Interpreting Tar Patterns at Former Manufactured Gas Plant Sites

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Why focus on tar?

- Dense, nonaqueous-phase liquid (DNAPL) that can sink into the saturated zone and contaminate groundwater
  - Expensive to remediate
- Insurance coverage litigation
  - How tar got there? (Expected and intended?)
  - When tar got there? (During coverage period?)
  - Is it still moving? (During coverage period?)

Outline

- What is manufactured gas plant (MGP) tar?
- How "tarry" is it?
- How fast does it move?
  - Distance and time scales
- How to interpret boring logs in terms of tar motion
- How can you identify source locations at a site where tar has migrated?

Nomenclature

- “Tar” generally = Density > Water
- “Oil” generally = Density < Water
- “Coal tar” = Tar from different processes
  - Coal gasification
  - Water gas
  - Carbureted water gas
  - Oil gas

Which may not involve the use of coal at all!

Different Processes for Manufacturing Gas

- Coal gas: Heat coal in the absence of oxygen
- Water gas (blue gas): Steam sprayed on incandescent coke $H_2O+C \rightarrow CO+H_2$
- Carbureted water gas: Petroleum is cracked and added to water gas—most popular Lowe process
- Oil gas: Cracked petroleum for low molecular weight gases

Initial Coal Gas Period

- 1812: First commercial plant chartered, London
- First U.S. gas companies incorporated
  - 1817 Baltimore
  - 1823 New York
  - 1829 Boston

