Integrated Evaluation of Petroleum Impacts to Soil

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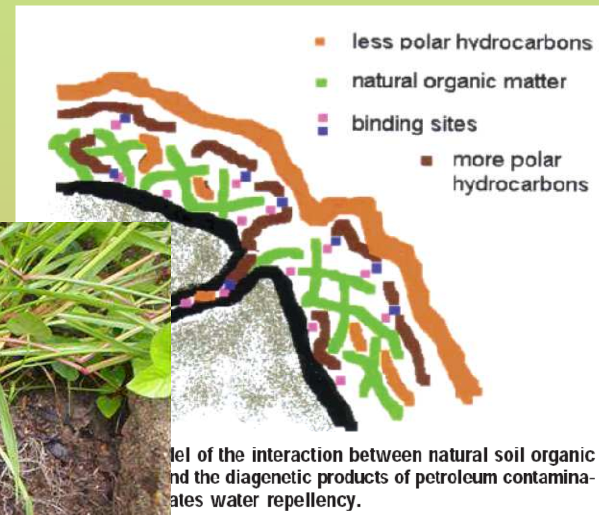

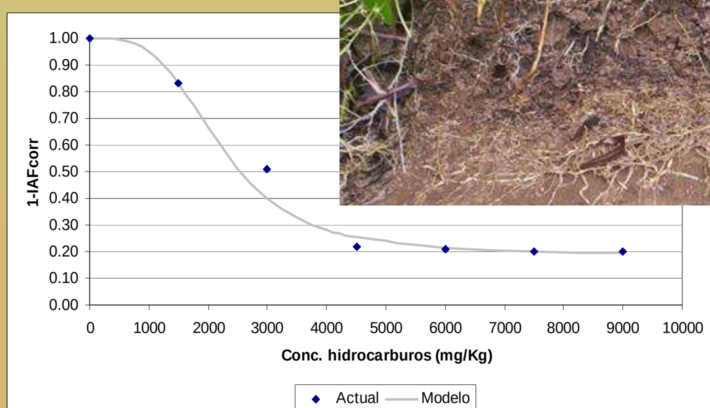

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BACKGROUND

- 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
- Subsequenty used as a basis for clean-up criteria for hydrocarbons in soils in many countries

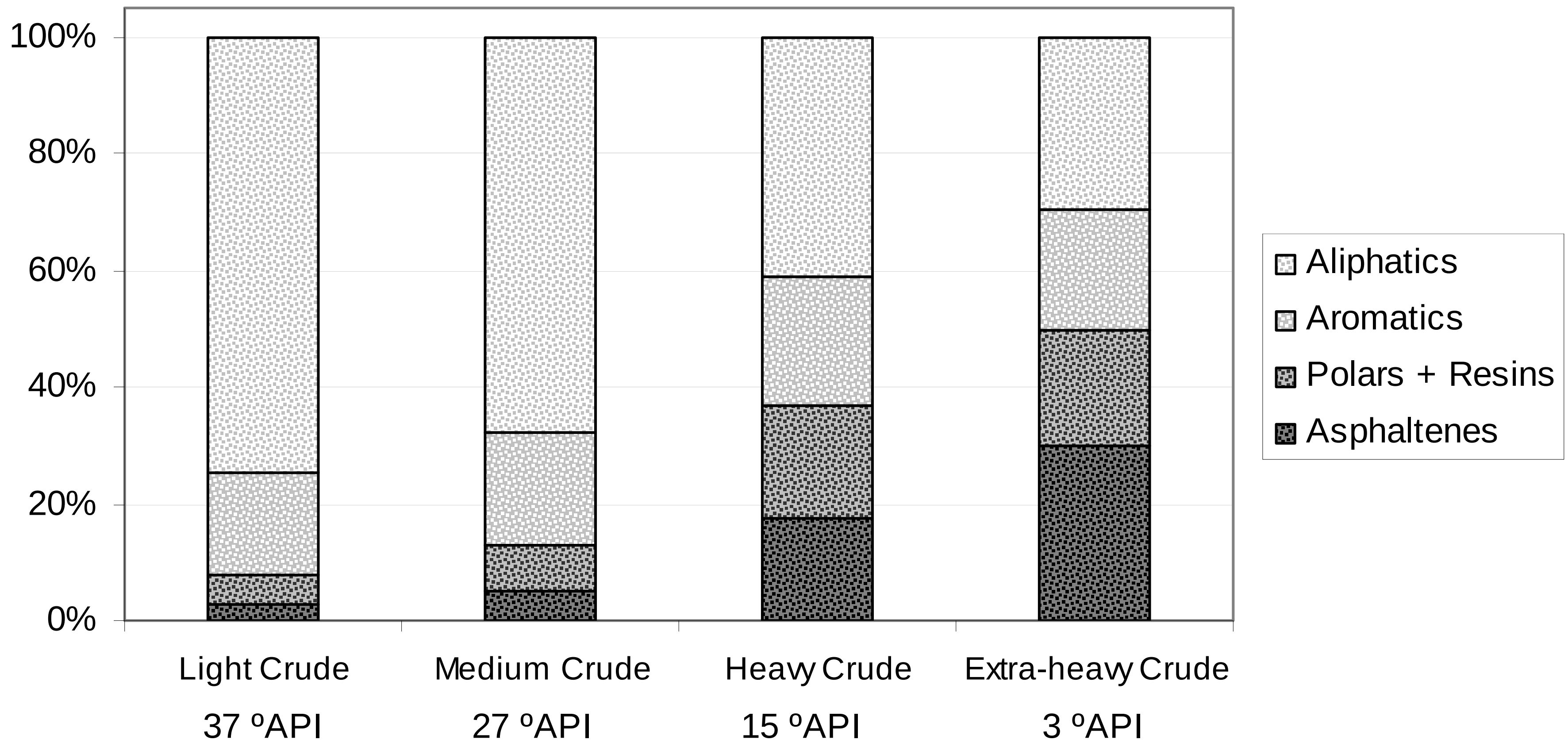
→ does not consider kind of hydrocarbons

→ does not consider kind of soil

SISTEMATIC EVALUATION

- **Selection of light, medium, heavy and extra-heavy crudes**
- **Selection of 5 soil types common in petroleum producing region of SE Mexico**
- **Contamination of soil at different concentrations**
  - **Measurement of acute toxicity (Microtox), and subchronic toxicity (28 d earthworm)**
  - **Measurement of impacts to soil fertility:**
    water repellency, soil moisure, compaction, complemented with *in situ* weathering experiments
  - **Measurement of plant growth: pasture, black beans**

Crude Petroleum Used in Study



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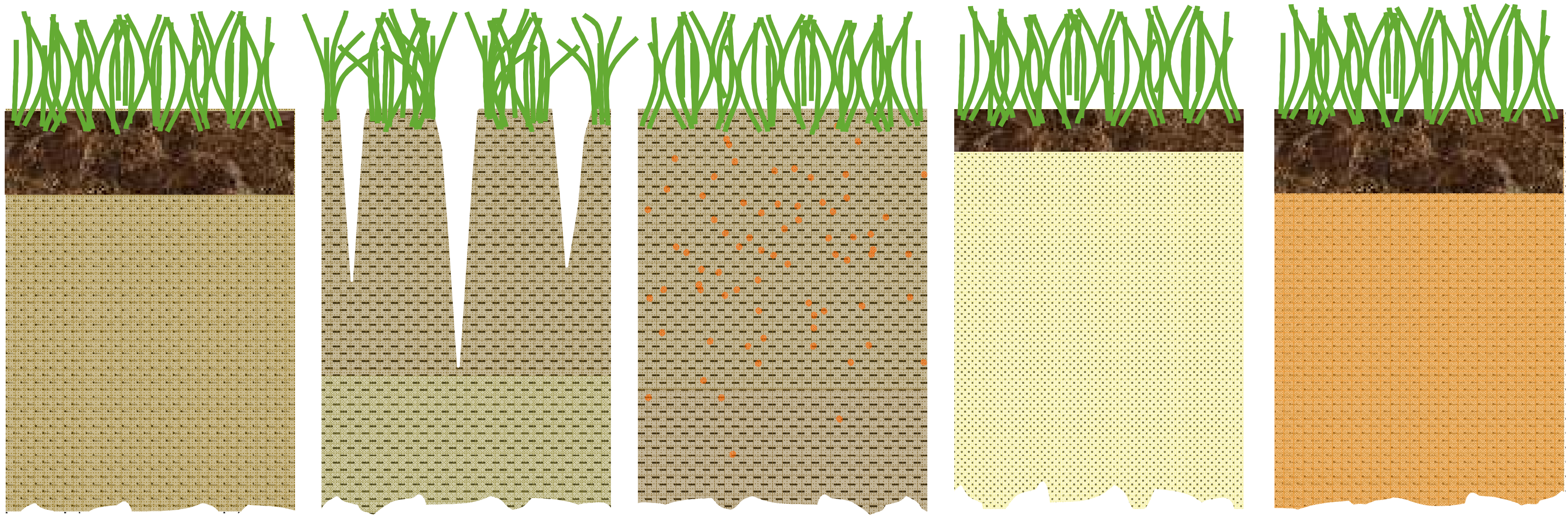


