



Alternative Method for Establishing Clean-up Criteria for Agriculture Based on API Gravity

Randy H. Adams, Carlos M. Morales-Bautista, and J. Gilberto Torres-Torres

**Universidad Juárez Autónoma de Tabasco
Villahermosa, Tabasco, Mexico**

drrandocan@hotmail.com





BACKGROUND

- **Clean-up criteria for petroleum contaminated soils developed in US in 60's and 70's on drilling cuttings**
- **1% considered OK – no or only slight damage to crops, only lasts one growing season**
- **Bioassays confirmed low toxicity of residual oil**
- **Subsequently used as a basis for clean-up criteria for hydrocarbons in soils in many countries**
 - **does not consider kind of hydrocarbons**
 - **does not consider kind of soil**



BACKGROUND

- In Mexico NOM-138-SEMARNAT-2003:
 - 1,200 ppm - mid-range HC in non-industrial sites
 - 3,000 ppm - heavy-range HC, non-industrial sites
 - Hydrocarbon range based on Carbon Number (C_{11-28} , C_{28+})
 - Criteria based on relative toxicity
- Analysis: mid-range: GC (EPA 8015)
Heavy-range: gravimetric/hexane (EPA 1664A)
- However, many remediated sites in SE Mexico present problems with soil fertility – at only 0.3%



BACKGROUND

- **Evidence from US, Canada, SE Mexico indicate potential fertility problems, especially with weathered hydrocarbons:**
 - **More weathered HC molecules act as chemical bridges between SOM and non-polar HC**
 - **Important in formation of hydrocarbon layers on soil particles:**
 - **Water repellency and field capacity**
 - **Cation Exchange Capacity**
 - **Compaction**

Model for Soil Water Repellency

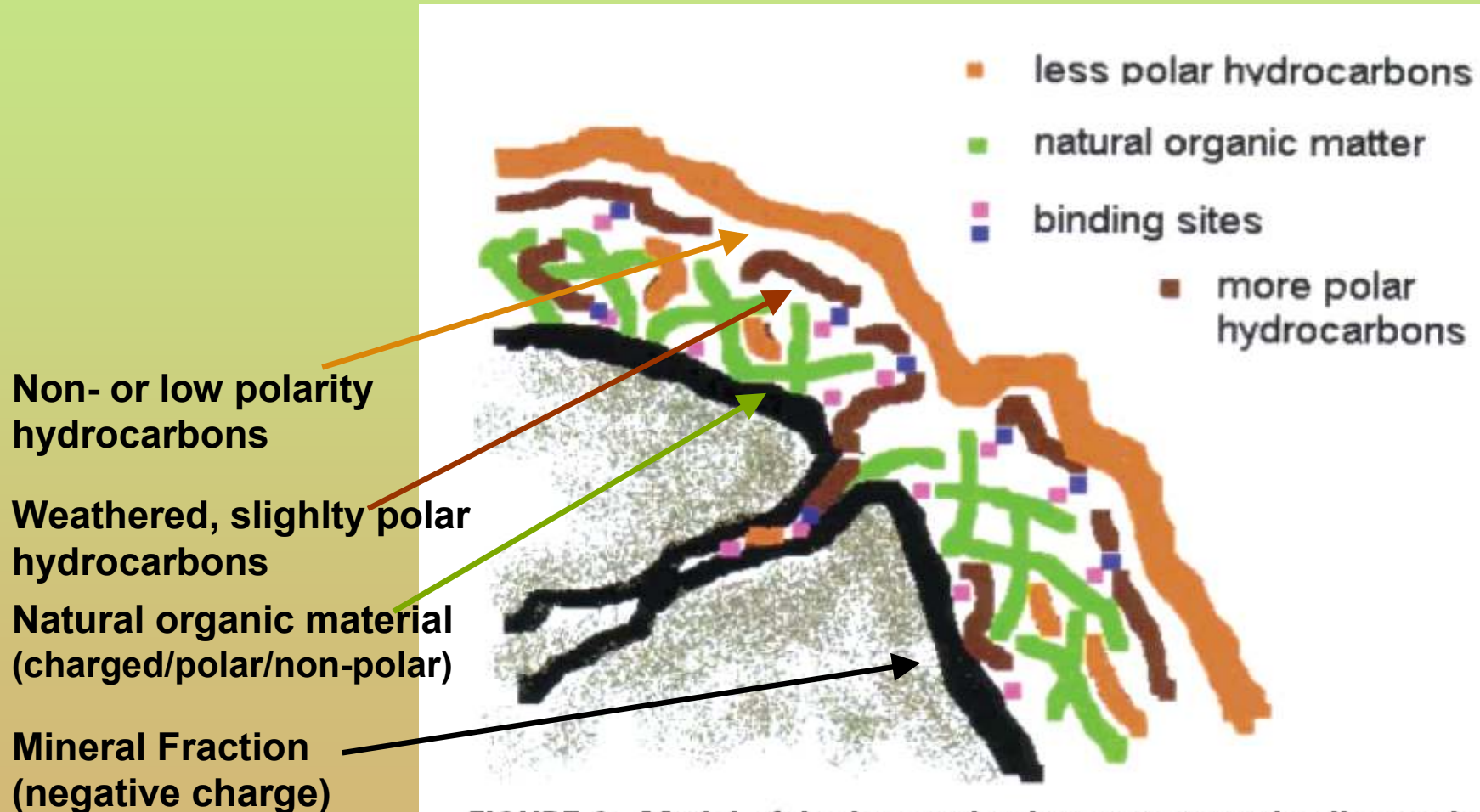


FIGURE 6. Model of the interaction between natural soil organic matter (NOM) and the diagenetic products of petroleum contamination that generates water repellency. (From: Litvina *et al.* 2003)

Soil Water Repellency



Soil Water Repellency



Soil Water Repellency



Soil Water Repellency





SISTEMATIC EVALUATION

- Selection of superlight, light, medium, heavy and extra-heavy petroleums
- PCE extraction of weathered and burned oil from contaminated sandy soil
- Determination of °API (SG) by hydrometer and dilution-extrapolation method (for extra-heavy, and low conc.)
- Group fractions by sequential column extraction with selective solvents and gravimetric analyses
- Predominant functional groups by FTIR
- Water repellency in alluvial soil by modified MED method



