

Environmental Effects of Asphalts: Discussion Topics

*Asphalt Workshop
UNH*

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ENTRIX, Inc.
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MM53 Incident



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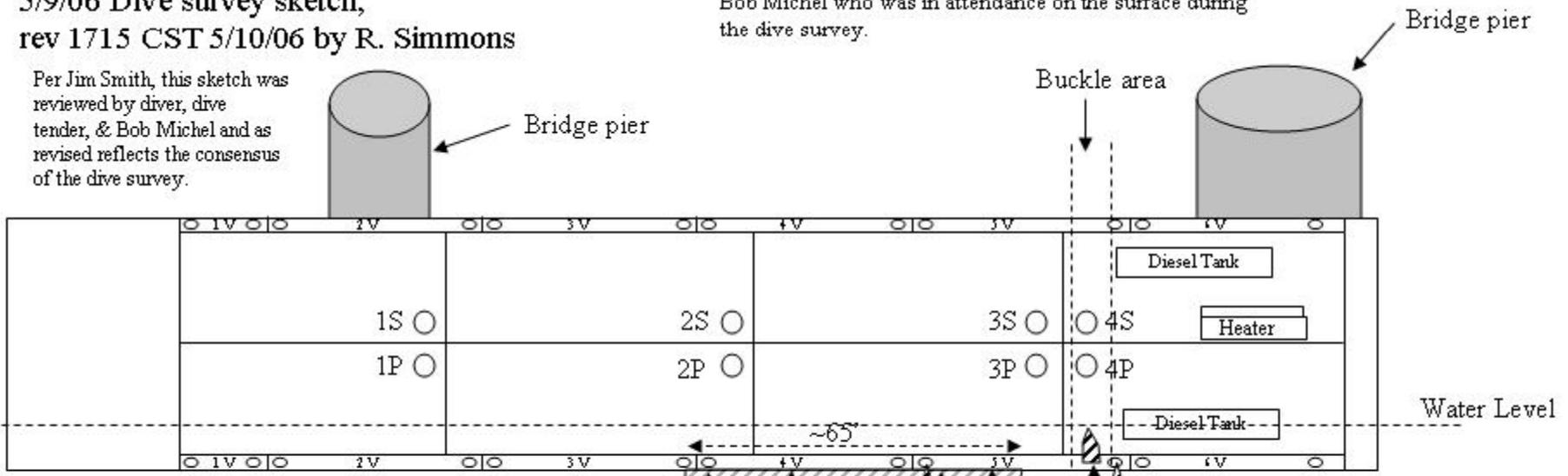
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10'

MM 53 – roughly to scale
5/9/06 Dive survey sketch,
rev 1715 CST 5/10/06 by R. Simmons

Per Jim Smith, this sketch was reviewed by diver, dive tender, & Bob Michel and as revised reflects the consensus of the dive survey.

Diagram produced by Robert Simmons based on dive survey by John Romans (diver) and information from Bob Michel who was in attendance on the surface during the dive survey.



Note: Displacement of stem end of MM 53 due to buckle is not depicted.

Asphalt in horizontal plane on river bottom on upriver side of barge; pliable; tacky, extruded; not smooth surface; **average thickness in question.**

Asphalt protruding from fore/aft hatches in #5 wing void; shiney-black.

Barge not touching bottom along this area, significant underflow.

3' x 3' protrusion of asphalt but does not touch river bottom; apparent breach.

Potential Injury Pathways

- Toxicity of dissolved components
 - acute
 - chronic
- Ingestion
- Physical fouling
 - smothering

Resources of Potential Concern

- Aquatic habitat
 - fish
- Sediment habitat
 - benthos
 - threatened and endangered species
 - freshwater mussels

Factors Influencing Hazards to Environment

- Solubility/toxicity of constituents
- Bioconcentration/Bioaccumulation
- Density
- Biodegradability

Asphalt

- LSU performed a water temperature experiment at the request of NOAA to determine properties of sunken asphalt at increasing temperatures
- Paving grade asphalt from sister barge MM54
- Asphalt introduced to 60°F water in beaker, gradually heated up to 125°F
- No sheen or oil visible at any temperature
- Low PAH concentrations in asphalt = low probability of PAH leaching into water column
- Hot asphalt hardens upon contact with water

LSU Asphalt Study



Figure 1.

Figure 1: Asphalt in water at 60°F



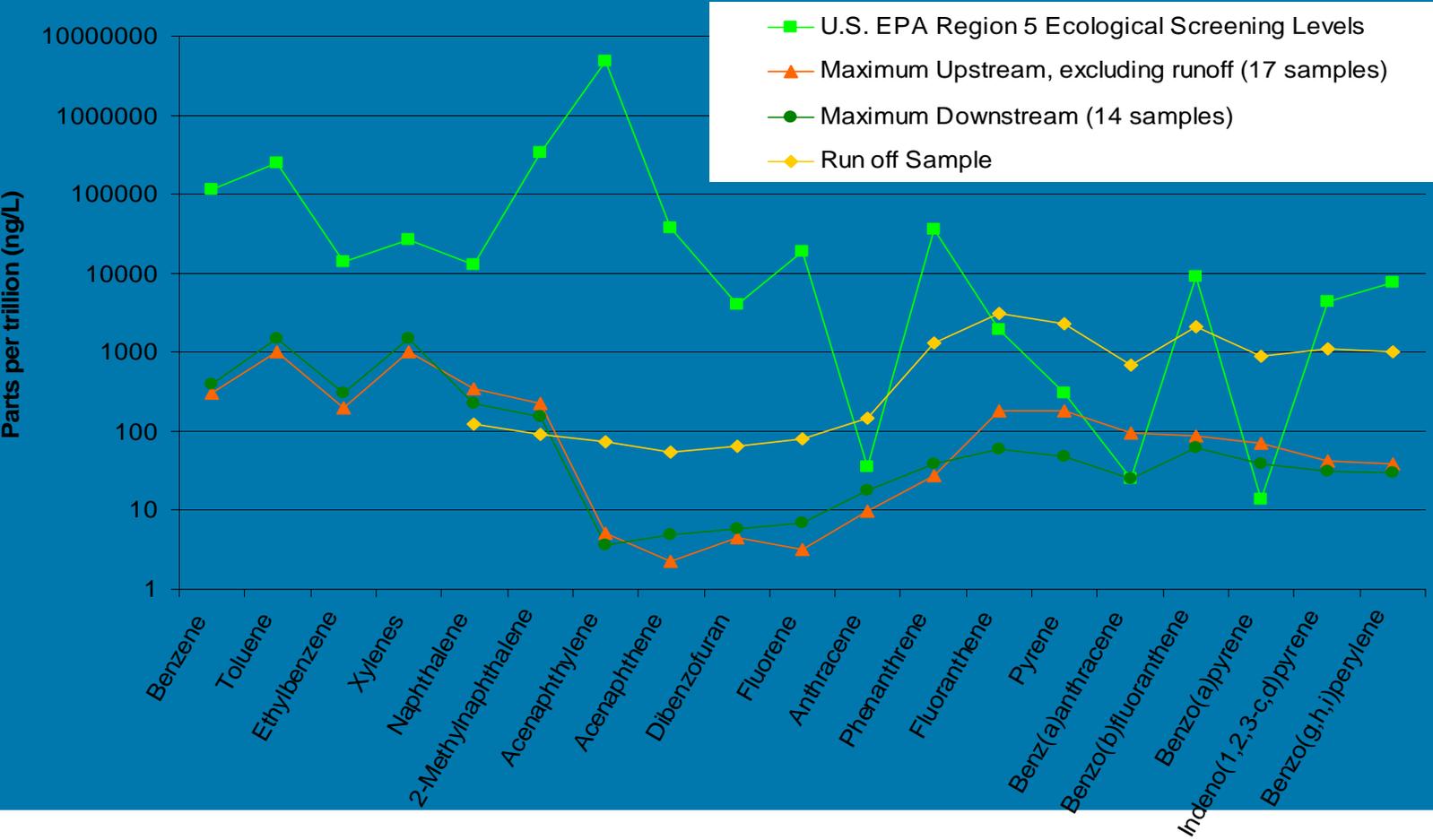
Figure 2.

