

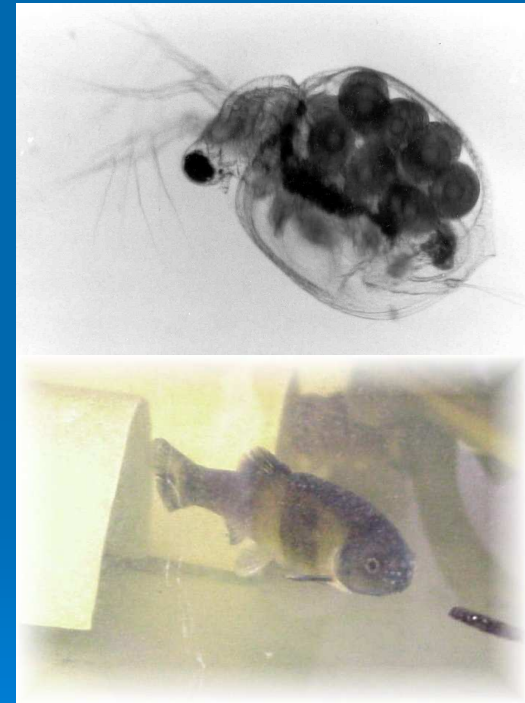
Identifying the Cause of Laboratory
Whole Effluent Toxicity to
Ceriodaphnia dubia from Fidelity's
CBNG Produced Water Discharges
and Assessing Potential Effects in
the Tongue River

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Whole Effluent Toxicity Tests Required in Discharge Permit

- 48-h acute whole effluent toxicity (WET) test using water flea *Ceriodaphnia dubia*
- 96-h acute WET test using the fathead minnow (*Pimephales promelas*)
 - WET Limit: median lethal concentration (LC50) at test termination > 100%



