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

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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 ↑, toxicity decreases

as LC50 ↓, 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 (unpublished data)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

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

where x_1, …, 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 *D. magna*
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

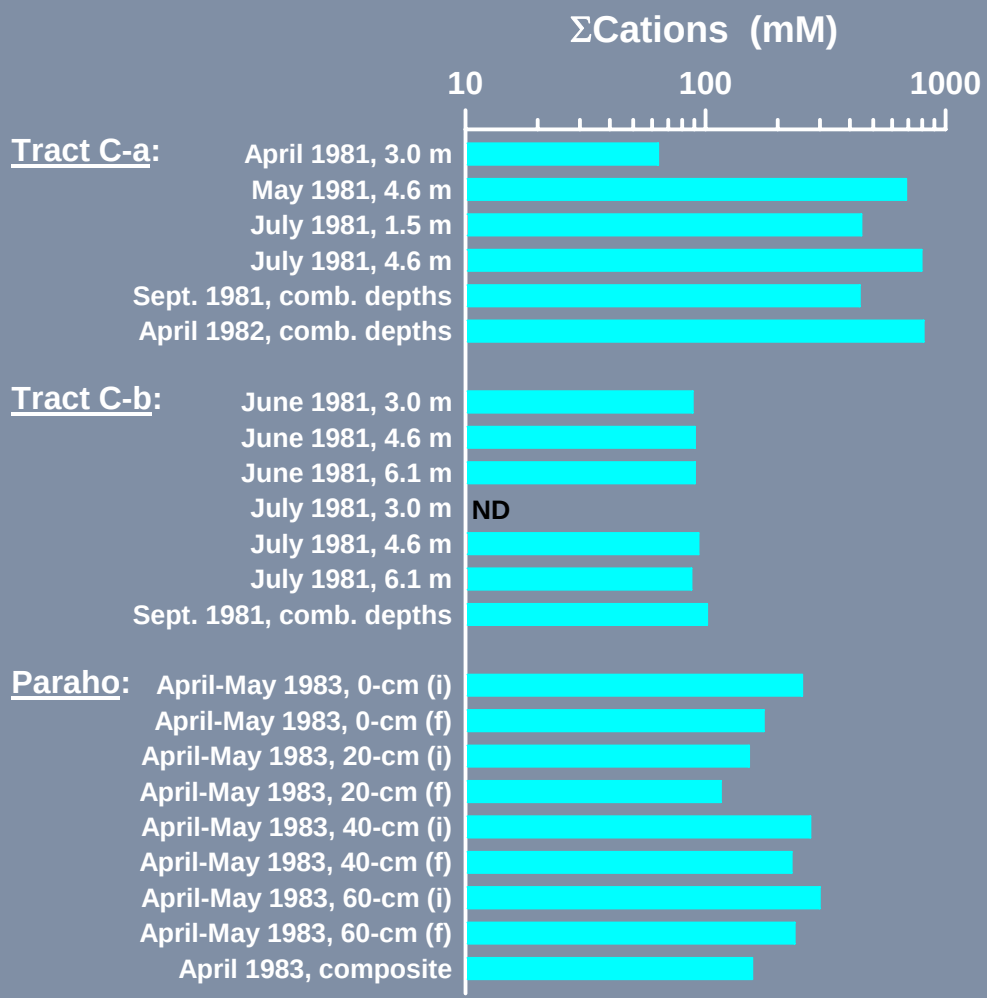
Methods (cont.)