Figure 2: Asphalt in water at 70 to 90 °F.

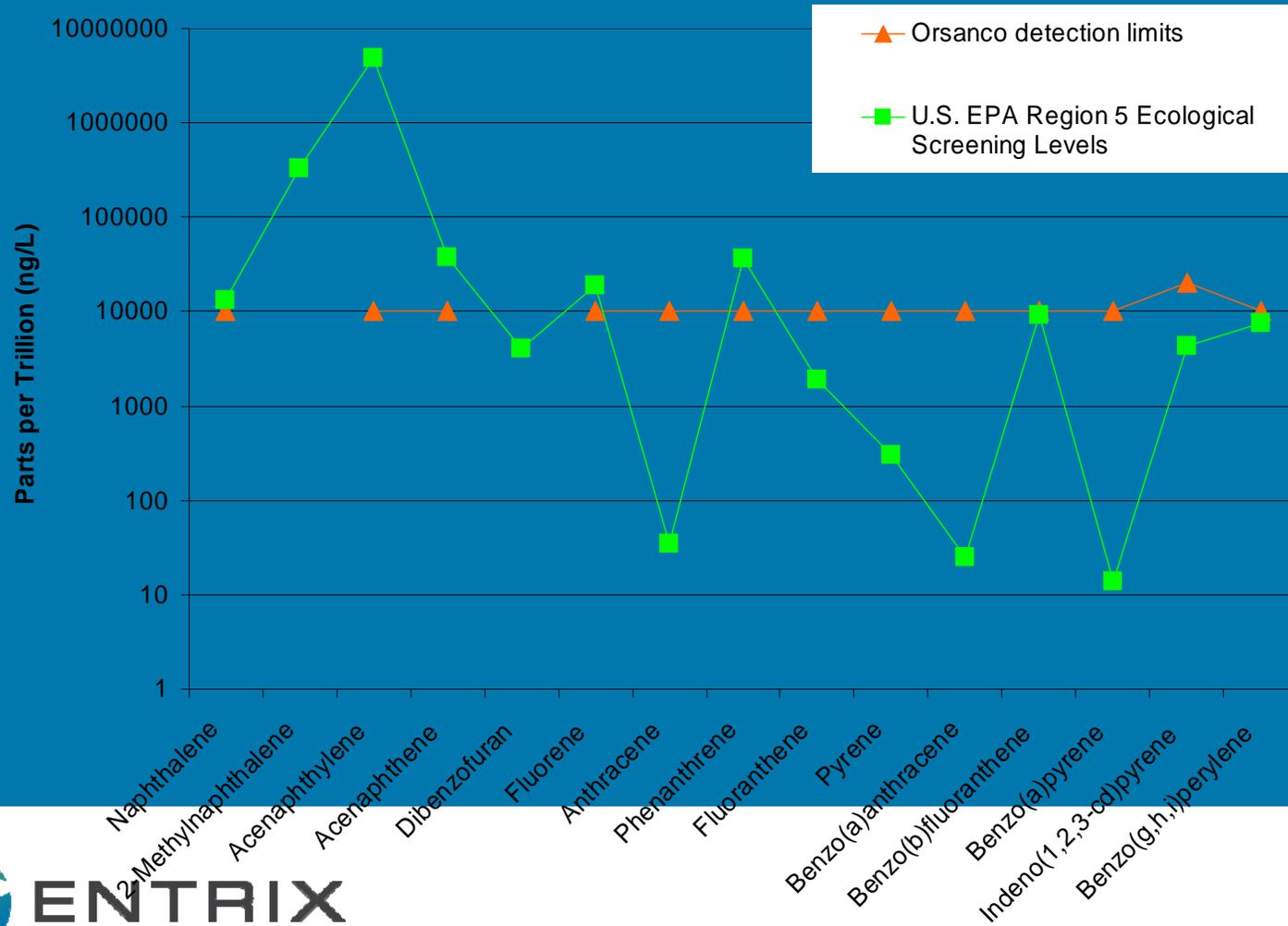
Toxicity

- **Acute and chronic effects are a function of**
 - concentration
 - duration of exposure
 - chemical type
- **Water sample data provides an estimate of concentrations and duration**
- **River flow and ambient conditions provide an idea of duration**
- **EPA criteria provide chemical thresholds**

