

Contribution of Major Ions to Toxicity of Oil Shale Leachates to Aquatic Organisms

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Imagine the result

Problem

- Leachates of raw (i.e., unprocessed) and spent (i.e., processed) oil shale from Colorado and Utah contain high concentrations of major ions (Ca^{2+} , Mg^{2+} , Na^+ , K^+ , Cl^- , HCO_3^- , SO_4^{2-})
[e.g., >20,000 mg/L (300 mM) total major ions]
 - Potential discharge to surface waters
 - Acute toxicity to fish and aquatic invertebrates
- How to predict that toxicity?
 - Previously predicted by comparing to reported toxicities of individual inorganic salts (e.g., NaCl , MgSO_4)
[e.g., Meyer et al. 1985, Woodward et al. 1985]
 - However, difficult to simultaneously take into account all major ions and their interactions

Potential Solution

Regression Model of Major-ion Toxicity

- Mount et al. (1997; *Environ. Toxicol. Chem.* 16:2009-2019)
“Statistical Models to Predict the Toxicity of Major Ions to *Ceriodaphnia dubia*, *Daphnia magna* and *Pimephales promelas* (Fathead Minnows)”
 - Based on acute toxicity tests with individual salts and binary mixtures of salts of all the major inorganic ions
 - Allows contributions of all major ions to be simultaneously incorporated into predictions of % survival of the three species

Objective

- Use the Mount et al. (1997) model to calculate the percentage contributions of major-ion mixtures to the toxicity of raw and spent oil shale leachates to *D. magna* and fathead minnow (FHM)

Definition

LC50 = median lethal concentration (i.e., the concentration that would cause 50% mortality of the test organisms)

Inverse relationship between LC50 and toxicity:

as LC50 \uparrow , toxicity decreases

as LC50 \downarrow , toxicity increases

Methods

Toxicity Data

- Meyer et al. (1985)
 - Leachates of raw shale from Tracts C-a & C-b, NW CO
 - FHM & *D. magna*
- Woodward et al. (1985)
 - Composite leachate of spent shale from Paraho above-ground retorting facility, Anvil Points, CO
 - FHM & *D. magna*
- Meyer et al. (unpublished data)
 - Leachates of spent shale from Paraho facility
 - FHM and *D. magna*

All tests conducted at University of Wyoming

Methods (cont.)

Mount et al. (1997) Logistic Regression Model

$$\text{survival (\%)} = 100 \cdot \frac{e^{b_0 + b_1 \cdot x_1 + \dots + b_n \cdot x_n}}{1 + e^{b_0 + b_1 \cdot x_1 + \dots + b_n \cdot x_n}}$$

where x_1, \dots, x_n are either (1) an ion concentration or (2) the number of cations at >10% of the total molar concentration of cations and at >100 mg/L

Methods (cont.)

Mount et al. (1997) Logistic Regression Model

Coefficients:

Parameter	96-h FHM	48-h <i>D. magna</i>
Constant	4.70	5.83
K ⁺	-0.00987	-0.0185
Mg ²⁺	-0.00327	-0.00510
Cl ⁻	-0.00120	-0.00395
SO ₄ ²⁻	-0.00075	-0.00255
HCO ₃ ⁻	-0.00443	-0.00397
NumCat	0	-0.511
NumCat·K ⁺	0	0.00677
NumCat·Cl ⁻	0	0.00146
NumCat·SO ₄ ²⁻	0	0.00132