WET Performance

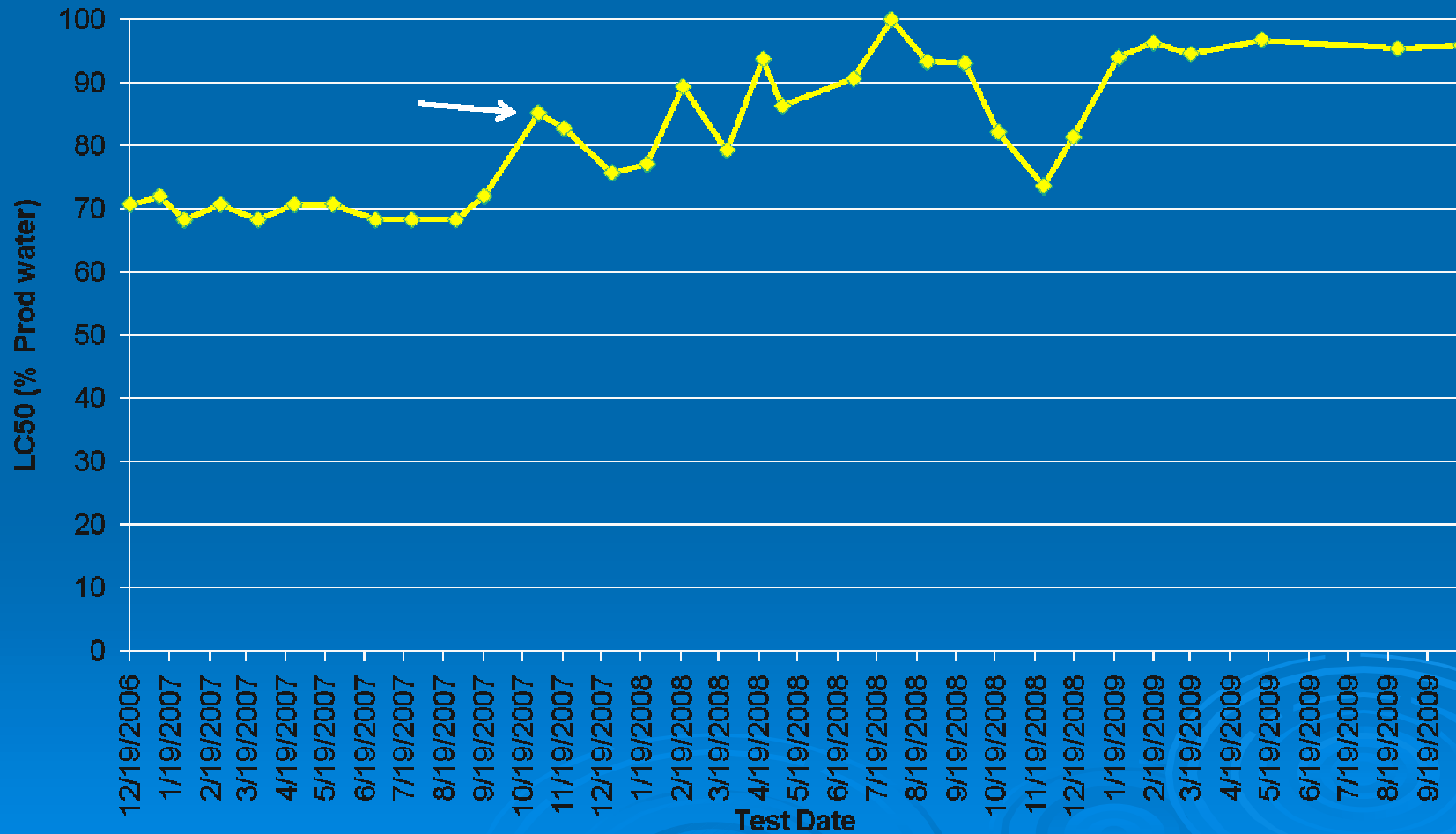
- Fathead minnow WET tests always pass at all discharge points
 - Survival effects to *C. dubia* often observed at very high concentrations of produced water
 - Toxicity Identification Evaluation (TIE) required
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- The bottom right corner of the slide features a decorative graphic of several concentric, light blue circles that resemble ripples on water, set against the dark blue background.