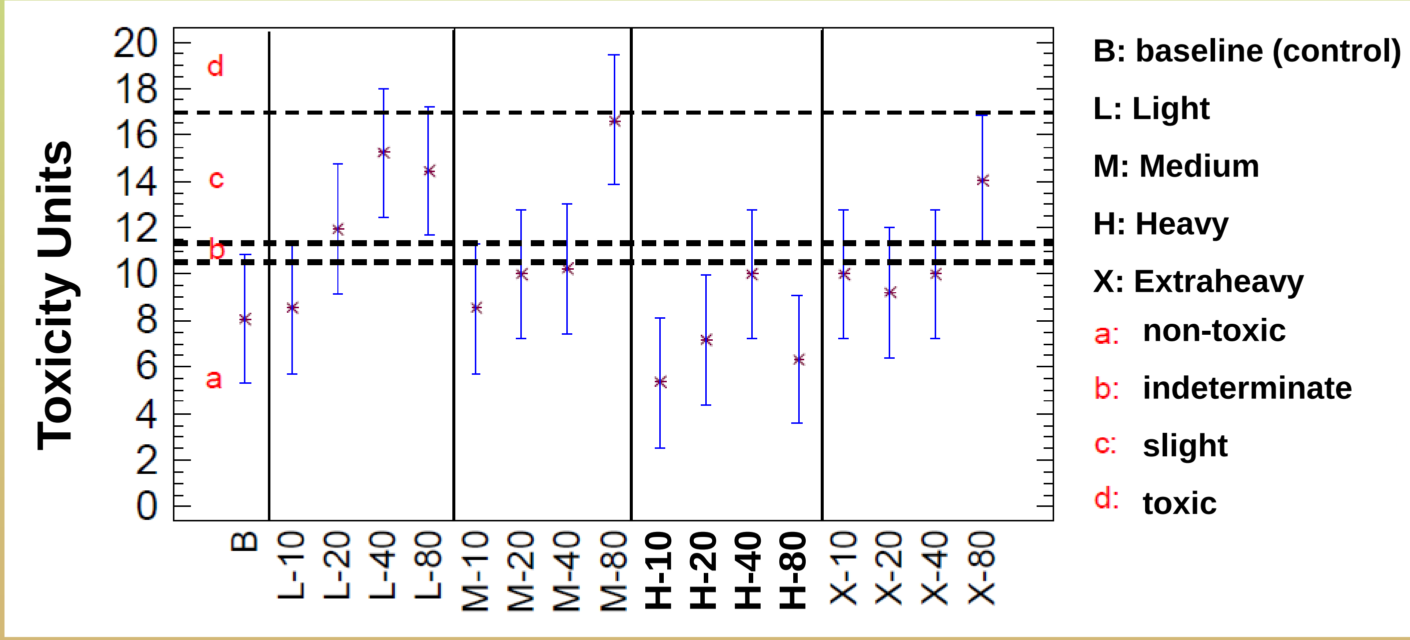
	FLUVISOL	VERTISOL	GLEYSOL	ARENOSOL	ACRISOL
FAO:	FLUVISOL	VERTISOL	GLEYSOL	ARENOSOL	ACRISOL
USDA:	FLUVENT	VERTISOL	GLEYSOL	PSAMMENT	ULTISOL
	• rich alluvial soil • medium texture • good internal drainage • aerobic conditions	• gilgai microrelief • high clay content • smectite clays: high shrink-swell capacity • poor internal drainage	• seasonally flooded • high clay content • smectite clays: high shrink-swell capacity • poor internal drainage	•coastal sandy soil •very low clay and silt content •excessive internal drainage	• weathered soil from Pleistocene Terrace • sandy-clay texture • clays: kaolinites and oxides of Fe/Al, – no shrink swell capacity
	cacao, maize, beans, pasture, sugarcane, watermellon, chiles, tomatoes	pasture, some maize	pasture, savannah oak (Macuilís)	pasture, coconuts	pasture, pineapple, citrus, sugarcane

Soils Used in Study

Acute Toxicity

•More toxic with lighter crude and in high concentrations

•However, at 1% non-toxic in acute test



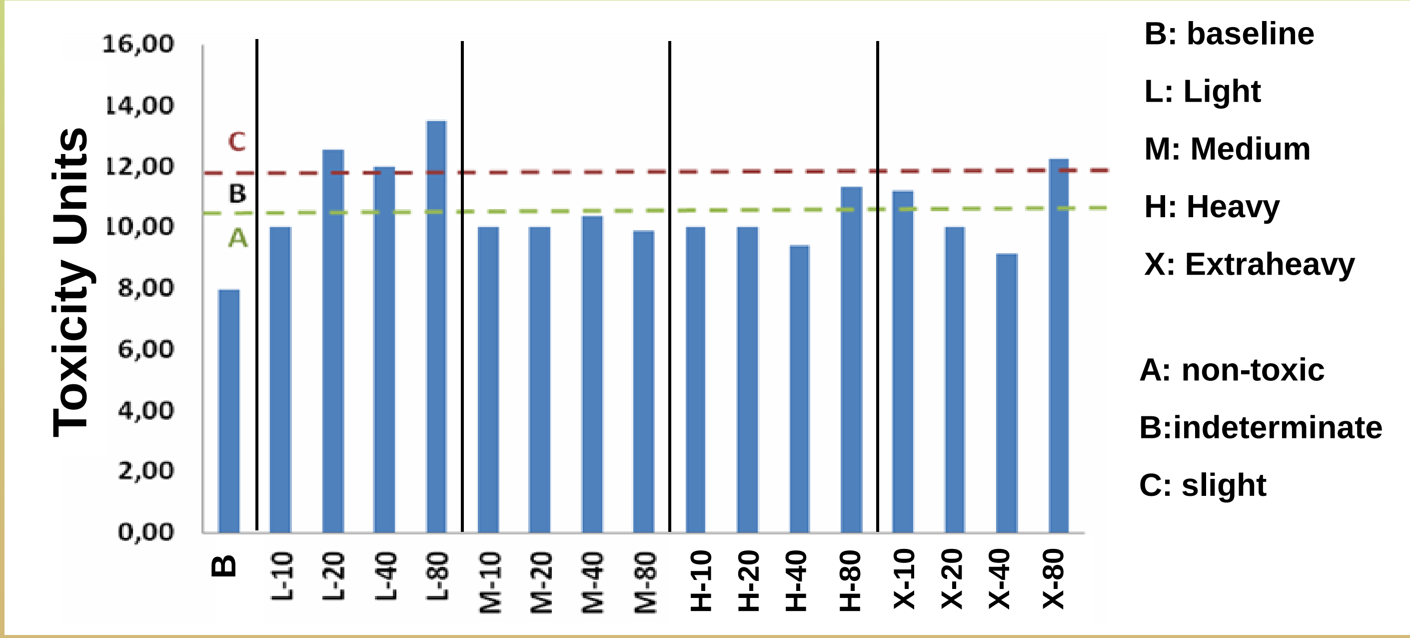
Arenosol

(Psamment)

sandy soil

Acute Toxicity

- More toxic with lighter crude and in high concentrations
- However, at 1% non-toxic in acute test



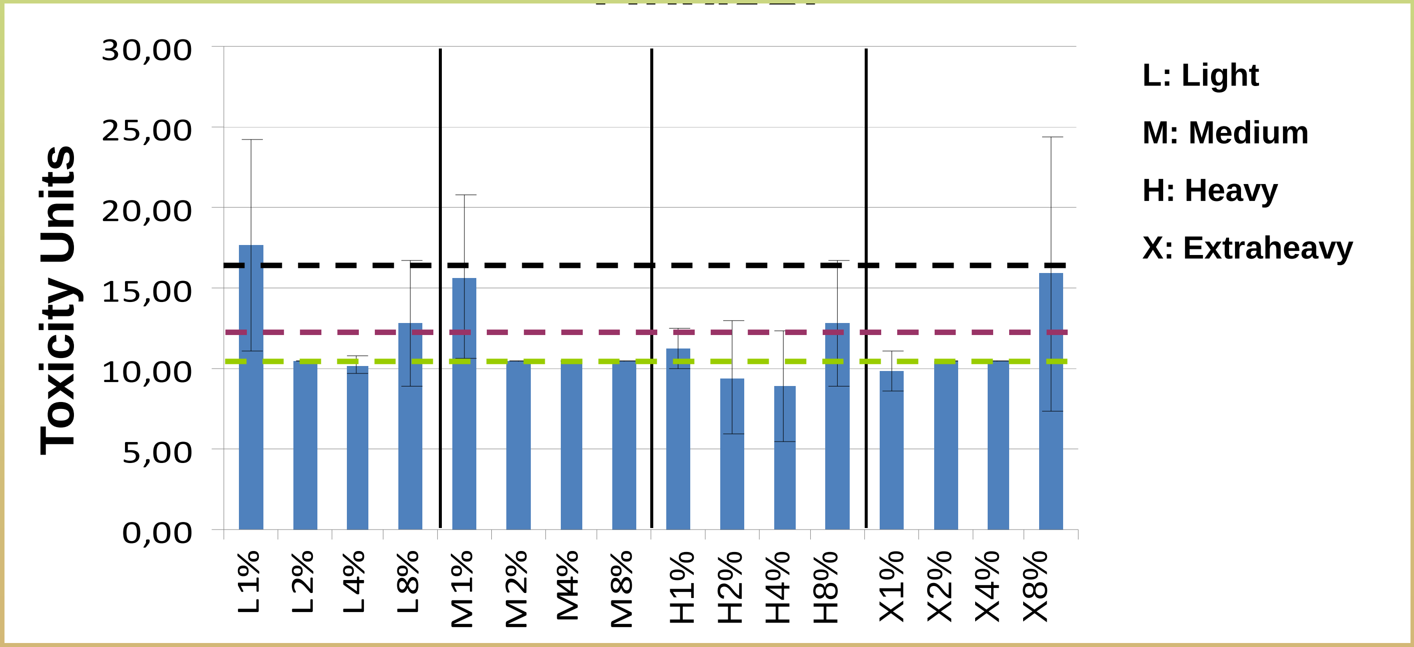
Acrisol

(Ultisol)

red clay soil

Acute Toxicity

- High variability with some samples
- In general, low-null toxicity in alluvial soils