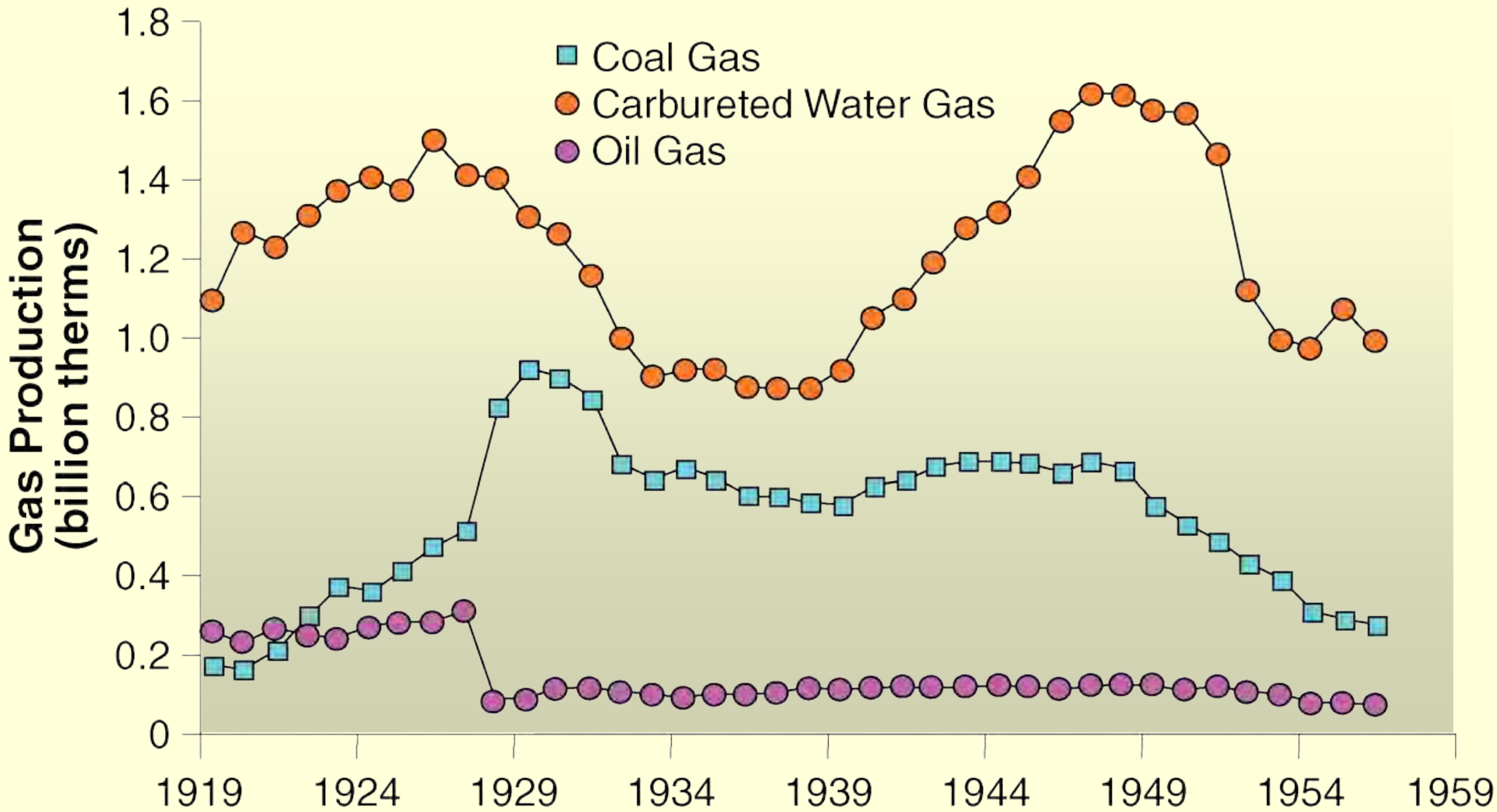
Advent of Water Gas

- 1873: Lowe Carbureted Water Gas (CWG) Process patented; water gas provided superior illumination
  - 1884: Patents sold to United Gas Improvement Company
  - 1892: Lowe's patents begin to expire
- 1900: CWG accounts for 75% of U.S. gas production
  - Coal gas retained at some plants to provide coke for water gas process

Arrival of Natural Gas

- 1943:
  - Big Inch and Little Big Inch pipelines constructed to carry crude and product from the Southwest to New York Harbor area
    - U-boat concern
    - Converted to carry natural gas at end of Word War II
- 1950s–1960s:
  - Plants convert to oil gas for natural gas compatibility
  - MGPs dismantled

U.S. Gas Production by Manufacturing Process



Source: Emsbo-Mattingly and Boehm adaption of Harkins et al. (1988)

Most Tar in the Ground is Water Gas

- In addition to greater gas production than coal gas:
  - More tar/cubic foot of gas
  - Can be more difficult to recover chemicals from than coal gas tar
  - Can be "off-spec" due to emulsions

Contemporary Citations Regarding Water Gas and Coal Gas Tar

"In former days it was a common custom to put all these tar tanks, settling tanks, etc. in the ground and to build them of wood. In time these became leaky and the contents would ooze out. Similarly, metal tanks would rust out and leak, and brick tanks would become more or less permeable. The present tendency is toward the use of better tanks, in order to avoid losses of valuable substances and in order to prevent pollution. The wastes from water gas plants are more troublesome in this respect than the waste from the coal-gas plants. …Often the floor of the tanks is built of concrete or brick and there is danger of leakage from such holders, as their area is considerable." (Whipple 1908)

Contemporary Citations Regarding Water Gas and Coal Gas Tar *(continued)*

"Experience has shown that a masonry tank will allow very little coal tar to seep through it but water-gas tar frequently escapes. Whenever possible water-gas tar should be stored in steel tanks of 10,000 gal capacity." (Russell 1917)

Tar Properties: Viscosity, μ

- Viscosity of tar
  - Low, light oil water gas/oil gas
  - Medium, heavy oil water gas/oil gas
  - High, coal gas/coke oven gas

Tar Viscosity at Time of Manufacture

	Water gas tar #1	Water gas tar #2	Light water gas tar	Low temperature coal tar	Coke oven coal tar	Pacific Coast oil gas tar
Dynamic Viscosity (cP)	9.1	9.9	12	60	1,470	119

Note: Viscosity converted from degrees Engler, T = 104° F = 40° C

Source: Harkins et al. (1988)

Present Tar Viscosity

Site Number	1B	2B	4	7	9	10	11
Dynamic Viscosity (cP)	63.6	425.3	144.6	32.0	51.0	62.9	34.7

Notes: T = 22° C

Samples 1A and 2A were high viscosity but not measured.
Samples1B and 2B are replacement samples.
Samples 3, 6, and 8 had large amounts of solids and were not used.
Generally small standard deviations not shown.

