



# Can Analytical Methods Predict Bioavailability?

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# Outline

- Contaminant Bioavailability
- Current in vitro methods
- Mobility/bioaccessibility
- Results
- Conclusions

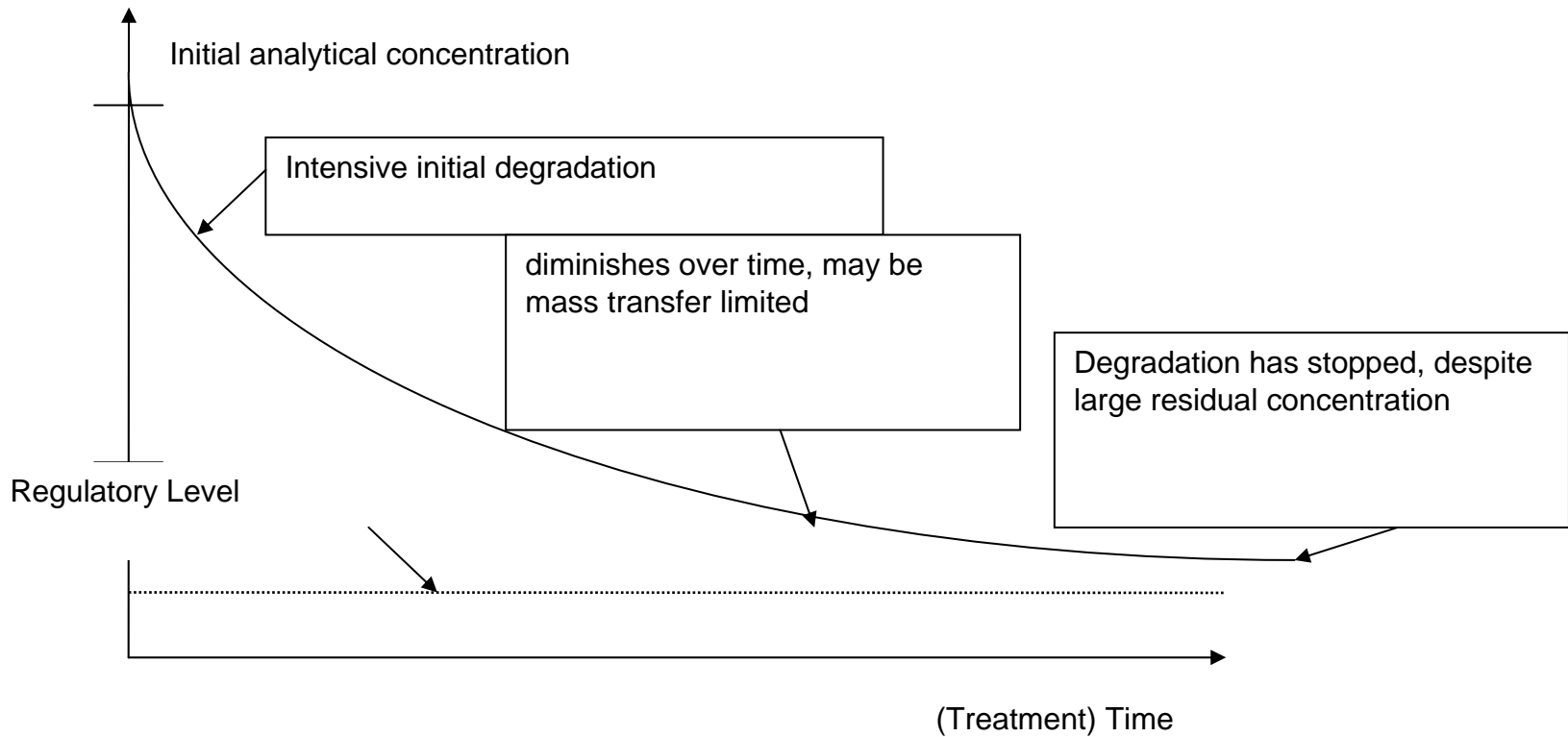


# Bioavailability Issues

- Sorption to soil surfaces or organic matter.
- Complex residues, which are protected from microbiological (enzymatic) attack
- Reduced bioavailability
- Mass transfer limitations (e.g., pore diffusion)
- Slow leaching in sites that have been remediated.



# Residual Concentration





# Definitions

- **Bioavailability** represents the fraction of a chemical that is freely available to cross an organism's (cellular) membrane from the medium the organism inhabits.
- **Bioaccessibility** encompasses what is actually bioavailable plus what is 'potentially bioavailable' (Semple 2004)



# Variables

- Source of contamination
- Soil texture
- Moisture level
- Time
- Degree of contamination