At What Concentration do Survival Effects Occur?

- Historically, LC₅₀ often ~70% because of very low survival in 100% PW but 100% survival in 50% PW
- Additional test treatments added to narrow down toxic threshold LC₅₀
- 65, 85 and 92% PW treatments

Historical LC50 Data, Outfall 016

C. dubia LC50s through August 2009, Outfall 016



What is a TIE?

- Series of studies designed to characterize, identify and confirm the cause of toxicity in the test medium, in this case, produced water
 - Phase I TIE (multiple manipulations)
 - Species sensitivity (Phase III)
 - Mock effluent tests (Phase III)
 - Modeling (***GRI- FWSTR***)

PHASE I Studies



Usual Phase I Manipulations

- Filtration
- Aeration
- pH adjustment (acidic [3] and basic [11])
- Solid Phase Extraction (SPE, C18)
- Chelation with EDTA
- Oxidant Reduction with sodium thiosulfate (STS)
- pH control (CO₂ atmosphere)
- Additional manipulations as needed

Phase I Results – Outfall 012 (2007)

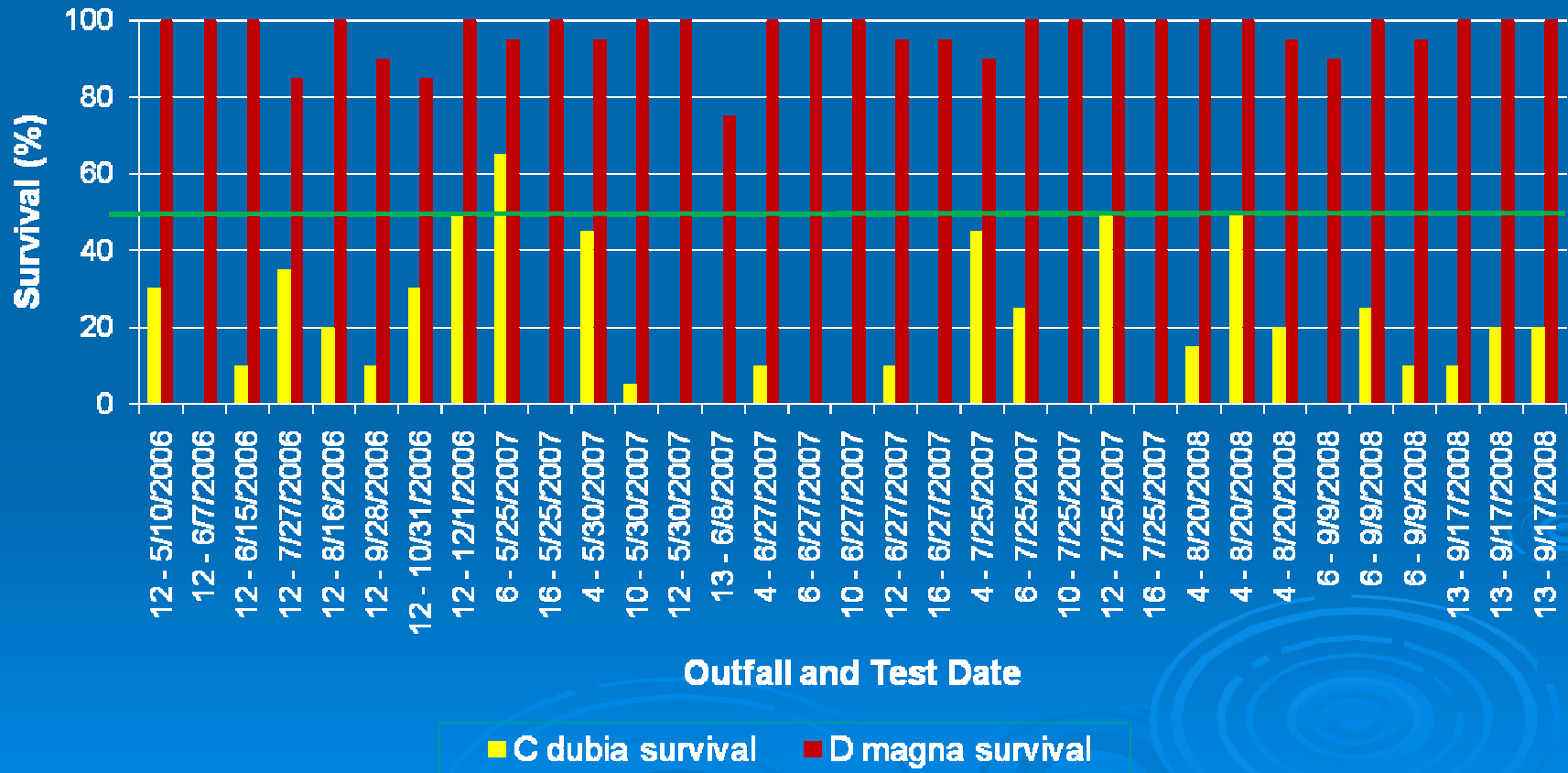
Description	Sample 20671 (13 June '07)			Sample 20767 (2 July '07)		
	Surv. 100% PW	LC50 (%)	Tox. Reduc.?	Surv. 100% PW	LC50 (%)	Tox. Reduc.?
Initial WET	0	57.53	NA	10	65.93	NA
Baseline	40	89.09	NA	0	70.71	No
1 um Filt	90	>100	Yes	0	70.71	No
C18 SPE	90	>100	Yes	90	>100	Yes
Aeration	30	82.03	No	10	73.49	No
pH 3	70	>100	Yes	90	>100	Yes
pH 3 Filt	100	>100	Yes	70	>100	Yes
pH 3 SPE	100	>100	Yes	80	>100	Yes
pH 3 Aer	100	>100	Yes	100	>100	Yes
pH 11	0	70.71	No	0	70.71	No
pH 11 Filt	0	70.71	No	0	70.71	No
pH 11 SPE	10	73.49	No	0	70.71	No
pH 11 Aer	0	70.71	No	0	64.84	No
EDTA	0	70.71	No	0	70.71	No
STS	50	100	No	0	70.71	No
CO2 (~7.5)	70	>100	Yes	50	100	Yes