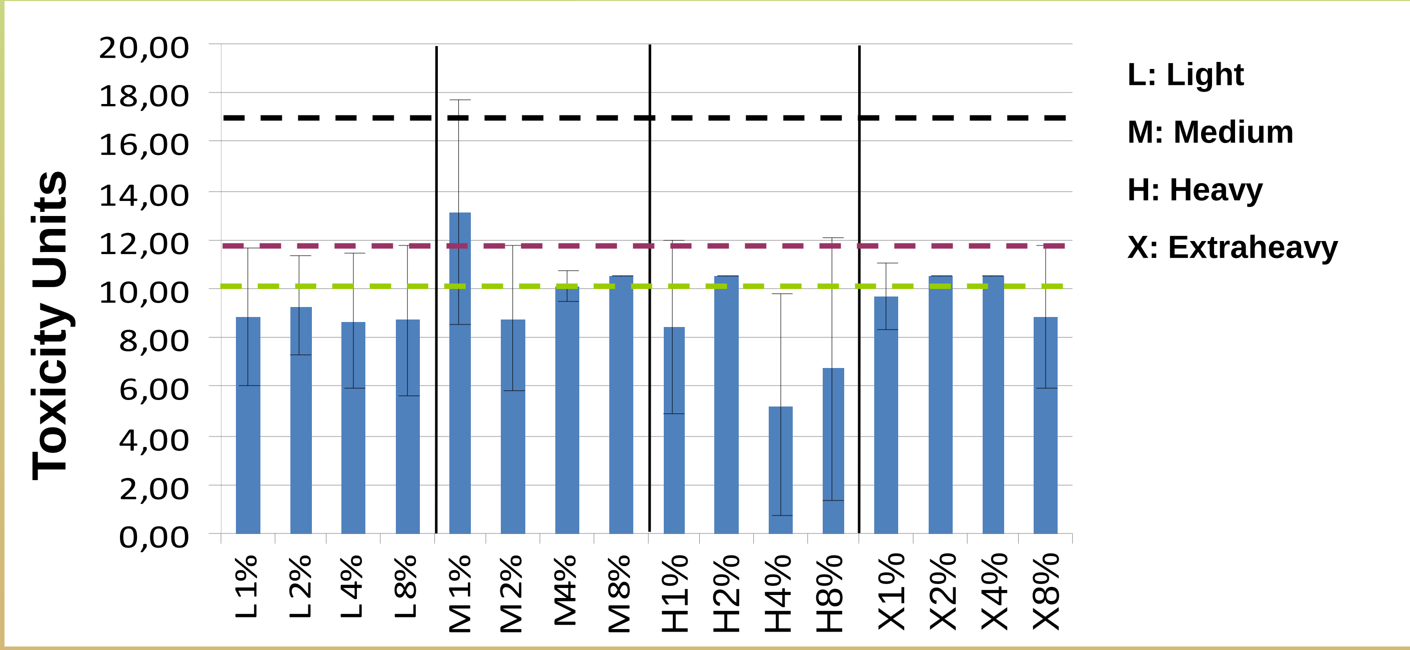
Fluvisol

(Fluvent)

river levee soil

Acute Toxicity

- High variability with some samples
- In general, low-null toxicity in alluvial soils

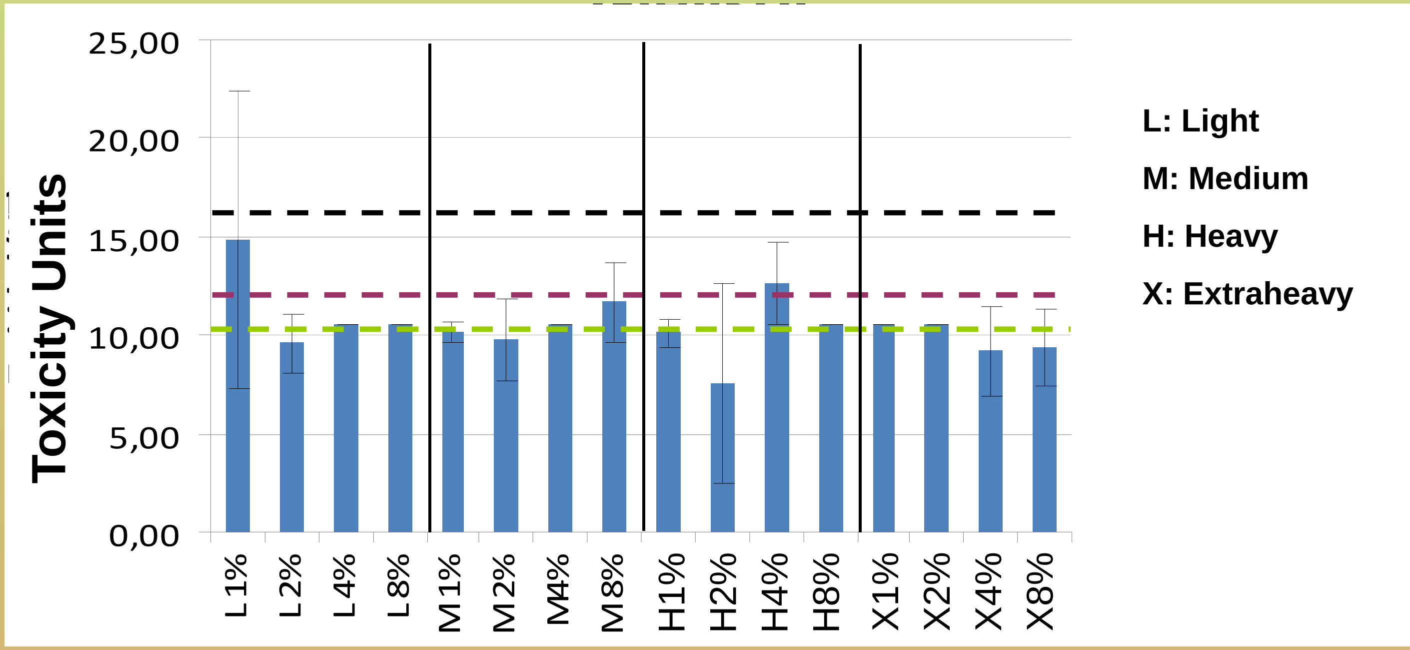


Vertisol

brown clay soil

Acute Toxicity

- High variability with some samples
- In general, low-null toxicity in alluvial soils



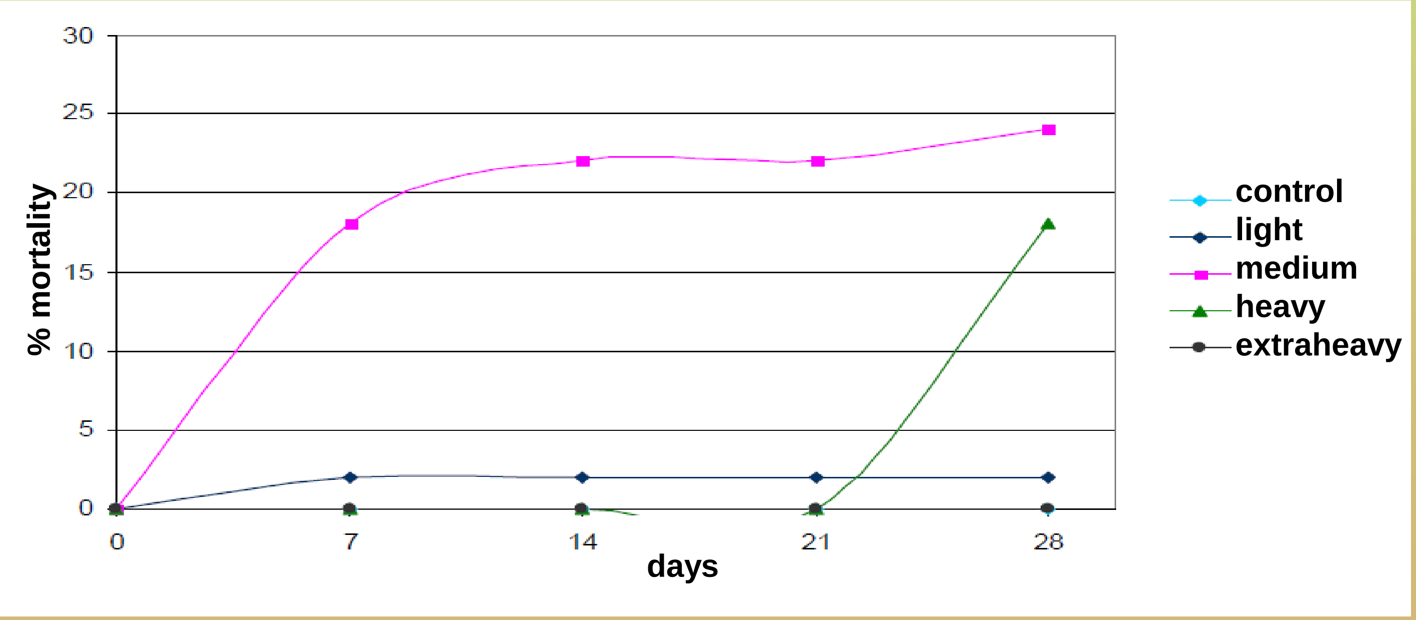
Gleysol

floodable brown clay soil

Subchronic Toxicity

•Limited toxicity with light crude, greater with medium crude

•No toxicity observed in heavy crude until 4 weeks (evasion?)



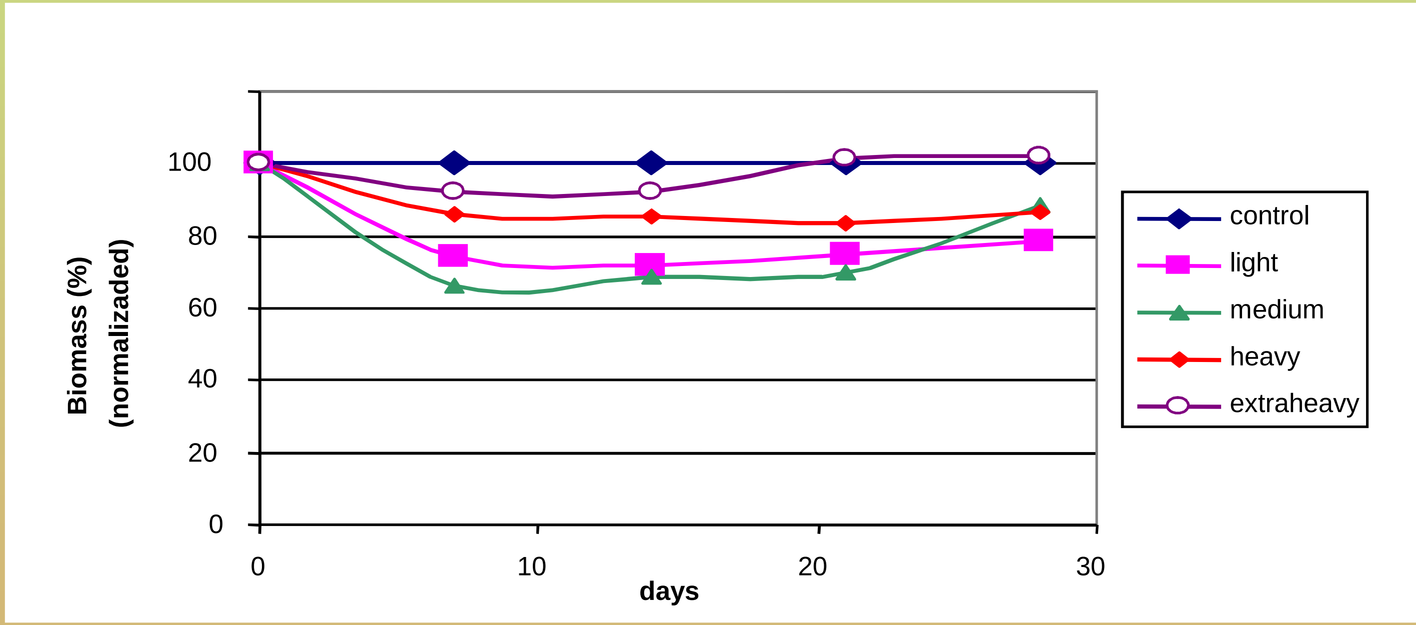
10000 ppm

Arenosol (Psamment)

sandy soil

Subchronic Toxicity

- •Biomass loss in first 2 weeks and then recovery (~2 mo. ?)
- •Recovery much slower with heavy crude



