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Bureau of Laboratories

Effect of Sample Collection Technique on the Concentration of Methane in Water

National Environmental Monitoring Conference

Orange County, CA

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Observed Variability

- Significant variation in results has been noted
- Possible sources of variation
  - Collection technique
  - Analytical technique
- Current study focuses on sample collection
  - Other studies on analysis method are in progress

Saturation & Effervescence

- *Saturation* - A solution in which no more solute can be dissolved.
  - Saturation has been achieved when additional solute is let off as a gas.
- *Effervescence* - "Fizzing" caused by release of dissolved gas from a solution.
  - Effervescence has been observed at methane concentrations as low as 20 mg/L.

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Loss of Analytes

- In an open system, lightweight analytes are lost to the atmosphere via volatilization.
  - Methane, ethane, propane, etc.
- Effervescence may exacerbate the loss of volatile analytes due to turbulence.

Collection Techniques

- Open Systems
  - Direct Fill
  - “Bowl method”
- Semi-Closed Systems
  - Inverted Fill (“Bucket method”)
- Closed Systems
  - IsoFlask®

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Collection Techniques – Open System

Bowl Method – A shallow bowl is filled with water, and the VOA vial is dipped in to fill.

It is generally agreed the bowl method is not appropriate for methane samples.

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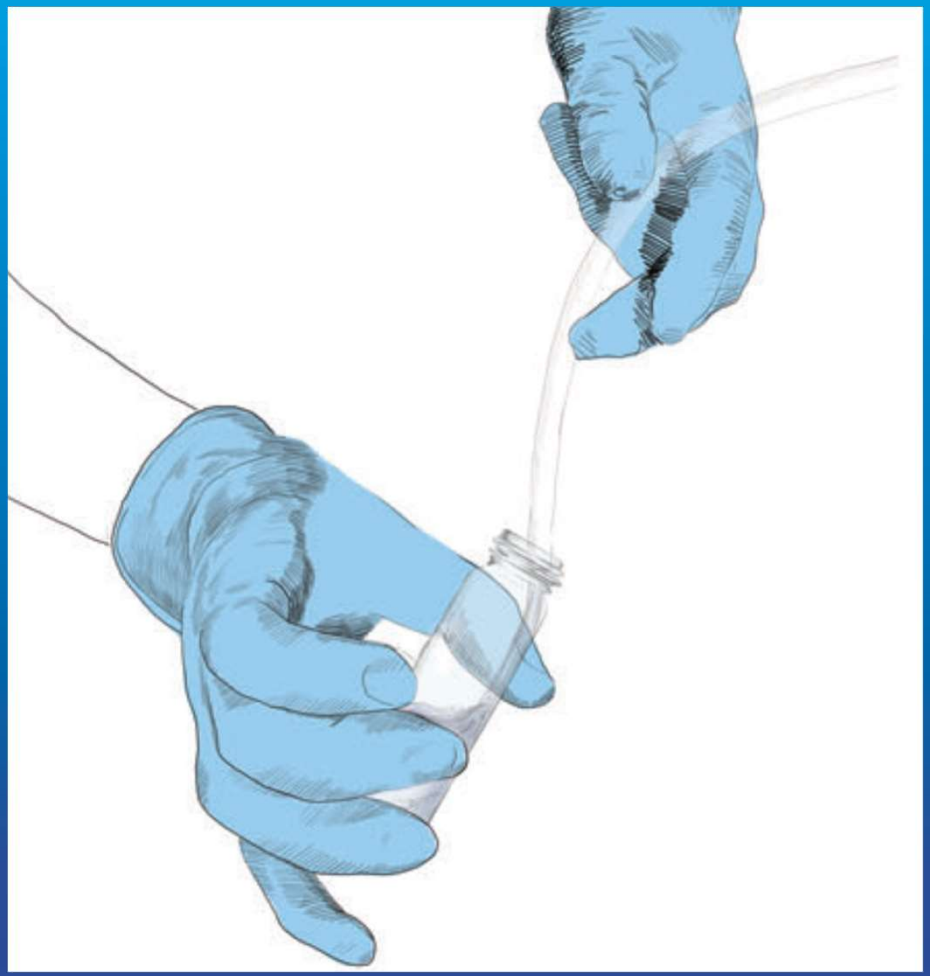
Collection Techniques – Open System



Direct Fill – A VOA vial is filled directly from the tap or tubing, using a low flow to prevent aeration or turbulence.

Illustration from http://onlinelibrary.wiley.com/journal/10.1111/%28ISSN%291745-6584

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Collection Techniques – Semi-Closed System

Inverted Fill – A VOA vial is inverted in a bucket of purge water and filled by displacement.

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Collection Techniques – Semi-Closed System

Inverted Fill

Theory:

- Use of inverted vial traps analytes that might be lost to volatilization.
- Submersion in water creates head pressure to inhibit effervescence.

