Ammonia and Sulfides Purging Triggers and Procedures

Revisions to the 2013 SMARM clarification paper

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US Army Corps of Engineers Seattle District

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Background

2013 Clarification Paper

- modified existing purging triggers
- purging triggers based on NOEC
- recommended ammonia ref tox test run at ½ NOEC
- pre-bioassay testing on overlying water
- larval test to be purged by aeration only

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Purging and Ref Tox Triggers

Trigger	Bedded sediment tests				Larval tests	
	Neanthes	*Ampelisca*	*Eohaustorius*	*Rhepoxynius*	*Bivalve*	*Echinoderm*
Unionized Ammonia (mg/L) Ref Tox	0.23	0.118	0.4	0.2	0.02	0.007
Unionized Ammonia (mg/L) Purge	0.46	0.236	0.8	0.4	0.04	0.014
Hydrogen Sulfide (mg/L) Purge	3.4	0.0094	0.122	0.099	0.0025	0.01

Comments Received

NewFields

Bill Gardiner
Brian Hester

NWAS/SEE

Dick Caldwell
Tim Thompson

Insightful but sometimes conflicting comments

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Comments Received

NewFields

- measure porewater for bedded sediment tests
- bioassay labs should do the pretesting, not the analytical labs
- alternative method proposed for purging larval test
- continued purging during bioassay may be necessary

NWAS/SEE

- porewater is more relevant than overlying water for *Eohaustorius*, *Rhepoxynius* and *Neanthes*
- pre-bioassay testing will increase costs; have analytical lab do more of the pretesting
- have analytical lab measure both bulk and porewater
- measure sulfides on composite, not individual core

Data Collection

- Additional ammonia/sulfides data were collected for four federal projects to answer the following questions:

  1. For sediment stored for bioassays, would bulk measurements taken after several weeks of storage be different from measurements made when the sediment first gets to the analytical lab?

  2. Would it be useful to have the analytical labs measure porewater concentrations in addition to, or instead of, bulk concentrations?

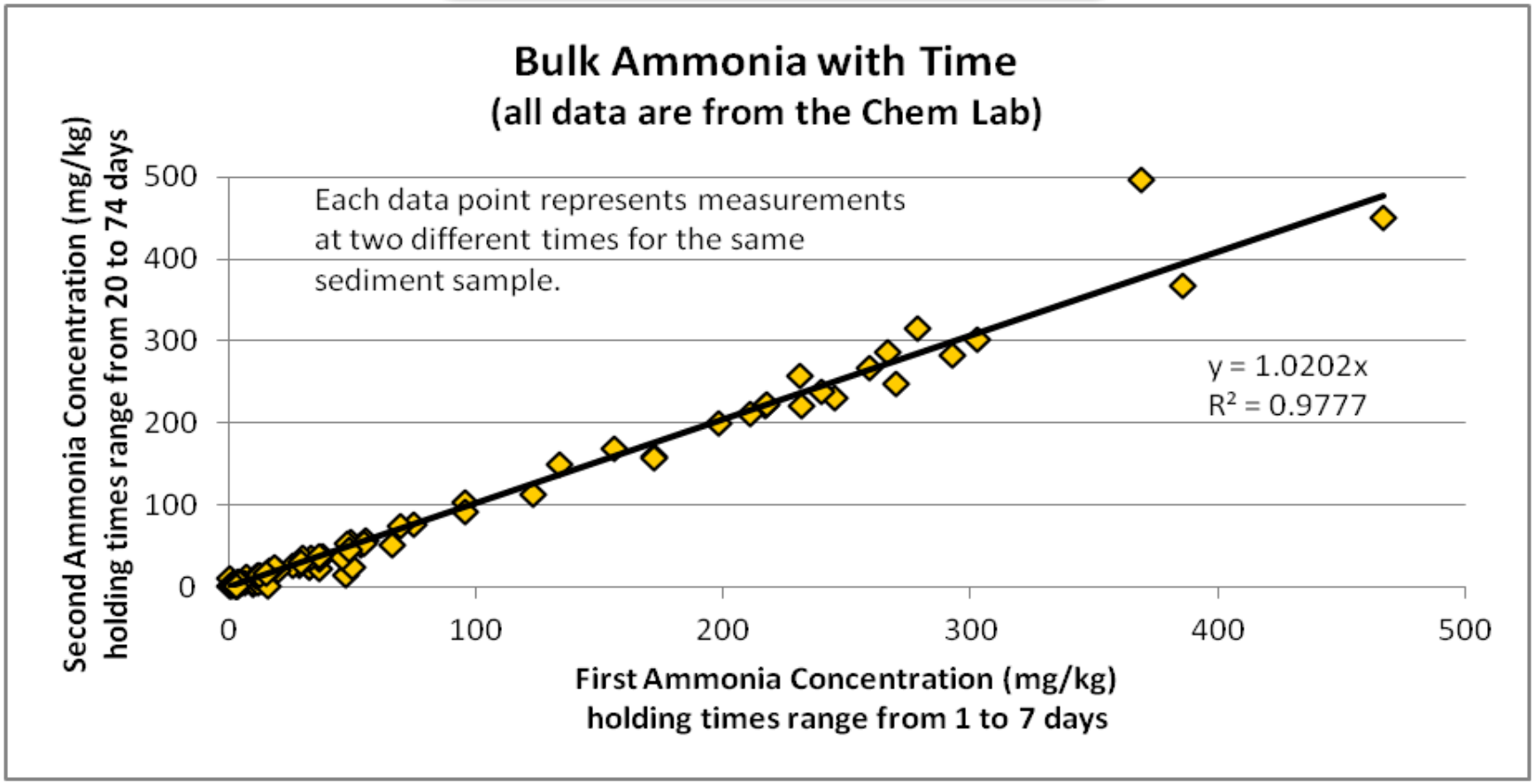
  3. How well do concentrations measured by the analytical labs match up with concentrations measured by the bioassay labs?