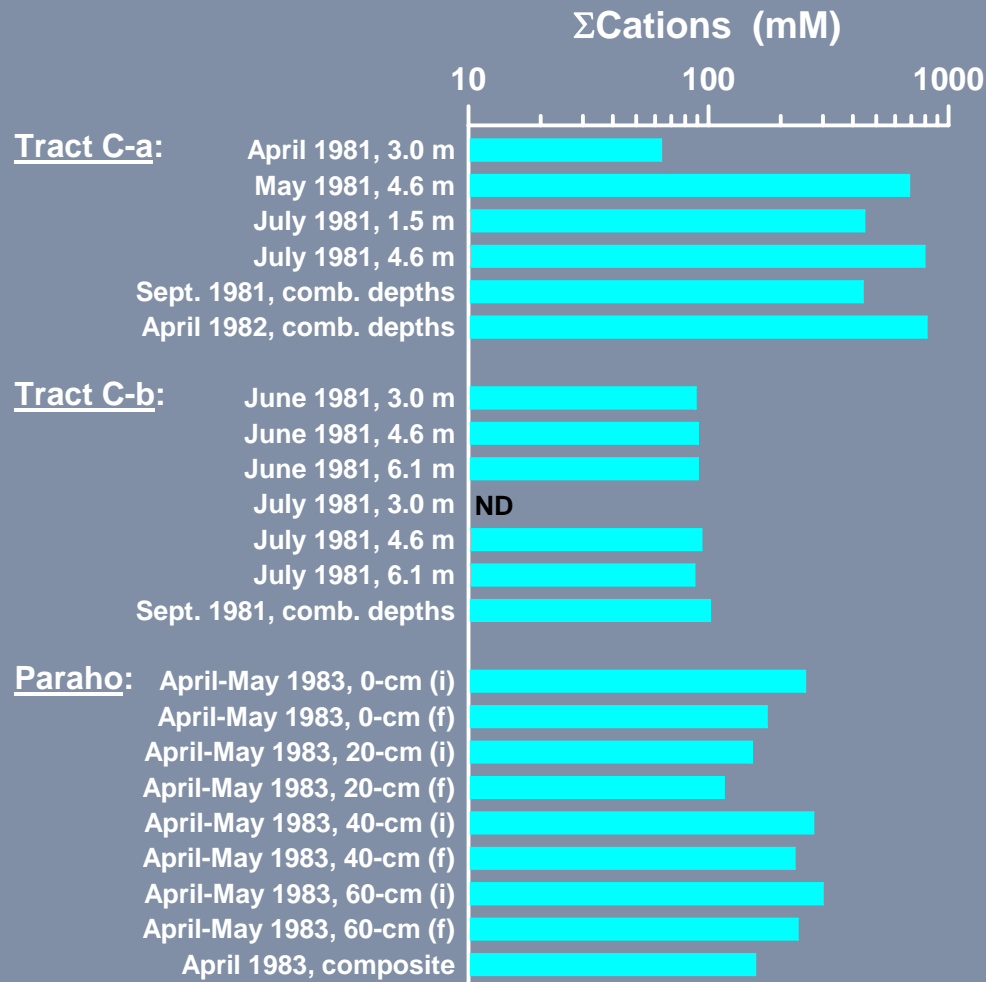
Methods (cont.)

Procedure

- Predict % mortality in each leachate using Mount et al. (1997) logistic regression model
- Calculate dilution of each leachate that would cause 50% survival (i.e., calculate LC50 as % of full-strength leachate)
- Compare predicted LC50 to reported LC50 for each leachate