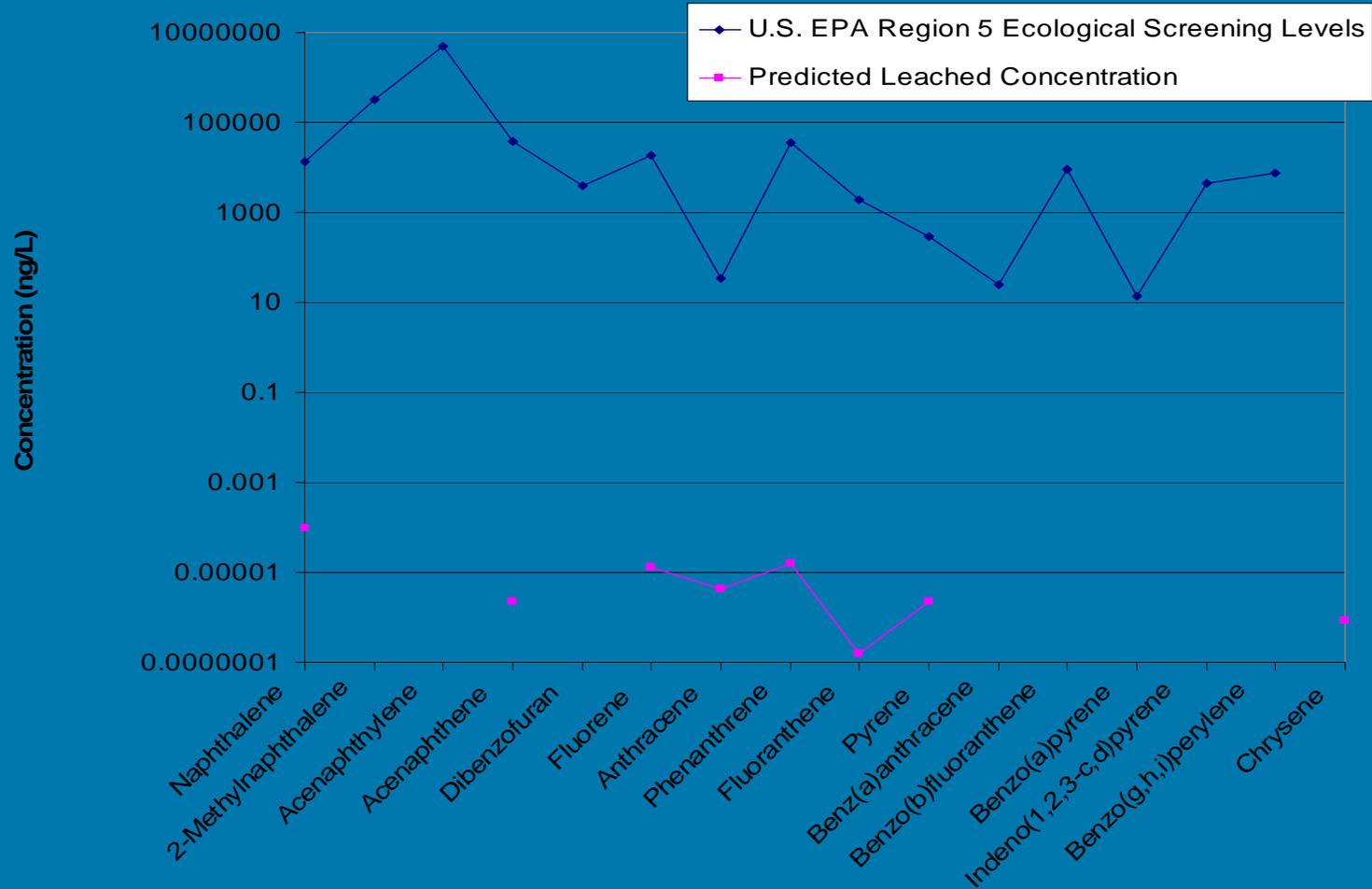
Water Column Results



Summary of ORSANCO Results



PAH Leaching from Asphalt



Estimated Mussel Tissue Concentrations

- Evaluate whether PAH would bioconcentration in mussel tissue at levels to cause chronic or acute effects
- Use accepted methods to calculate tissue concentrations
- Compare tissue concentrations to EPA benchmark

Method to Estimate Mussel Tissue Concentrations

- Use empirical water concentration data
- Calculate a Bioconcentration Factor (BCF) for each PAH based on EPA regression equation
 - the ratio of a substance's concentration in tissue of an aquatic organism to its concentration in the ambient water
- Estimate tissue concentrations using equation
 - $C_{\text{tissue}} = \text{BCF} * C_{\text{water}}$

Method to Estimate Mussel Tissue Concentrations

- Convert C_{tissue} (ng/g wet wt) to $\mu\text{mol PAH/g lipid}$
 - normalize to lipid concentration
- Sum individual PAHs
- Compare to EPA Final Chronic Value

EPA Tissue Benchmark

- EPA Final Chronic Value 2.24 $\mu\text{mol/g}$ lipid
- Source: USEPA, 2003. *Procedures for the Derivation of Equilibrium Partitioning Sediment Benchmarks (ESBs) for the Protection of Benthic Organisms: PAH Mixtures.**
 - Acute value (9.31 $\mu\text{mol/g}$ lipid) is derived from water LC50 studies from a wide range of PAHs and species
 - Threshold is based on total μmol present (PAHs effect additive)
 - Chronic value - based on acute:chronic ratio from paired studies
 - Designed to be protective of 95% of benthic organisms as per EPA guidance for deriving water quality criteria.

*USEPA, 2003. *Procedures for the Derivation of Equilibrium Partitioning Sediment Benchmarks (ESBs) for the Protection of Benthic Organisms: PAH Mixtures.* EPA-600/R-02-013. U.S. Environmental Protection Agency. Office of Research and Development. Washington D.C. 175 pp.

Estimated Mussel Tissue Concentrations

- Surface water data used:
 - Scenario 1:* Downstream sample collected February 15th, 1 mile south of spill
 - Scenario 2:* Maximum concentrations of PAH in sample with sheen
- Results range in $\mu\text{mol PAH/g lipid}$
 - Scenario 1* = 0.12
 - Scenario 2* = 0.58



*USEPA, 2009. Procedures for the Derivation of Equilibrium Partitioning Sediment Benchmarks (ESBs) for the Protection of Benthic Organisms: PAH Mixtures. EPA-600-R-02-013. U.S. Environmental Protection Agency. Office of Research and Development. Washington D.C. 175 pg.