# Example of Medium Crude - Unweathered

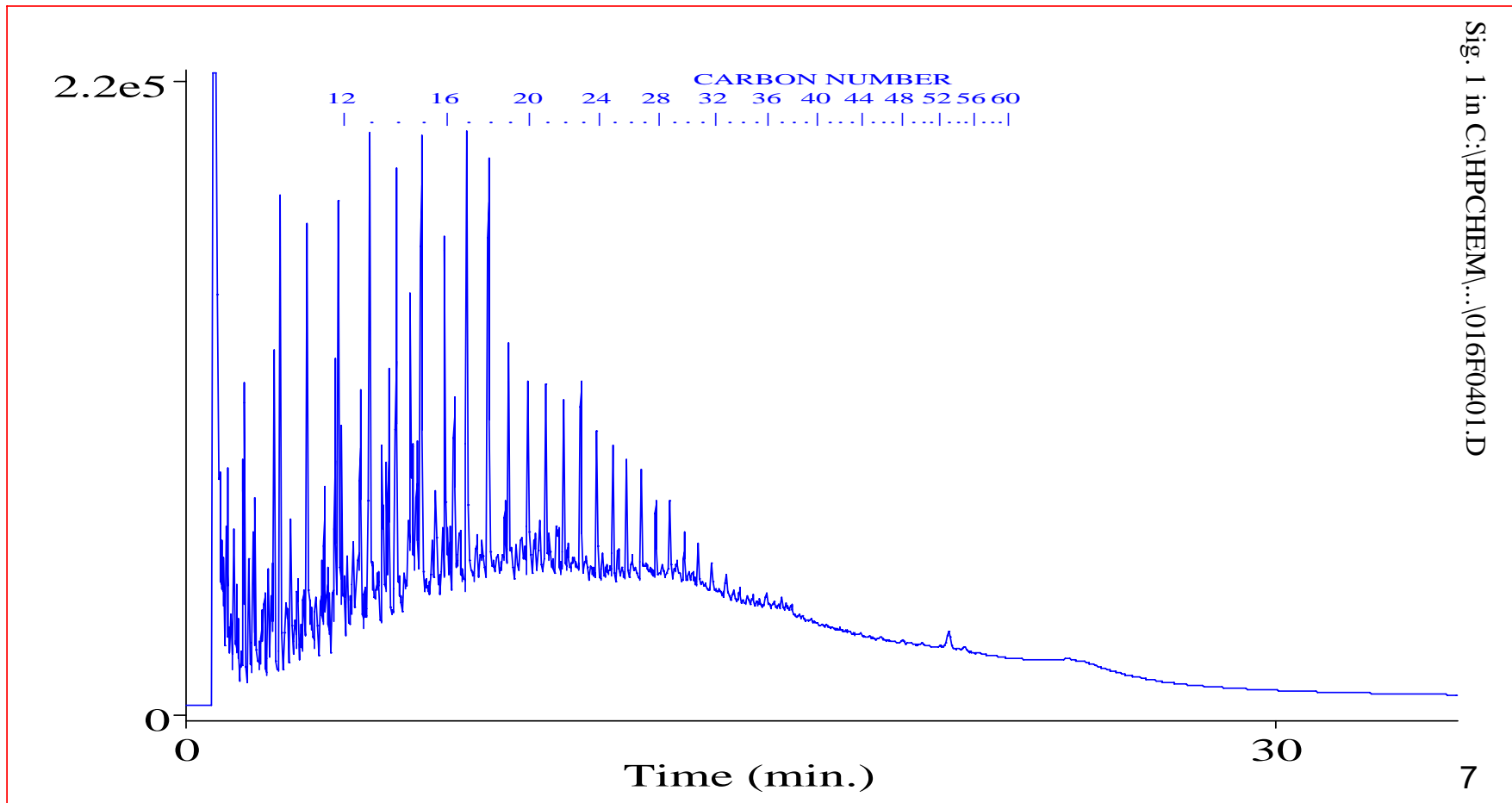
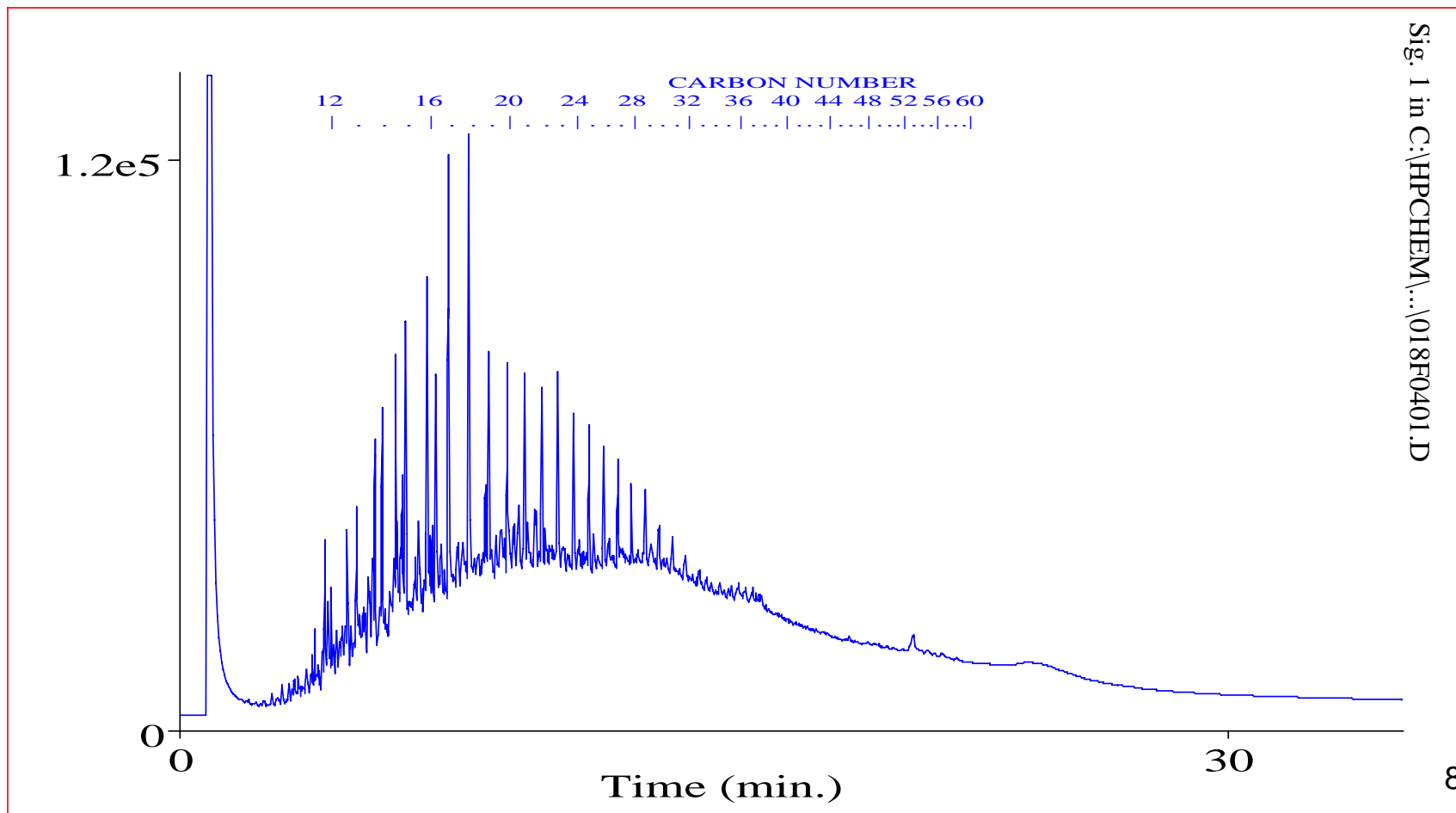