10000 ppm

Arenosol (Psamment)

sandy soil

Subchronic Toxicity

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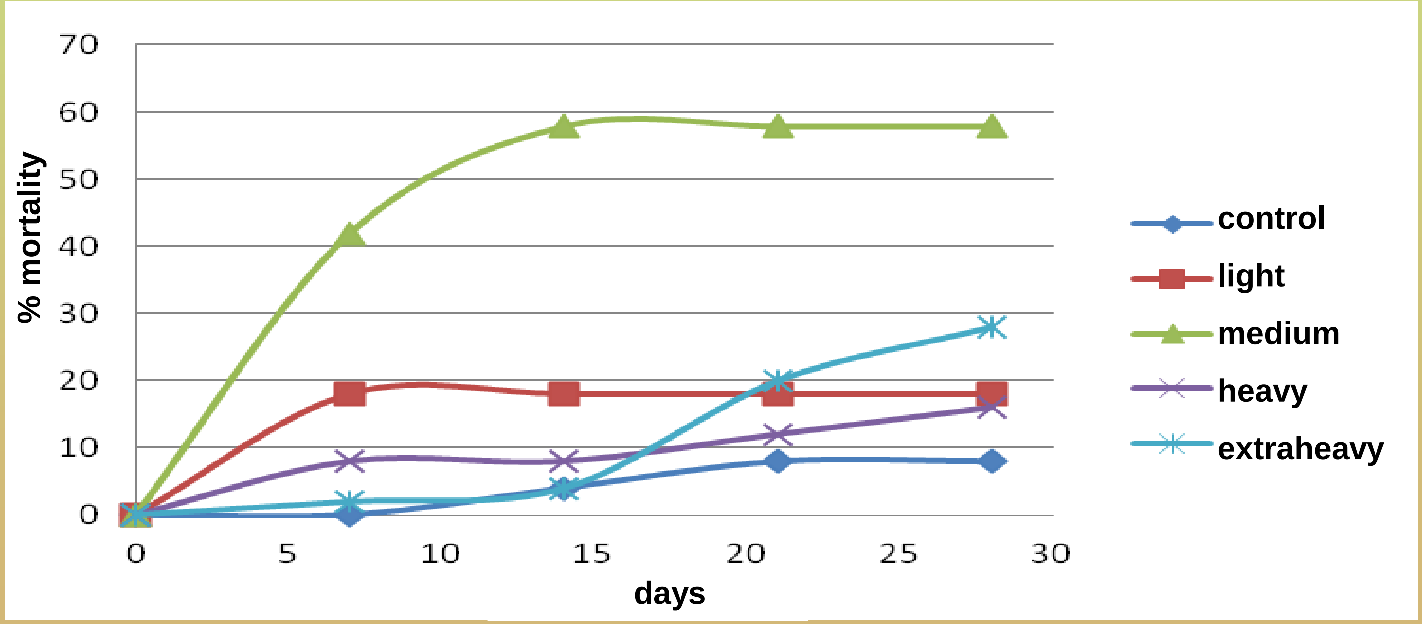
•**Limited toxicity with light crude, greater with medium crude**

•**Very low toxicity with heavy crude, but with extraheavy crude after 3 weeks →formation of compacted clumps**



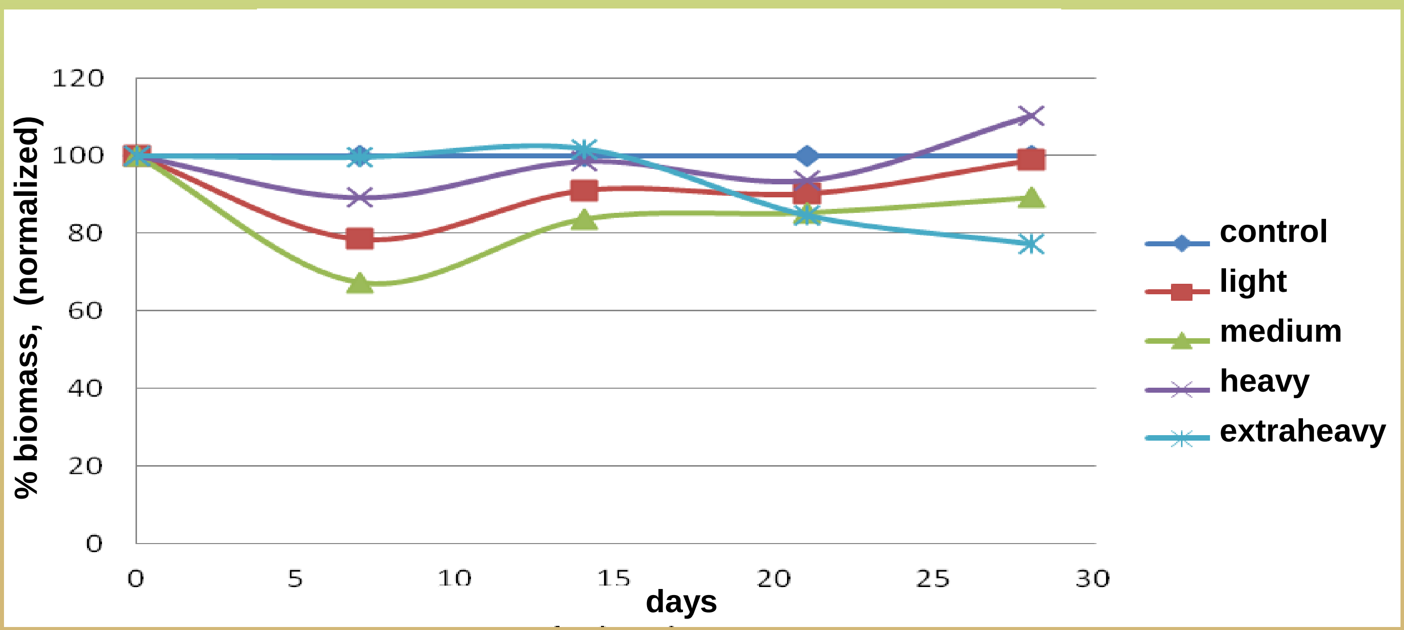
10000 ppm

Acrisol (Ultisol)

red clay soil

Subchronic Toxicity

- Biomass loss in first 2 weeks, then recovery (~3-8 weeks)
- No evidence of recovery for extraheavy crude (clumps)



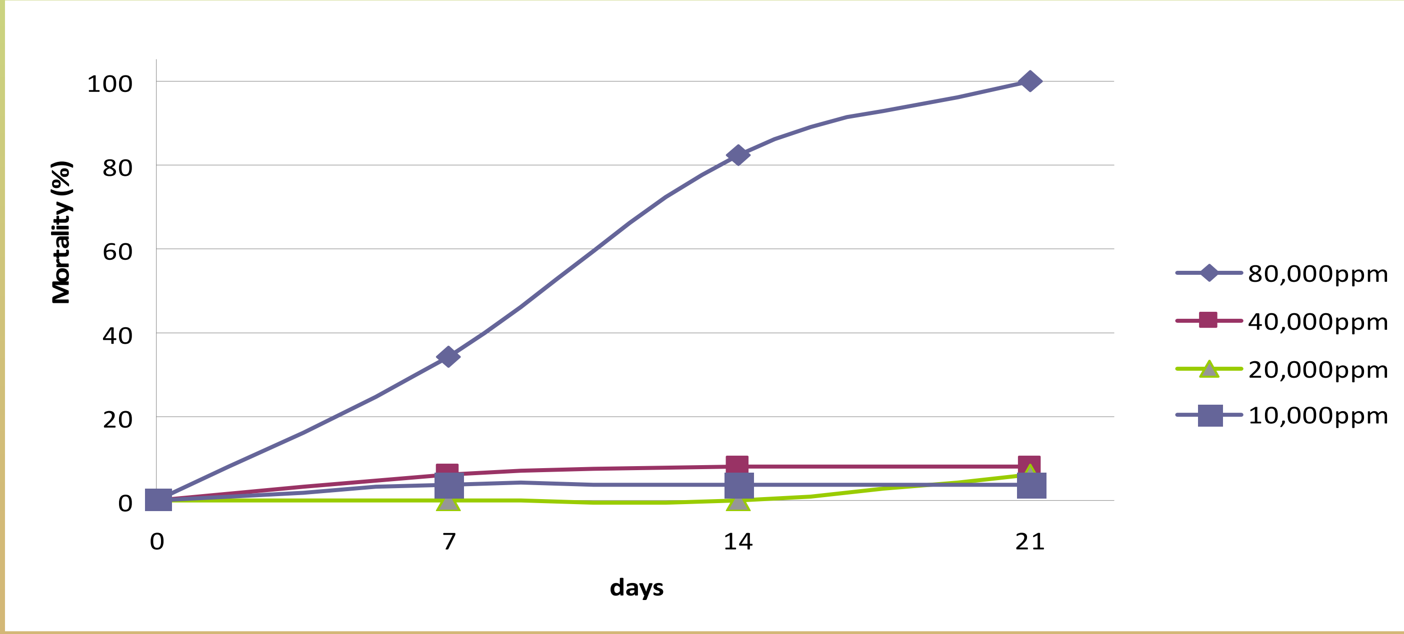
10000 ppm

Acrisol (Ultisol)

red clay soil

Subchronic Toxicity

- Very low mortality in alluvial soils (only 4%, in heavy crude)
- Bioavailability limited by presence of silts and clays;
  Clays with shrink-swell capacity → no clumping