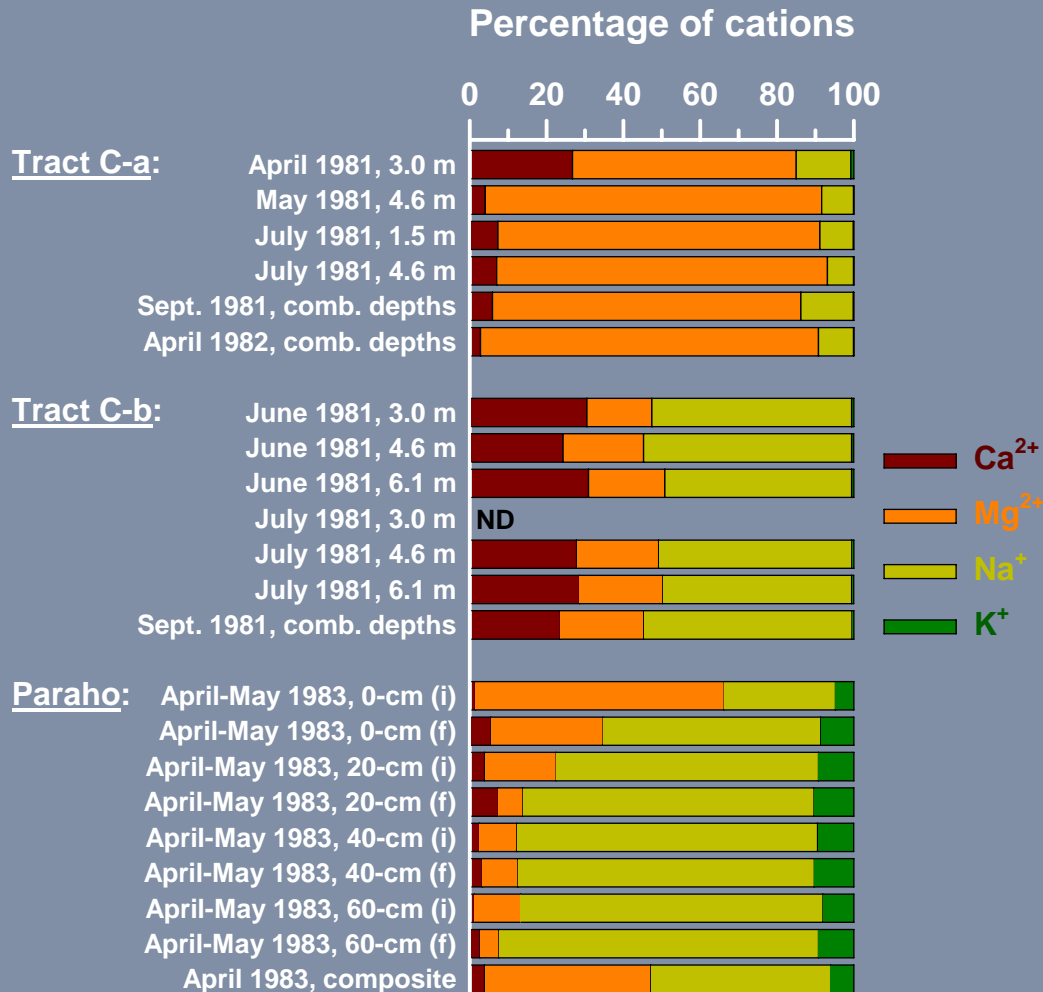
Results

All Leachates: Σ Cations and Conductivity



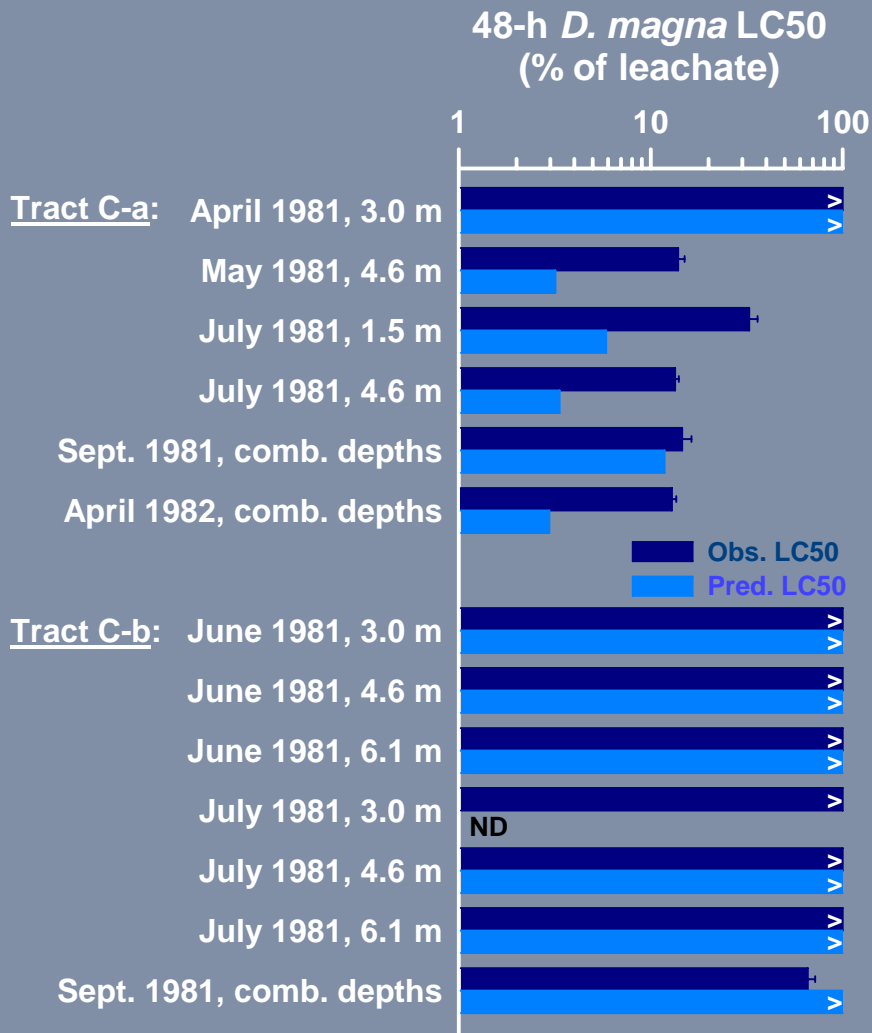
Results

All Leachates: Percentage Composition of Ions



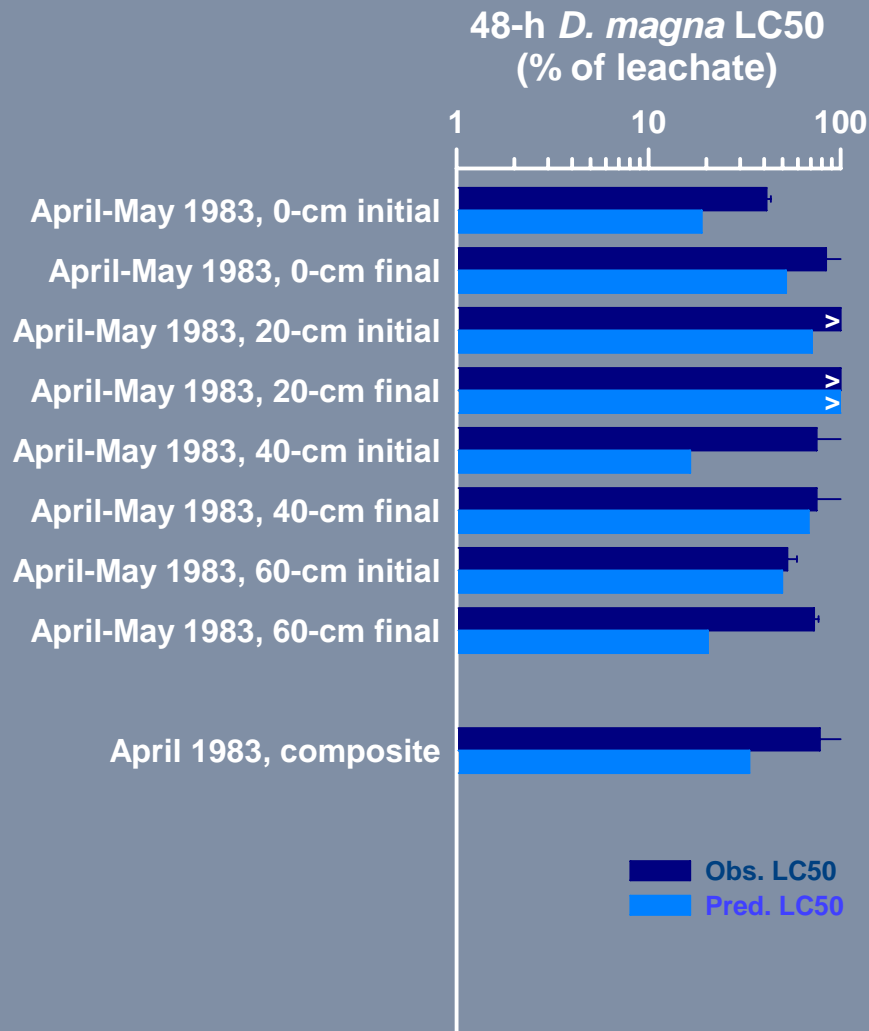
Results

Tracts C-a & C-b: Observed vs. Predicted LC50s



Results