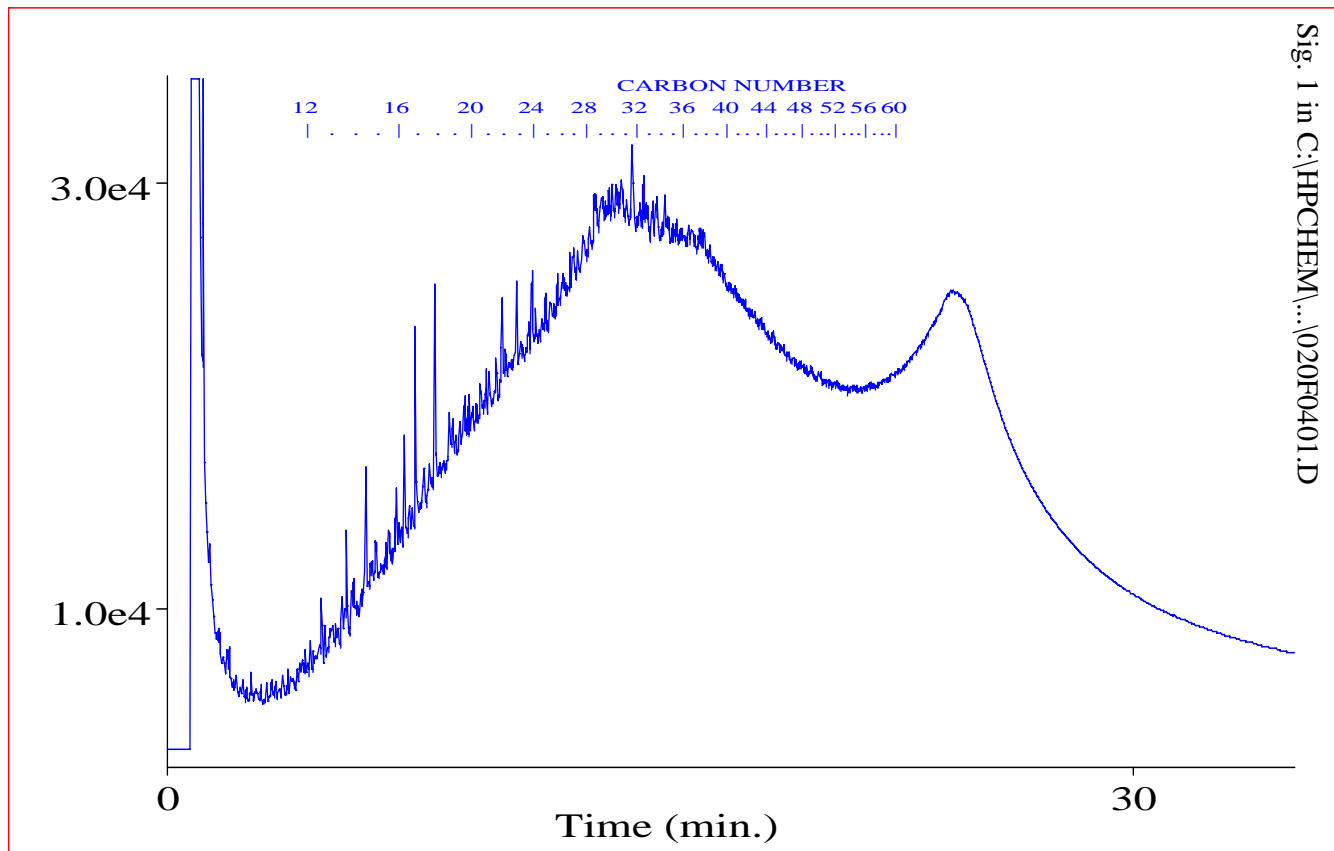
Fig. 1 in C:\HPCHEM\...\016F0401.D

# Example of Medium Crude - Weathered





# Heavy Weathered Crude





# Mild Extraction tests approaches

- solid with bound contaminant is extracted into a solvent phase: mild (methanol) extractions, subcritical water extractions, supercritical fluid extractions (CO<sub>2</sub>)
- solid or solid slurry is extracted into a solid phase sorbent: Tenax, XAD, C-18 or SPME, or cyclodextrin (Puglisi 2003)
- solid slurry is extracted through a membrane into a solvent phase (PBET, Ruby 1996)
- solid or solid slurry is extracted through a membrane into a solid phase sorbent (resin capsules)



# Extraction tests --issues

- Overestimate the bioavailability of contaminants.
- Milder extraction tests may correlate more
- Extractions are never specific