Results

- Estimated body burdens are at least 4 times lower than the EPA chronic benchmark (2.24 $\mu\text{mol/g}$ lipid)
- Upstream sample has the highest potential body burden because it has the highest concentrations of heavy PAHs (contributes more on a μmol basis)
- Contribution of spill related body burden estimated by the percent of body burden due to naphthalenes (and alkylated naphthalenes) in the barge sample (worst case)
 - 25% of PAH body burden is due to naphthalenes
 - 75% of calculated body burden could be from background PAH

Summary of Potential Exposure Pathway Completion

	Resource	Constituents	Toxic	Duration of	Pathway
Resource	Present	Present	Concentration	Exposure	Completed?
Fish	?	Yes	No	Short	NO
Benthos	?	Yes	No	Short	NO
mussels	?	Yes	No	Short	NO

Models Used to Predict Transport in River

- Flows
- Temperatures:
 - Water
 - Asphalt
- Density
- Size /shape of Asphalt

MM53 Release Investigation

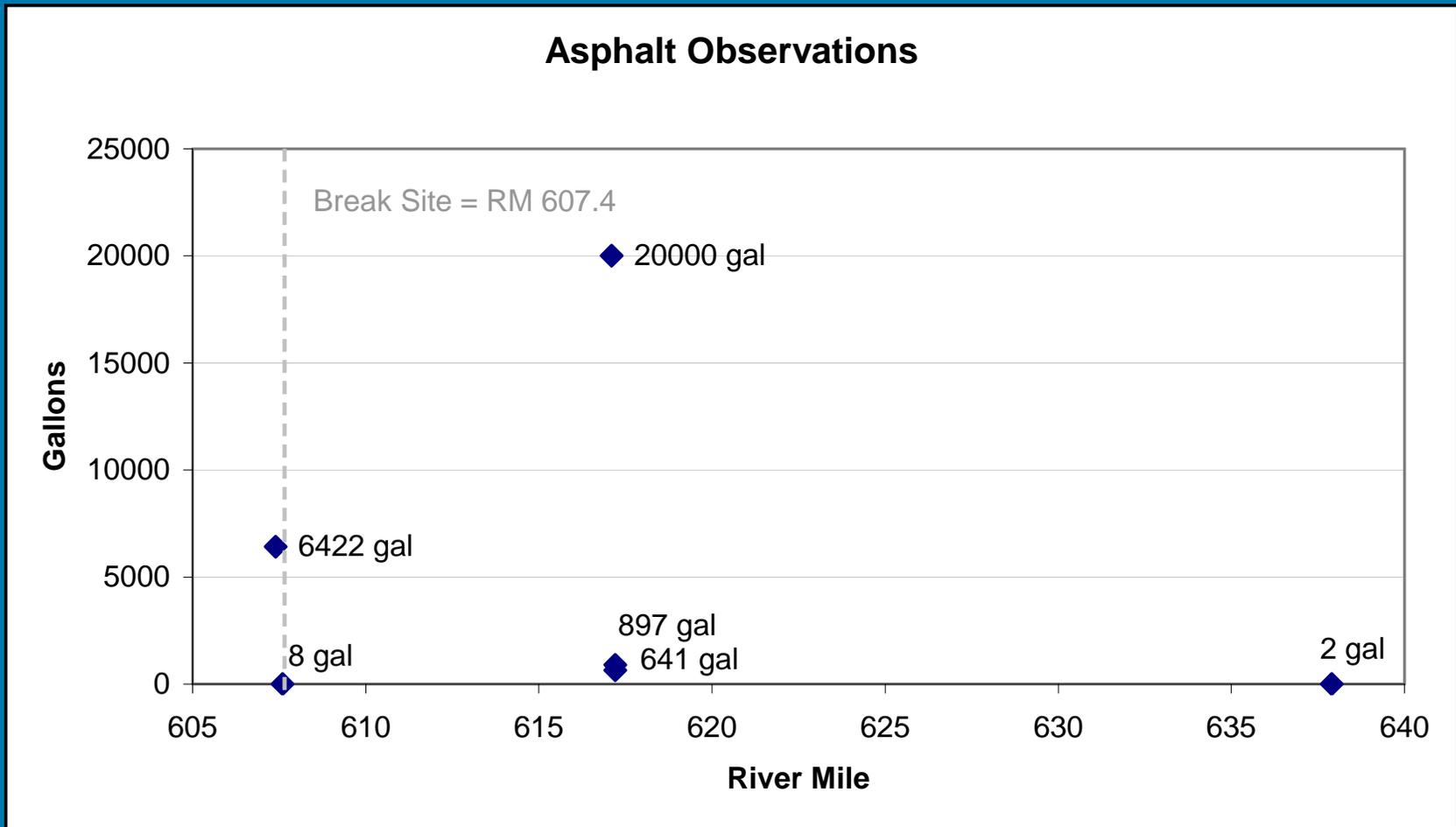


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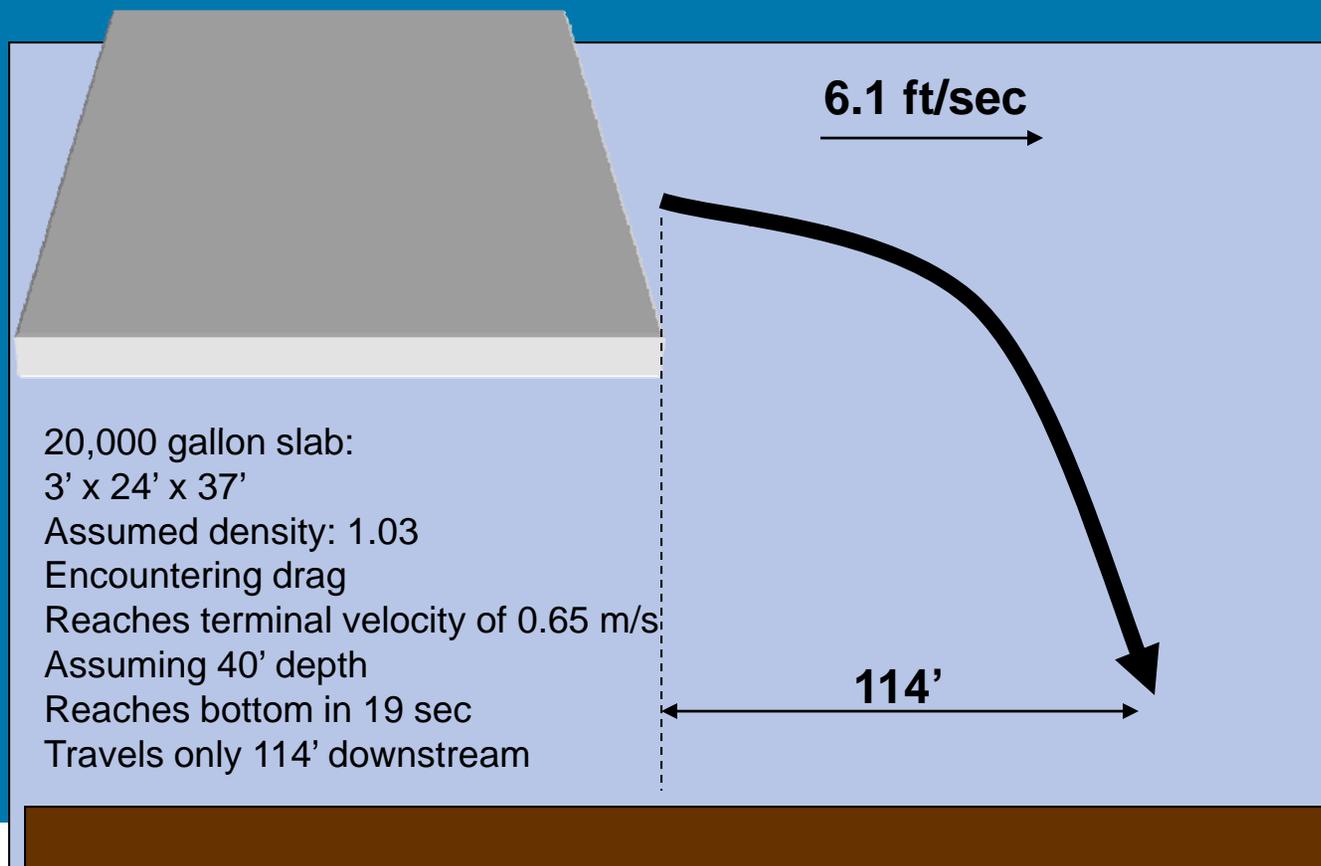
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Where was asphalt observed?