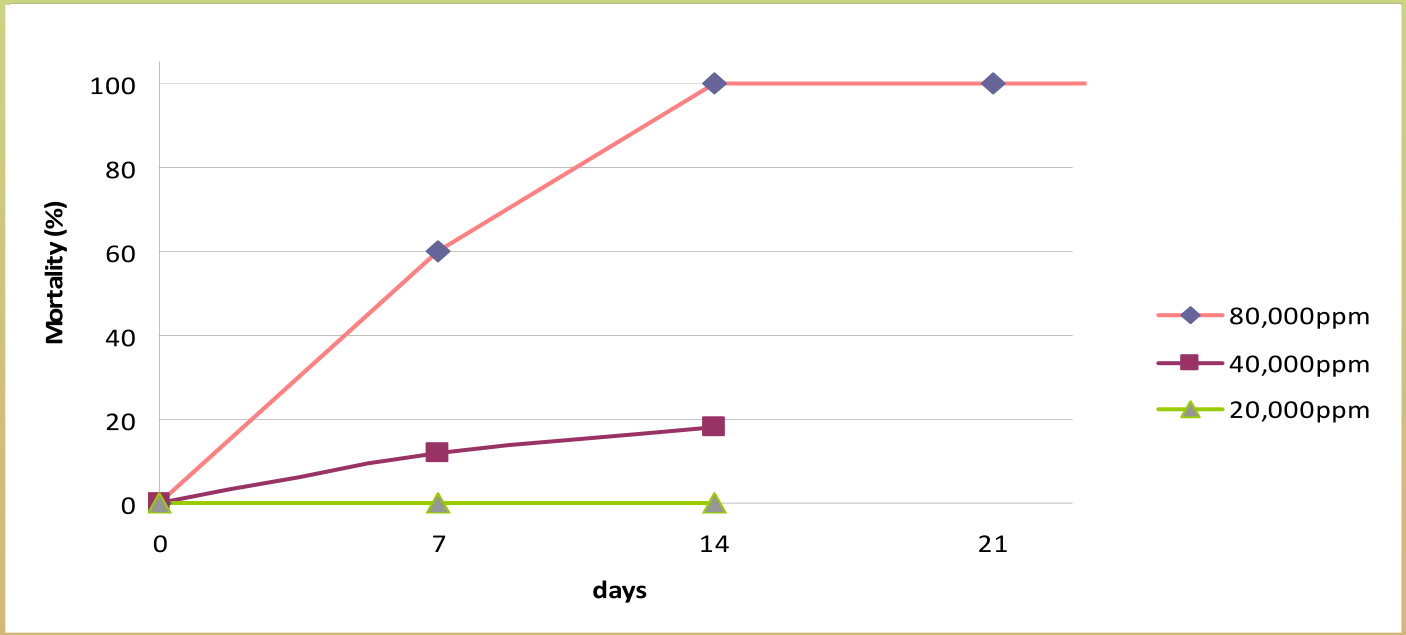
Heavy Crude

Fluvisol (Fluvent)

river levee soil

Subchronic Toxicity

- **Low-nul mortality in alluvial soils (0%, in heavy crude)**
- **Bioavailability limited by presence of silts and clays; Clays with shrink-swell capacity → no clumping**



Heavy Crude

Vertisol

brown clay soil

Problems with Fertility

- 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, field capacity
        - Aglomeration and compaction

Model for Soil Water Repellency

Non- or low polarity hydrocarbons

Weathered, slighlty polar hydrocarbons

Natural organic material (charged/polar/non-polar)

Mineral Fraction (negative charge)

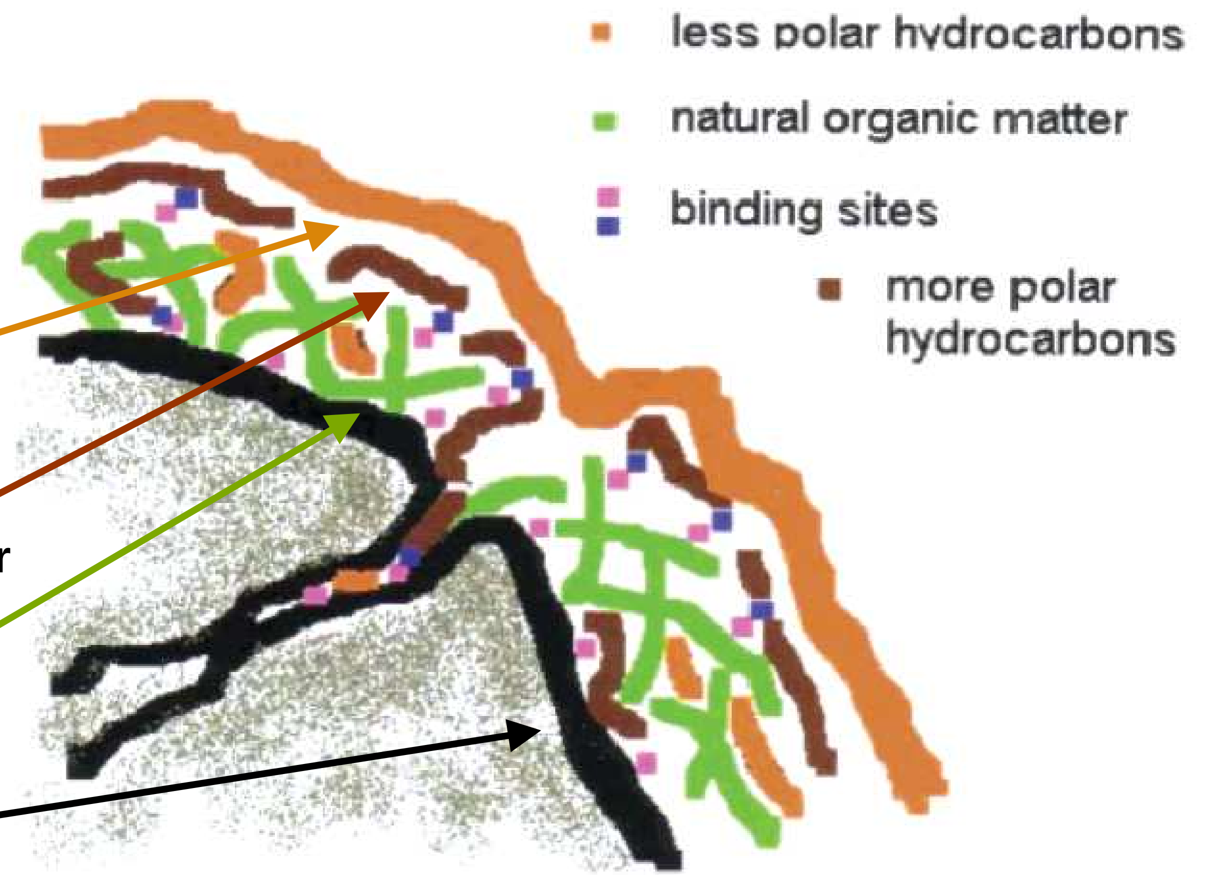


FIGURE 6. Model of the interaction between natural soil organic matter (NOM) and the diagenetic products of petroleum contamination that generates water repellency. (From: Litvina *et al.* 2003)

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Soil Water Repellency

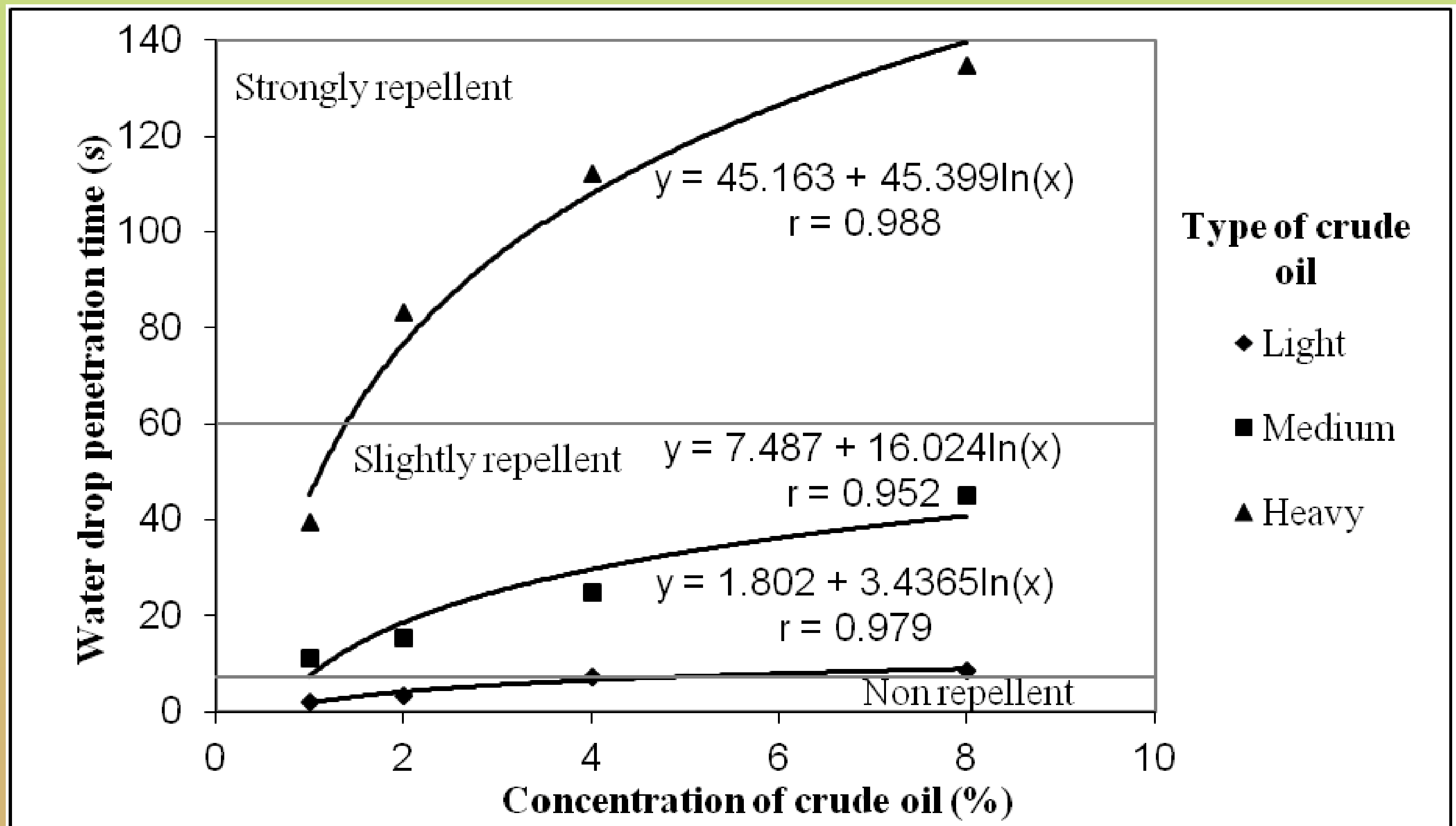
Water Repellency at 10,000 ppm

crude oil type	water repellency per soil type (WDPT in seconds)				
	Fluvisol (river levee)	Vertisol (expansive clay)	Gleysol (floodable)	Arenosol (sandy)	Acrisol (red clay)
light	8.7	2.1	<1	$>10^5$	<1
medium	8.6	11.1	8.5	$>10^5$	4.3
heavy	9.3	39.4	10.2	$>10^5$	$>10^7$
extraheavy	191	NC	NC	$>10^5$	NC

NC – not calculable, very variable data.