- Comparison of extraction tests to those from an in vivo model (e.g. piglets) are very costly
- Could be used in Tier 2 assessment



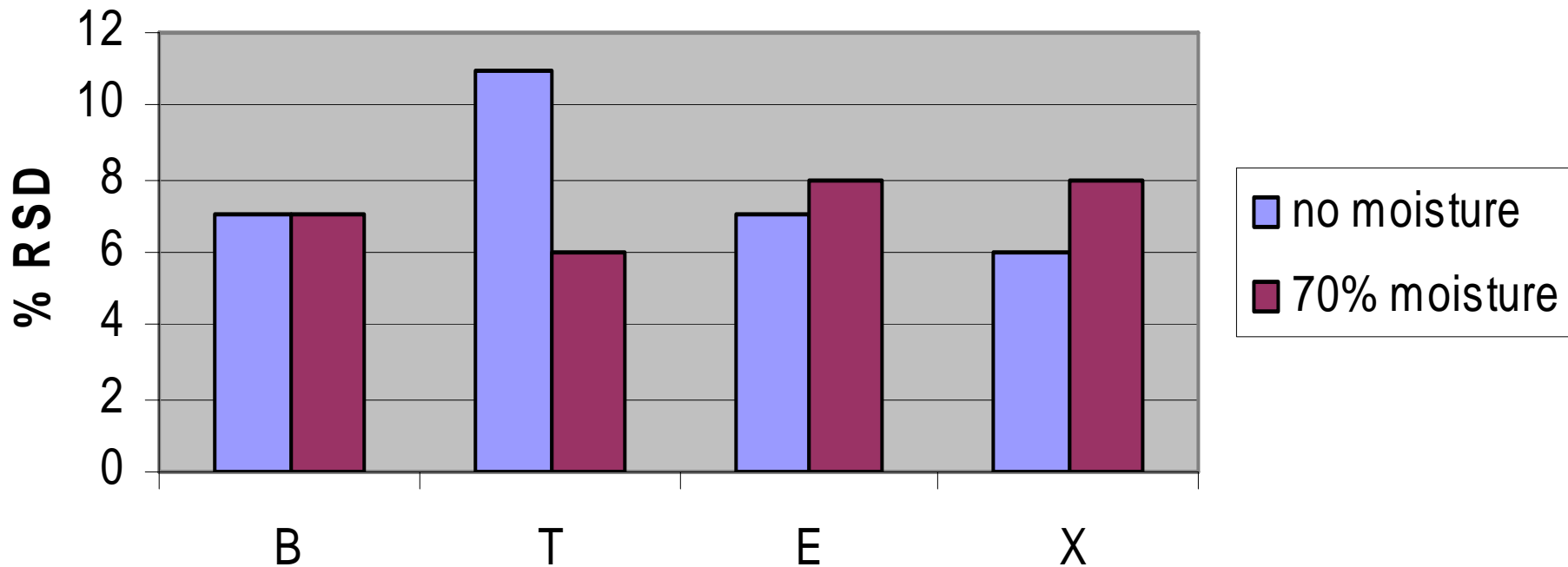
# Leachate tests

- Simple regulatory leaching test, such as the TCLP, EPA method 1311, or the SPLP, method 1312 have been used to determine the bioaccessibility of metals from soil.
- They were designed to simulate leaching in a landfill environment or leaching in rainwater.
- They are only useful for evaluating the mobility of the contaminants in soils.
- Their use as a first level, commercially available test to evaluate the mobility in soils may be appropriate for particular situations.



## LBTEX Precision

### Effect of moisture





**Table 1. leachate extraction efficiency of fresh spikes in sand (%)**

<b>Benzene</b>	<b>Toluene</b>	<b>Ethyl benzene</b>	<b>Xylenes</b>	<b>Average</b>
89	92	84	82	87