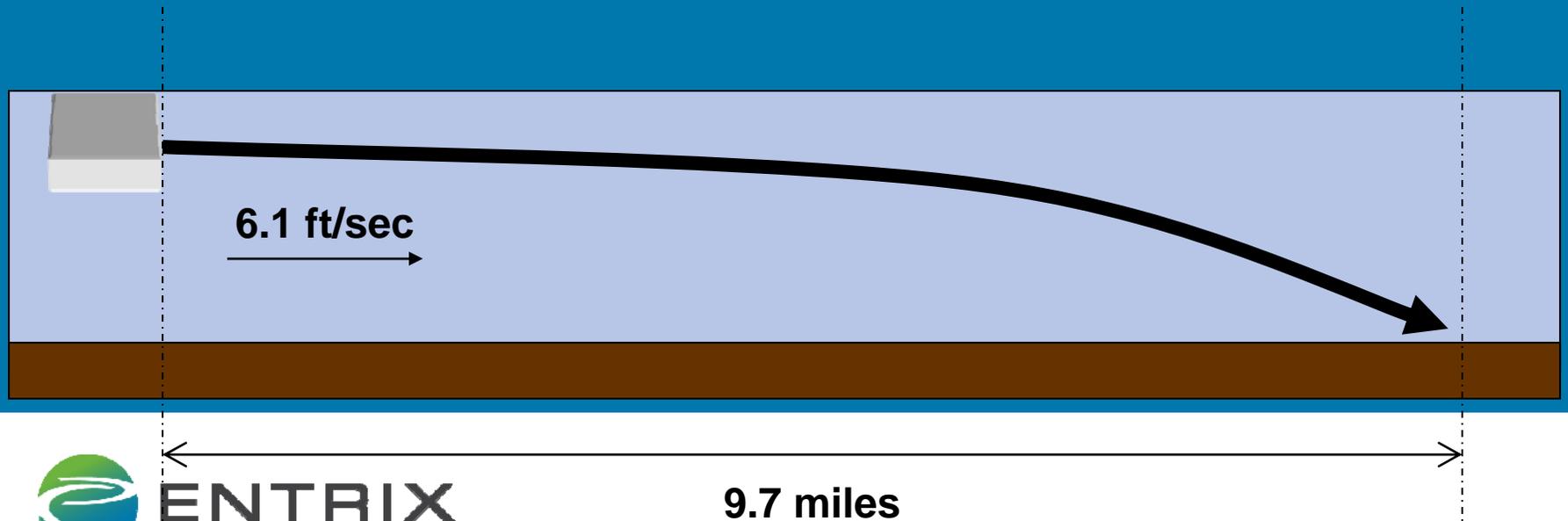
Simplified model projects large slab settling close to release site



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However, asphalt found ~10 miles downstream
How did it get there?



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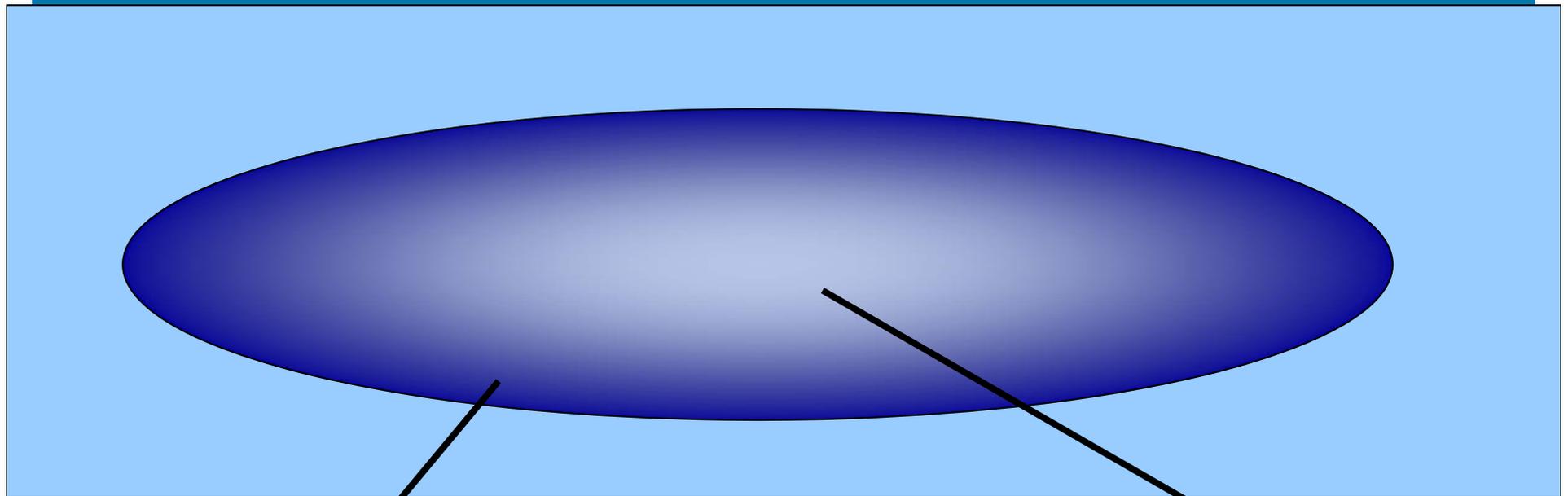
9.7 miles

Possible causes for transport

- Asphalt emerged hot at a density <1
- Water's density = 1.0
- The asphalt traveled with flow ~neutrally buoyant
- Once cooled, density increased to >1 , then sank quickly

Time to cool

- The time necessary to cool and sink a function of the shape / thickness of the mass and temperature differential