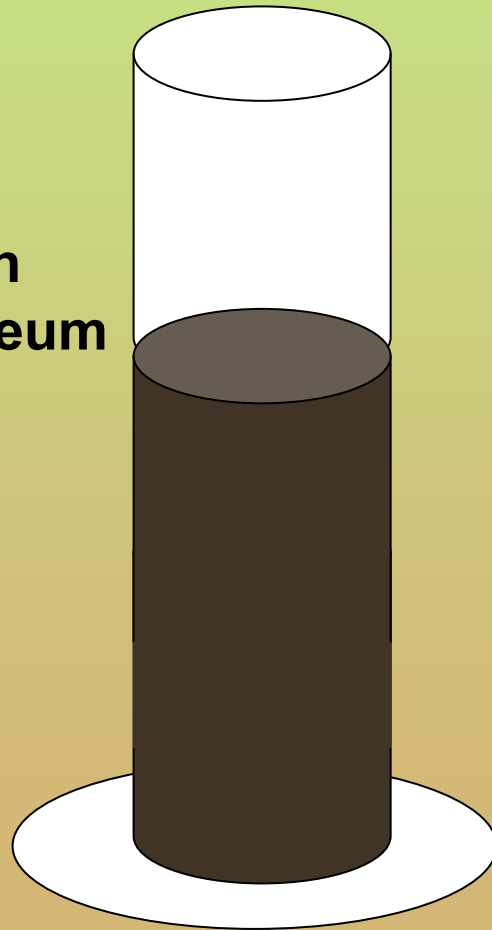
Alternative Method for °API

- °API – used in petroleum industry to classify petroleum according to density (specific gravity)
- Normalized for temperature (60 °F, 15.6 °C)
- Standard hydrometer method uses ~ 1/2 L of petroleum)
- Not practical for viscous hydrocarbons (extra-heavy/weathered)
- Not practical for hydrocarbons in soil (in low concs.)