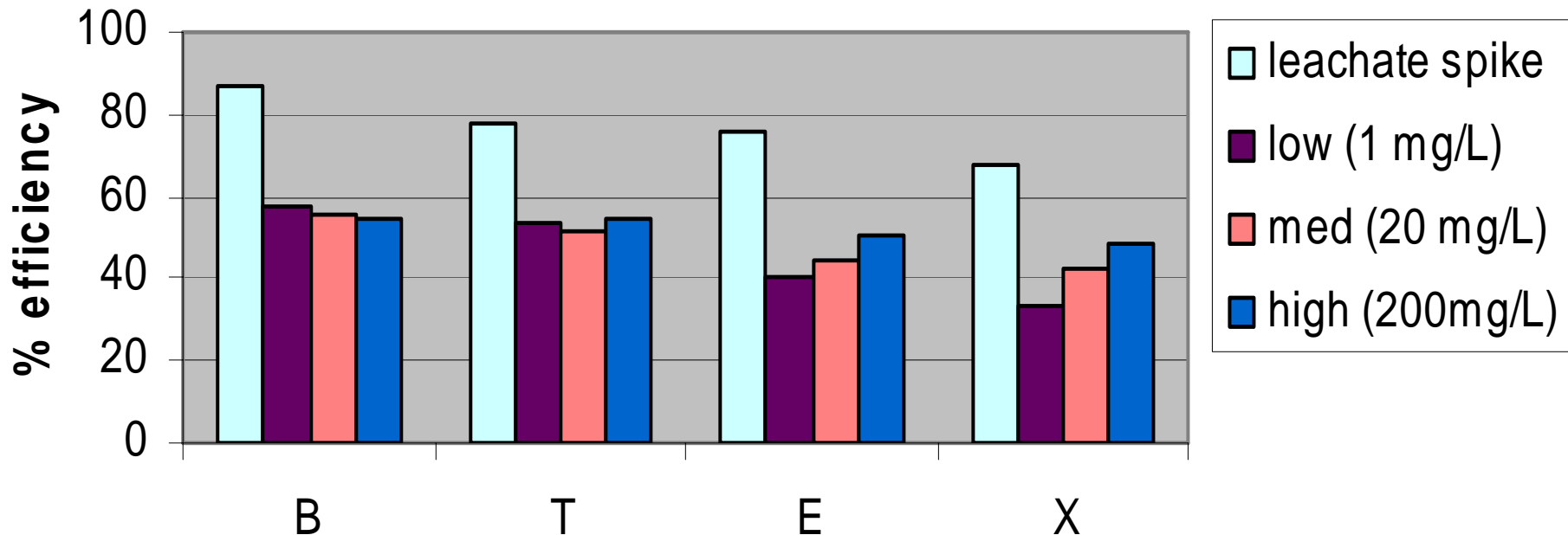
**Table 2. Leachate extraction efficiency of fresh spikes in loam (%)**  
(average from duplicates at each concentration)

<b>Concentration</b>	<b>Benzene</b>	<b>Toluene</b>	<b>Ethyl benzene</b>	<b>Xylenes</b>	<b>Average</b>
Low (1 mg/L)	58	54	40	33	46
Med (20 mg/L)	56	52	44	42	48
High (200 mg/L)	55	55	51	48	52
Average	56	54	45	41	49



## Lab spikes -- Loam

(Average from duplicates at each conc. Level)