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Collection Techniques – Closed System

Isoflask® – A flexible plastic bag is filled by direct connection to the sample tubing.

Illustration from http://onlinelibrary.wiley.com/journal/10.1111/%28ISSN%291745-6584

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Study Design

- Samples collected side-by-side using open, semi-closed, and closed techniques.
  - Samples collected from wells with a wide range of historically observed concentrations.
  - Direct Fill (DF) and Inverted Fill (IF) samples sent to PADEP Bureau of Laboratories (BOL) for analysis.
  - Isoflask® samples sent to Isotech for analysis.

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Direct Fill (DF) vs. Inverted Fill (IF)

Observation 1:

- DF vials had less headspace than IF vials.
  - 17% of DF vials had headspace.
  - 54% of IF vials had headspace.
  - 21% of IF vials had bubbles characterized as “large”.

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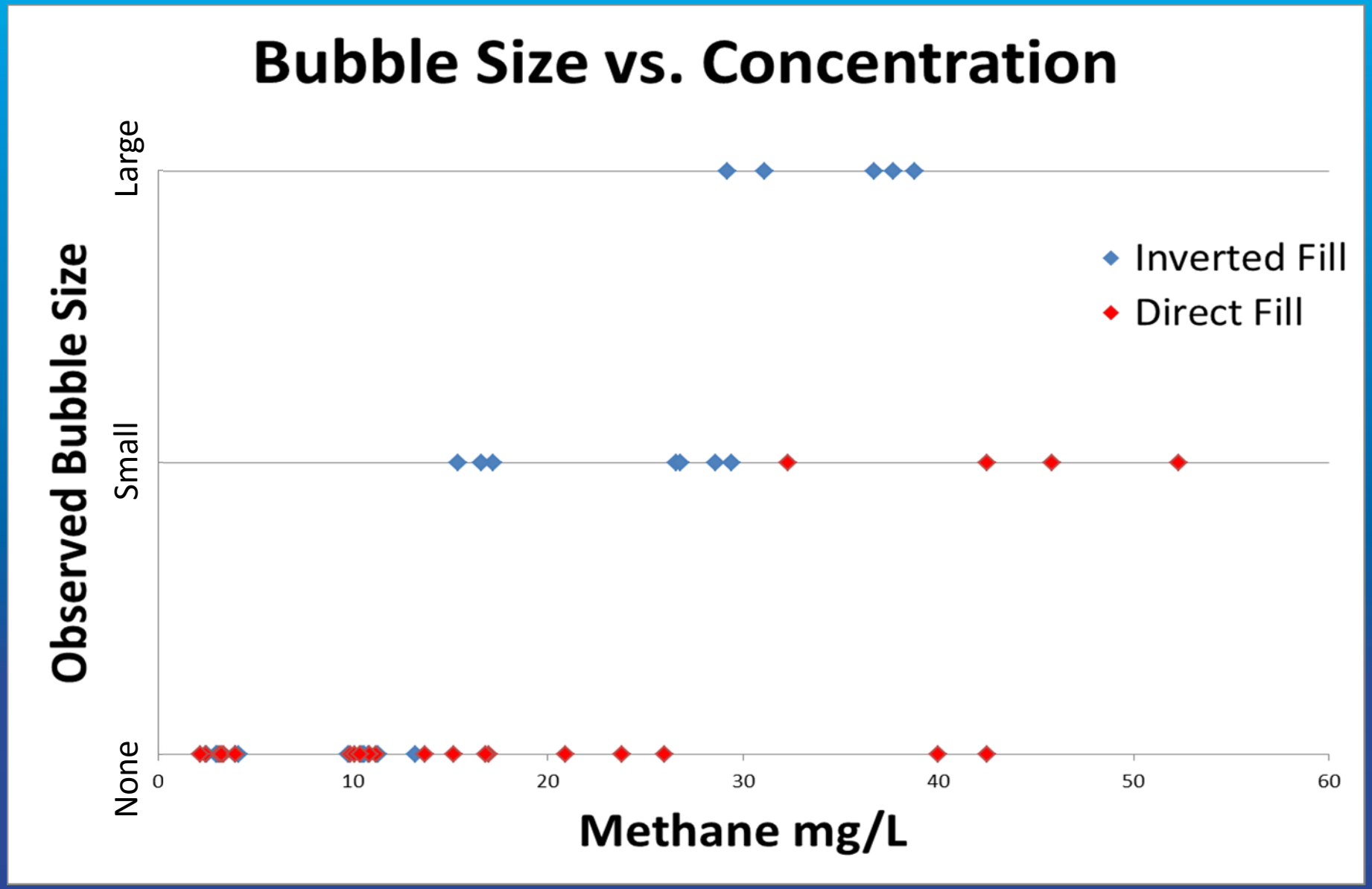
Direct Fill vs. Inverted Fill