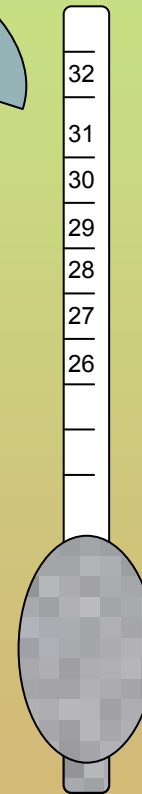


Standard Method for °API

Cylinder with
crude petroleum

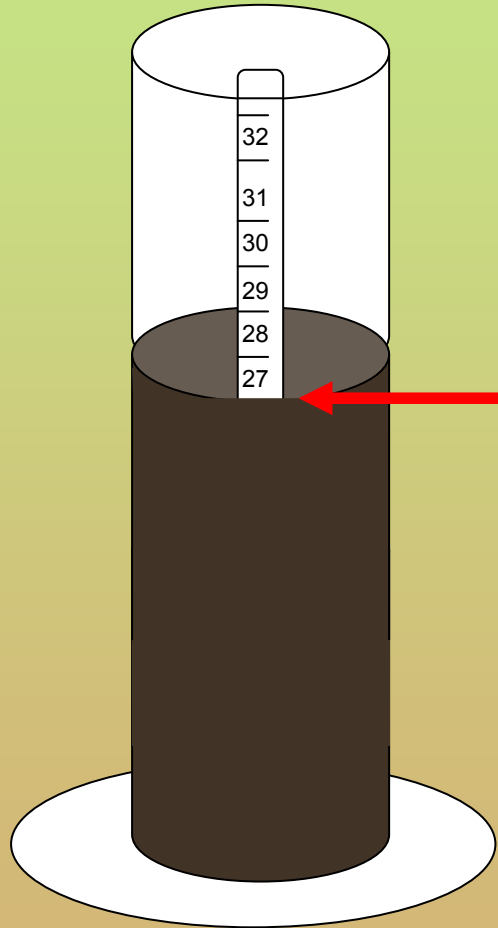


Calibrated Hydrometer





Standard Method for °API



°API Reading

$$^{\circ}\text{API} = (141.5/\text{SG}) - 131.5$$

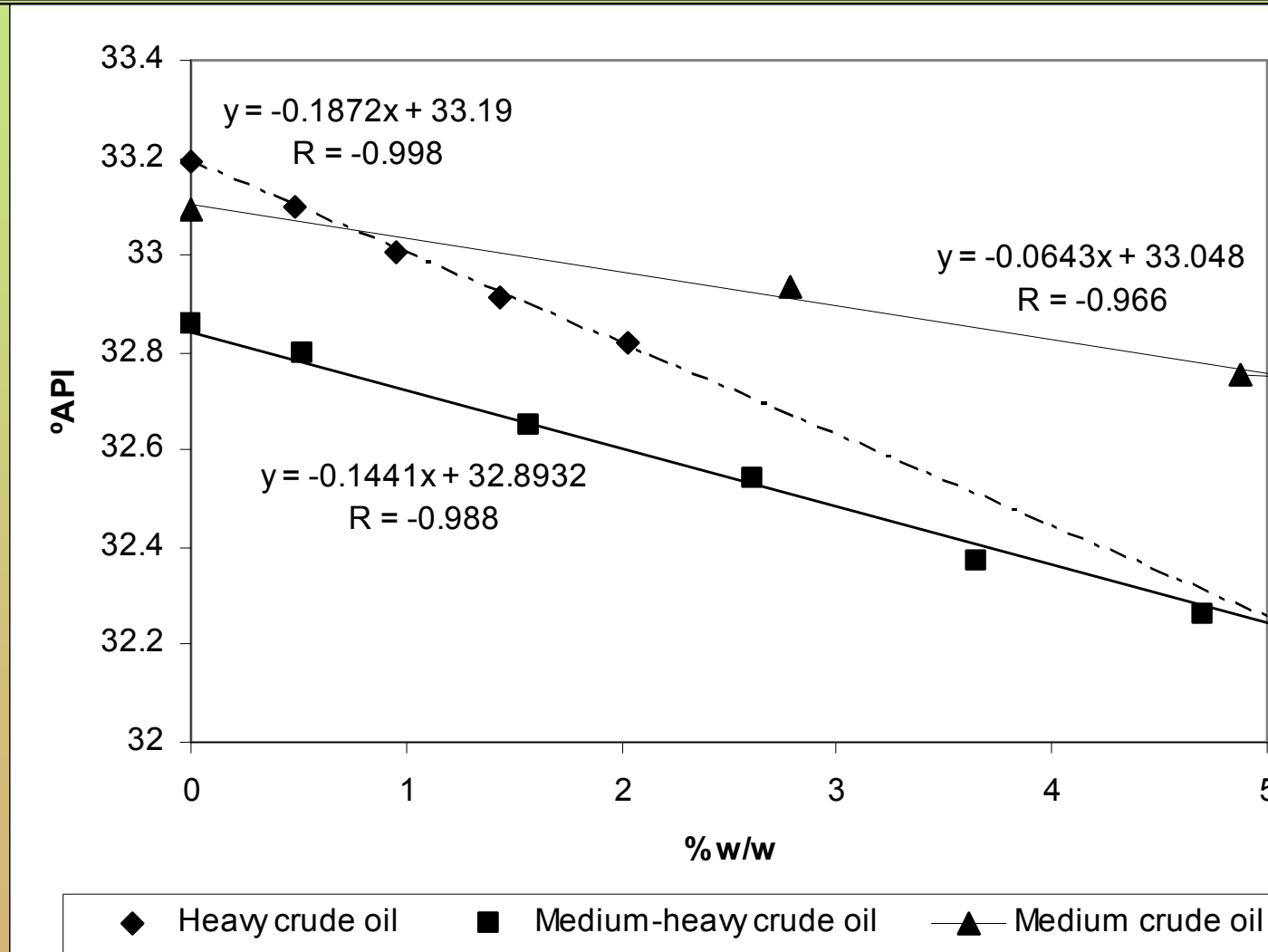


Alternative Method for °API

- **Solvent: evaporated diesel + automotive lubricant to obtain a mixture with approx. 28 – 34 °API**
- **Add crude petroleum in small quantities (0.5 – 5%) reading °API at each dilution (correct for temp.)**
- **Extrapolate to 100% petroleum to determine °API and specific gravity**
- **Uses small quantities (2 – 10ml) of petroleum**
- **Works well for extra-heavy/weathered oil**
- **Simple, materials easily available**
- **Good reproducibility, good precision and exactness**



METHODS



Dilution-Extrapolation Method for °API Determination



RESULTS

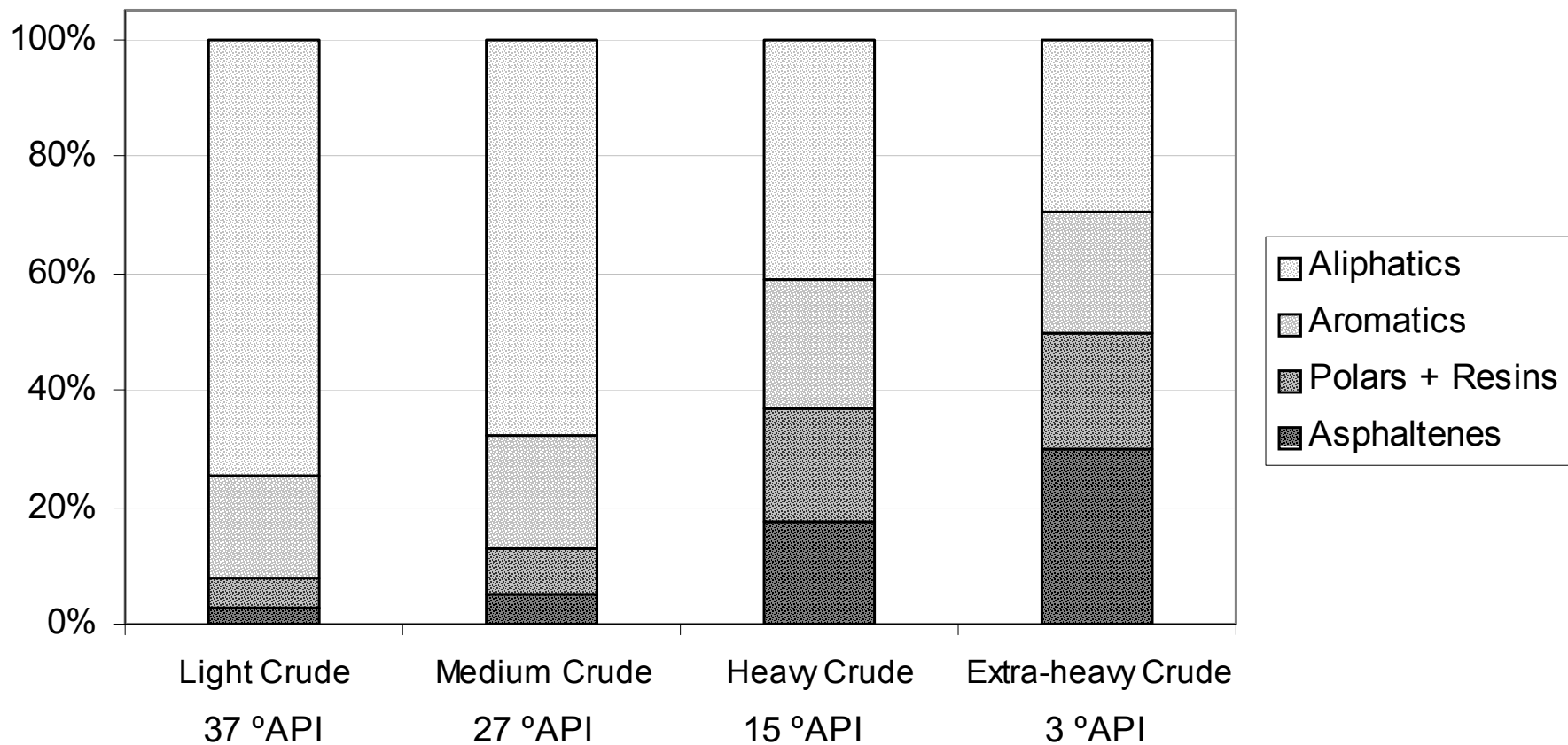
API Gravity and Specific Gravity of Petroleums