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

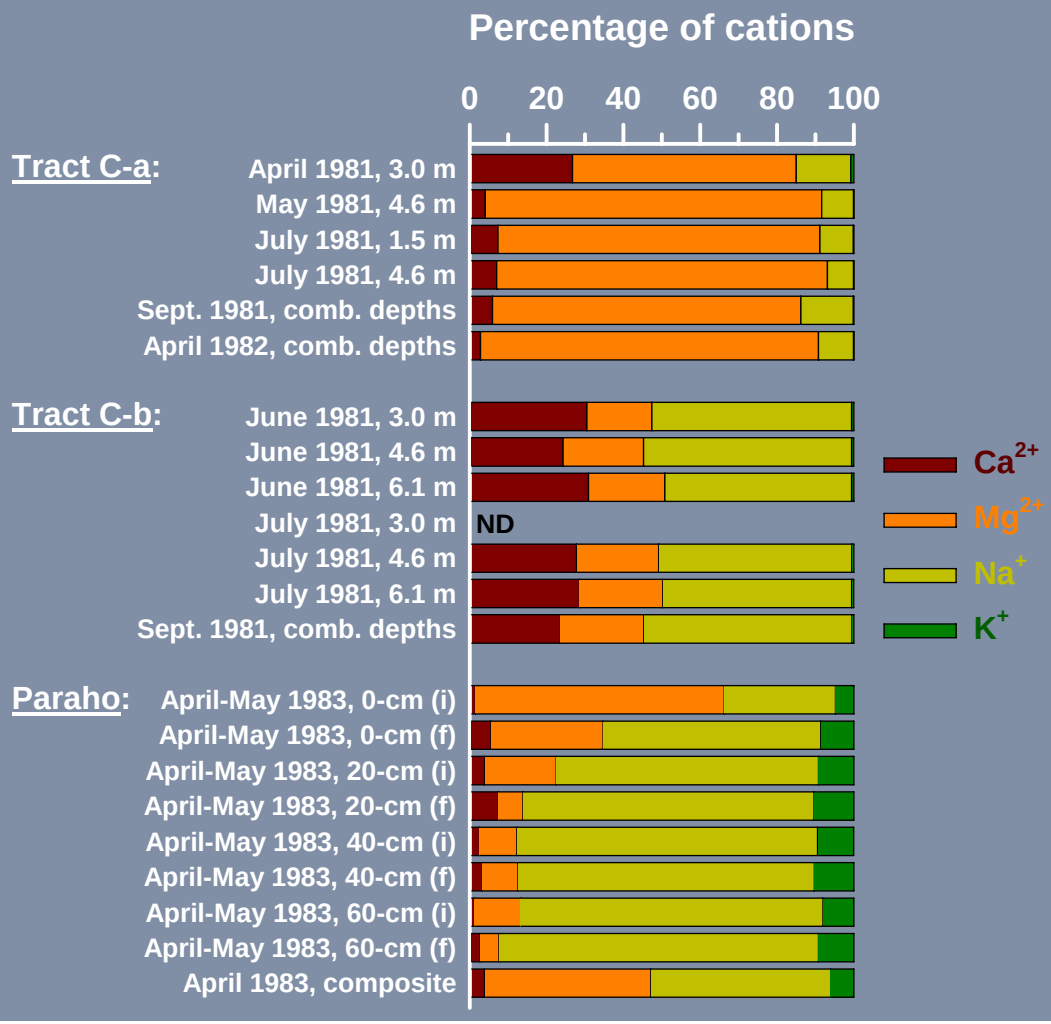
Results

All Leachates: ΣCations and Conductivity



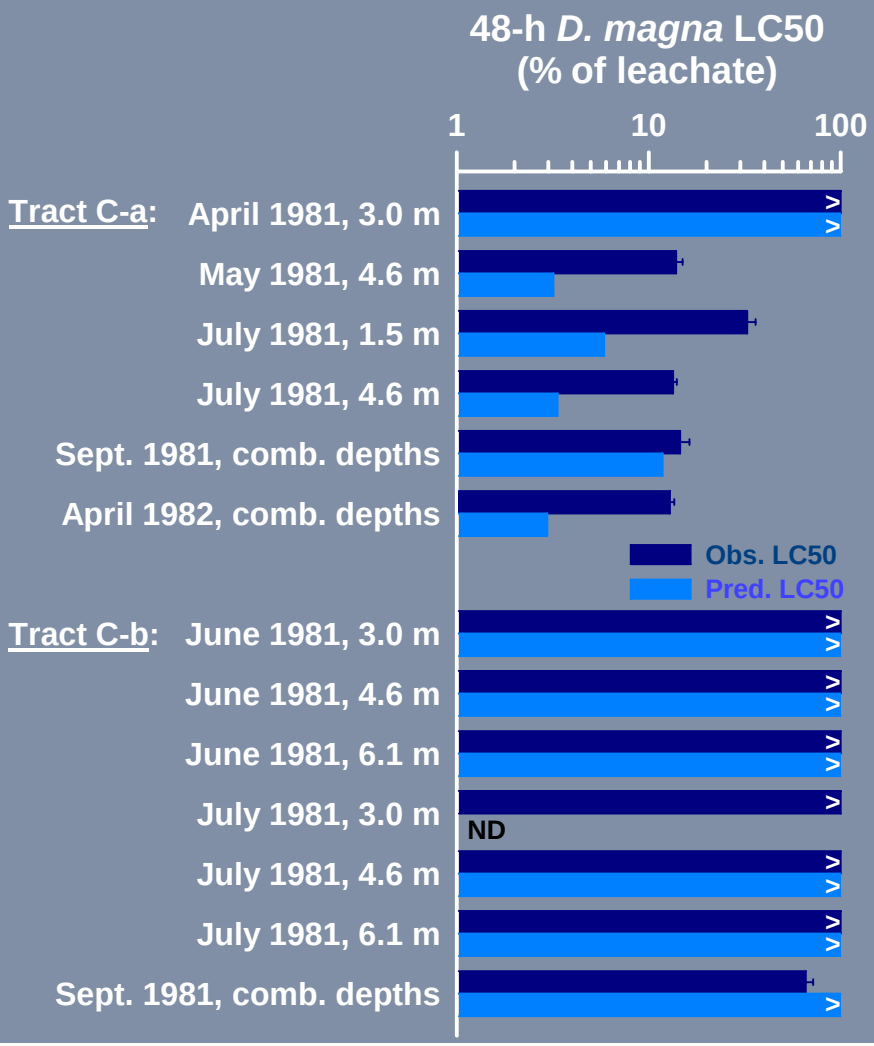
Results