Soil Water Repellency

- In Fluvisol and Vertisol water repellency could be modeled based on ºAPI and TPH concentration



Vertisol

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In situ Moisture Content

- **open air weathering experiments (1 yr)**

In situ moisture content after weathering (1yr)

approx. final concentration and crude oil type used	Reduction in moisture content with respect to uncontaminated control		
	Arenosol (sandy)	Gleysol (floodable)	Fluvisol (river levee)
0.5 – 4 %, medium, heavy	~70%	~10%	
0.15 – 1%, medium crude			~10%
0.15 – 1%, heavy crude			~18%

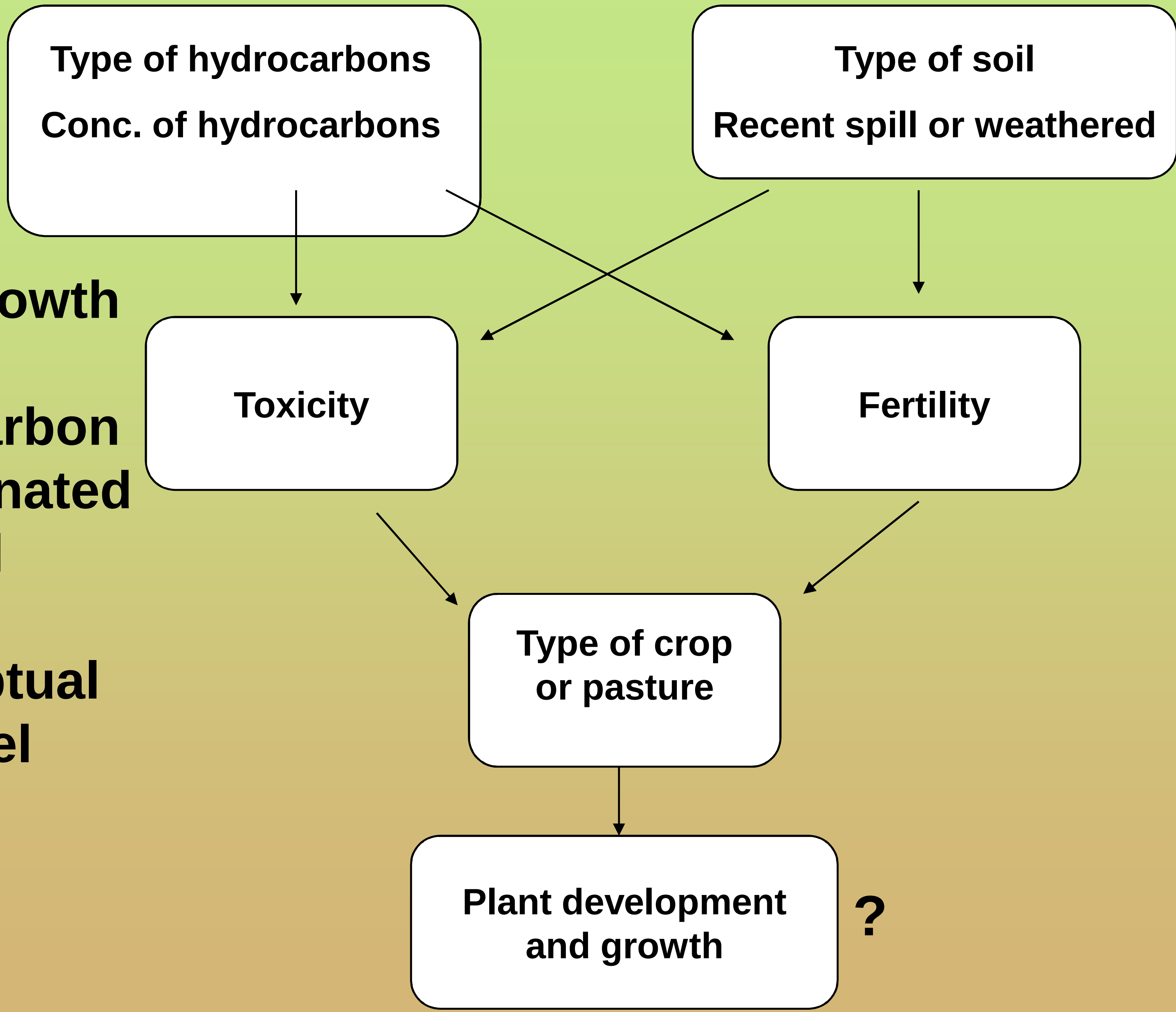
Compaction

- measured with soil penetrometer after weathering expts. (1 yr)
- observations from worm assays

soil type	experimental conditions	observations
Arenosol (sandy)	• 1 year weathering • medium and heavy crude • final concs. ~0.5 – 4%	penetrometer values very low (<25 PSI) in all treatments
Gleysol (floodable)	• 1 year weathering • medium and heavy crude • final concs. ~0.5 – 4%	tendency to decrease with medium crude and increase with heavy crude, however all values < 90 PSI
Fluvisol (river levee)	• 1 year weathering • medium and heavy crude • final concs. ~0.15 – 1%	tendency to increase with medium and heavy, however all values < 70 PSI
Acrisol (red clay)	• without weathering • extraheavy crude • conc. 1%	formation of hard compacted clumps in worm bioassay, trapped worms (increased mortality)

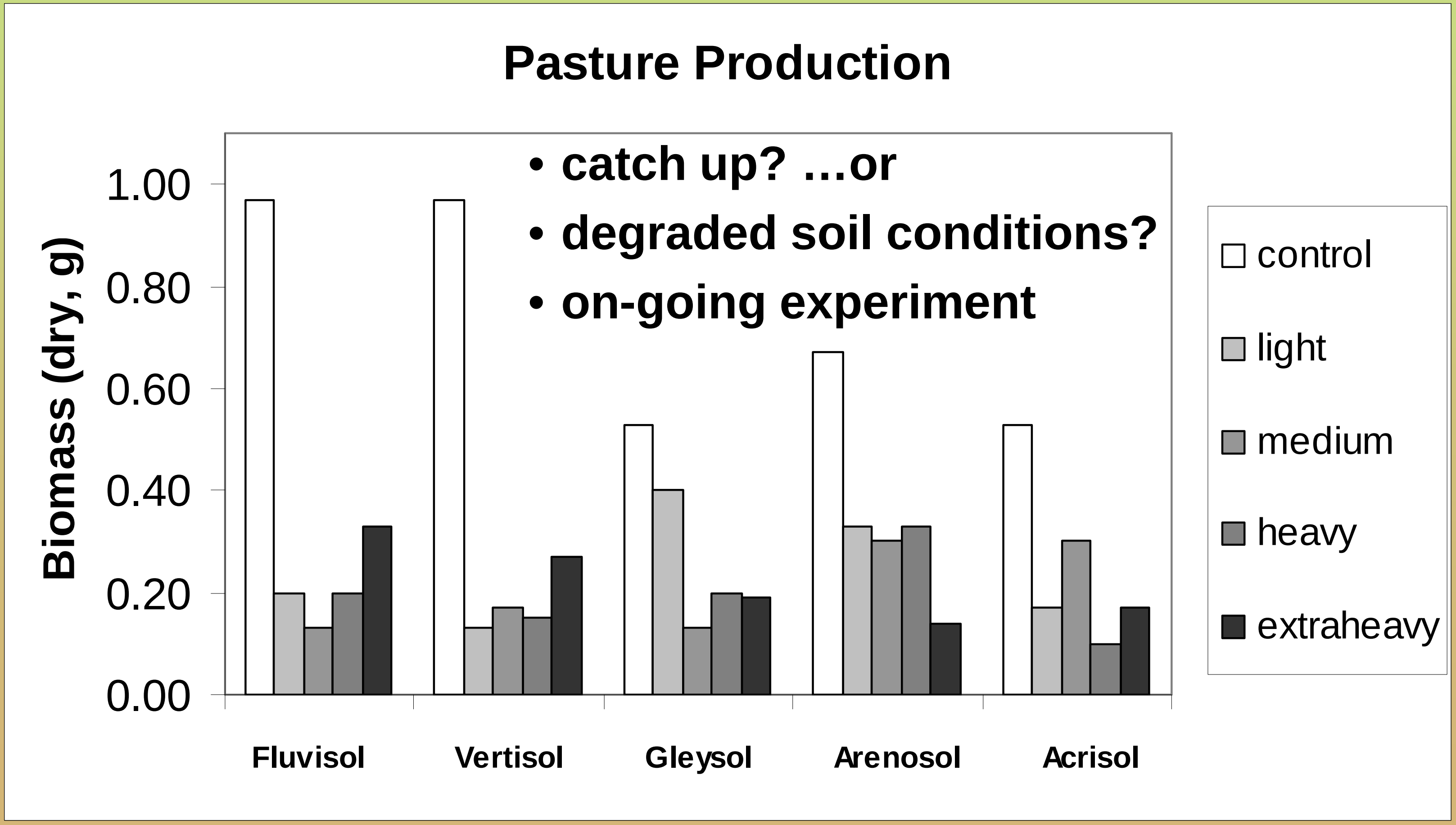
Plant Growth in Hydrocarbon Contaminated Soil

Conceptual Model



Plant Growth

- pasture planted by stolons
- cut every 2 mo. and above ground biomass measured



CONCLUSIONS

Impacts of petroleum contamination in soil are affected by:

- **Type of Petroleum:**
  - **→lighter crudes are more acutely toxic (but temporary)**
  - **→heavier crudes are more likely to impact fertility:**
    - **polar groups lead to formation of HC laminates**
      - **→water repellency/soil moisture**
      - **→soil compaction**

    - **recovery may be very, very slow**

CONCLUSIONS

Impacts of petroleum contamination in soil are affected by:

- **Type and abundance of soil clays:**

  smectites: high surface area, expansive (in brown-grey soils)

  →reduce toxicity (low bioavailability)

  →very little water repellency (lots of reactive surface area)

  →very little compaction (shrink-swell properties)

  non-smectites: kaolinites, amorphous Fe/Al oxides low surface area, non-expansive (in red-clay soils)

  →med-high toxicity (more bioavailability)

  →med-high water repellency (less reactive surface area)

  →a lot or compaction (no shrink-swell properties)

CONCLUSIONS

Impacts of petroleum contamination in soil are affected by:

- **Type and abundance of soil clays:**
  - **very sandy soils: practically no clay (<1%)**
    - **→med-high toxicity (almost complete bioavailability)**
    - **→high water repellency (very little reactive surface area)**
    - **→no compaction (absence of clays: → basically no aggregates)**

Thank you for your attention

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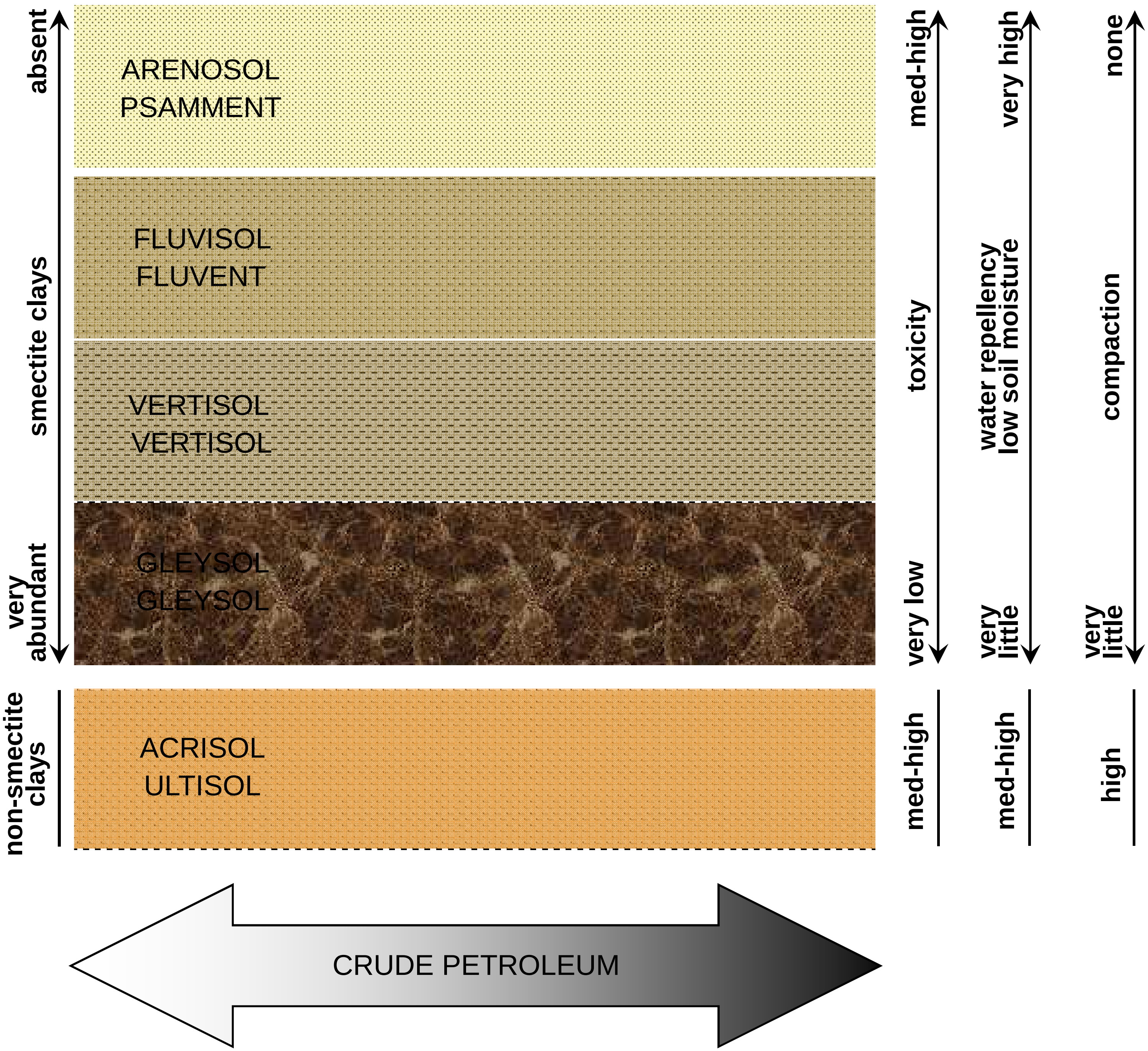
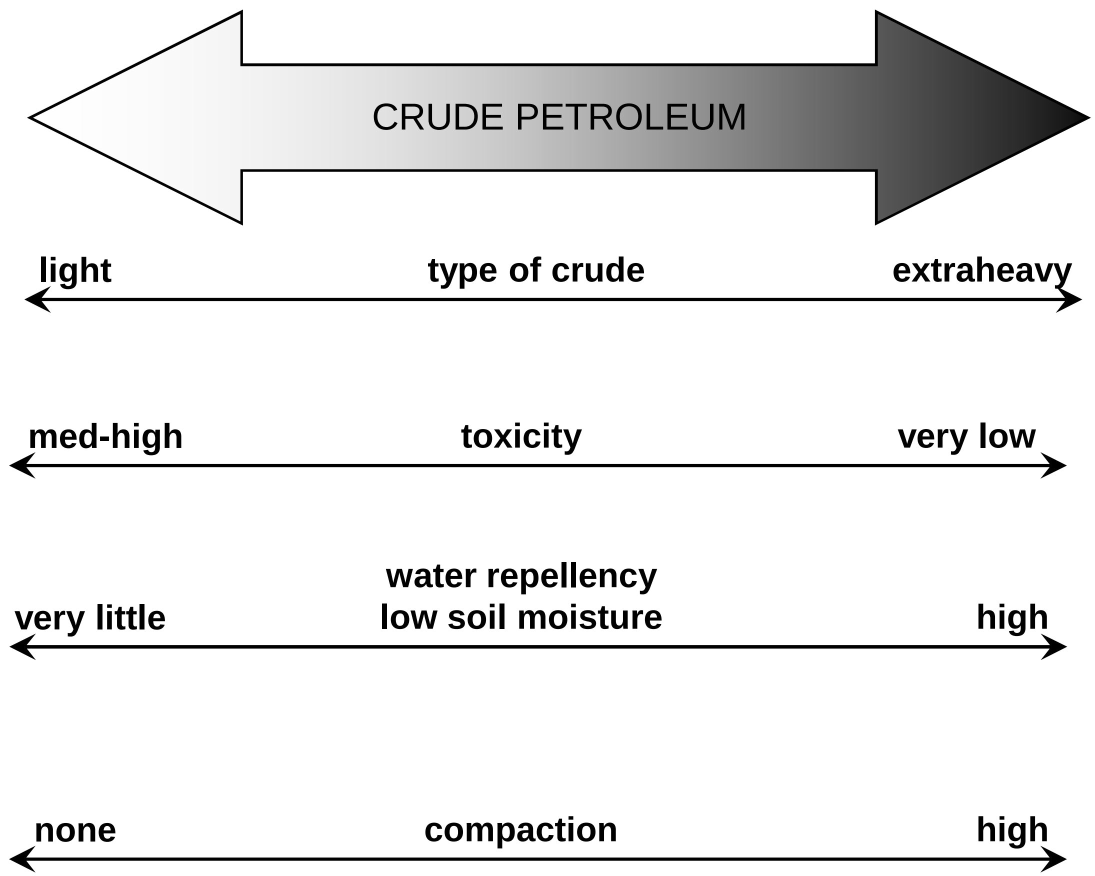
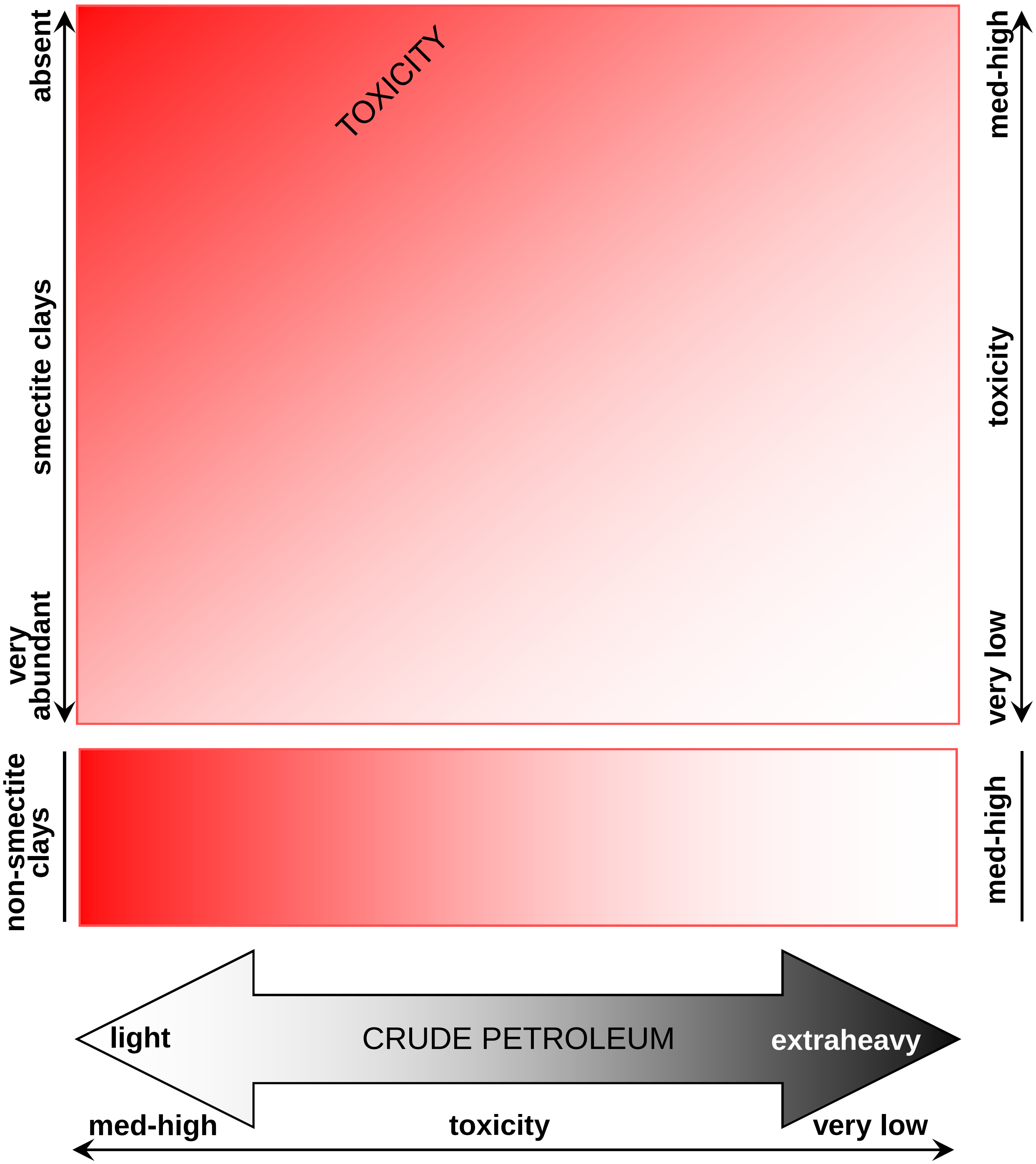
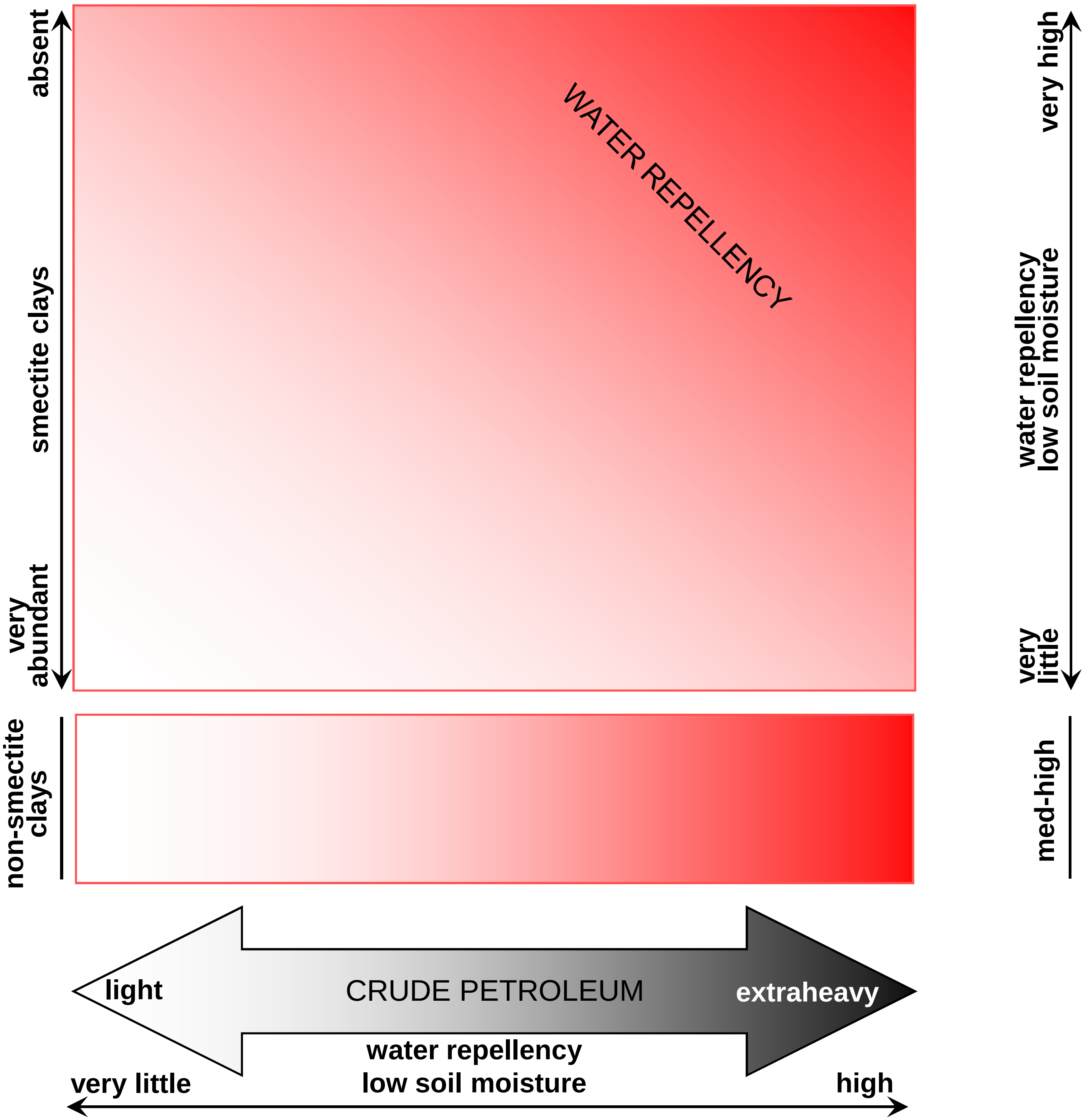


