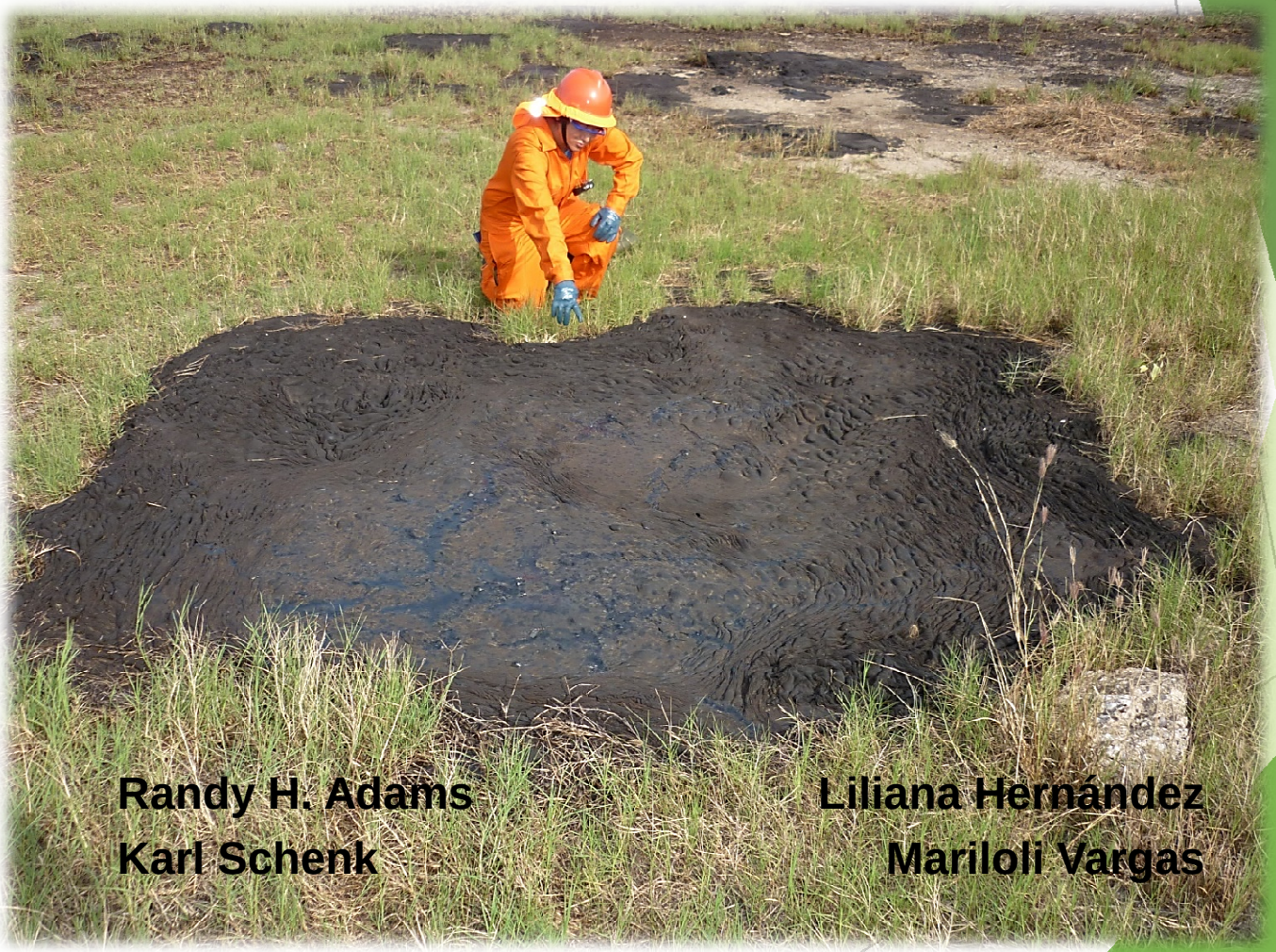
Treatment of Asphaltic Geysers by Chemical Stabilization and Solidification



Randy H. Adams
Karl Schenk
Liliana Hernández
Mariloli Vargas

Site Background

- Periferal underused area of old refinery

- Property transfer for construction of a gas processing plant ~2002

- During operations of the refinery, this area was used to dump waste, apparently tank bottoms (probably diesel or gasoil)

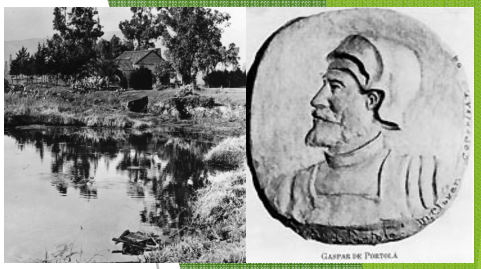
- Oily waste is very viscous, groundwater is not contaminated

- Prior to property transfer, surface was covered with rubble and sand to leave a clean looking site

- However, due to differences in densities and tropical climate, the oil rises through the overfill, creating emanations:

→ “asphaltic geysers”

Natural Asphaltic Geyers (~50,000 yrs old)
La Brea (Hollywood, CA)



- The Portolá expedition, a group of Spanish explorers led by Gaspar de Portolá, made the first written record of the tar pits in 1769.

- Father Juan Crespí wrote:

While crossing the basin the scouts reported having seen some geysers of tar issuing from the ground like springs; it boils up molten, …

We christened them *Los Volcanes de Brea* [the Tar Volcanoes].

Kielbasa, John R. (1998). "Rancho La Brea". Historic Adobes of Los Angeles County. Pittsburg: Dorrance Publishing Co. ISBN 0-8059-4172-X..