Species Sensitivity



Sensitivity of Two Cladocerans

Daphnia magna and *Ceriodaphnia dubia* Survival in 100% Produced Water (values on or below red line (50% mortality) represent a WET failure)



Mock Effluents



Mock Effluents

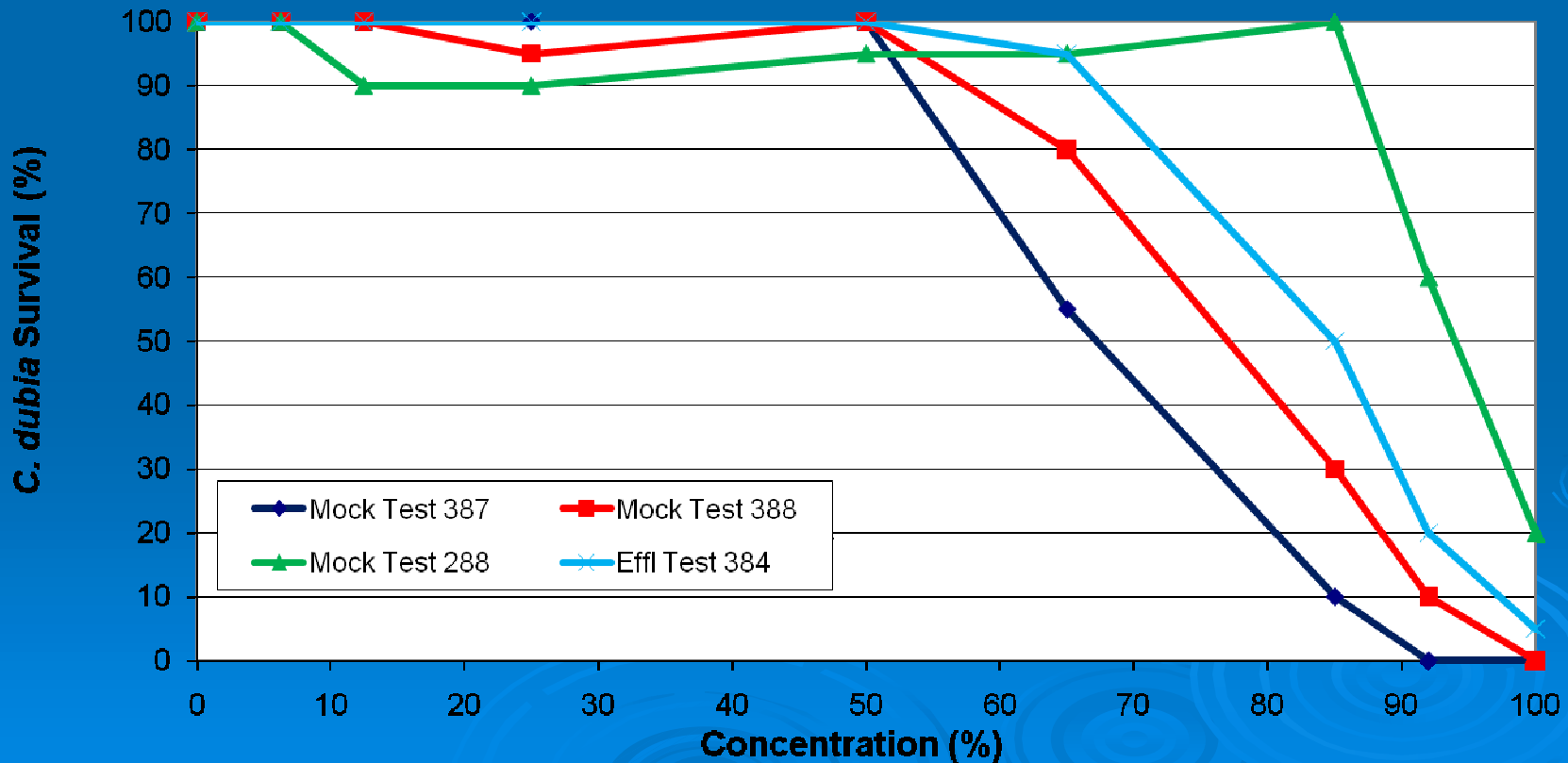
- Match the concentration of the particular suspect parameter(s)
- Can be particularly effective in identifying toxicity due to total dissolved solids (TDS)
- Prepared with clean laboratory water and reagent-grade chemicals
- For Fidelity studies, mocks prepared by matching concentrations of seven major freshwater ions: Ca, Na, K, Mg, Cl, SO₄ and HCO₃