Data Collection

4. Would measurements of bulk sulfides on composites be better than our traditional way of measuring on samples from individual cores?
5. How well does the purging method suggested by NewFields for the larval test compare to the aeration-only method?
6. How much sediment is lost using the NewFields method?
7. Does either purging method result in a loss of contaminants?

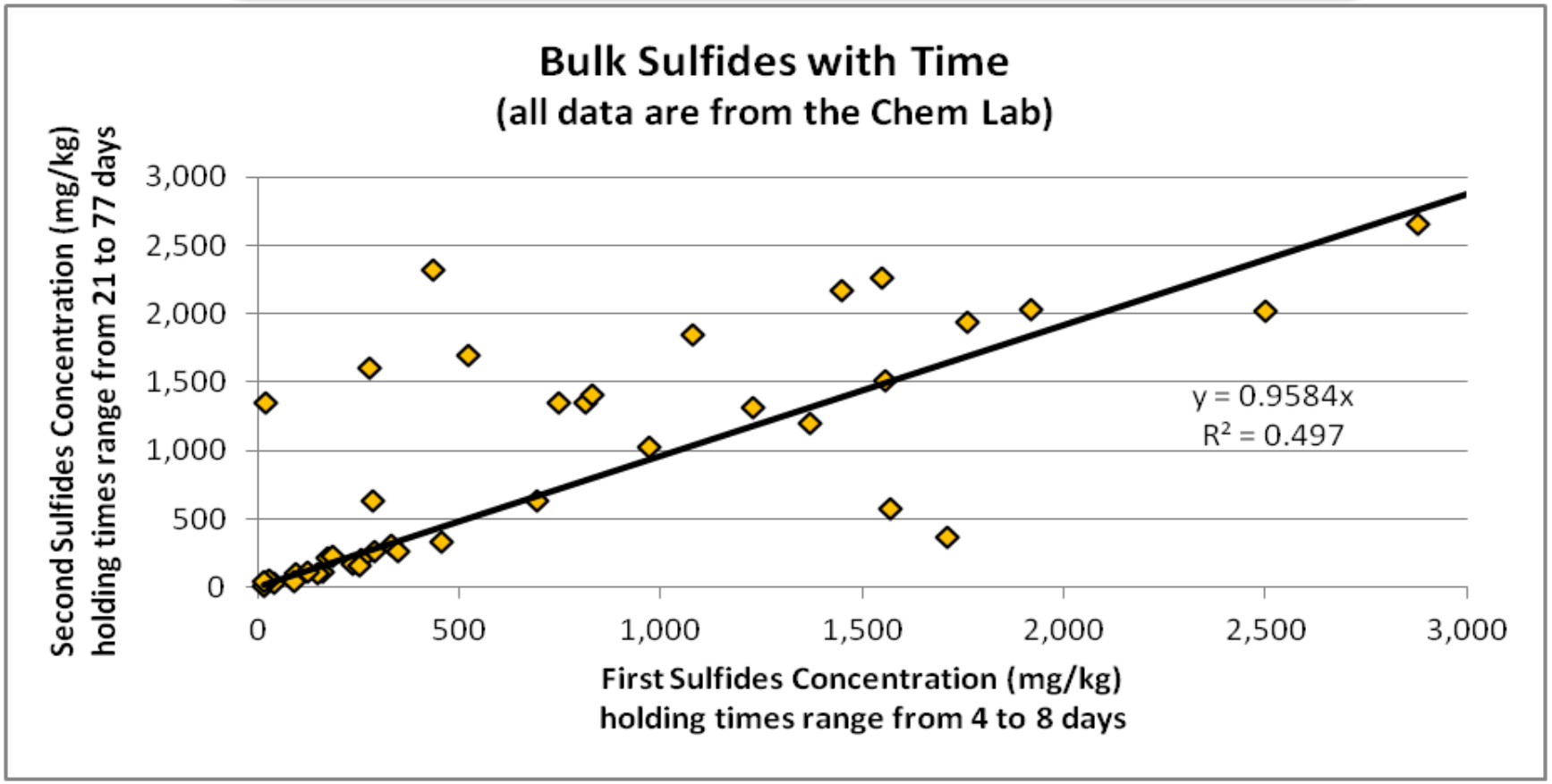
1. Experimental Findings

Bulk ammonia stable with time
(as measured by analytical lab)



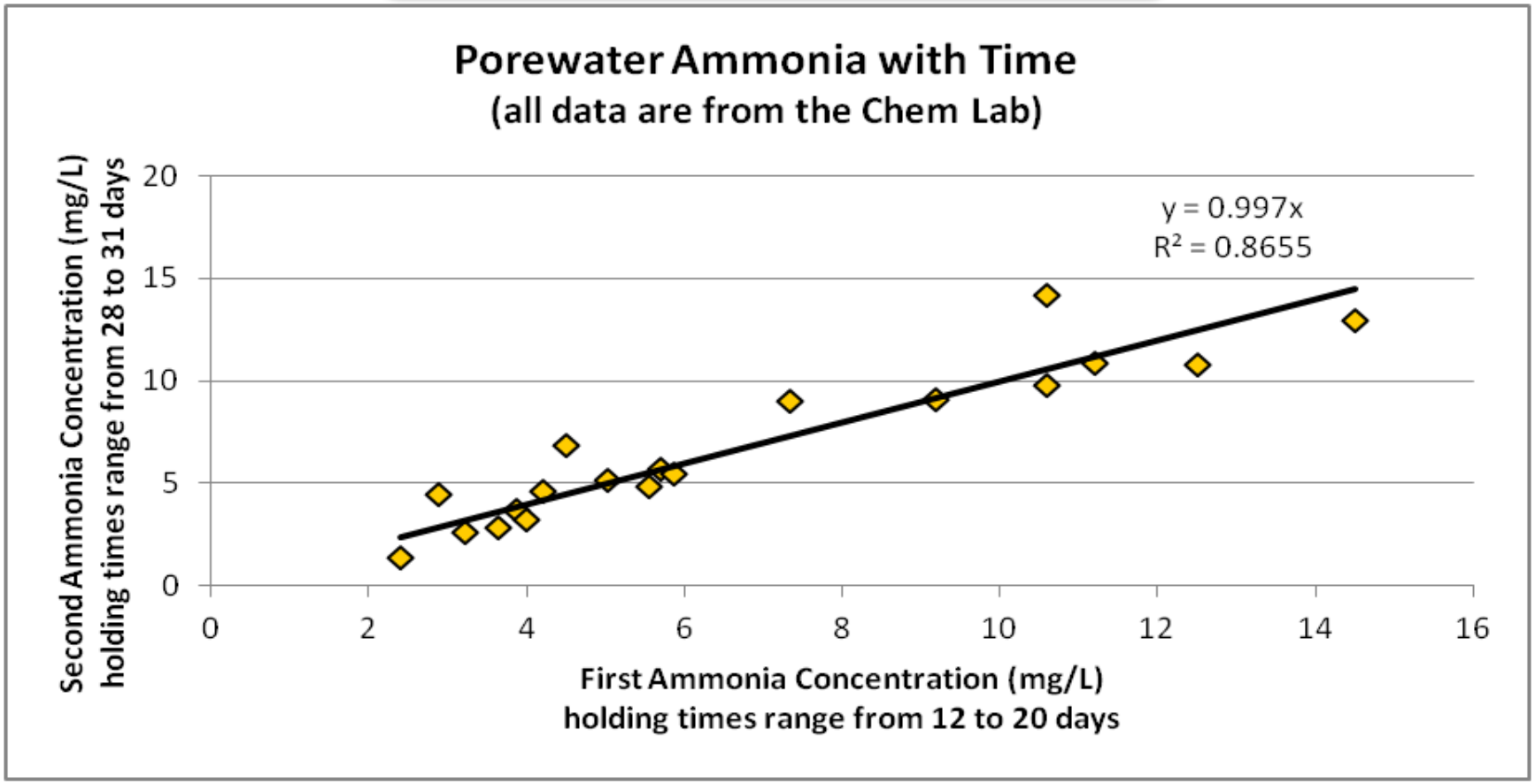
1. Experimental Findings

Bulk sulfides measurements highly variable over time (as measured by analytical lab)