Natural Asphaltic Geyers (~50,000 yrs old)

La Brea (Hollywood, CA)

Man-made Asphaltic Geysers

Man-made Asphaltic Geysers


Emanation begins


Extension of the geyser


Formation of a hydrocarbon carpet


Emanation in vegetated area

Site Background

Site Background

Site Background

Oily Residue Sampling

Asphaltic Geysers

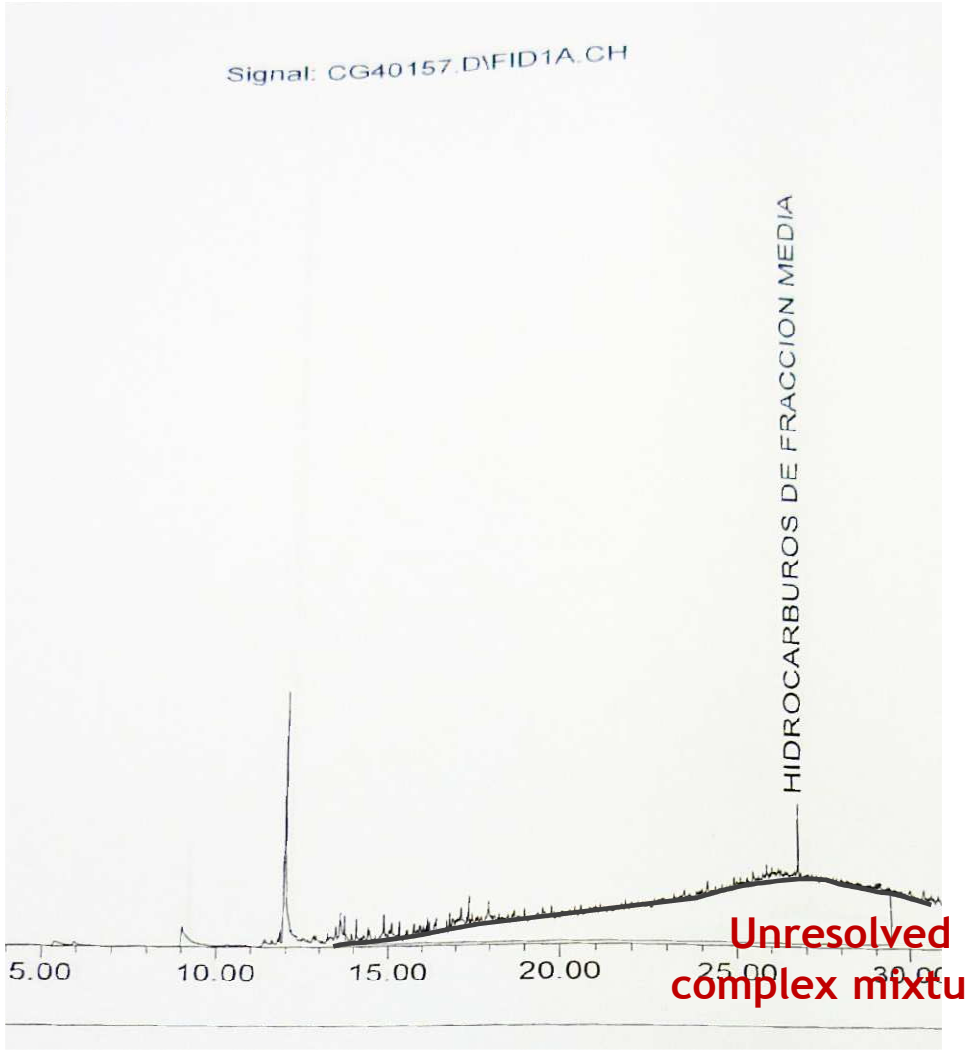
Asphaltic Geysers

Asphaltic Geysers

Asphaltic Geysers

Gas Chromatograph

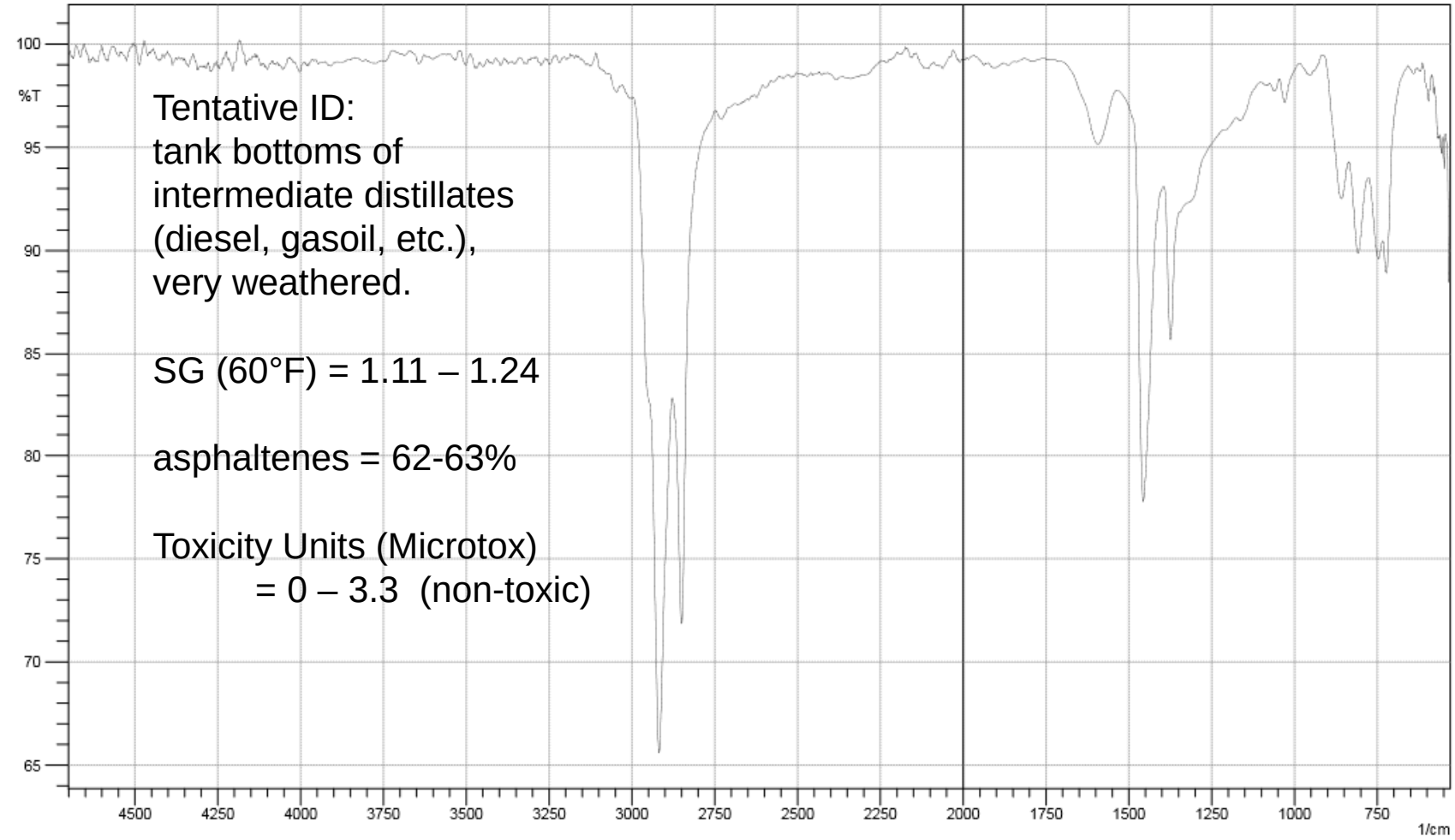
Sample with internal standard



