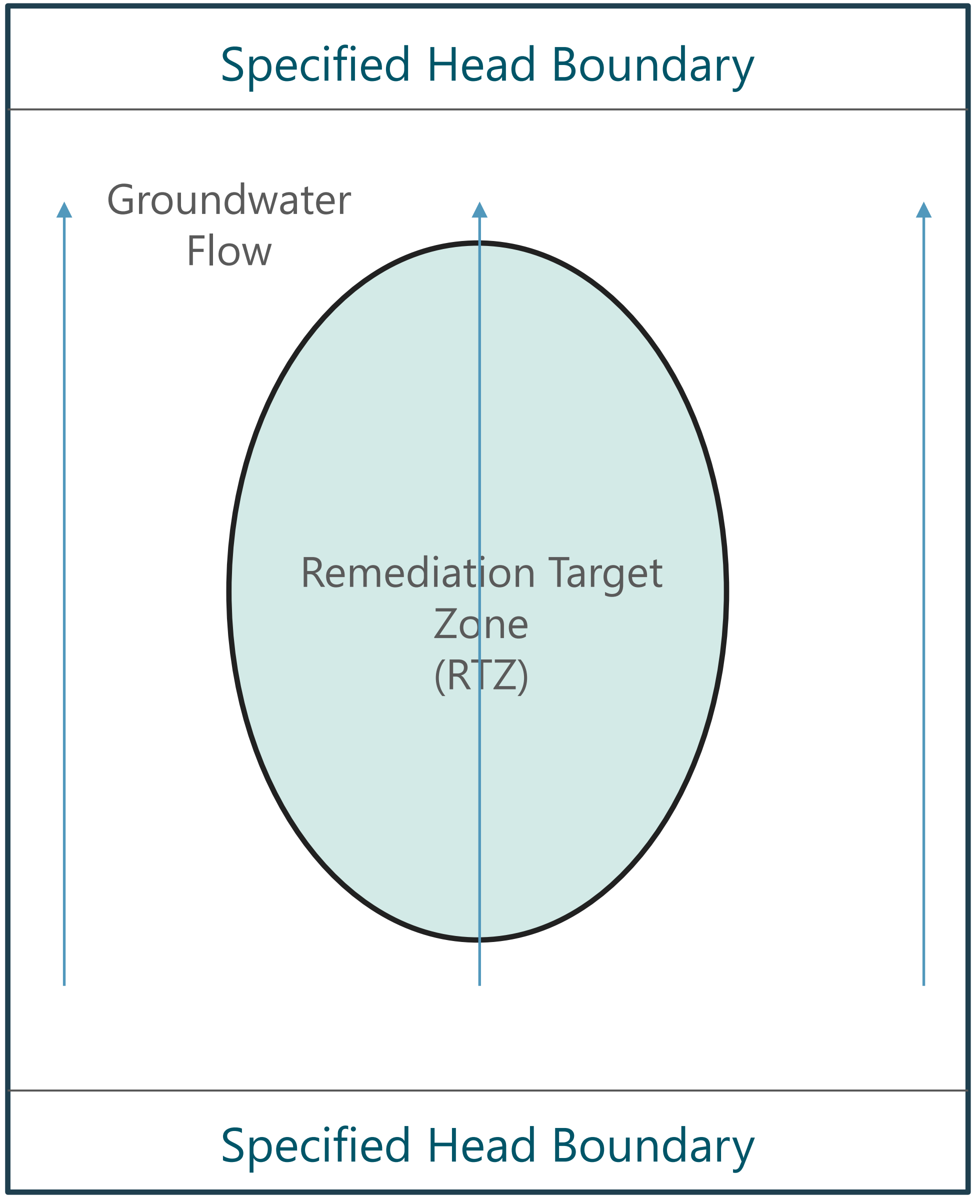


- Conditions at wells outlined in blue are best suited for DNAPL dissolution modeling for benzene and naphthalene
- High percent of total effective solubility (81% average)
- Low DNAPL mass fraction (9% average)

FS Dissolution Modeling Approach

- Develop simplified, generic, 2D model with average effective solubility and DNAPL mass fraction for naphthalene and benzene
- Run model to predict concentrations over time for naphthalene and benzene
- Adjust model parameters to represent remediation and re-run model

Model Conceptual Design



Specified Head Boundary

Groundwater Flow

Remediation Target Zone (RTZ)