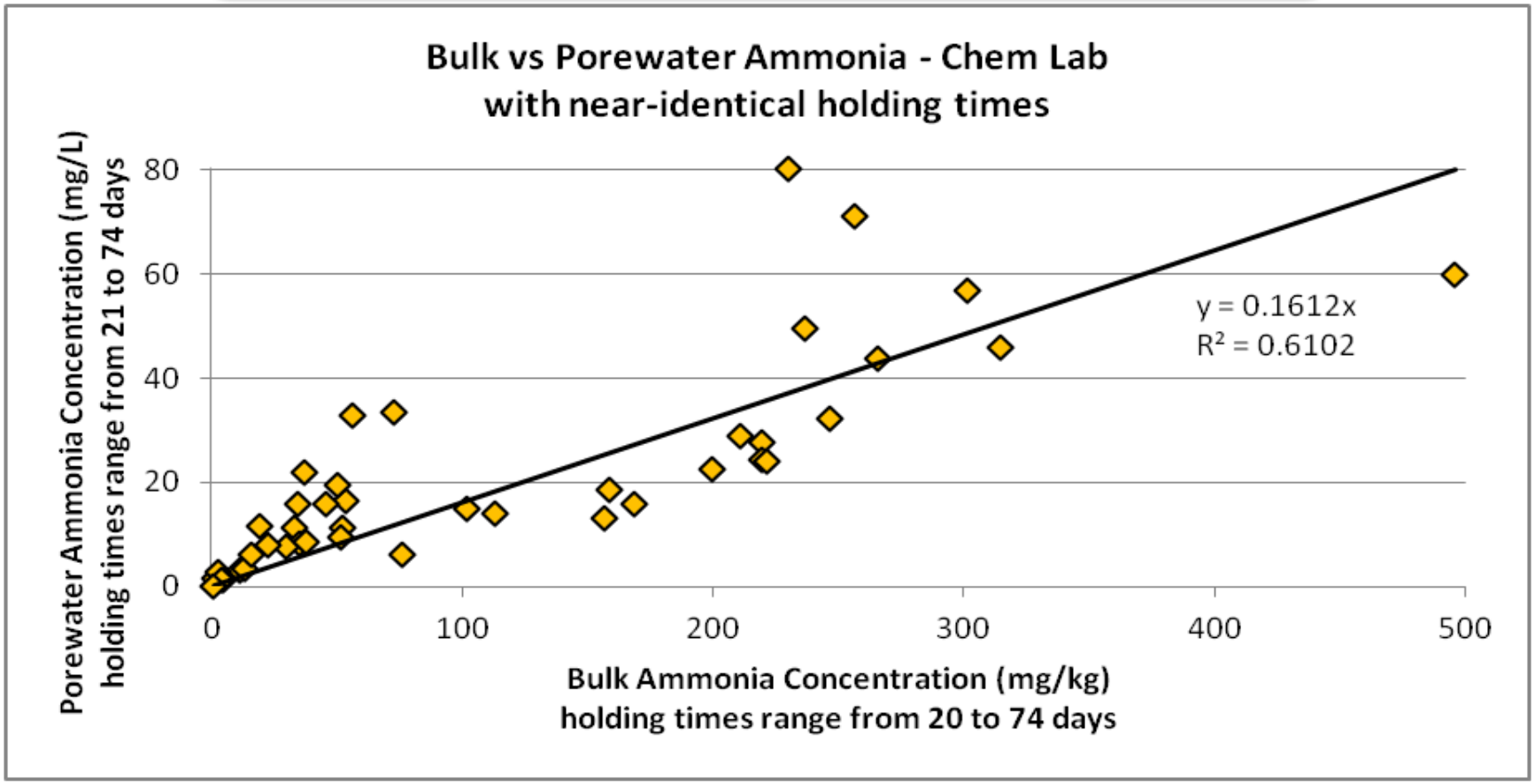
2. Experimental Findings

Porewater ammonia stable with time
(as measured by analytical lab)



2. Experimental Findings

Bulk and porewater ammonia not highly correlated
(as measured by analytical lab)