- Low biodegradation potential
- Low leachate potential
- Practically non-toxic

Chemical-Toxicologica Evaluation of Hydrocarbons

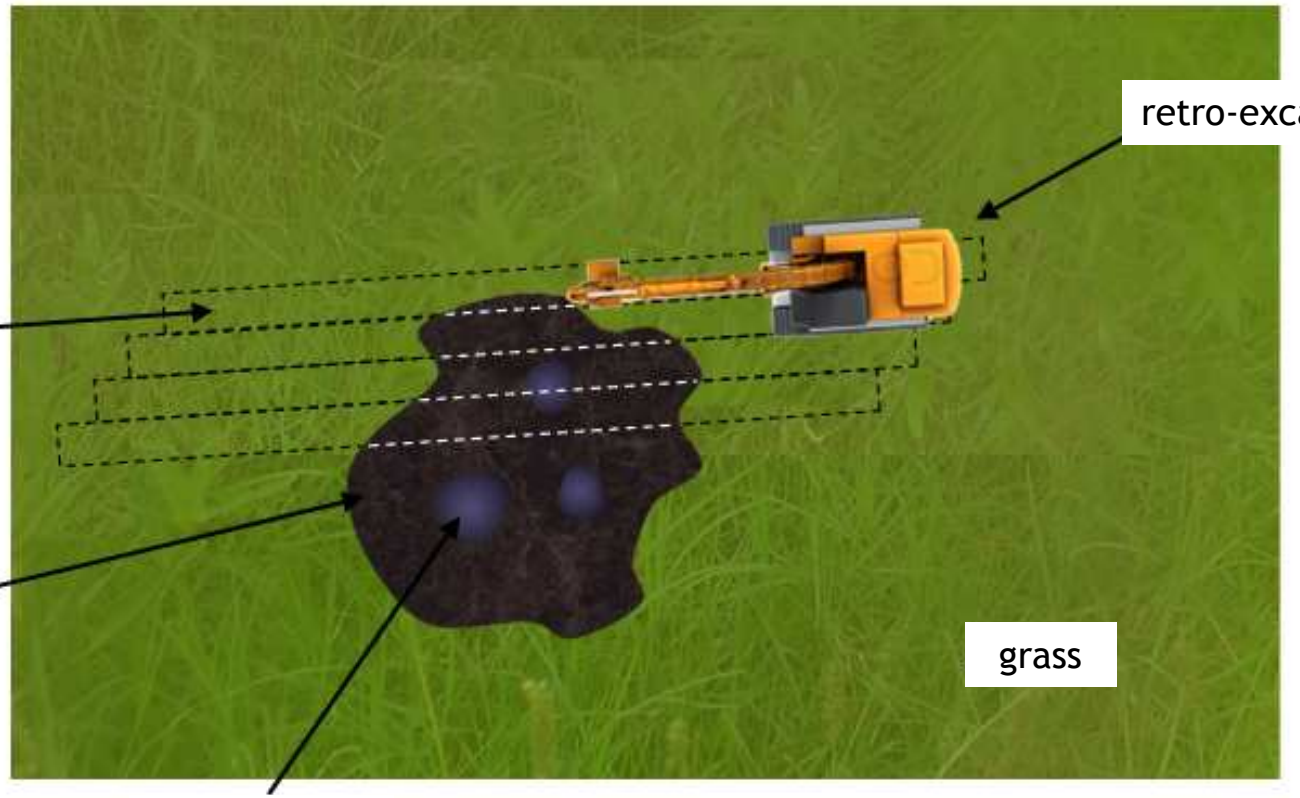
FTIR Spectra Evaluation



Exploratory Excavations

Excavation of emanation in low-lying area

Transversal Cuts

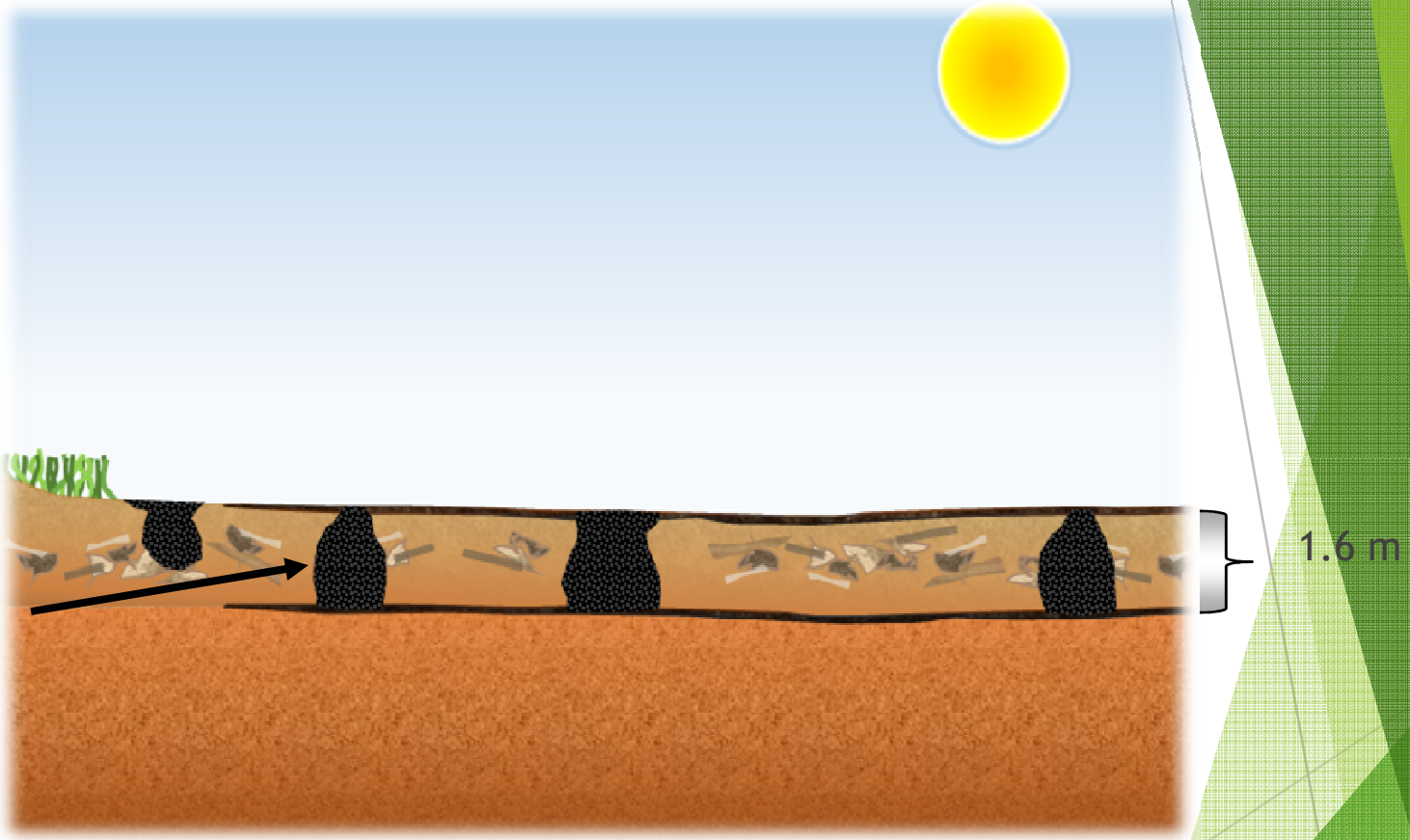


Exploratory Excavations

Exploratory Excavations

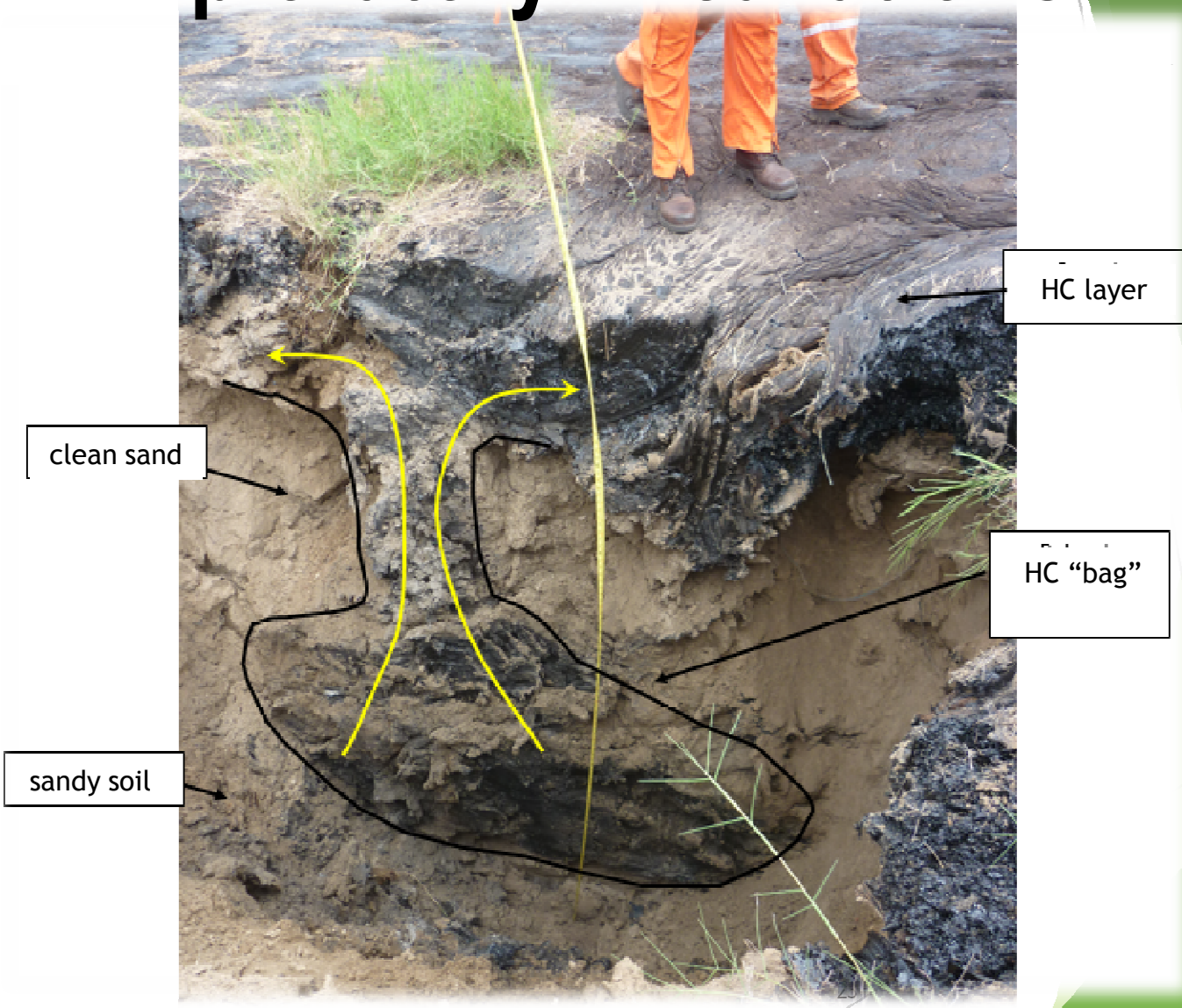
Emanation Source

Schematic of Emanation Source