Concentrations of Major Ions in Effluent from Outfall 016

Ion	Ion Concentrations (mg/L)	
	#21808 (rec. on June 4, '08)	#21913 (rec. on July 1, '08)
Ca	7.6	4.9
Na	590	480
K	12	10
Mg	5.8	3
Cl	NM	19
HCO ₃	1707	1707
SO ₄	71	42
Sum of Ions	~2393	~2266

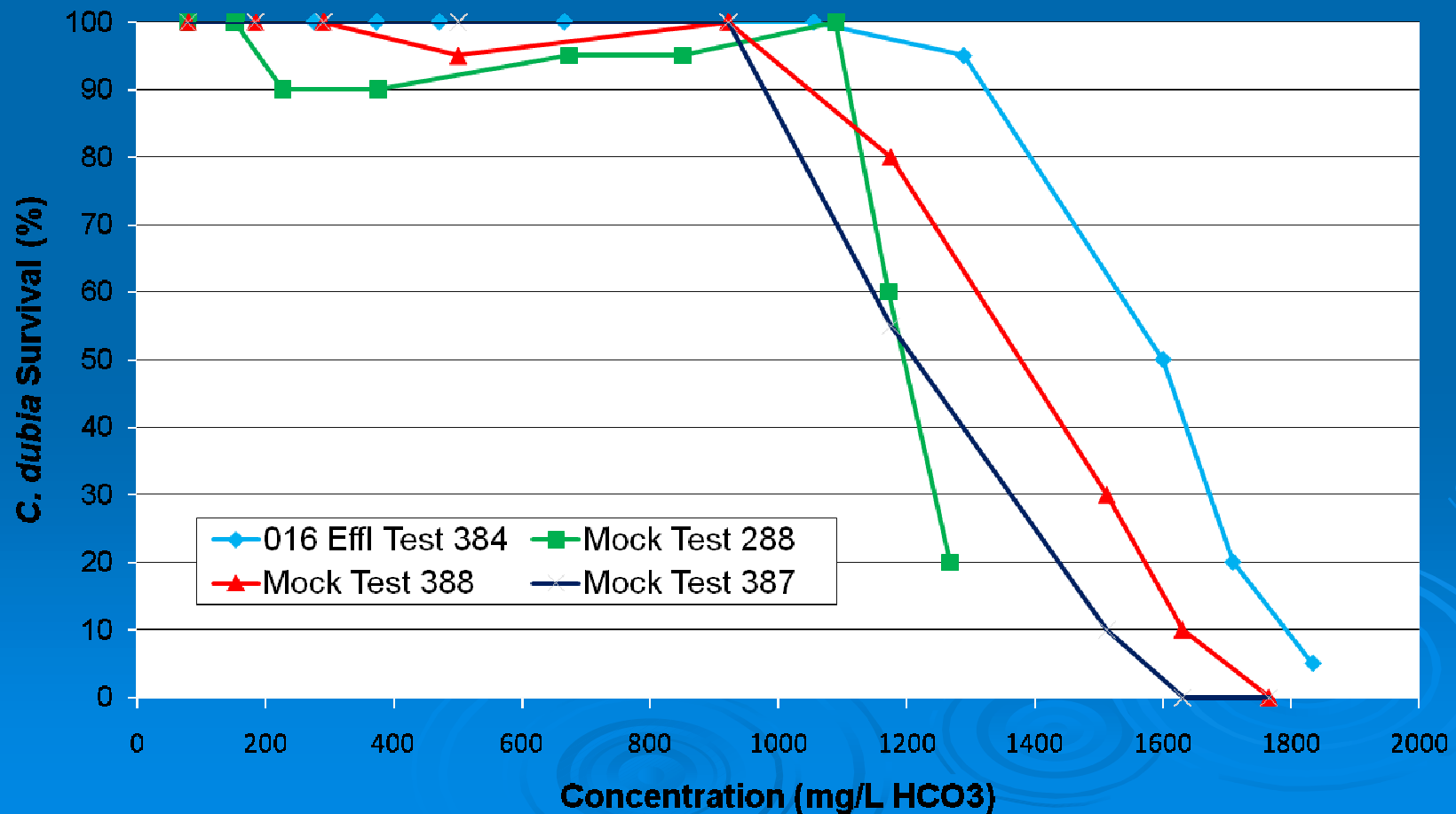
Comparison of Toxicity in Mock Effluents and Effluent