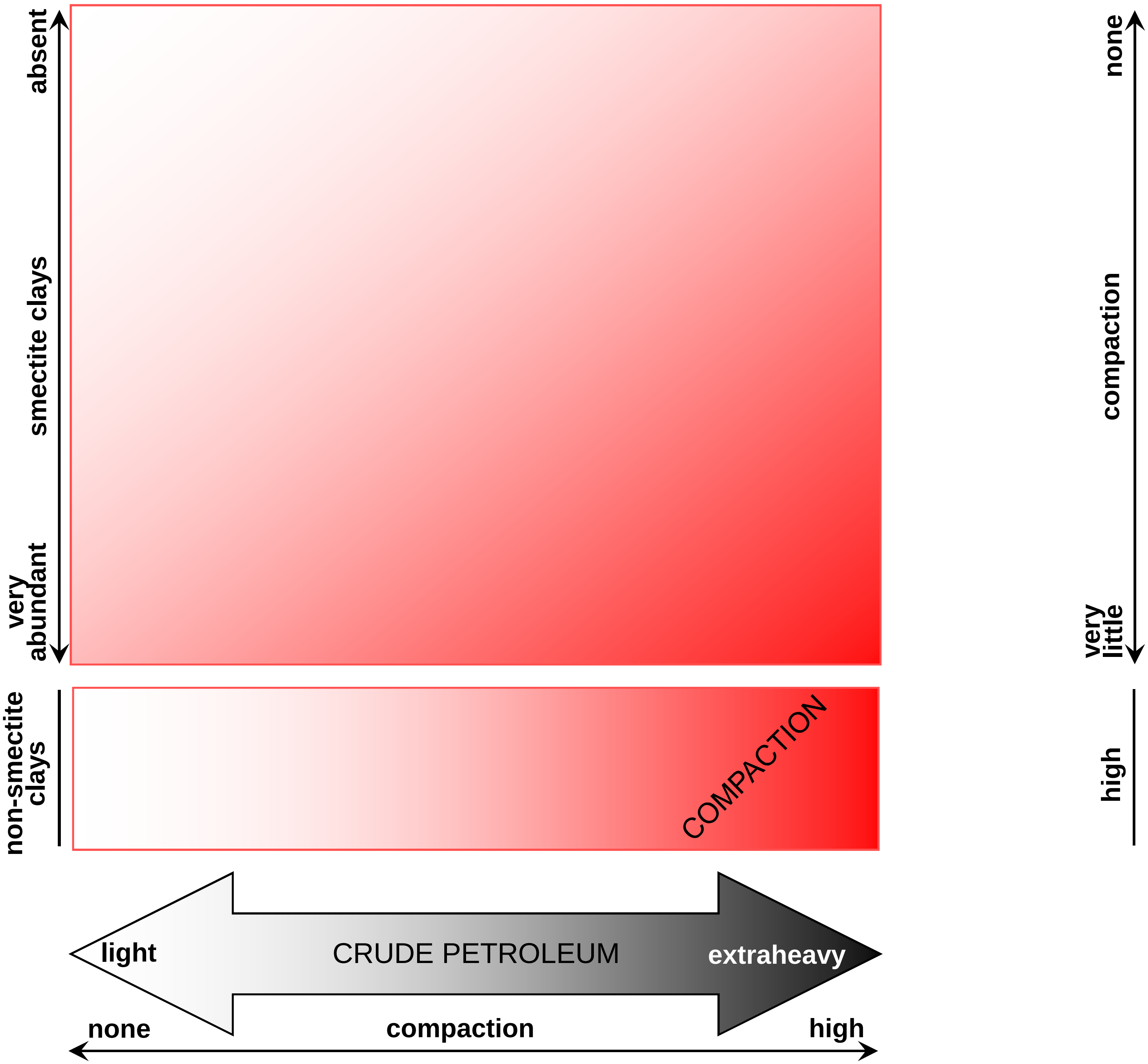
absent
smectite clays
very abundant
non-smectite clays
ARENOSOL
PSAMMENT
FLUVISOL
FLUVENT
VERTISOL
VERTISOL
GLEYSOL
GLEYSOL
ACRISOL
ULTISOL
med-high
toxicity
very low
med-high
very high
water repellency
low soil moisture
very little
med-high
none
compaction
very little
high
CRUDE PETROLEUM


CRUDE PETROLEUM
light
type of crude
extraheavy
med-high
toxicity
very low
water repellency
low soil moisture
very little
high
none
compaction
high


absent
smectite clays
very abundant
TOXICITY
med-high
toxicity
very low
non-smectite clays
med-high
light
CRUDE PETROLEUM
extraheavy
med-high
toxicity
very low



absent
smectite clays
very abundant
WATER REPELLENCY
very high
water repellency
low soil moisture
very little
non-smectite clays
med-high
light
CRUDE PETROLEUM
extraheavy
water repellency
low soil moisture
very little
high


absent
smectite clays
very abundant
non-smectite clays
none
compaction
very little
high
COMPACTION
light
CRUDE PETROLEUM
extraheavy
none
compaction
high