Paraho: Observed vs. Predicted LC50s



Results

Interpretation of Predicted vs. Observed LC50s

- Mount et al. (1997) logistic regression model over-predicted toxicity of oil shale leachates by up to 7.7×
- However, organisms could have differed in sensitivity between the two studies conducted in different labs with different strains of the *D. magna* and FHM

Results

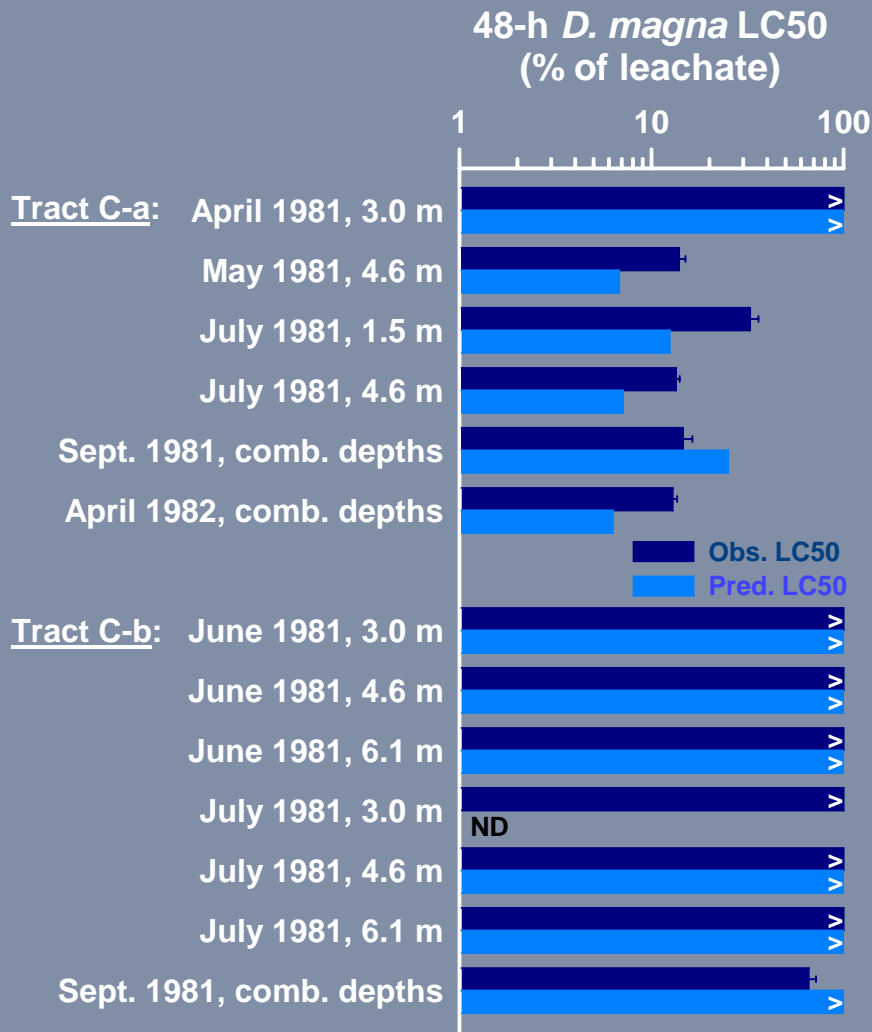
Reference-toxicant Tests

Species & duration	Toxicant	Meyer et al. (1985) LC50 (mg/L)	Mount et al. (1997) LC50 (mg/L)
<i>D. magna</i> 48 h	Na ₂ SO ₄	8,600	4,580
	MgSO ₄	4,300	1,820
FHM 96 h	Na ₂ SO ₄	15,200	7,960
	MgSO ₄	7,900	2,820