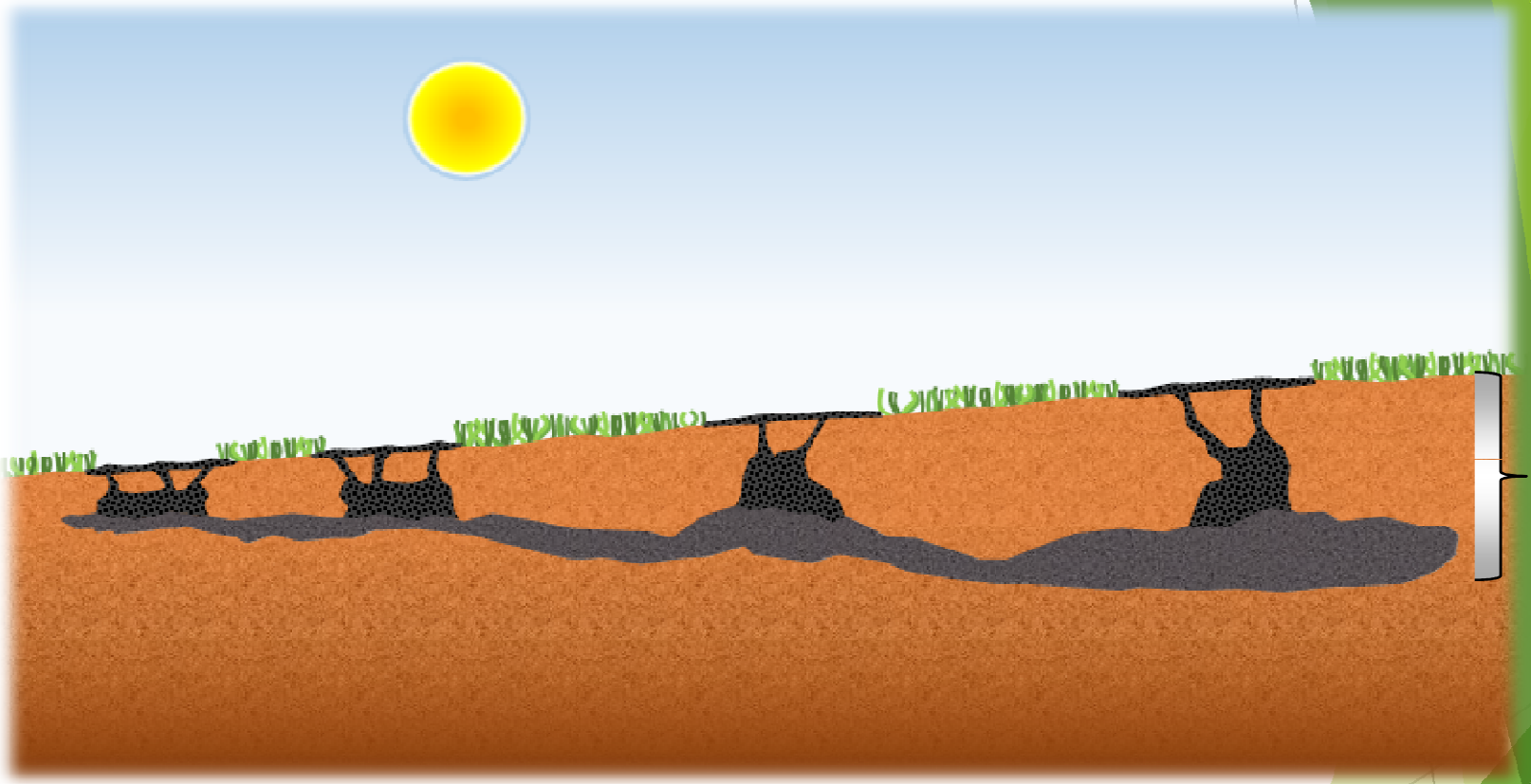
- **Underlying layer (original?)**
- **Overlay with sand and rubble**
- **Formation of hydrocarbon “bags”, emanations and “carpet”**
- **HC consistency is very similar in all areas**

Exploratory Excavations



Excavation of emanation in hilly area

Schematic of Emanation Source



Sources of hard and viscous HC bags in hilly area

- Underlying layer – hard, immobile, up to 78% asphaltenes
- Overlying viscous but mobile HC
  → formation of hydrocarbon “bags”, emanations and thick HC surface layer

Field Test – Stabilization (low-lying area)

- **Excavation of HC, sandy fill and rubble**
- **Breaking of large rubble into soccer-sized balls with pressure hammer**
- **Crushing of rubble and HC plast with ALLU crusher**
- **Mixing with ALLU mixer and cement *in situ***

Excavation of HC, sand and rubble

Field Test – Stabilization (low-lying area)

Breaking large rubble

Field Test - Stabilization (low-lying area)

Crushing rubble

Field Test – Stabilization (low-lying area)