Classification	Origin	°API	Specific Gravity
Light Crude	Pipe-line spill (Cumuapa, Tabasco)	36.6	0.842
Medium Crude	Tank storage facility (Comalcalco, Tab.)	27.4	0.891
Heavy Crude	Sulphur well (Texistepec, Veracruz)	15.0	0.966
Extra-heavy Crude	Holding pond (Texistepec, Veracruz)	3.4	1.049
Super Light Crude	Separation battery (Cunduacán, Tab.)	39.9	0.826
Weathered and Burned Oil	Separation battery (Pailebot, Tabasco)	-----	1.273

$$\text{°API} = (141.5/\text{SG}) - 131.5$$



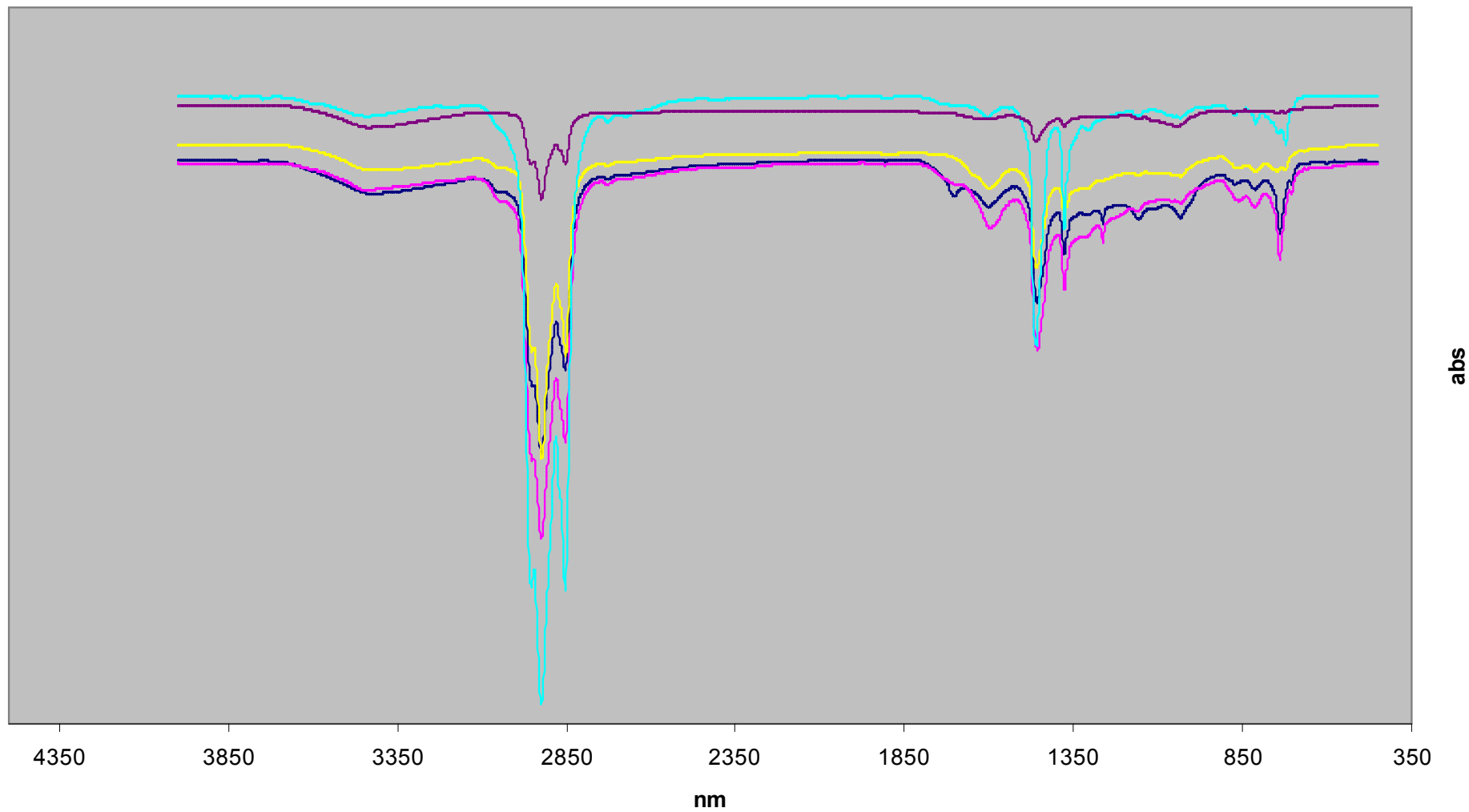
RESULTS



Crude Petroleum Fraction Compositions