Source: EPRI, 2004

How “Tarry” is MGP Tar: Comparison with Common Fluids

Fluid	Viscosity (cps)	Tar	Viscosity
Water (65°F)	1		
Milk	3	Water gas tar #1	9.1
Blood	10	Water gas Tar #2	9.9
Gasoline	11	Light water gas tar	11
Beer	18	#7	32.0
Cream	20	#11	34.7
Vegetable oil	40	Low temperature coal tar	60
SAE 10	88–206	#9	51.0
		#1B	63.6
		#10	62.9
Peanut oil	103	Pacific Coast oil gas tar	119
Tomato juice	180	#4	144.6
Maple syrup	435	#2B	425.3
Latex paint	750		
Honey	1,500	Coke oven coal tar	1,470
Chocolate syrup	2,250		

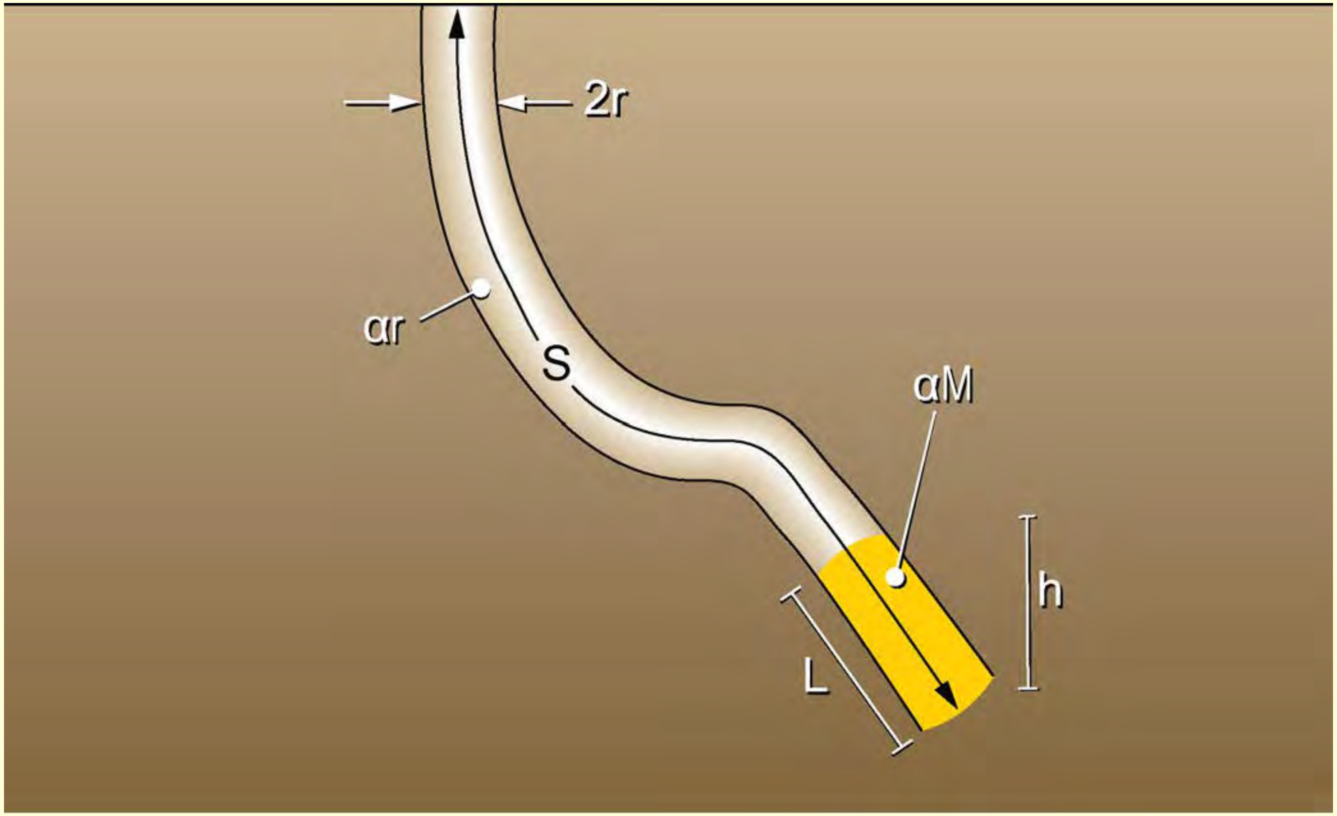
Question: How "Tarry" is the Tar? Answer: Not Very