⇒ Need to multiply Mount et al. LC50s by average ratio to adjust predicted LC50s to account for different sensitivity

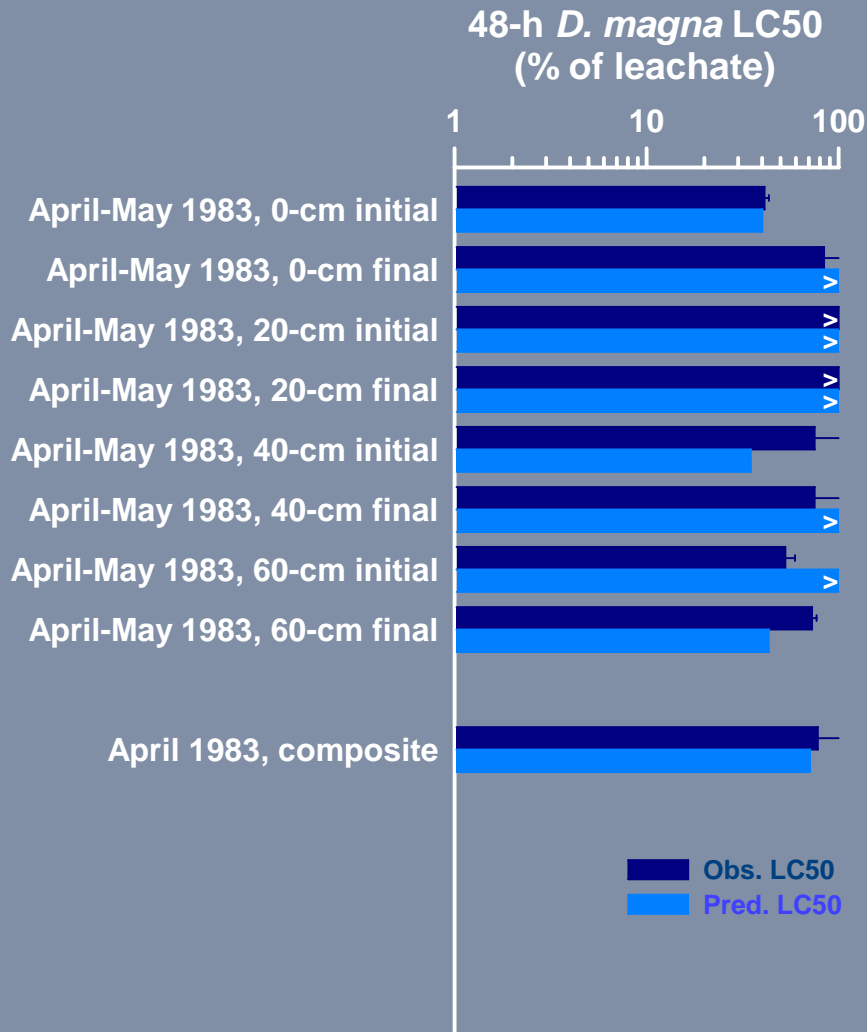
Results

Tracts C-a & C-b: Observed vs. Adj. Predicted LC50s



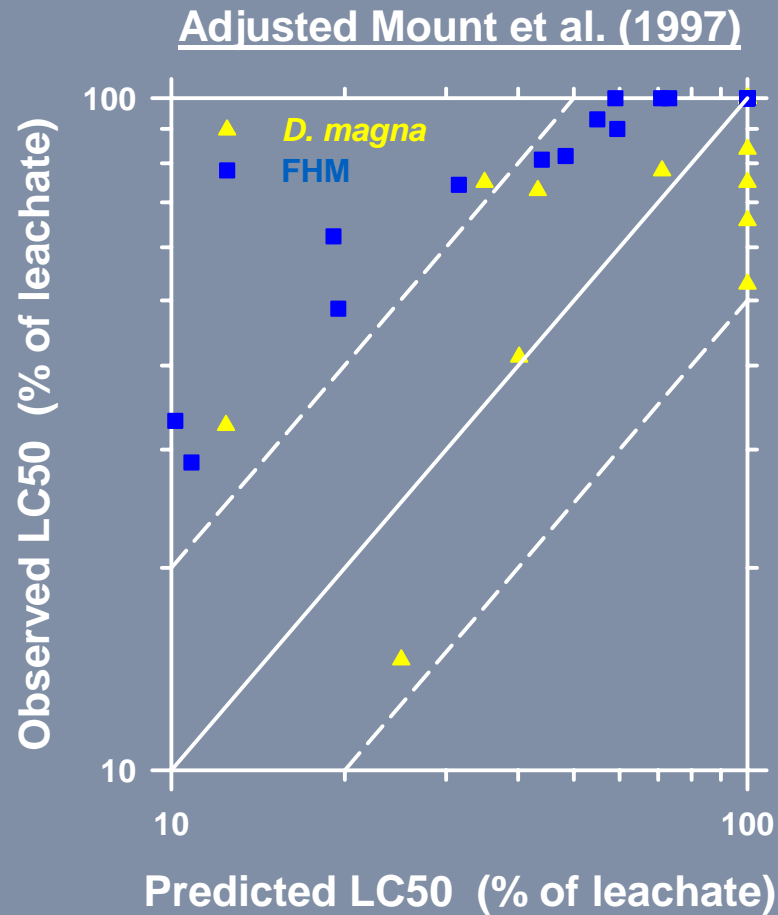
Results

Paraho: Observed vs. Adj. Predicted LC50s



Results