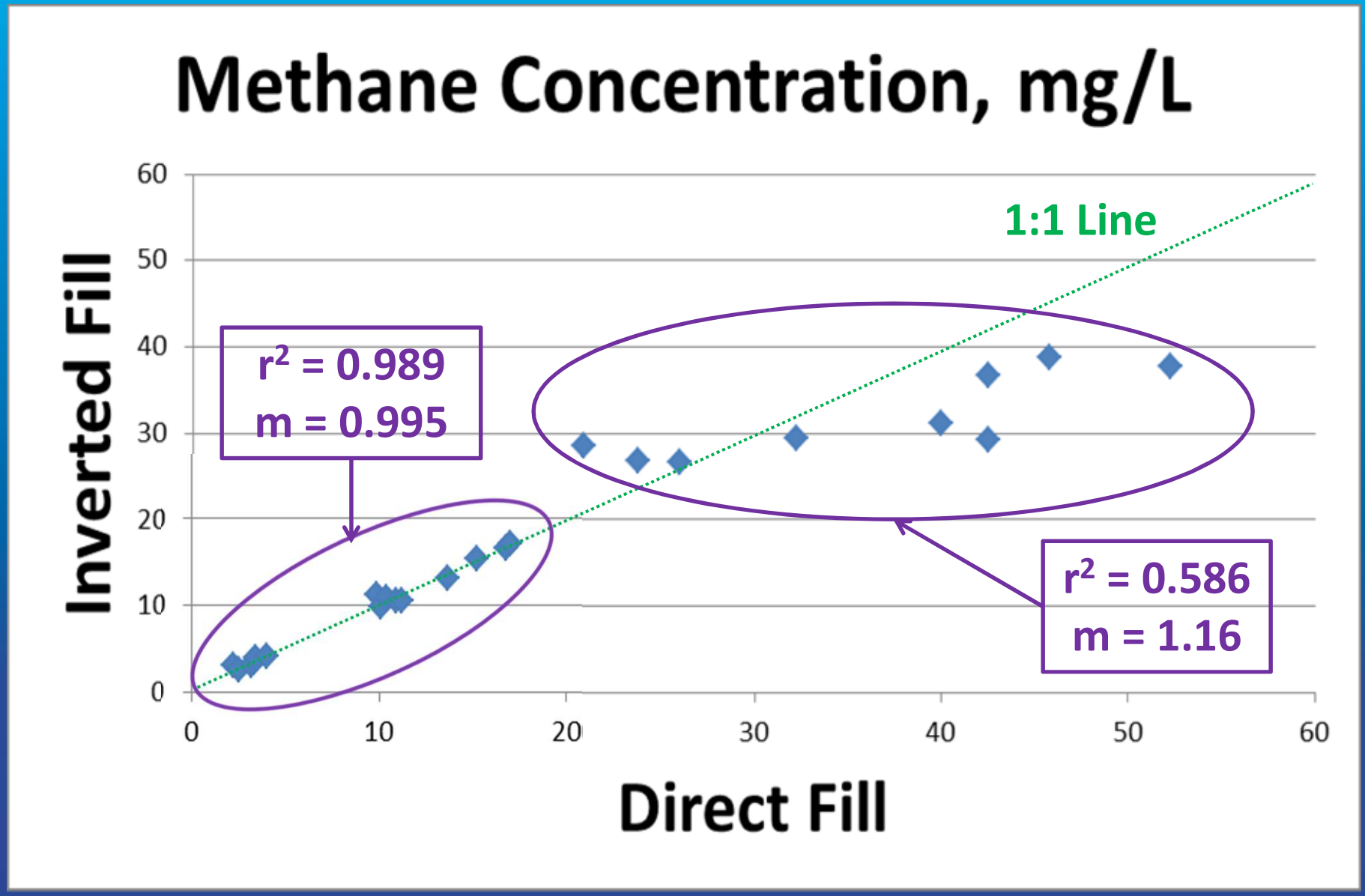


Direct Fill vs. Inverted Fill

Observation 2:

- DF & IF results correlate up to ~ 20 mg/L.
  - Divergence occurs at a concentration similar to the saturation point.
  - Divergence also corresponds to largest bubbles observed in the Inverted Fill vials.

Direct Fill vs. Inverted Fill



Direct Fill vs. Inverted Fill

Lower concentrations – why?

- Large headspace allows methane to off-gas in the vial prior to analysis.
- When little or no headspace is present, rigid vial emulates hydrostatic pressure to keep methane in solution.

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Direct Fill vs. Inverted Fill

Below the saturation or effervescence point, DF & IF provide equivalent results.

Above the saturation or effervescence point, DF provides better results.

Conclusion: No advantage to using the Inverted Fill technique.