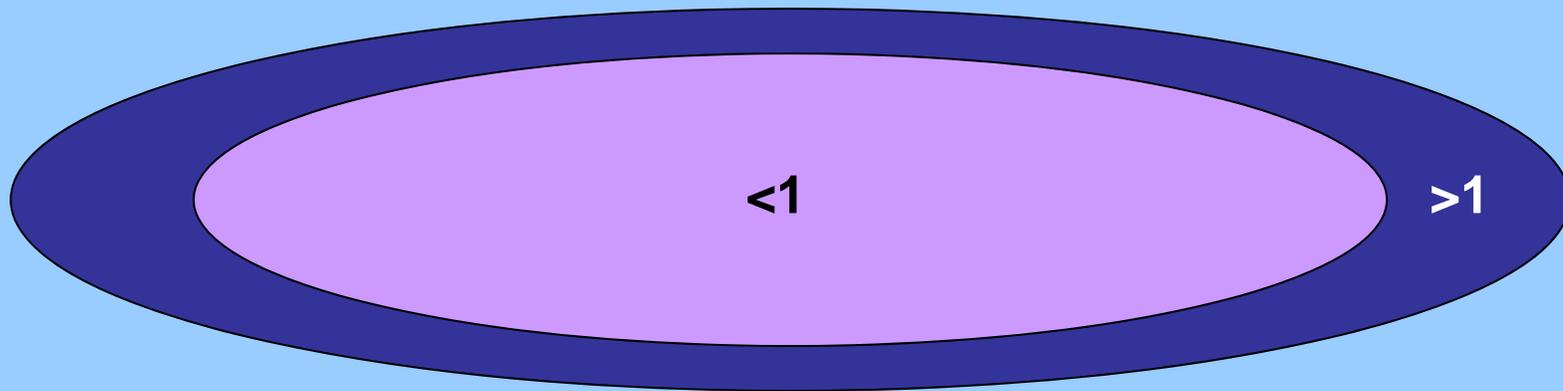
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Exterior cools / hardens first

Hot center, lower density

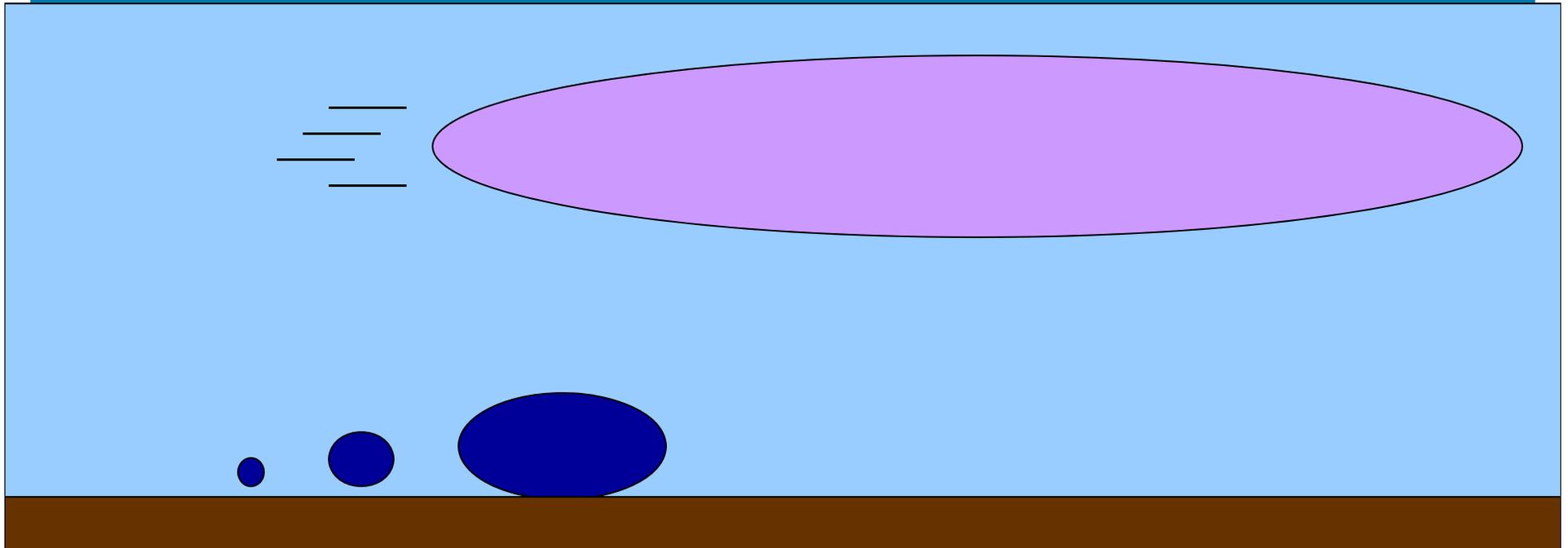
Time to cool

- The net density of the mass may be less than water while the exterior forms a more dense crust.