- What about samples that were not used?
  - 1A, 2A "High viscosity"
    - Could be coal tar or weathered (evaporated) samples from the surface/near surface

How Fast Does Tar Move

- An EPRI program provides site-specific tar and soil properties allowing for the calculation of movement

Schematic



Equations of Motion

- Tar Motion: Controlled by three forces
  - Gravity: $F_g = \Delta\rho g h \pi r^2$
  - Capillary: $F_c = 2\delta cos\theta\, \pi r$
  - Viscous: $F_{v=} \dfrac{v\mu nL\, \pi r^2}{k}$

Equating Gravitational and Viscous Forces Results in D'Arcy's Law

$$\boldsymbol{v = \frac{dS}{dt} = \frac{kg\Delta\rho h}{n\mu L}}$$

v = Tar front migration speed (m/s)

s = Path length (m)

t = Time (s)

k = Intrinsic permeability (m^2)

g = 9.81 (m/s^2)

Δρ = ρ_{tar}-$\rho_{other\ fluid}$ (gm/m^3)

h = Vertical extent of saturated tar column (m)

n = Effective porosity

m = Dynamic viscosity (cP, gm/m-s)

l = Length of saturated tar column (m)

Saturation, α

- “Mobile” saturation
  - Fraction of pore volume filled when the tar is moving through
  - Can approach 1 although water is the “wetting” fluid
  - Mobile saturation values can exist when motion has ceased
- “Residual” saturation
  - Left sorbed to soil or trapped by capillary forces after the tar has drained
  - Residual tar does not contribute to hydraulic head

Supplement D'Arcy's Law with Conservation of Mass to Relate S and L

$$L_0\alpha_m = L\alpha_m + (S - L)\alpha_r$$

$$\frac{dL}{dS} = \frac{\alpha_r}{\alpha_r - \alpha_m}$$

S = Path length (m)

L = Saturated tar length (m)

L_0 = L(t=0)

α_r = Residual soil concentration (cm^3/cm^3)

α_m = Mobile soil concentration (cm^3/cm^3)

Resulting Solution

- $S = \frac{\alpha_m}{\alpha_r} L_0 - \left(\frac{\alpha_m}{\alpha_r} - 1\right) L$
- $L = L_0 - \mathrm{ut}$
- $u = \left(\frac{\alpha_r}{\alpha_m - \alpha_r} \frac{\Delta\rho}{\mu}\right)\left(\frac{k}{n}\right) g < cos\varphi >$
- $< cos\varphi > = \frac{1}{t}\int_0^t \cos\varphi \, dt \cong \frac{1}{t}\int_0^t \frac{h}{L} dt$
- φ = Time weighted average angle from the vertical
- $h \cong L \cos\varphi$

Elapsed Time

- $\frac{dS}{dt} = \left(\frac{\alpha_m}{\alpha_r} - 1\right) u$
- $t = \frac{L - L_0}{u} = \frac{\mu n}{\Delta \rho g k < cos\varphi >} (S - L_0)$
- $L_0 \cong \frac{\alpha_r}{\alpha_m} S$

Parameters Determining Tar Migration

- Tar properties
  - Viscosity, μ
  - Density, ρ
  - Surface tension, σ (ST)
  - Interfacial tension, σ (IT)
  - Contact angle, θ
  - Residual saturation, α_r
- Soil properties
  - Intrinsic permeability, k
  - Porosity, n

Tar Properties

Site/Sample	1B	2B	4	7	9	10
Density (g/cm^3)	1.066	1.104	1.062	1.076	1.054	1.062
Dynamic viscosity (cP)	63.6	425.3	144.6	32.0	51.0	62.9
Surface tension (dynes/cm)	33.75	26.67	34.35	34.17	23.44	33.63
Interfacial Tension (dynes/cm)	26.70	27.83	22.55	25.79	22.37	24.43
α_r (cm^3/cm^3)	0.159	0.226	0.131	0.156	0.192	0.077
θ (degrees)	15.8	22.4	26.8	17.4	19.3	21.6

Source: EPRI (2004); Kong (2004). θ is the average at pH 4.7 and 7.1.