All Leachates: Percentage Composition of Ions



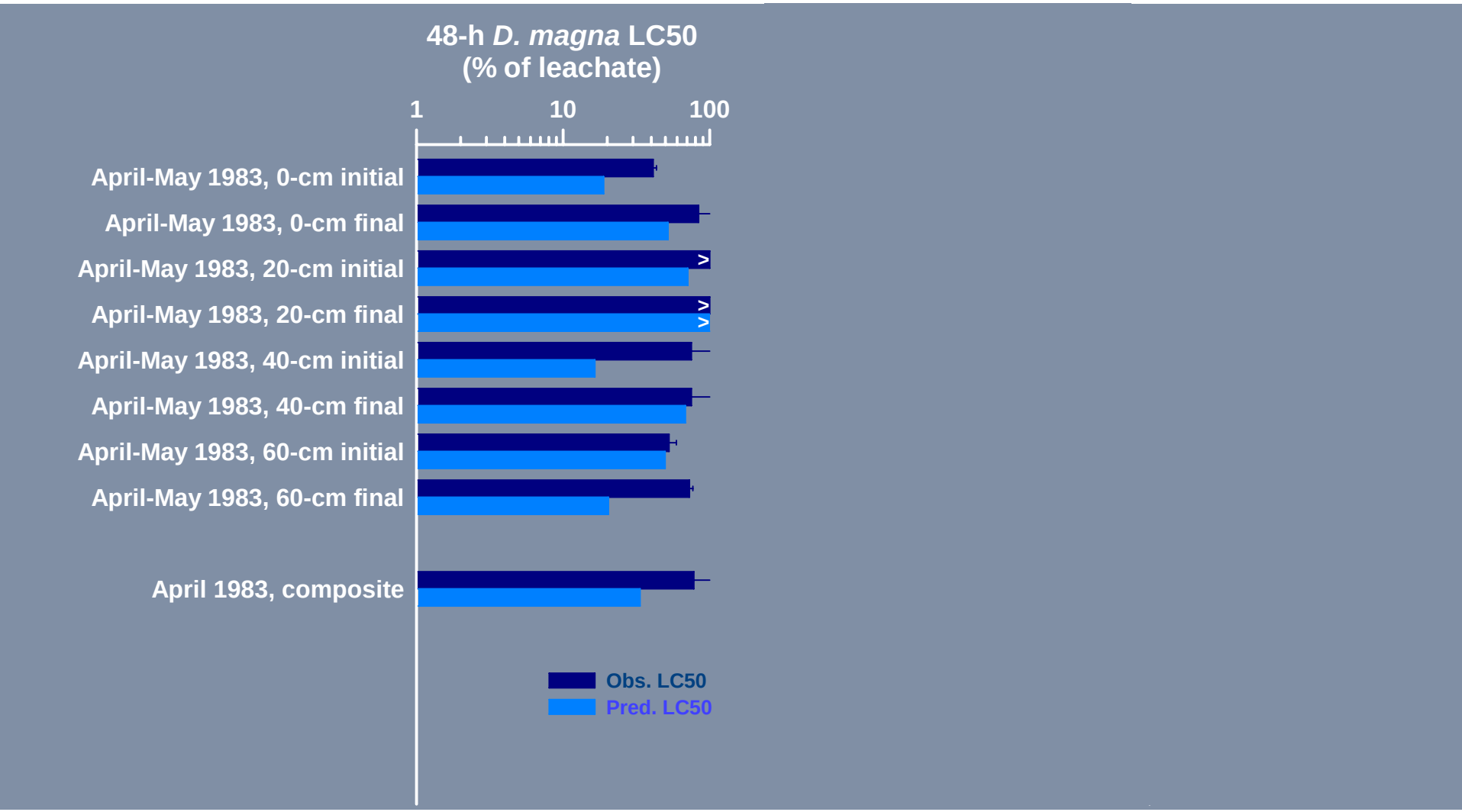
Results

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

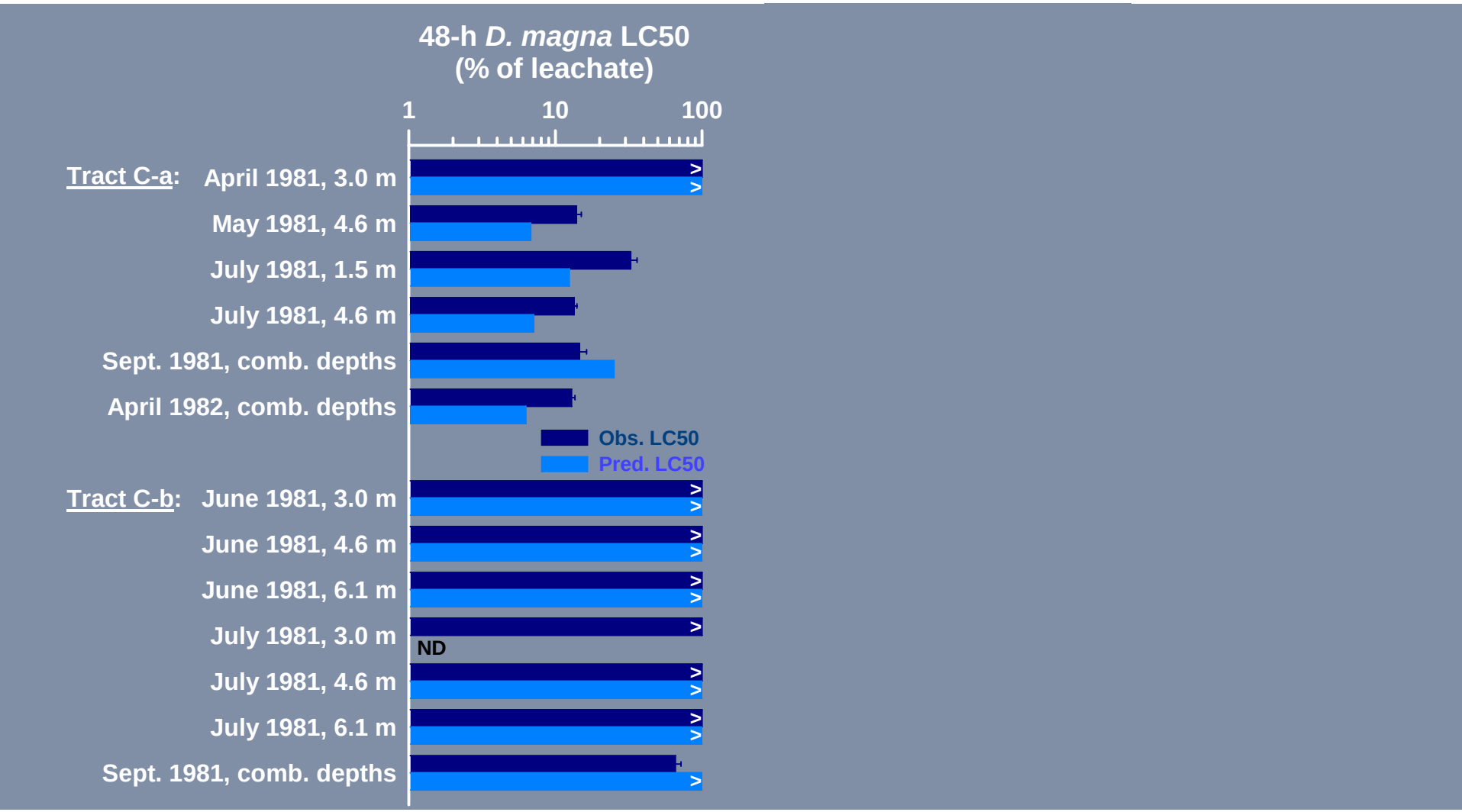
Reference-toxicant Tests

Species & duration	Toxicant	Meyer et al. (1985) LC50 (mg/L)	Mount et al. (1997) LC50 (mg/L)
D. magna 48 h	Na_2SO_4	8,600	4,580
	$MgSO_4$	4,300	1,820
FHM 96 h	Na_2SO_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**