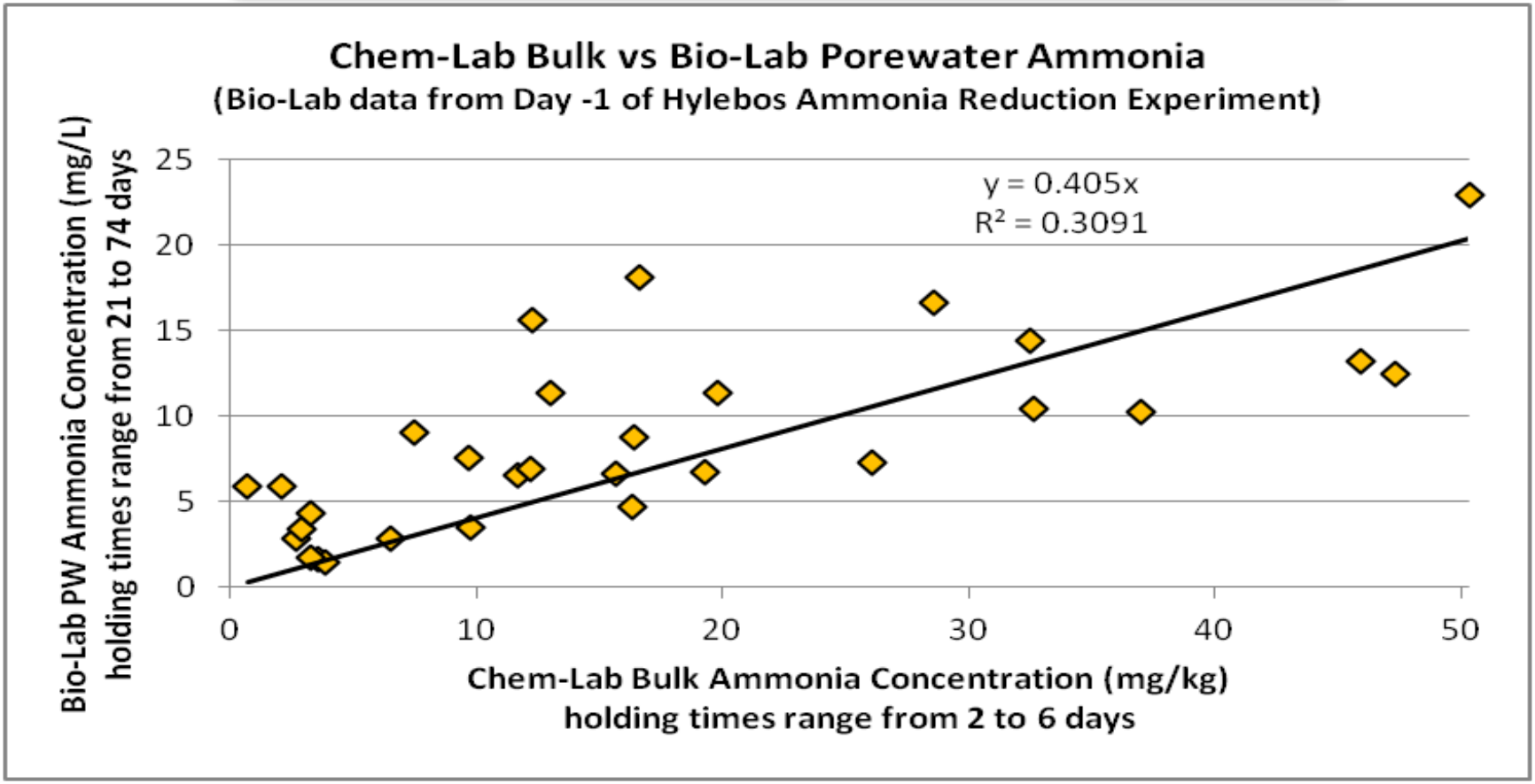
2. Experimental Findings

Porewater sulfides mostly undetected
(as measured by analytical lab)

- porewater sulfides were measured at two different times for only one of the projects (Hylebos) so determination of stability was only possible for a single project
- Hylebos bulk sulfides were as high as 4,300 mg/kg for single cores and 2,500 mg/kg for composites, but porewater concentrations were mostly non-detects
- of all the porewater measurements made for the four projects, only 15 out of 90 had detected concentrations even though there were a lot of high bulk sulfides concentrations