Soil Properties

	1	2	4	7	9	10
N	0.420	0.435	0.343	0.451	0.383	0.530
$k(m^2) \times 10^{-11}$	5.46	4.58	1.93	4.61	1.13	14.6

Source: EPRI (2004). k calculated based on the method of Kruger using the article size distributions.

Conservative Case

- All motion in the saturated zone
- At an average 60° from the vertical

Time to Migrate 100 m at 60° from the Vertical

Site/ Sample number	1B	2B	4	7	9	10
Years	4.0	19.4	23.3	2.2	16.7	2.2
L_0 (m)	15.9	22.6	13.1	15.6	19.2	7.7

How long does the tar take to move 100 m in the saturated zone?

- Generally a few years
- Worst case about two decades
  - High viscosity
  - Low conductivity
  - Near neutral buoyancy
- Requires a large initial input of tar from 7.7 to 22.6 m thick to go 100 m
- Much faster in the vadose zone

Can "mobile tar" persist longer?

- Bond number N_b is the ratio of gravitational to capillary force

$$N_b = \frac{F_g}{F_c} = \frac{\Delta\rho g h r}{2\sigma cos\theta}$$

  - As h decreases, capillary pressure overcomes gravitational force ($N_b \cong 1$) and motion ceases
  - r~ Pore radius, capillary radius, grain radius (m)
  - **σ** = Interfacial tension between tar and other fluid (dynes/cm = gm/s^2)
  - **θ** = Contact angle

Value of h(r) in Meters for $N_b = 1, \varphi = 0$

r (m)↓ Site/Sample→	1B	2B	4	7	9	10
1×10^{-4} Sand	7.94E-01	5.04E-01	9.36E-01	6.60E-01	7.97E-01	7.47E-01
5×10^{-5} Transition	1.59E+00	1.01E+00	1.87E+00	1.32E+00	1.59E+00	1.49E+00
1×10^{-5} Silt/clay	7.94E+00	5.04E+00	9.36SE+00	6.60E+00	7.97E+00	7.47E+00

Source: USDA Soil classifications

Conclusion "Mobile Tar"

- A column of height h can exist over tight soils
- For silt/clay this column can be from 5 to 9.4 m high below the water table
- Finding saturated tar in soils does not indicate that tar is still moving!

Some Effects Can Produce Local Tar Movement

- Radically falling water table
  - Buoyancy reduced
- Installation of wells
- Test pits

Interpreting Boring Logs

Log	Interpretation	α
Solid	Weathered saturated tar if mixed with soil, otherwise disposal of 100% tar	$= \alpha_m \cong 1$
"Saturated"	"Mobile" tar held in place by capillary forces at a lower elevation	$= \alpha_m \leq 1$*
"Interbedded"	"Mobile" tar held in place in a layered stratigraphy by capillary forces at a lower elevation	50%?
Blebs, ganglia, lenses	Residual tar with capillary trapping	Upper end of range $= \alpha_r = 7.7–22.6\%$
"Coated soil grains"	Residual tar without capillary trapping	Lower end of range $= \alpha_r = 7.7–22.6\%$
Stains	Tar related if characterized by a naphthalene or "tar" odor. A continuum with "coated grains" or possibly dissolved phase tar components.	Low 3% ?