Stabilization with ALLU mixer

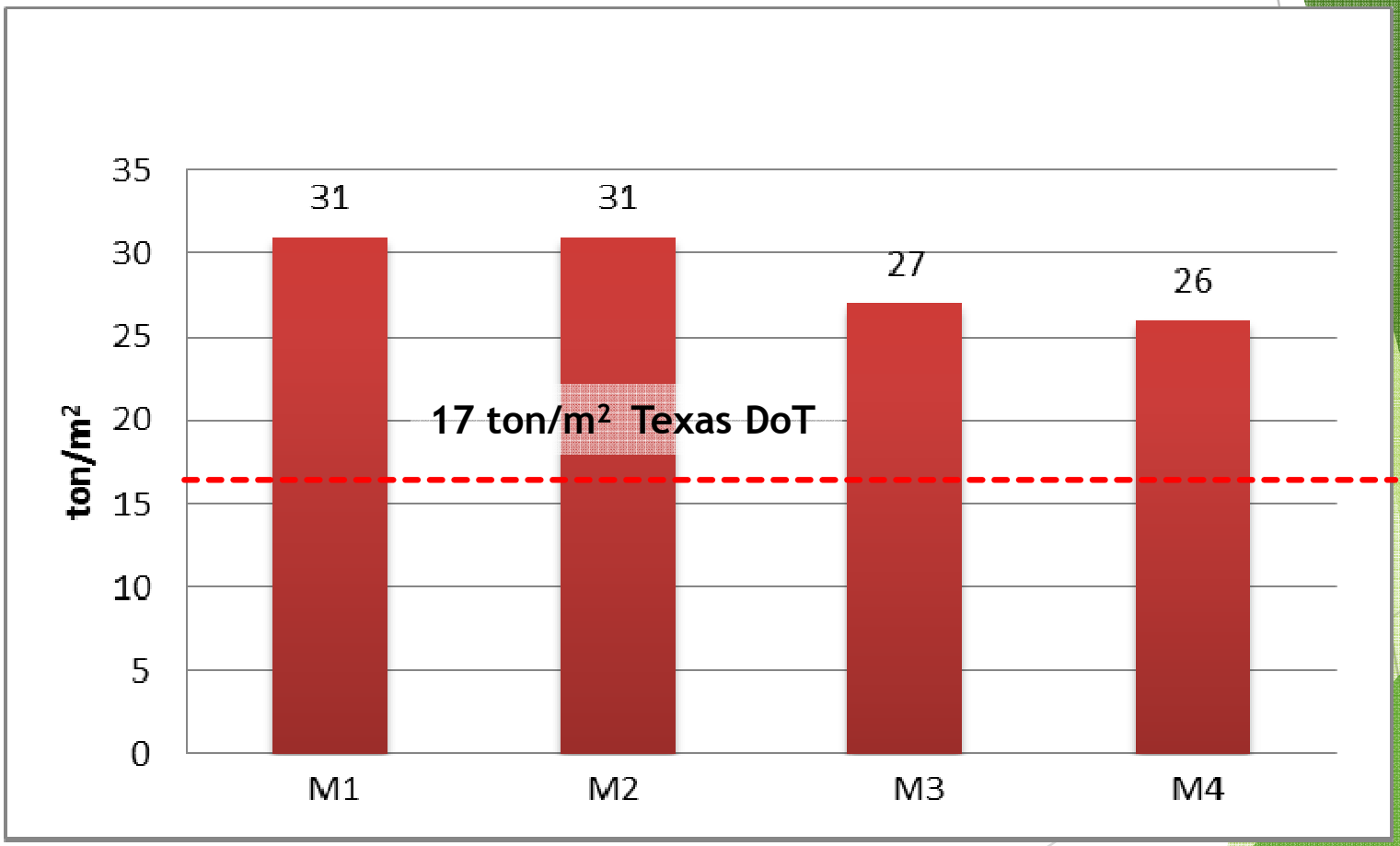
Lab Scale Solidification Test

Preliminary Tests – feasibility for re-use as road base

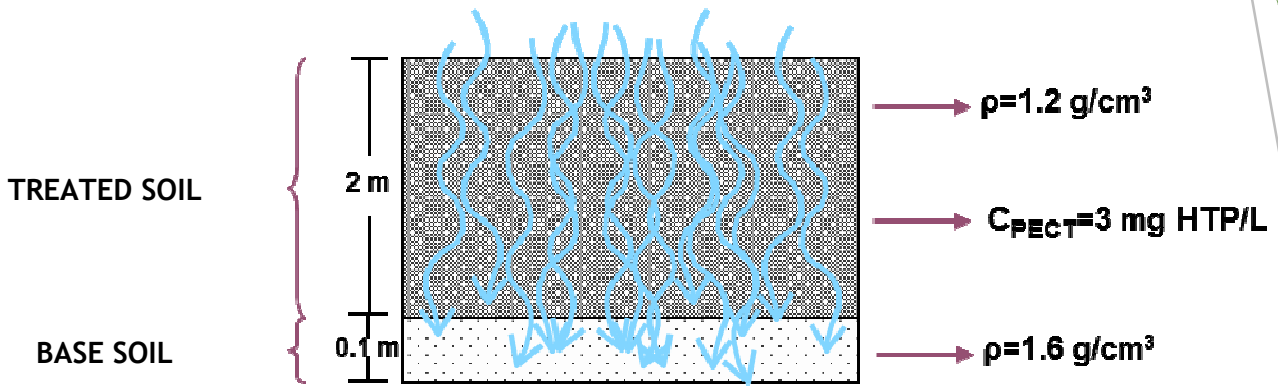
- **Different mixtures of HC, sandy soil, gravel, clay, cement, lime**
- **Resistance to unconfined compression (Kg/cm^2)**
- **TCLP leachate test for TPH**
- **Subsequent optimization tests for Marshall Stability (Kgf) (HC, sandy soil, gravel and a little cement)**