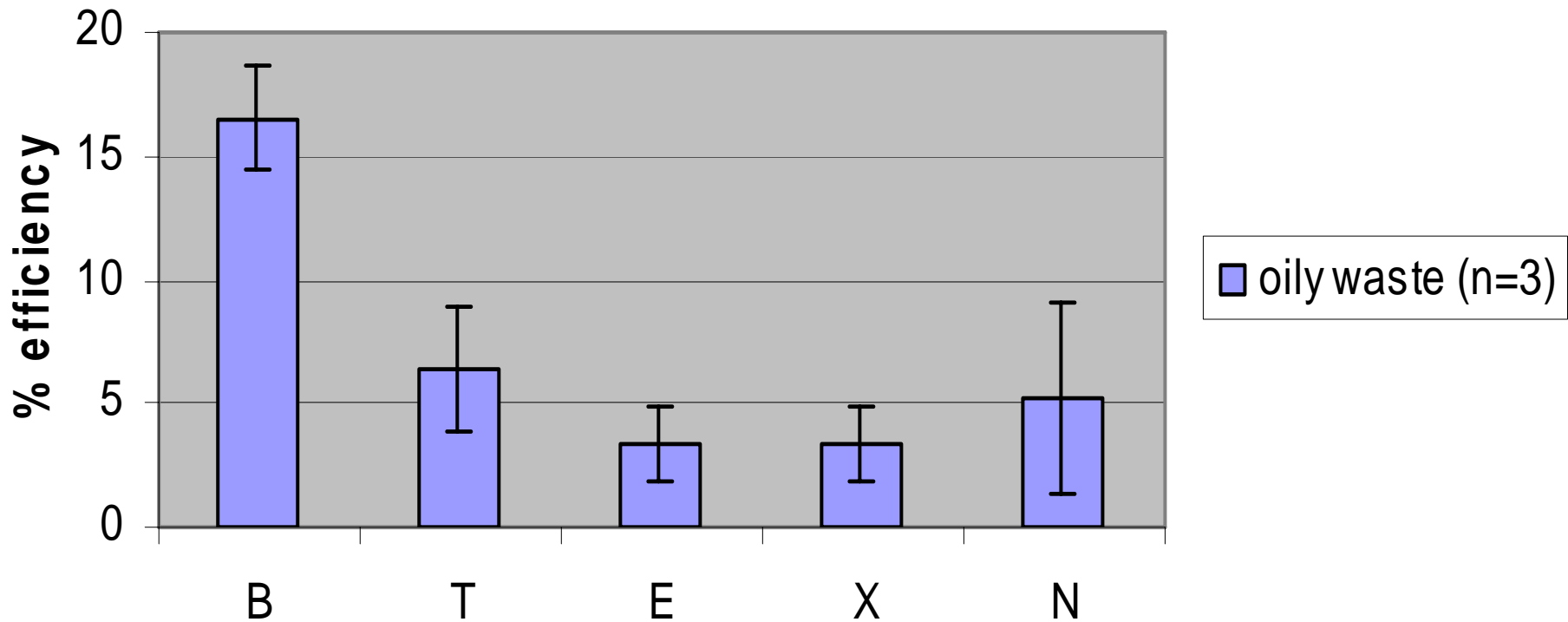


**Table 3. Leachate extraction of an oil (n=1)**

	<b>Total concentration</b> mg/kg	<b>Leachate concentration</b> mg/L	<b>% efficient</b>
Benzene	0	<0.01	-
Toluene	516	1.01	4%
Ethylbenzene	99	0.009	2%
Xylenes	566	0.50	2%



## Oily waste



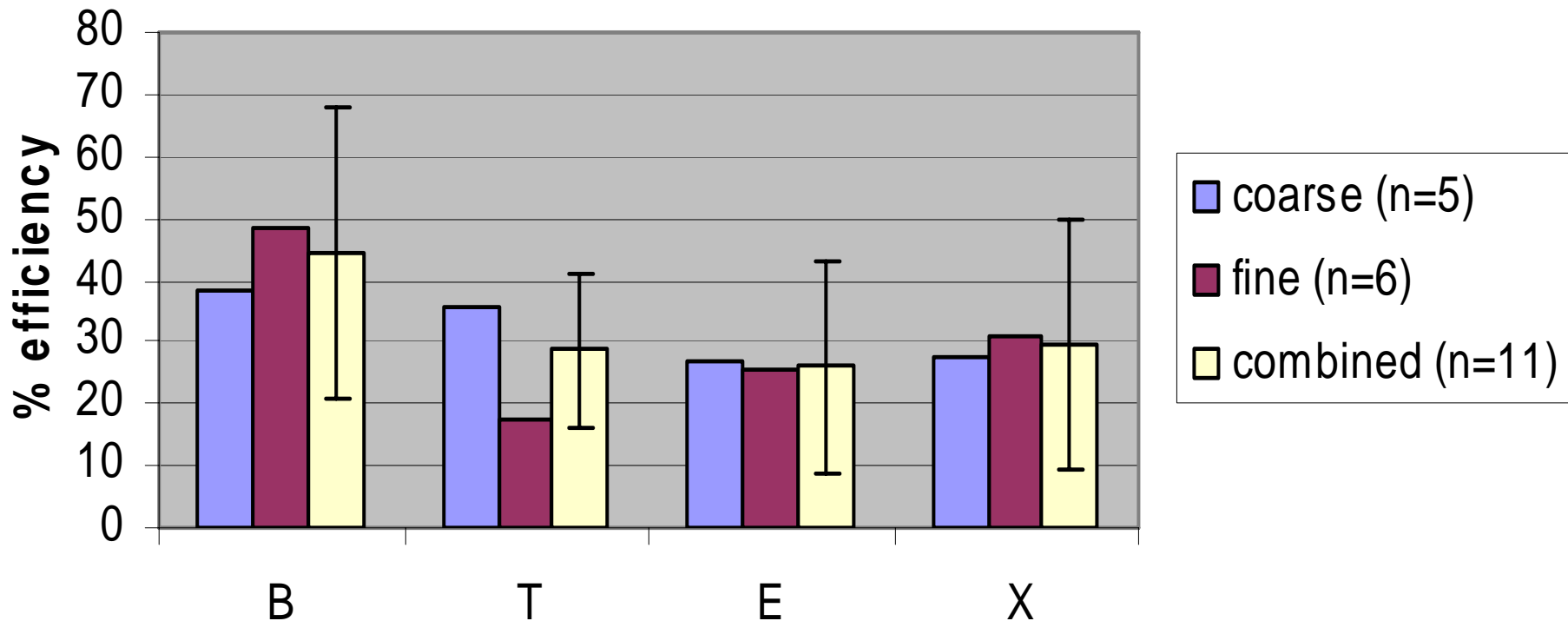


**Table 4. Leachate extraction efficiency as a function of texture (%)**  
(n=4 for each soil type)

<b>texture</b>	<b>Benzene</b>	<b>Toluene</b>	<b>Ethylbenzene</b>	<b>Xylenes</b>
Coarse (sand)	37	42	38	35
Fine (clay)	35	18	20	22