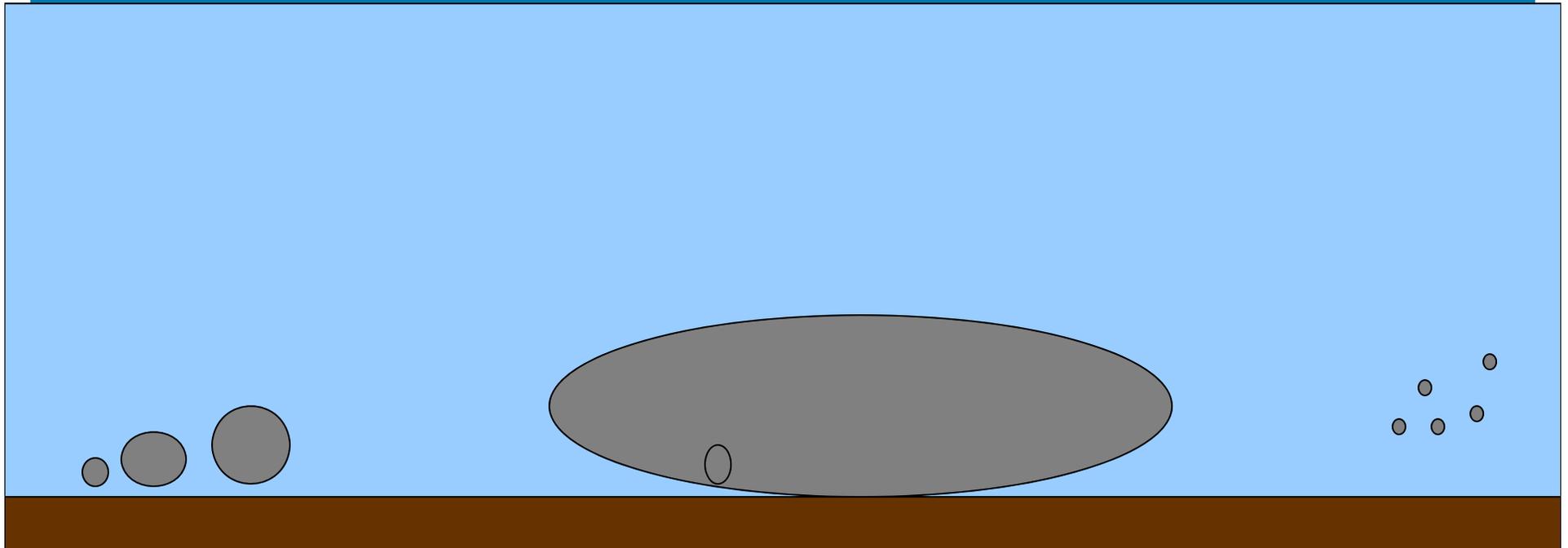
Time to cool

- Smaller particles cool faster, sink faster



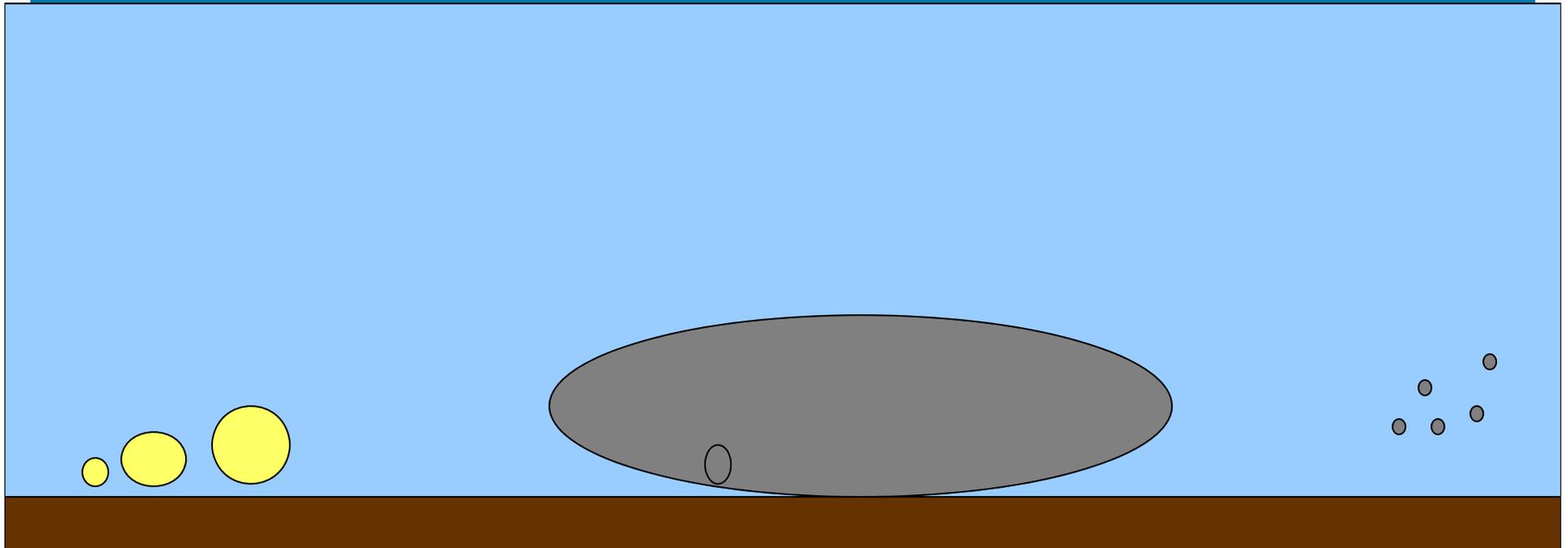
4 Transport Categories

- The asphalt may have transported in 4 different ways



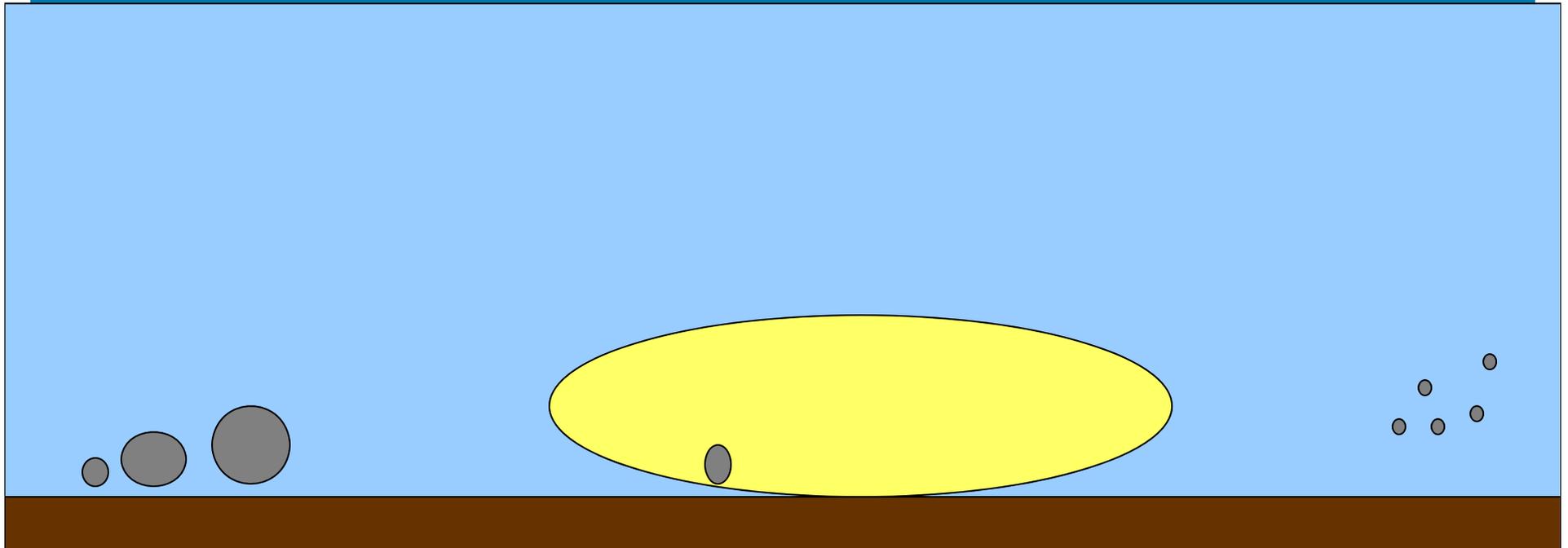
4 Transport Categories

- First – smaller pieces of asphalt cooled quickly and settled close to the break site