All Leachates: Observed vs. Predicted LC50s



Results

Interpretation of Adj. Predicted vs. Observed LC50s

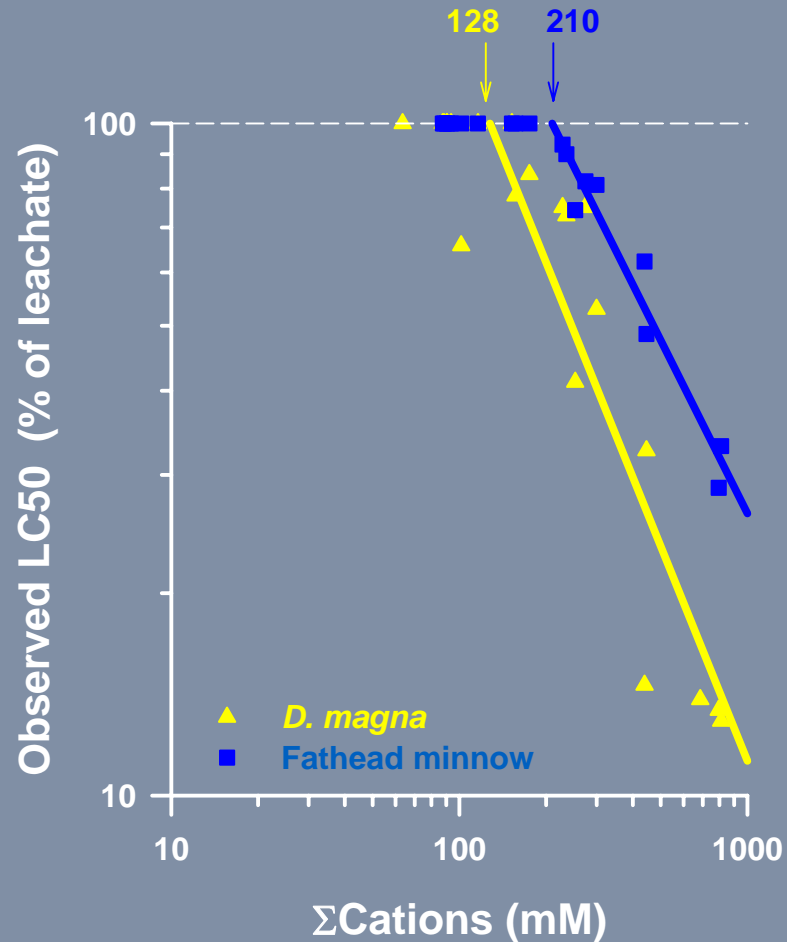
- LC50-adjustment ratio decreased the over-prediction of LC50s by the Mount et al. (1997) model to $<3.3\times$

⇒ **Better than before!**

- However, can LC50s of oil shale leachates be predicted even more accurately?