Comparison of Three Mock Effluent Tests and One Effluent (016) Test, Based on Percent Test Water



Comparison of Toxicity in Mock Effluents and Effluent

Comparison of *C. dubia* survival in Three Mock Effluent Tests and One Effluent (016) Tests, Based on Bicarbonate Concentration




Salinity-Toxicity Relationship (STR) Model Results



Actual vs Predicted Survival of *C. dubia* in Produced Water

Outfall	Ion Concentration (mg/L)							Actual/Predicted 48-h Survival of <i>C. dubia</i> (%)		
	Ca	Na	Mg	K	SO4	Cl	HCO3	Test 1	Test 2	STR
006	3.2	410	1u	8.1	2u	22	1341	35	55	9
013	7.5	600	5.1	12	99	16	1829	10	30	0.2

2009 – Additional TIE Tests

- Effluents and mock effluents from outfalls 006 and 013
 - TDS ions
 - TDS ions + methane
 - Aeration (to reduce methane)
 - Storage for 1 week
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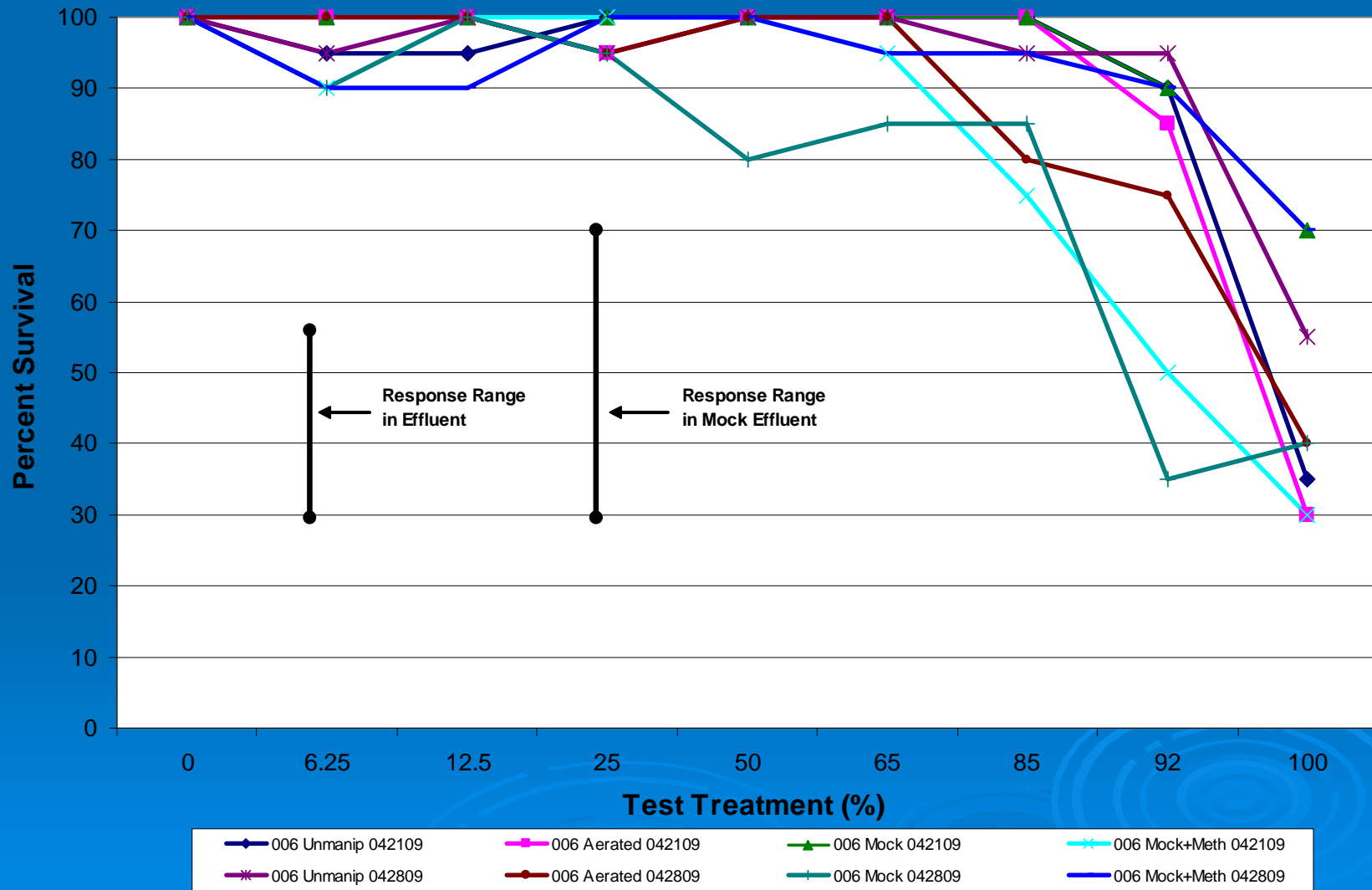
Results of 2009 Studies

- Methane in the effluent was quickly reduced by agitation of the sample
- Presence of methane in the effluent or mock effluent had no apparent impact on survival of *C. dubia*