## Soil type



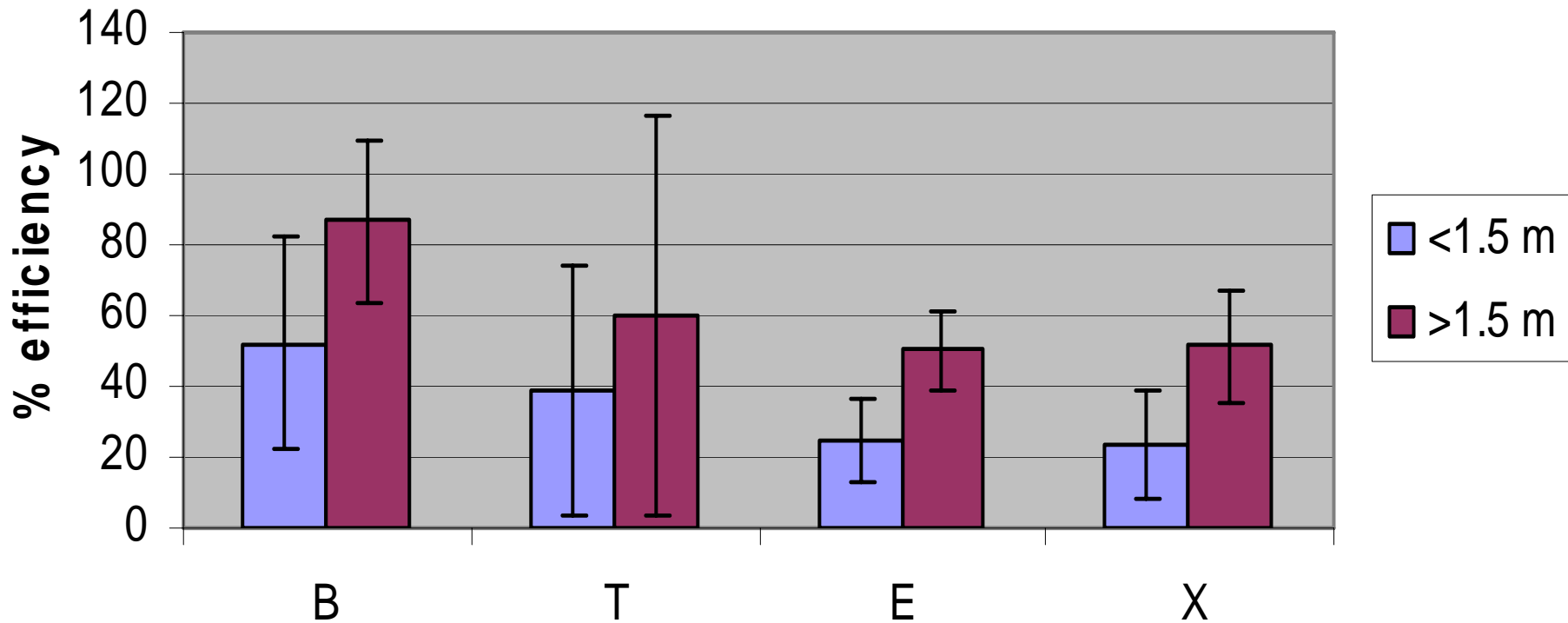


**Table 5. Leachate extraction efficiency as a function of depth (%)**  
(n=6 for each depth).

depth	Benzene	Toluene	Ethylbenzene	Xylenes
<1.5 m	46	44	28	23
>1.5 m	87	60	52	42



## Depth





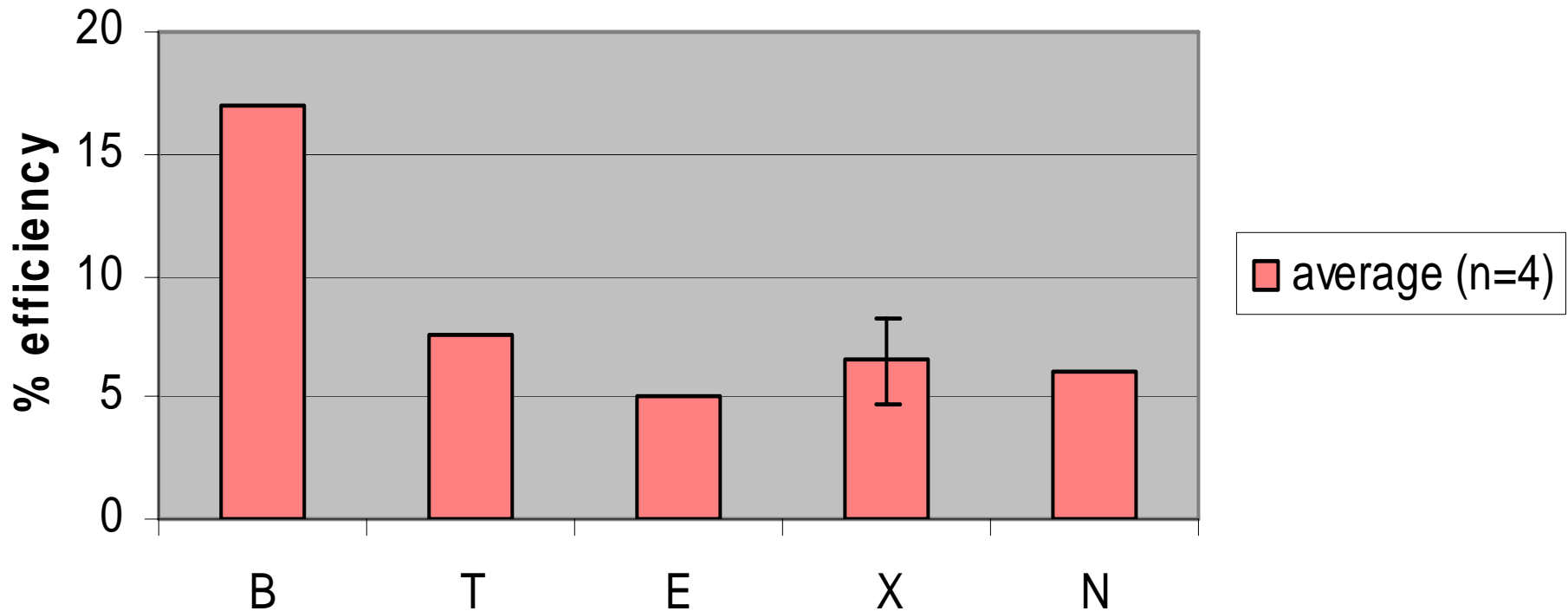
## Table 6. Leachate extraction efficiency in windrows (%)