MGP Locations

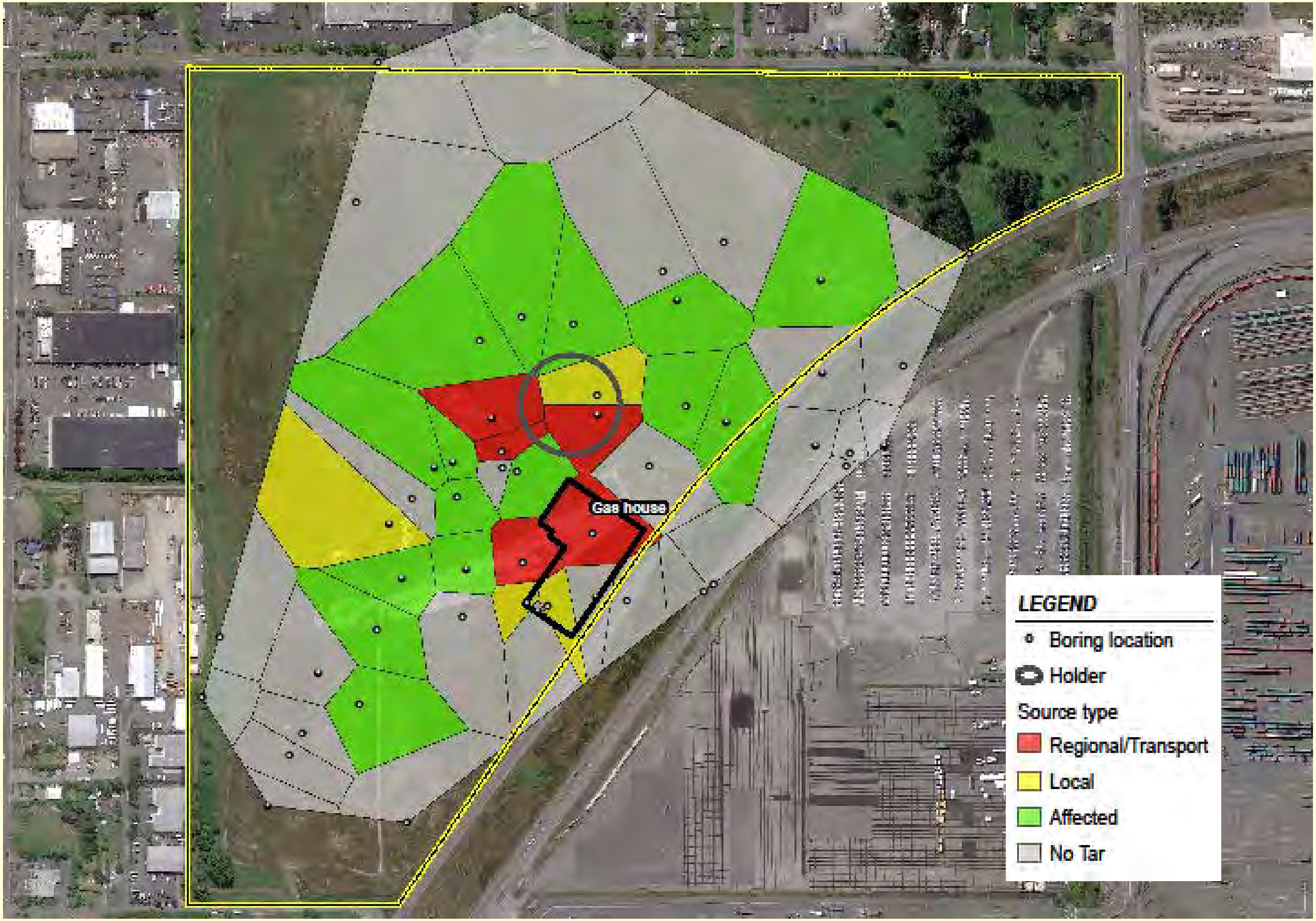
- Usually located on water bodies
  - Fuel transport
    - Later residuals (coke, tar, ammonia liquor) transport out
  - Steam and cooling water supply
  - Landlocked exceptions on a rail spur with ground water supply
- Often on reclaimed bay, estuary, marsh land

Fill

- Because fill lacks bedding planes it does not facilitate transport over substantial distances
- Determining depth of fill
  - Boring log notation
  - Buried debris
  - Peat layer
  - Shells

Tar in Fill

- Tar in fill only
  - Local source
- Tar in fill and native soil
  - Possibly a regional source
- Tar in native soil only
  - A result of transport


Gas house
LEGEND
Boring location
Holder
Source type
Regional/Transport
Local
Affected
No Tar

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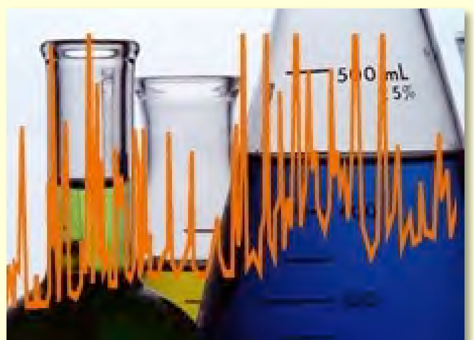

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