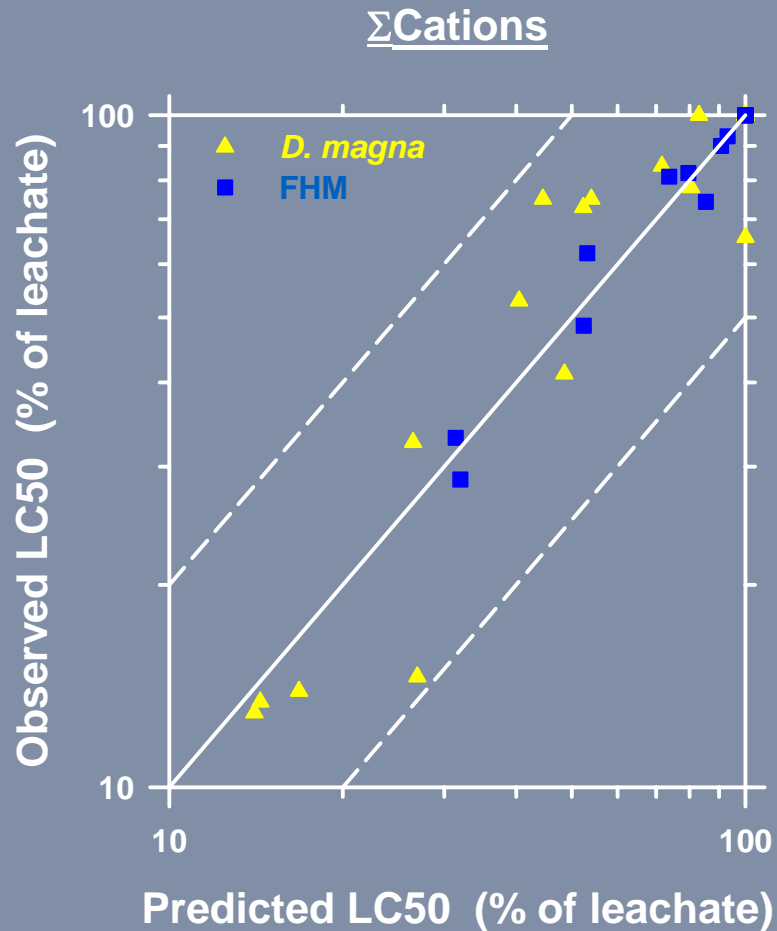
Results

All Leachates: LC50s vs. Σ Cations or Conductivity



Results

All Leachates: Observed vs. Predicted LC50s



Results

Interpretation of Σ Cations & Conductivity Regressions

- Predicted LC50s differ from observed LC50s by $<2\times$ using Σ cations (on a mM basis) or conductivity
 - ⇒ **Even better than with Mount et al. (1997) model!**
- However, beware of using these Σ cations and conductivity regressions for waters with different major-ion composition

Summary

- Raw and spent oil shale leachates were saline and were dominated by MgSO_4 and/or Na_2SO_4

$\Sigma\text{Cations} = 64 - 812 \text{ mM}$

Conductivities = 5,500 - 29,500 $\mu\text{S/cm}$

- Observed LC50s of leachates ranged 13 - >100% for *D. magna* and 29 - >100% for fathead minnows
- LC50s predicted by adjusted Mount et al. (1997) model over-predicted observed LC50s by <3.3×
- However, regressions of LC50 vs. $\Sigma\text{cations}$ or conductivity predicted observed LC50s even better

Conclusions

- Much (if not all) the toxicity of oil shale leachates might be caused by major ions
- ⇒ **The potential contribution of major ions to the toxicity of oil shale leachates should not be overlooked**

Imagine the result