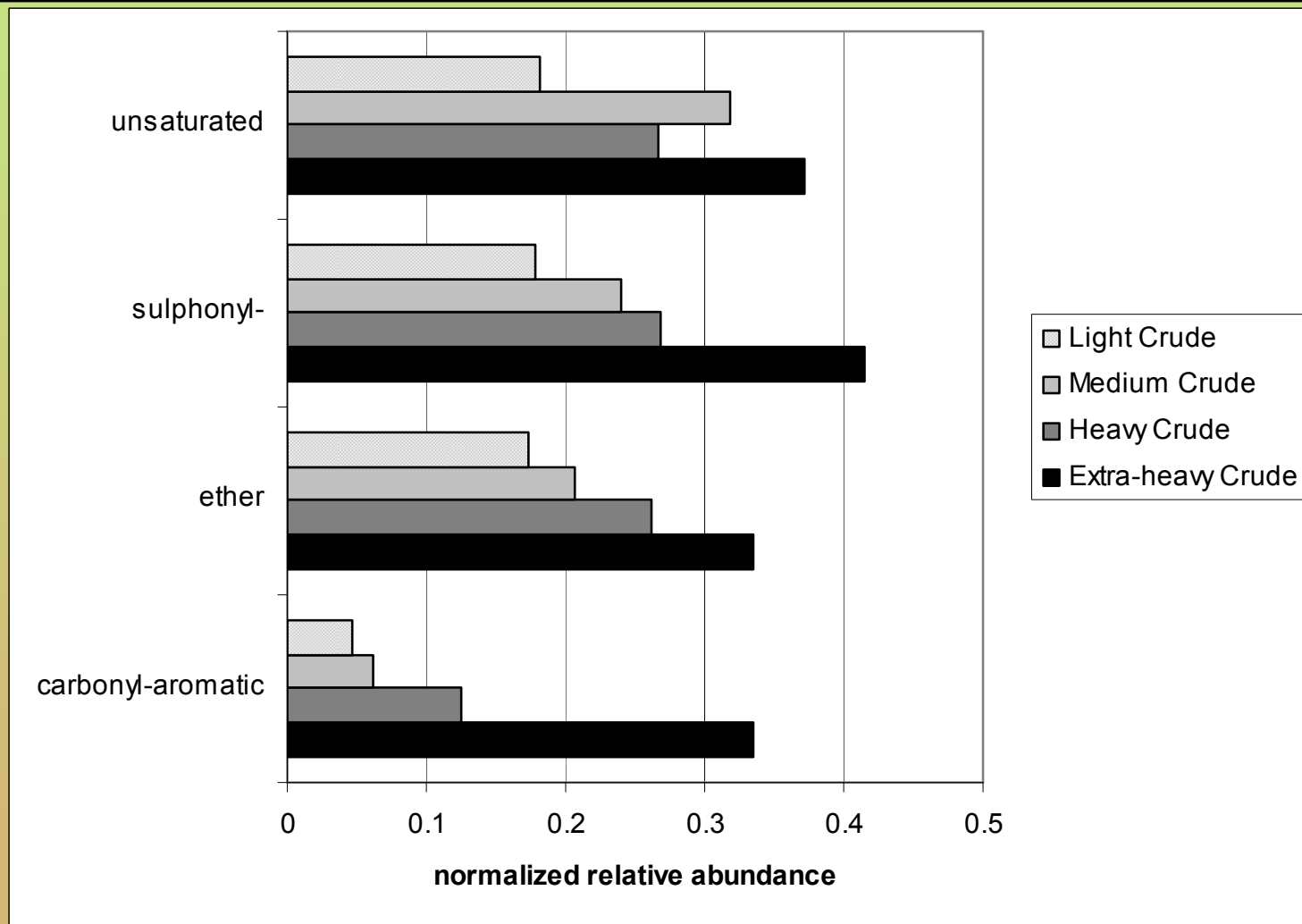
IRFT-A

— PI — PP — PM — PL — PSL





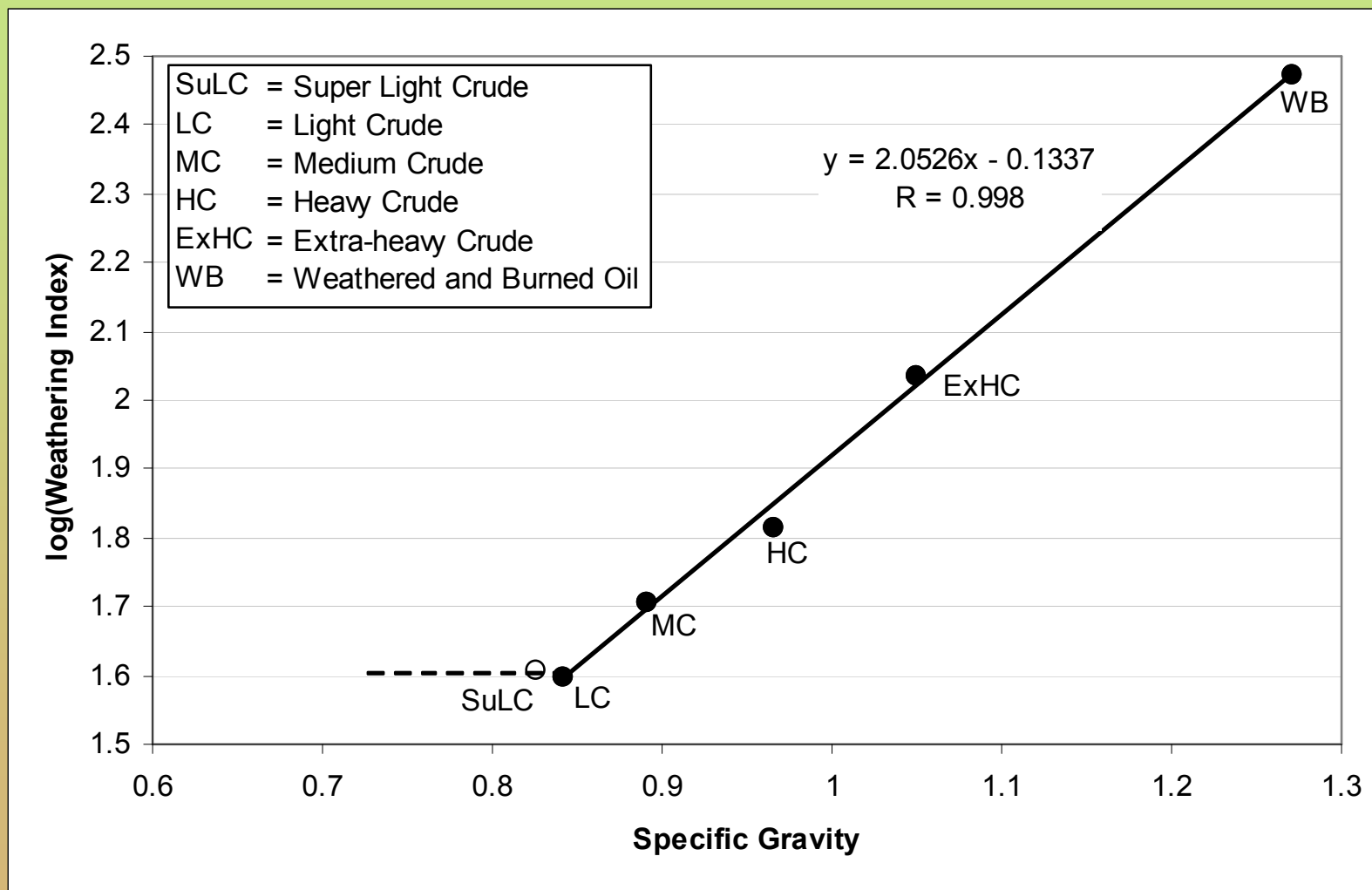
RESULTS



Relative Abundance of Functional Groups in Crude Petroleums



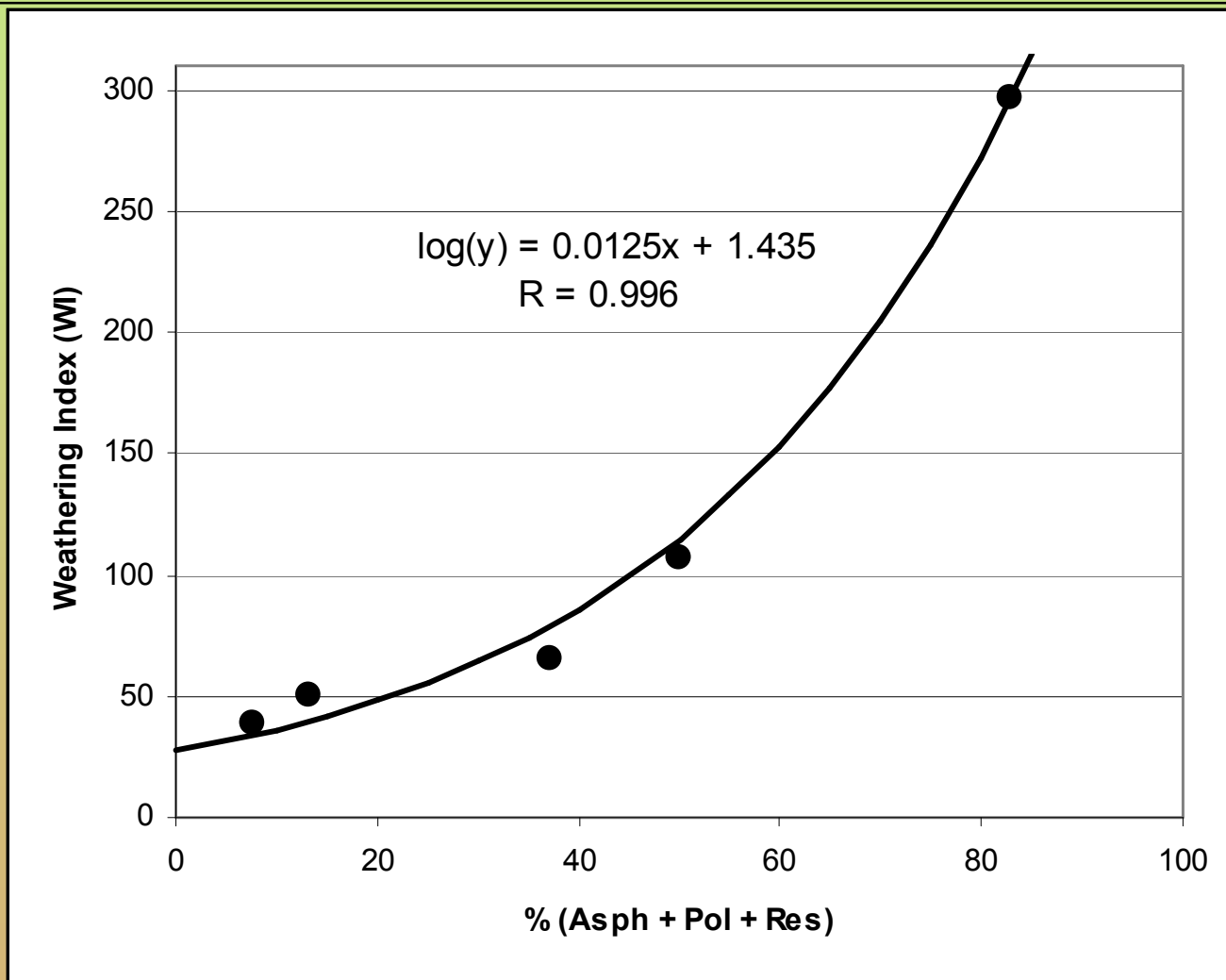
RESULTS



Relationship between Specific Gravity and the Weathering Index



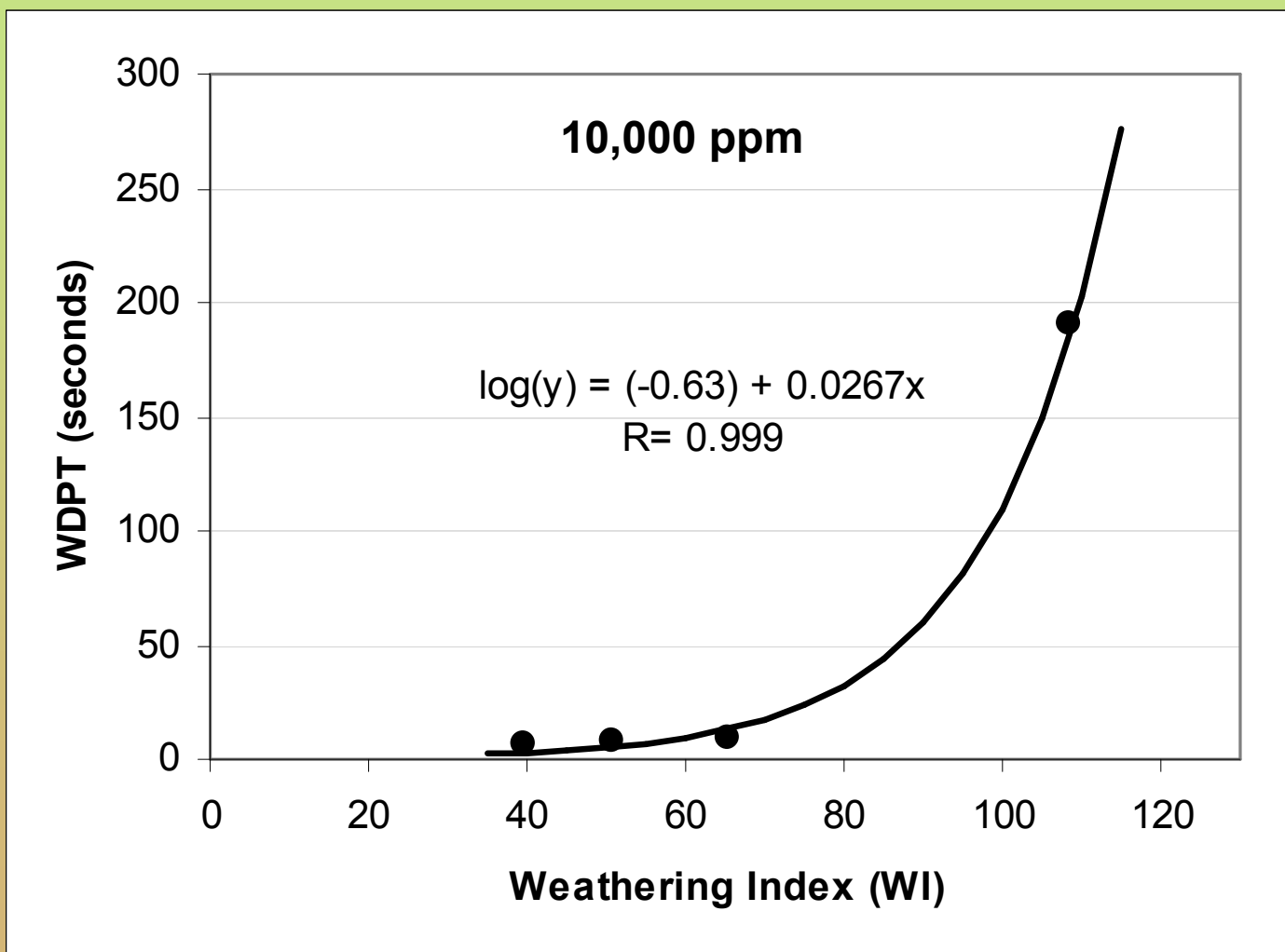
RESULTS



Relationship between Asphaltene, Polars and Resin Content vs. Weathering Index



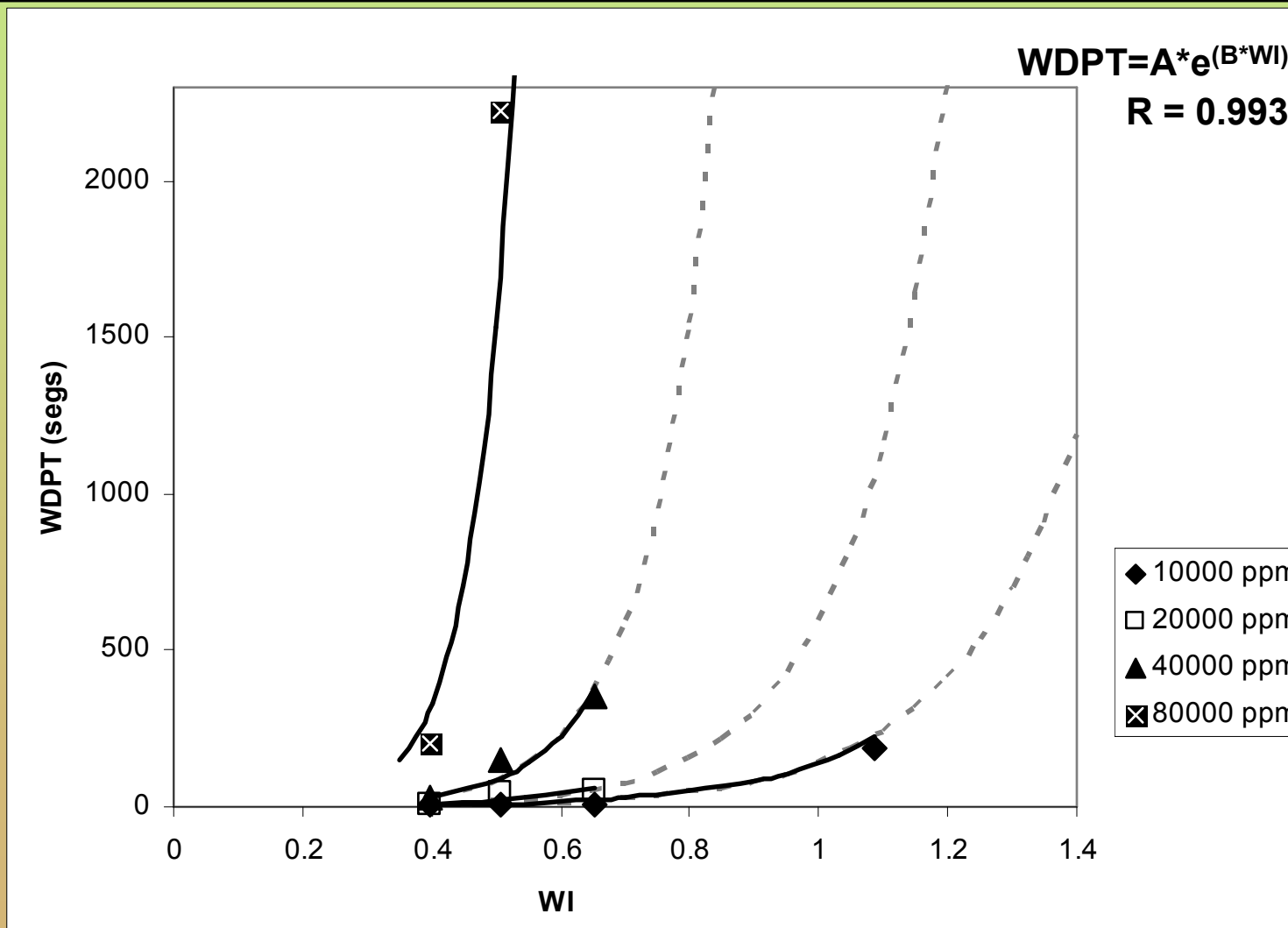
RESULTS