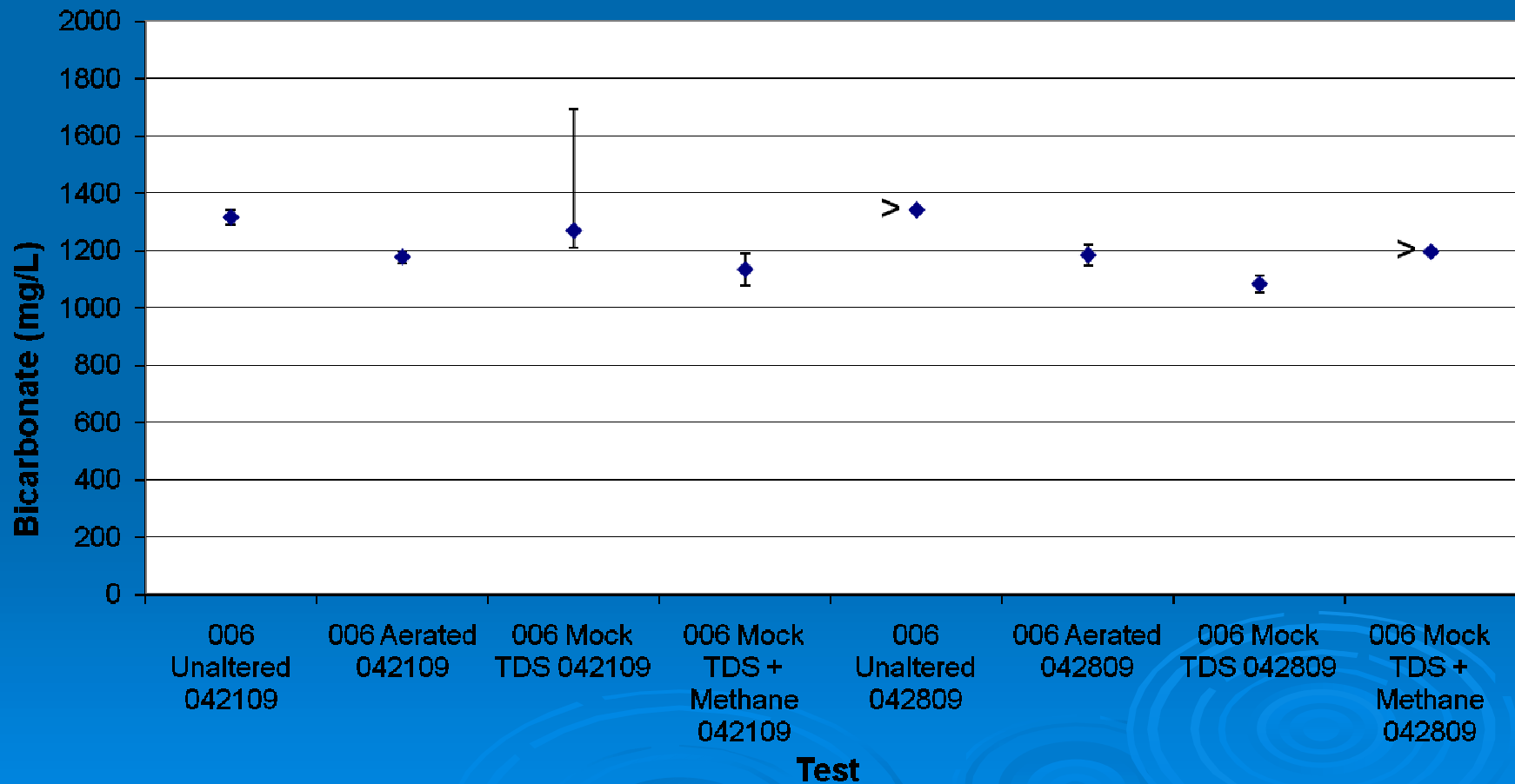
All 006 Effluents and Mock Effluents

Figure 1. Survival of *C. dubia* in April 21 & 28 Tests of Outfall 006 Effluents and Mock Effluents



LC50s of 006 Effluent and Mock Effluent Tests when Normalized to Bicarbonate

2009 TCIP Studies
Outfall 006 48-Hr LC50s Based on Bicarbonate (mg/L)



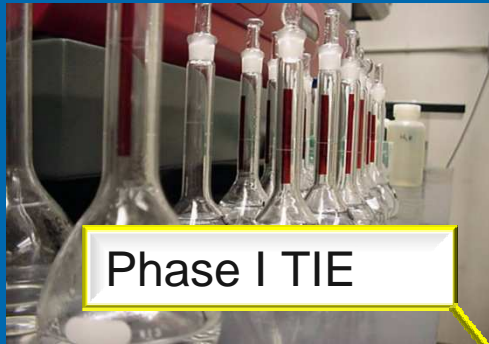
Summary

- Produced water from Fidelity outfalls often toxic to *C. dubia* in laboratory WET tests at high (near 100%) concentrations
- Treating with acid to $\text{pH} \leq 3$ (followed by readjustment) in Phase I TIE studies often reduced or eliminated toxicity
- Raising the pH increased toxicity because of the increase in ion concentrations from bases and acids
- Produced water was never toxic to *Daphnia magna*, a cladoceran that is less sensitive to TDS

Summary (Cont)

- Mock effluent tests to match TDS ion concentrations usually demonstrated toxicity \geq effluent (lower LC50s)
- When normalized to TDS ion concentration or bicarbonate concentration, mock effluents were at least as toxic as effluents
- Analysis with the STR model indicated TDS ions accounted for all of the observed toxicity

Conclusion



Failure of *C. dubia* WET tests in the laboratory is due to TDS