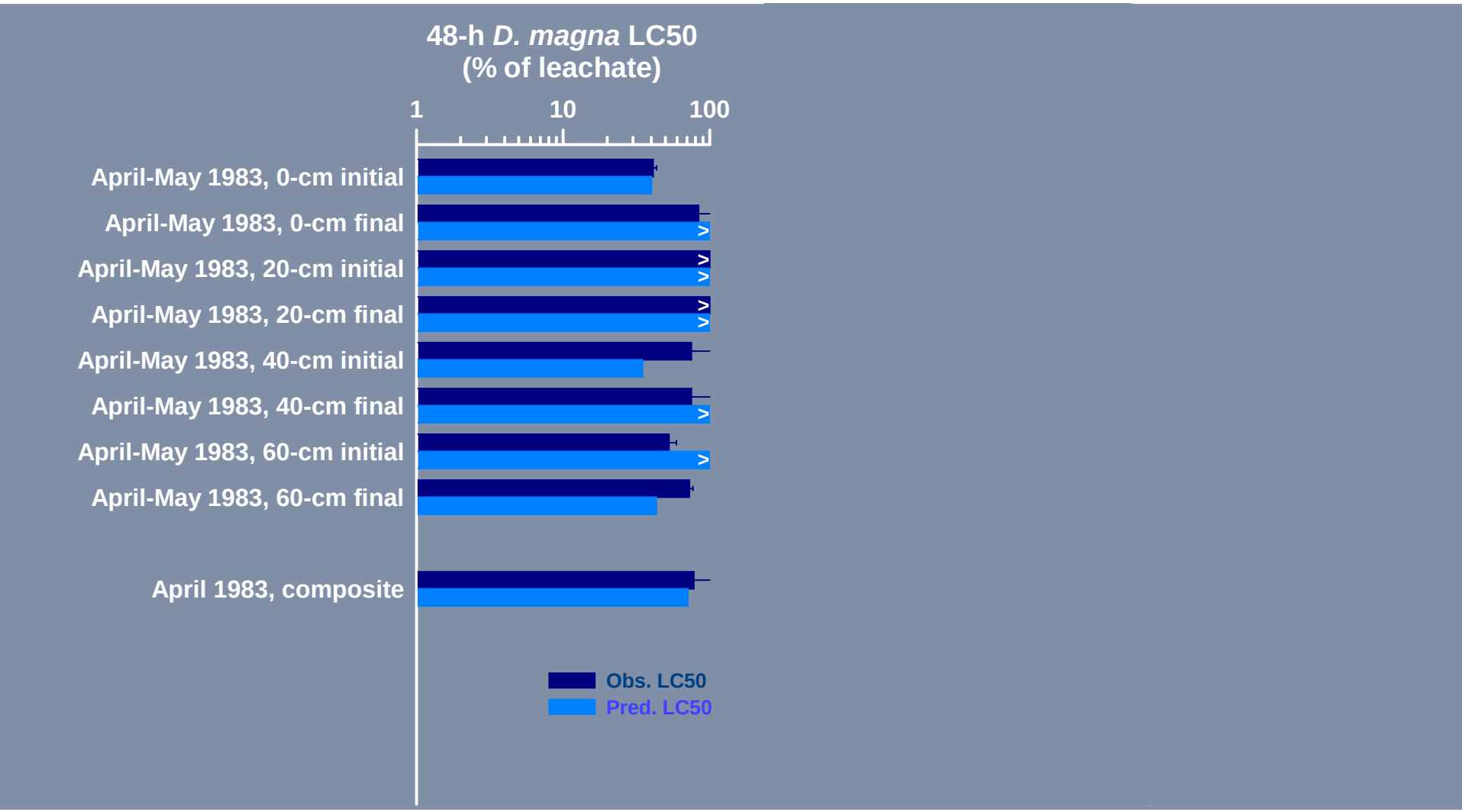
Results

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



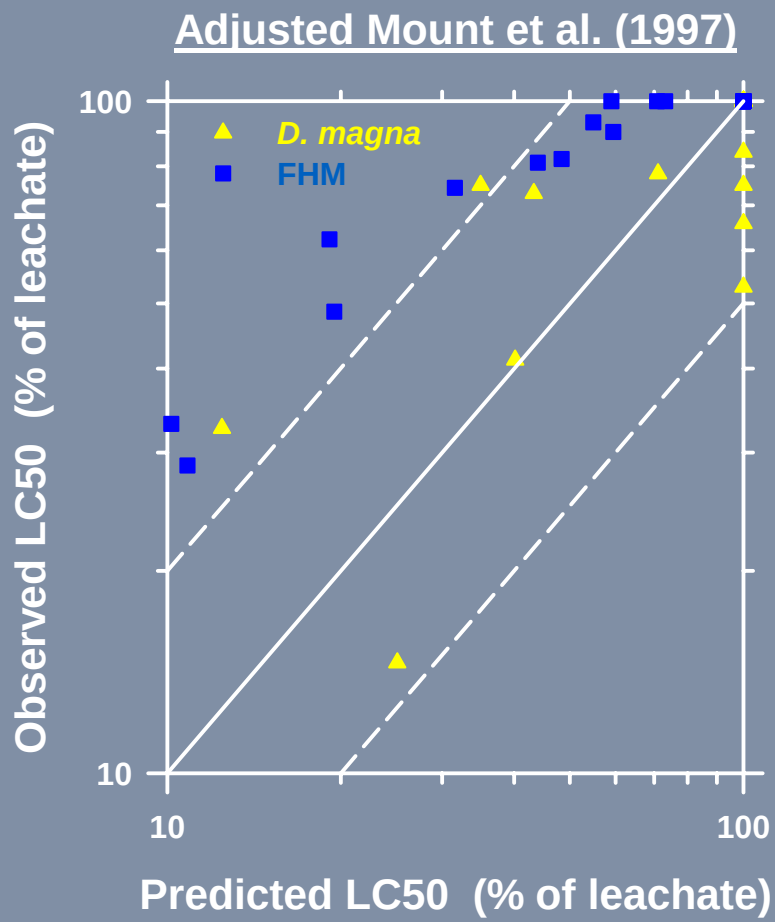
Results

Paraho: Observed vs. Adj. Predicted LC50s



Results

All Leachates: Observed vs. Predicted LC50s



Results

Interpretation of Adj. Predicted vs. Observed LC50s

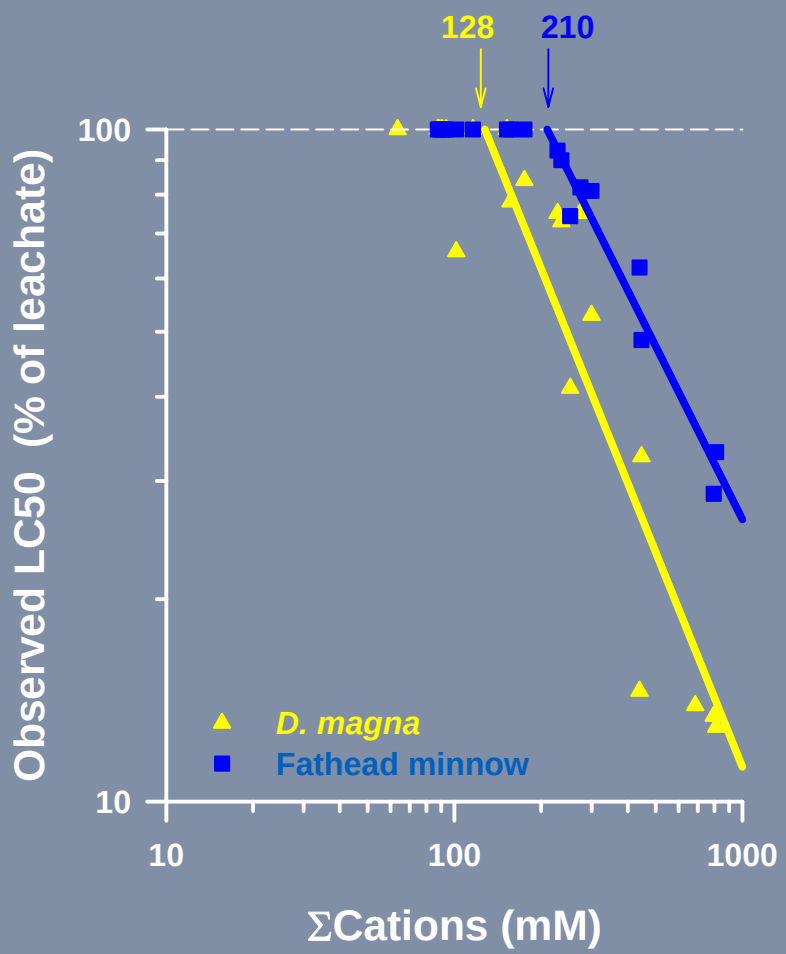