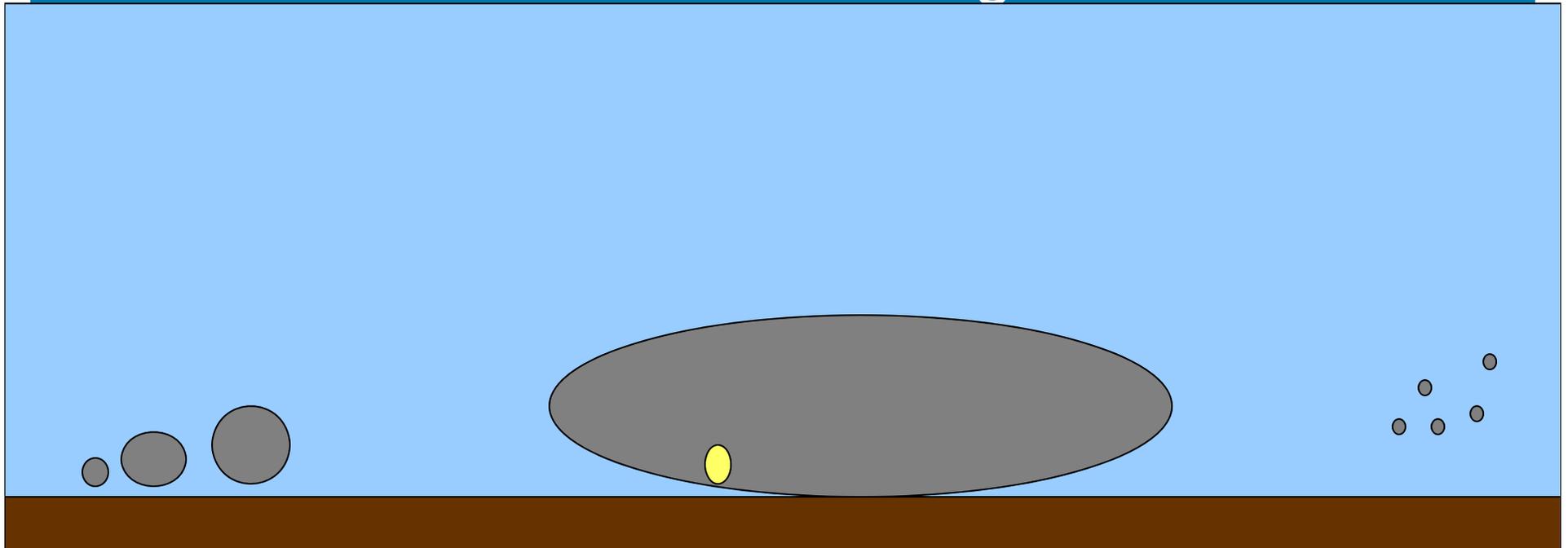
3 Transport Categories

- Second – large mass of asphalt was carried aloft until it cooled and sank farther downstream



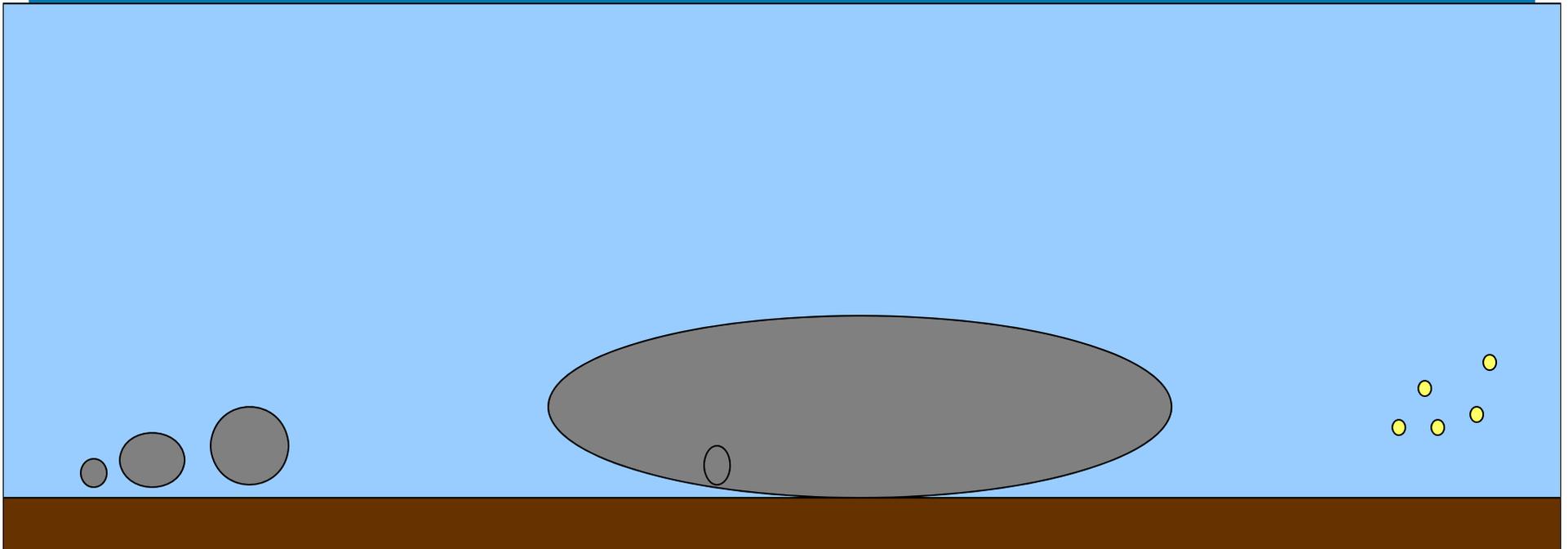
3 Transport Categories

- Third – pieces of the large mass could have broken off and landed close to the large mass OR rolled downstream during storm conditions with strong flow



3 Transport Categories

- Fourth, particles ~ 0.1 meters and smaller likely too small to remain settled and traveled farther downstream



Transport, Fate of Asphalt

- Assume that density/specific gravity and flow are primary factor governing settling location
- Assuming the 20,000 gal. slab initially emerged as one piece (found at mile 617)
- In order to travel further downstream, a slab would have had to cool more slowly, ie be larger than that found

Transport, Fate of Asphalt

- Searched depositional areas to mile 642 (approx 25 miles below large mass)
- Appears likely that additional large slabs would have been found via SSS in depositional areas between mile 617 and 642?