Preliminary Proctor Tests
Resistance to Unconfined Compression

Preliminary Proctor Tests
Resistance to Unconfined Compression



Simple Leachate Model

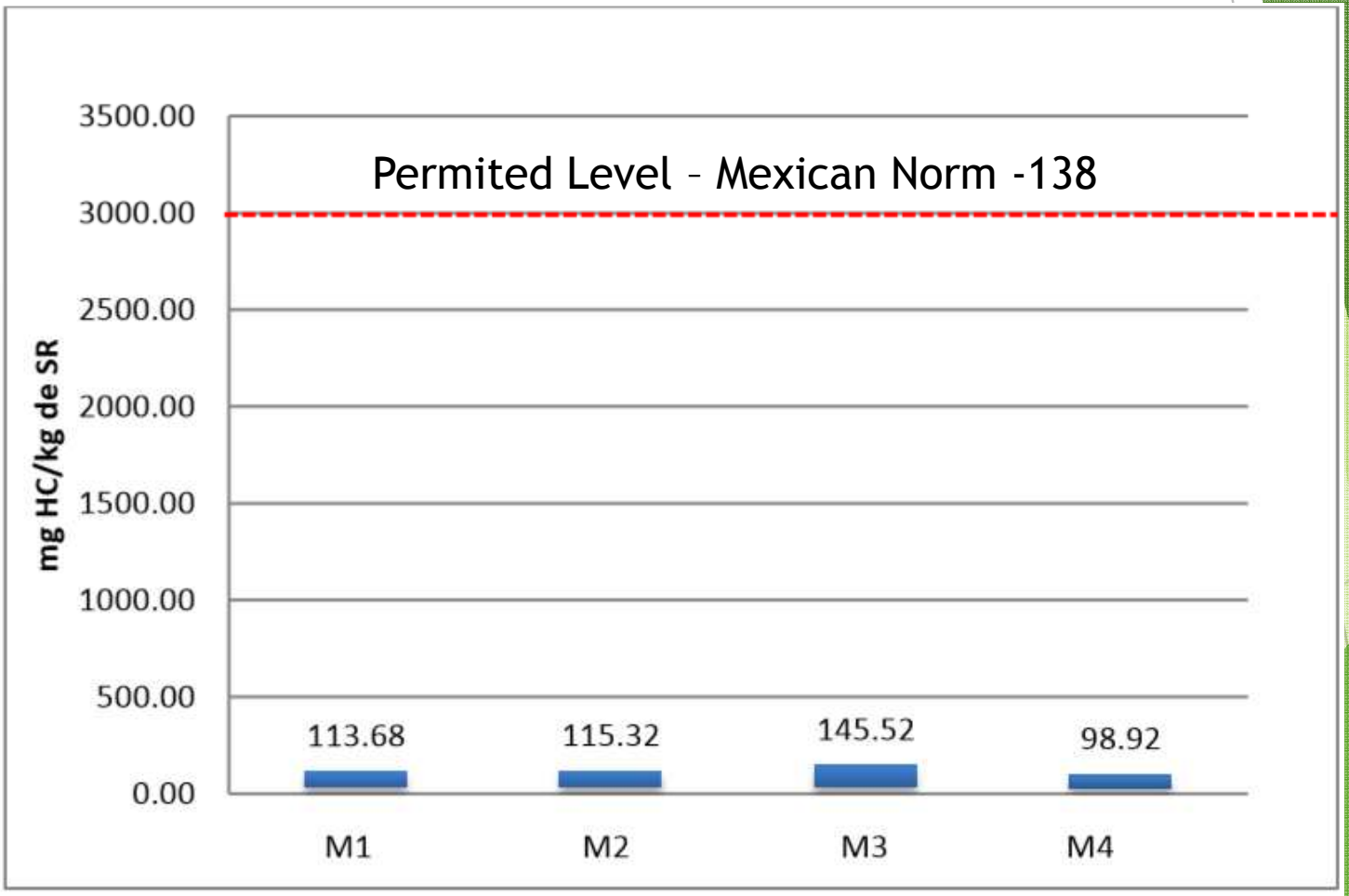


Model Assumes:

- TCLP is reasonable approximation to real site conditions
- All leachable hydrocarbons leach out into subsoil
- For conservative calculation, we assume all leached hydrocarbons accumulate in first 10 cm of subsoil
- Must meet Mexican Norm – 138 limits in subsoil (<3000 mg/kg)

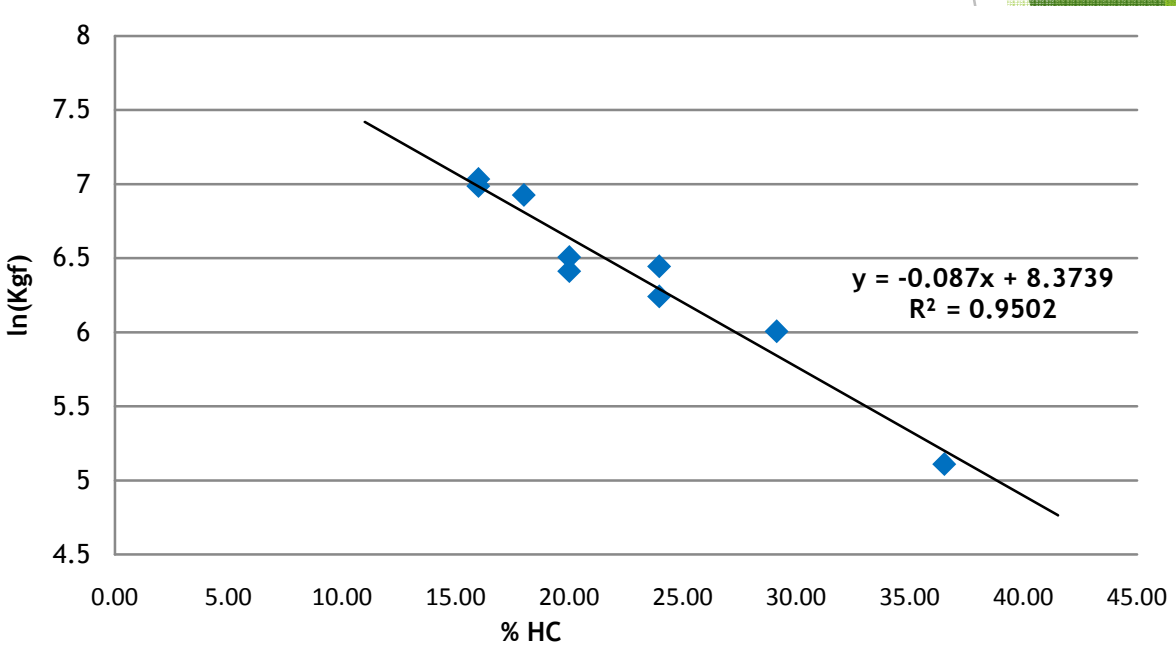
TCLP Leachate Tests Results

Leachate → Hydrocarbon concentration in subsoil (equiv.)