Specified Head Boundary

Basic Model Setup

- Assign representative K, i, Θ based on site data and site-wide groundwater flow model
- Identify representative average effective solubility and DNAPL mass fractions for benzene and naphthalene based on sampling results
- Calculate effective K_d using those data and midpoint DNAPL saturation (S_d) values
  - Inside RTZ: potentially mobile DNAPL (44%)
  - Outside RTZ: residual, immobile DNAPL (14%)
- Assign degradation rates based on literature for redox conditions
- Set diffusion and dispersion coefficients based on literature values

Remedial Simulations

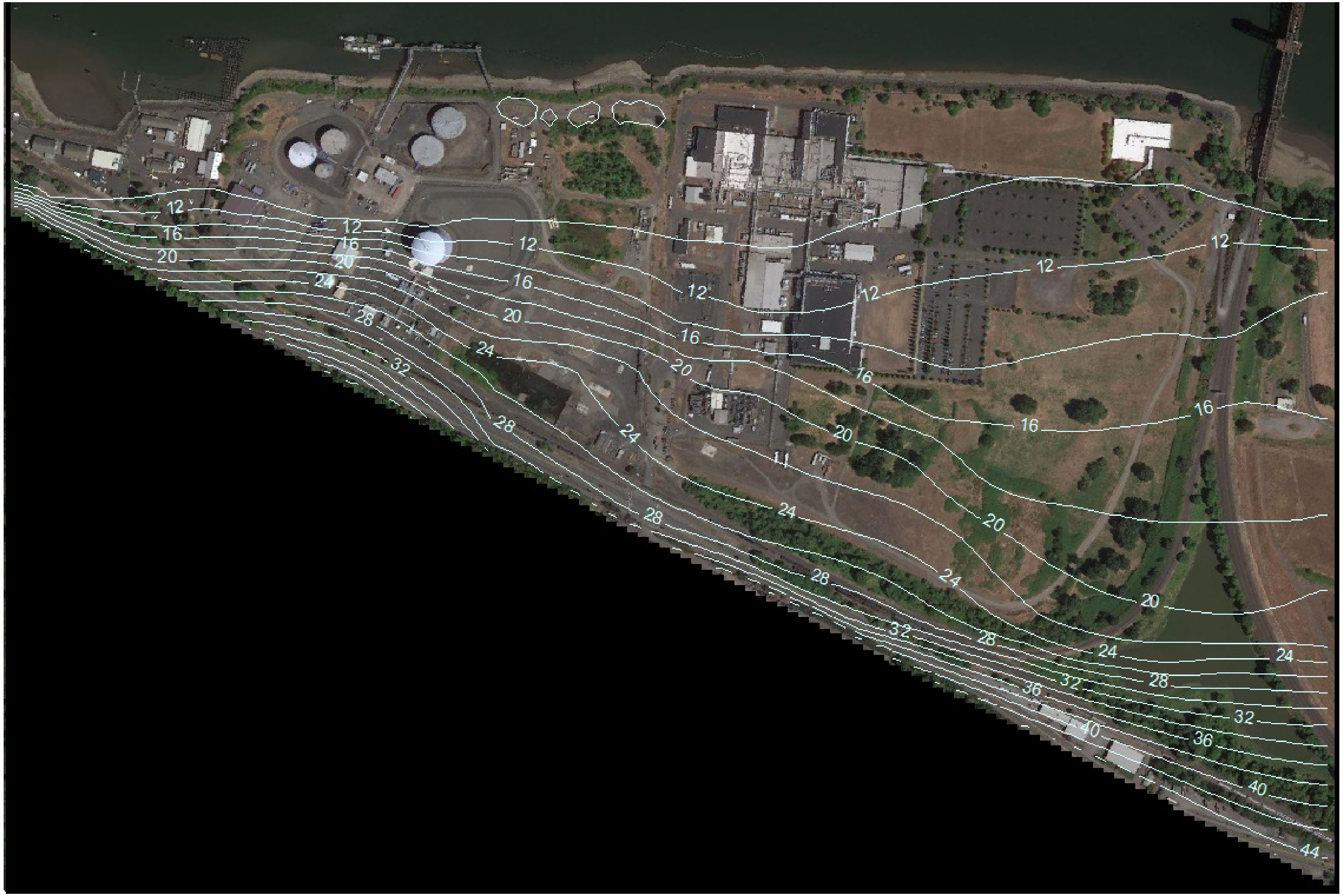
Remedial Scenario	Modeling Process
No action	Run model until benzene and naphthalene reach Table 17 values throughout model.
DNAPL recovery	Convert S_d inside RTZ to residual DNAPL value. Also calculate DNAPL recovery time and add that to total simulated restoration time.
ISS	Reduce K and Θ and potentially increase S_d and degradation half life inside ISS zone.
Enhanced biodegradation / groundwater warming	Decrease degradation half life.
Containment	Add barrier wall around perimeter of RTZ.
Excavation	Convert S_d to zero in area of interest and replace K and Θ with backfill properties.