- **LC50-adjustment ratio decreased the over-prediction of LC50s by the Mount et al. (1997) model to <3.3×**

  ⇒ Better than before!

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

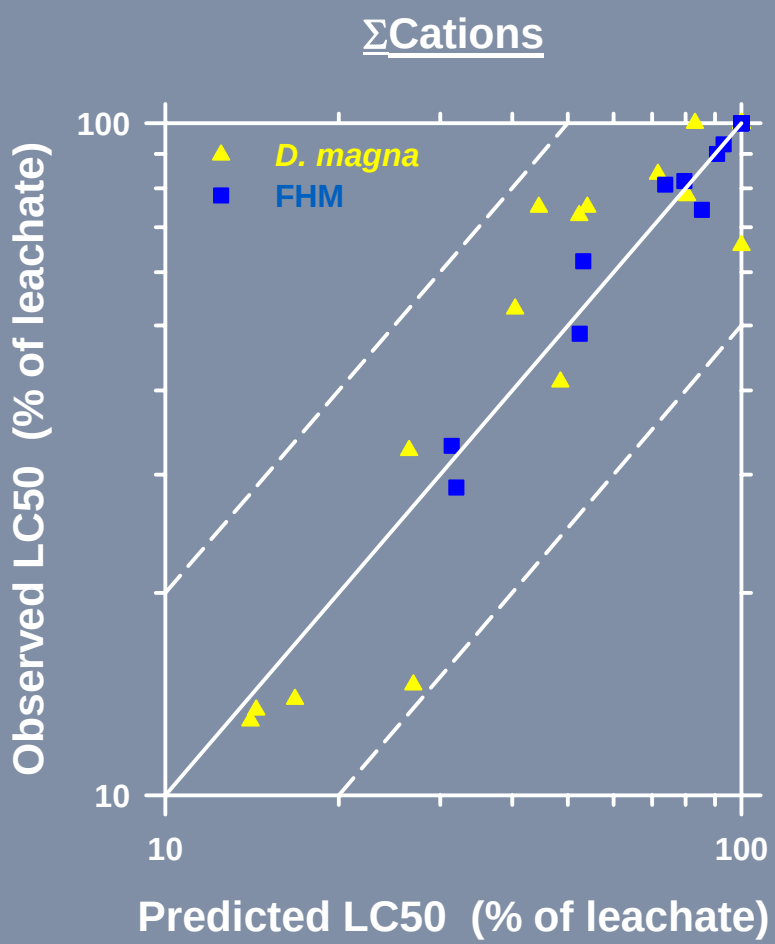
Results

All Leachates: LC50s vs. ΣCations or Conductivity



Results

All Leachates: Observed vs. Predicted LC50s



Results

Interpretation of ΣCations & Conductivity Regressions

- **Predicted LC50s differ from observed LC50s by <2× using Σcations (on a mM basis) or conductivity**

  ⇒ Even better than with Mount et al. (1997) model!

- **However, beware of using these Σcations 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

  ΣCations = 64 - 812 mM
  Conductivities = 5,500 - 29,500 μS/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. Σcations 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