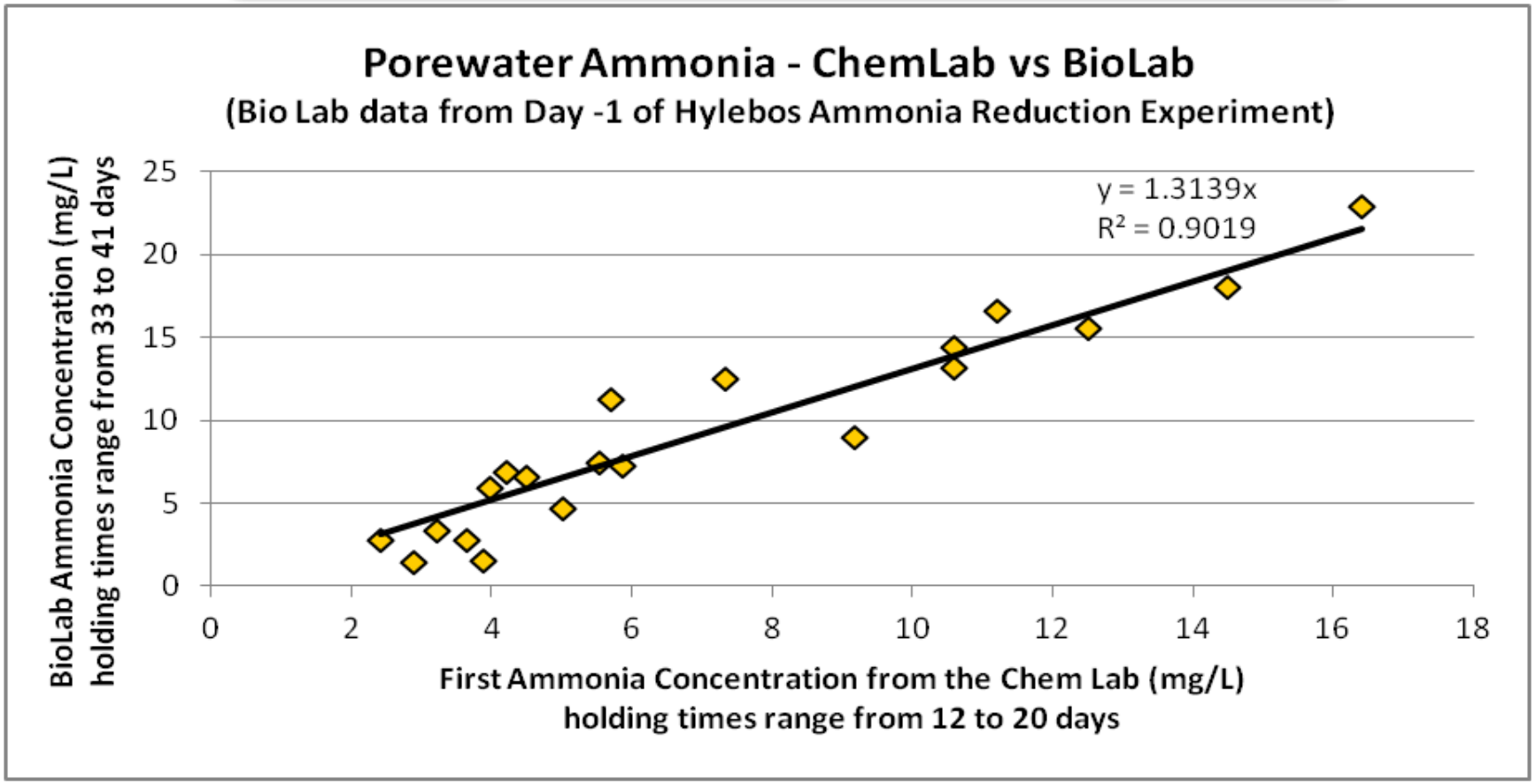
3. Experimental Findings

Bulk ammonia by analytical lab not highly correlated with porewater ammonia by bioassay lab