Note:
Remedial technologies can also be run in sequence (treatment train).

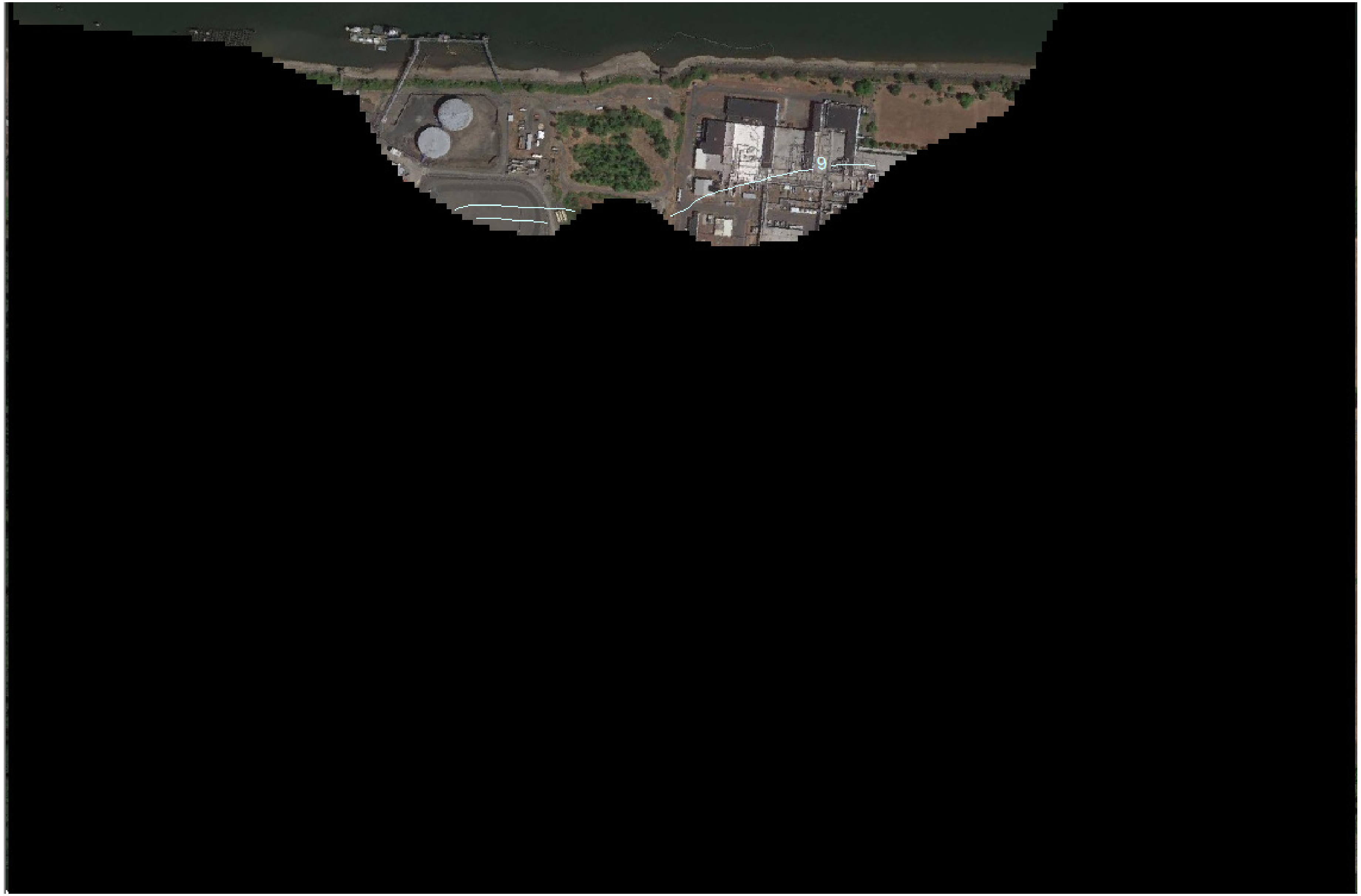
What questions do you have?

Layer 1

Layer 4



Layer 7



Layer 9