Optimization Tests for Marshall Stability

- **Objective 1) use as much HC as possible – and still pass test (avoid stabilization as much as possible - $)**
- **Objective 2) use as little gravel as possible – and still pass test (simplify logistics and reduce costs)**



Maximum passing test (700 Kgf) = 18% HC

CONCLUSIONS

- **Very weathered HC - non-toxic, non-leachable, non-biodegradable**
- **Formation of Man-made Asphaltic Geysers – nuisance**
- **Treatment options: stabilization cells – OK**
  solidification for beneficial use – road base
- **Field test for stabilization cells had excellent results**
  →but is more costly
- **Preliminary test for road-base:**
  → pass unconfined resistance and leachate
- **Optimization tests for maximum HC in road base: up to 18%!**
- **Don't put sandy overfill on old oily residues → they bubble back up!**

Natural Asphaltic Geyers (~50,000 yrs old)

La Brea (Hollywood, CA)

Oil field in 1870s

Comparison of Natural and Man-made Asphaltic Geysers

Sample	SG (60°F)	asphaltenes (%)	weathering (%)
MCH-1 chapopote CPGA	1.24	62	97
MCH-2 chapopote CPGA	1.11	62	87
MCH-3 chapopote CPGA	1.15	63	91
La Brea (Holloywood) ~50,000 yrs	1.42	--	100+

Comparison of Natural and Man-made Asphaltic Geysers

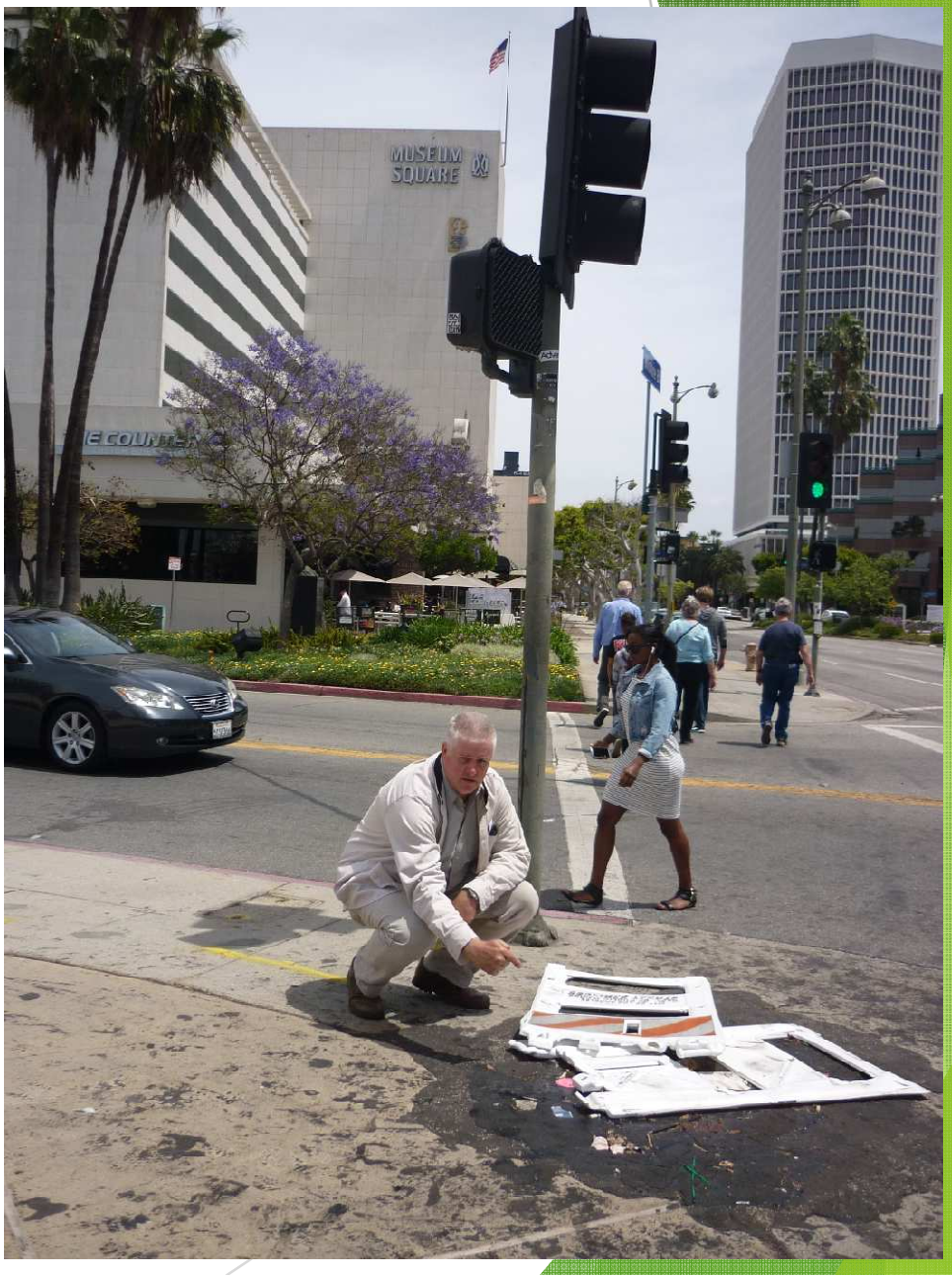
Natural Asphaltic Geyser
~50,000 yrs old

La Brea
(Hollywood, CA)

Oil field since 1870s

Urbanized 1910-20s

…and they still can't stop the flow!



Thank you for your attention and enjoy New Orleans!

Natural Asphaltic Geyser
~50,000 yrs old

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Oil field since 1870s

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