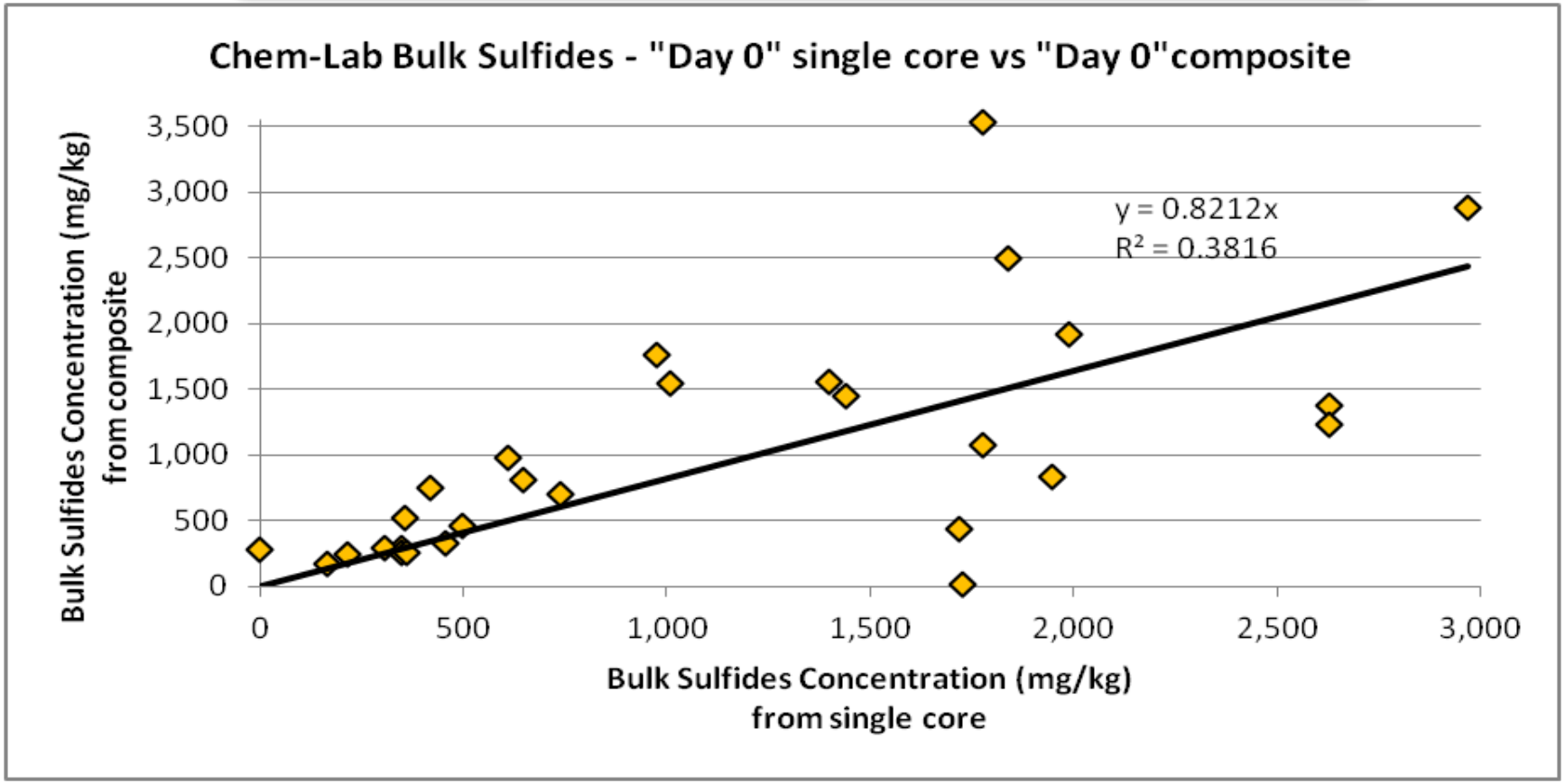
3. Experimental Findings

Porewater ammonia by analytical lab
predictive of porewater ammonia by bioassay lab



4. Experimental Findings

Bulk sulfides from single core not well-correlated with bulk sulfides from composite

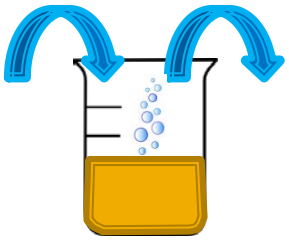


5. Experimental Findings

Purging the Larval Test

aeration only

renewal plus aeration



Purge

Run Bioassay

5. Experimental Findings

Comparison of Purging Methods

- 12-day purging period
- 18 g/beaker for aeration-only method
- 200 g in 'combined' beaker for renewal/aeration method
- both methods reduced overlying NH_3
- only aeration method reduced porewater NH_3
- sulfides data difficult to interpret

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6. Experimental Findings

Sediment Loss During Renewal Method

- all removed water from one treatment was filtered
- the sediment remaining on the filter was weighed
- loss of solids was only 0.04% of the total wet-weight mass