(n=4)

Benzene	Toluene	Ethylbenzene	Xylenes	Naphthalene	Overall
16	7	8	9	6	~10%



## Windrows





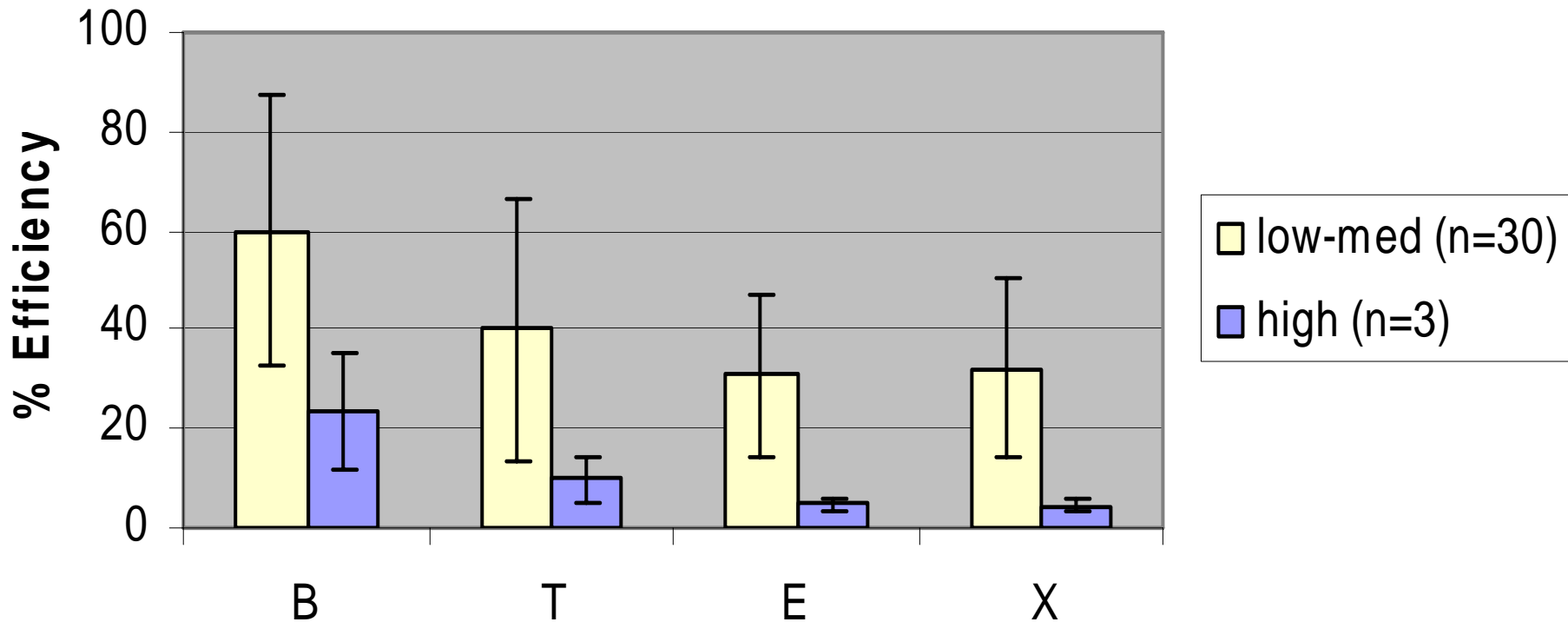


**Table 7. Leachate extraction efficiency as a function of concentration level (%)**  
(n=6 for each level)

<b>Concentration</b>	<b>Benzene</b>	<b>Toluene</b>	<b>Ethylbenzene</b>	<b>Xylenes</b>
Low	37	36	44	32
Med	62	52	34	38
High	22	21	14	14



## Concentration Level





# Conclusions

- The leachate extraction efficiency results indicate that at a first level, a commercially available test such as the leachate test can be used appropriately to evaluate, not only the mobility, but also the bioaccessibility of contaminants in soils.



# Examples of research studies

- Bioavailability studies that have the aim of developing standardized in vitro bioavailability methods
- Investigating the effects of mixtures of substances and determining whether these substances show additive, synergistic or antagonistic properties
- Re-evaluating the toxicity of PCBs, petroleum hydrocarbons (PHCs), PAHs, etc. with the aim of revising the toxicological reference value (TRV) for these substances



# References

- Stantec Consulting Ltd. (2004). Framework Foundation and Guidance for Tier 2 Site-specific development of Soil Contact Standards for PHC-contaminated Sites: Literature review. ERAC Soil and Groundwater Project 2002.
- ERAC (2004). Environmentally Acceptable Endpoints for Weathered and Aged Petroleum Hydrocarbons Fraction F3 in Soil. Report on 2004 Research Projects. Environmental Research Advisory Council



# Can analytical methods predict bioavailability?