Relationship between Weathering Index and Water Repellency in a Fluvisol



RESULTS



Relationship between Weathering Index and Water Repellency in a Fluvisol



CONCLUSIONS

- Heavier petroleum has more asphaltenes, polars and resins:
 - increase density ($^{\circ}\text{API}$ or SG)
 - increase relative abundance of polar functional groups
 - derivation of Weathering Index, proportional to SG ($^{\circ}\text{API}$)
- WI and HC concentration are proportional to water repellency
- By determining $^{\circ}\text{API}$ of oil in soil + HC conc. can predict impacts to soil water repellency – soil fertility
- Can use to establish clean-up criteria to avoid problems with soil fertility



CONCLUSIONS

- Criteria based on HC conc. + °API (not Carbon Number)
- Criteria is gradual, not in steps (°API vs. C_{5-10} , C_{10-28} , C_{28+})
- Dilution-Extrapolation method developed to measure °API of oil in soil with extra-heavy oil and also in small quantities (10 g)
- Simple and easy, does not require specialized equipment (only a hydrometer)

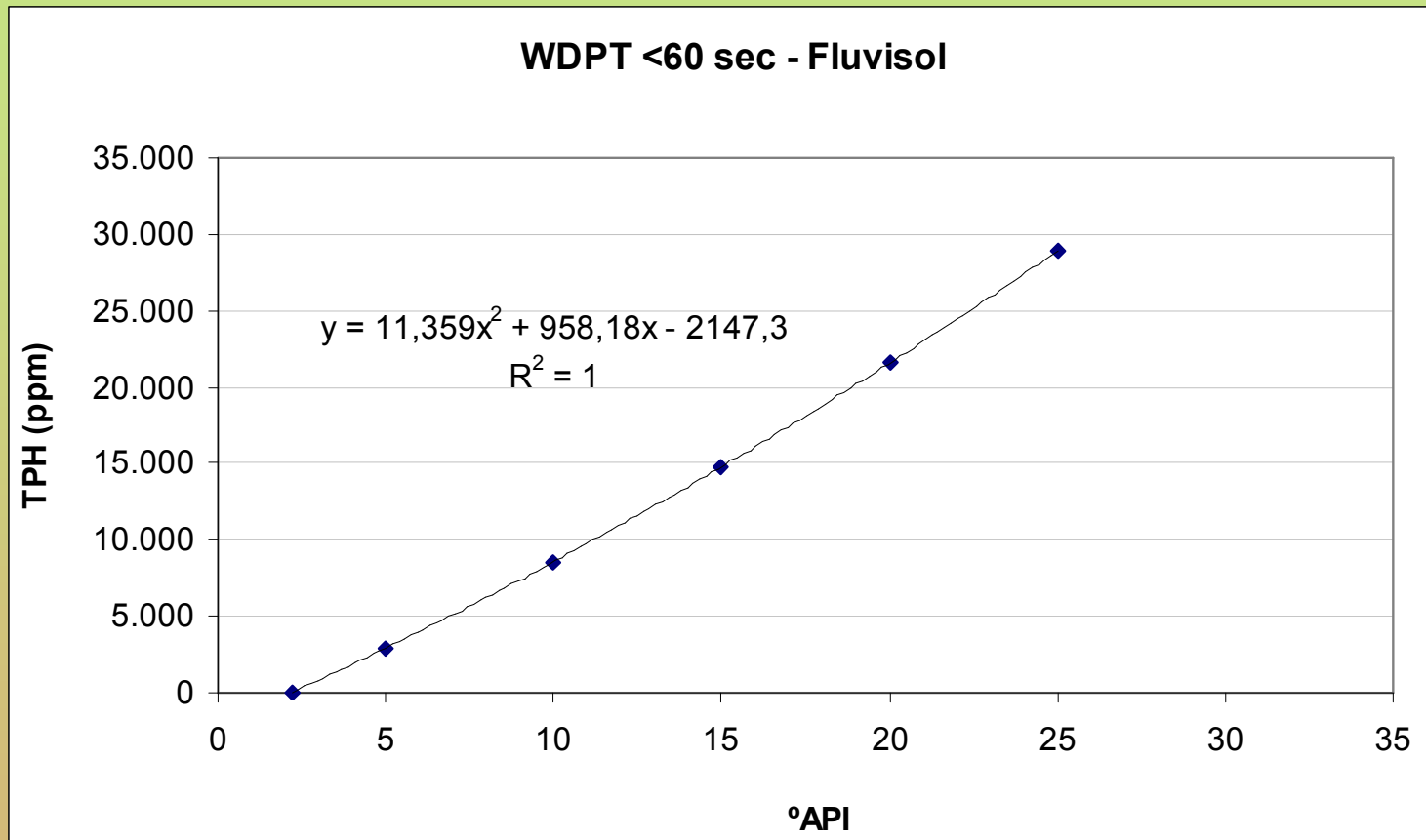


CONCLUSIONS

- **Up to 30% of heavy oil may be asphaltenes: not toxic but cause fertility problems**
- **Important to measure TOTAL HC conc. (not only hexane soluble)**
 - **DCM/Sohxlet-gravimetric or PCE/IR Spectrometry**
- **Note criteria are MORE demanding for heavier oil than medium or light oil (opposite of Mexican Norm, and many US states)**



CONCLUSIONS



- Note: specific to soil type (type and quantity of clays and SOM)
- Sandy soils even more sensitive, clayey soils more resilient
- May modify soil to improve fertility (soil amendments or chemical treatment)

Gracias por su atención