7. Experimental Findings

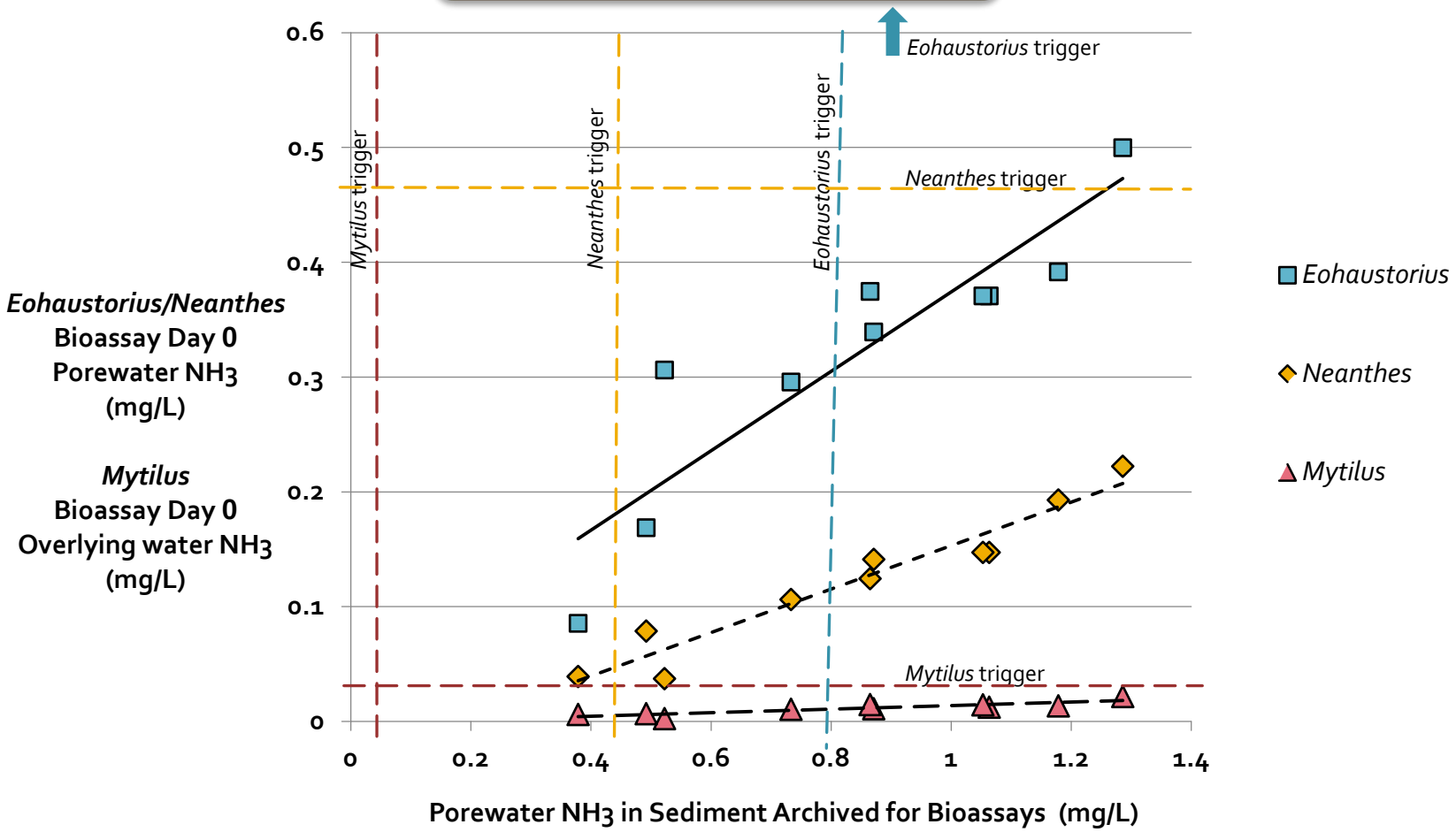
Contaminant Loss from Purging
Hylebos Waterway Sediment Samples

- post-purge sediment concentrations compared to pre-purge concentrations
- aeration-only; renewal/aeration; unpurged
- semi-volatiles and metals
- no apparent contaminant loss from either purging method

NORTHWESTERN AQUATIC SCIENCES

Richard Caldwell and Gerald Irissarri

Dilution during bioassay set-up may eliminate need for purging



A Few Conclusions…

Conclusions

- ammonia is stable during storage, so no need for more than one measurement by the analytical lab
- porewater ammonia measurements by the analytical lab better predict porewater measurements by the bioassay lab than do bulk measurements, but…
- it's difficult collecting enough sediment for porewater testing by the analytical lab AND for sacrificial beakers for purging
- composited sediment is a better analogue of sediment stored for bioassays than samples from single cores

…And Several More

Conclusions

- the renewal method for purging the larval test appears to be less effective than aeration-only
- contaminant loss from purging doesn't appear to be a problem, at least for the chemicals and sediment samples tested for the Hylebos experiment
- the bioassay set-up itself reduces the concentrations of ammonia and sulfides, especially for the larval test, and may obviate the need for purging to begin with
- we don't have all the answers (imagine that) so…provide consultants/labs flexibility

Developing Recommendations

Factors Considered

- input from labs and consultants
- conclusions from Corps testing
- experimental results provided by NWAS
- logistics required – keep it simple
- volume of sediment required

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Recommendations

2015 Clarification Paper

- bulk sulfides on composites, not individual cores
- for DMMUs requiring bioassays:
  - set up single amphipod/*Neanthes* beaker for pretest; measure NH_3 and sulfides in porewater after 24 hours; compare to purging triggers
  - set up single larval beaker; measure NH_3 and sulfides in overlying water after 4 hours (also applies to *Ampelisca*); compare to purging triggers

Recommendations

2015 Clarification Paper

- if renewal method of purging is proposed for the larval test, the NewFields method of purging a "combined" beaker must be used
- continue water renewals for bedded sediment tests (not the larval test) during bioassays if necessary

Questions ?