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Isoflask® vs. Direct Fill

Observation 1:

- More headspace was observed in the Isoflasks® than the DF vials.
  - Every Isoflask® had headspace.
  - Only 17% of DF vials had headspace.

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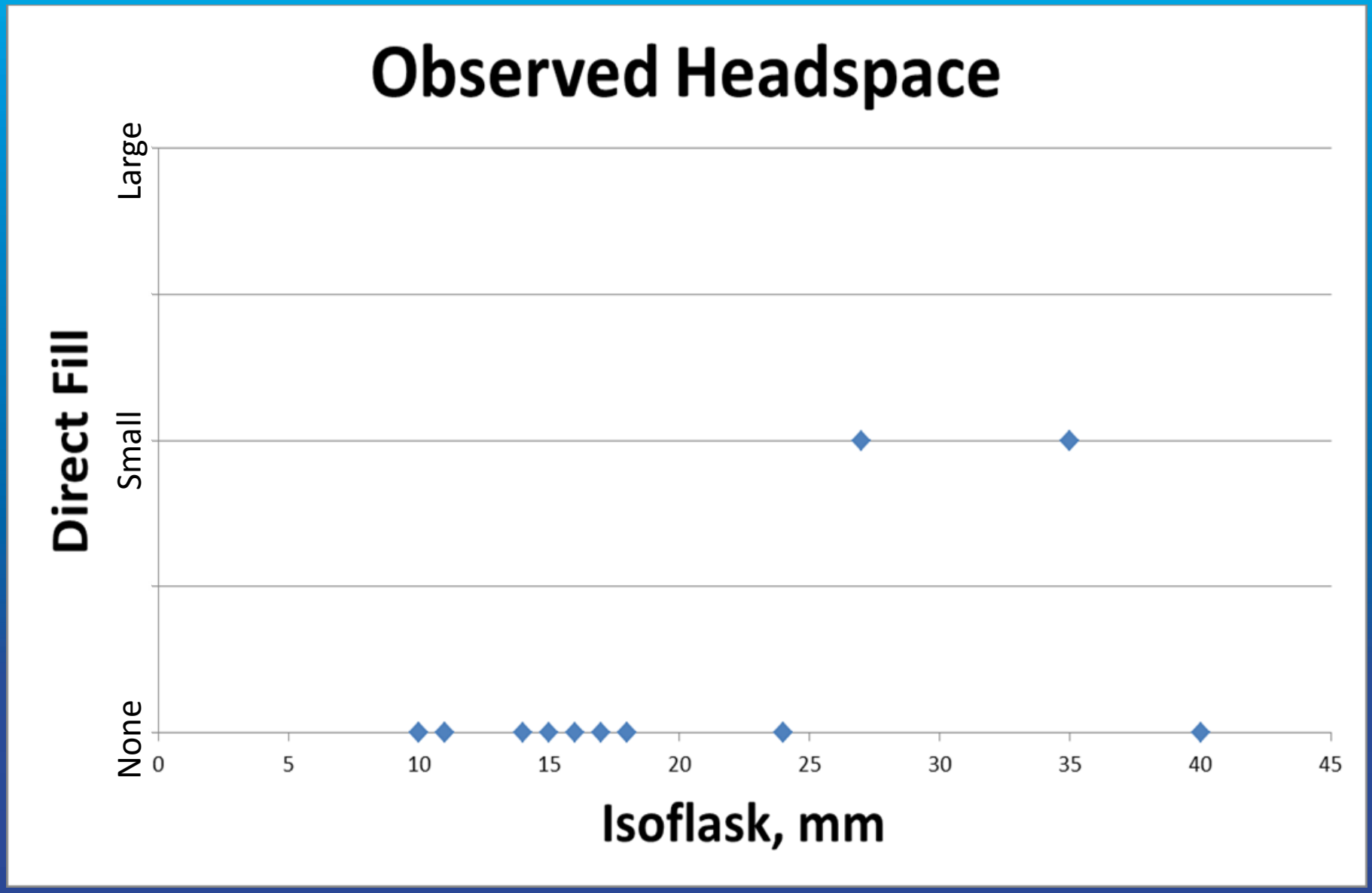
Isoflask® vs. Direct Fill



Isoflask® vs. Direct Fill

Increased headspace – why?

- Ex-solved gases lost during DF sampling are captured with Isoflask®.
- Low tensile strength of Isoflask® bag encourages ex-solvation of gases.

Conclusion: Samples collected in Isoflasks® MUST have both aqueous and gaseous phase analysis for accurate results.

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Isoflask® vs. Direct Fill

Observation 2:

- DF and Isoflask® results correlate up to ~ 20 mg/L.
  - Divergence occurs at a concentration similar to the saturation point.
  - Isoflask® results were consistently higher than DF results.

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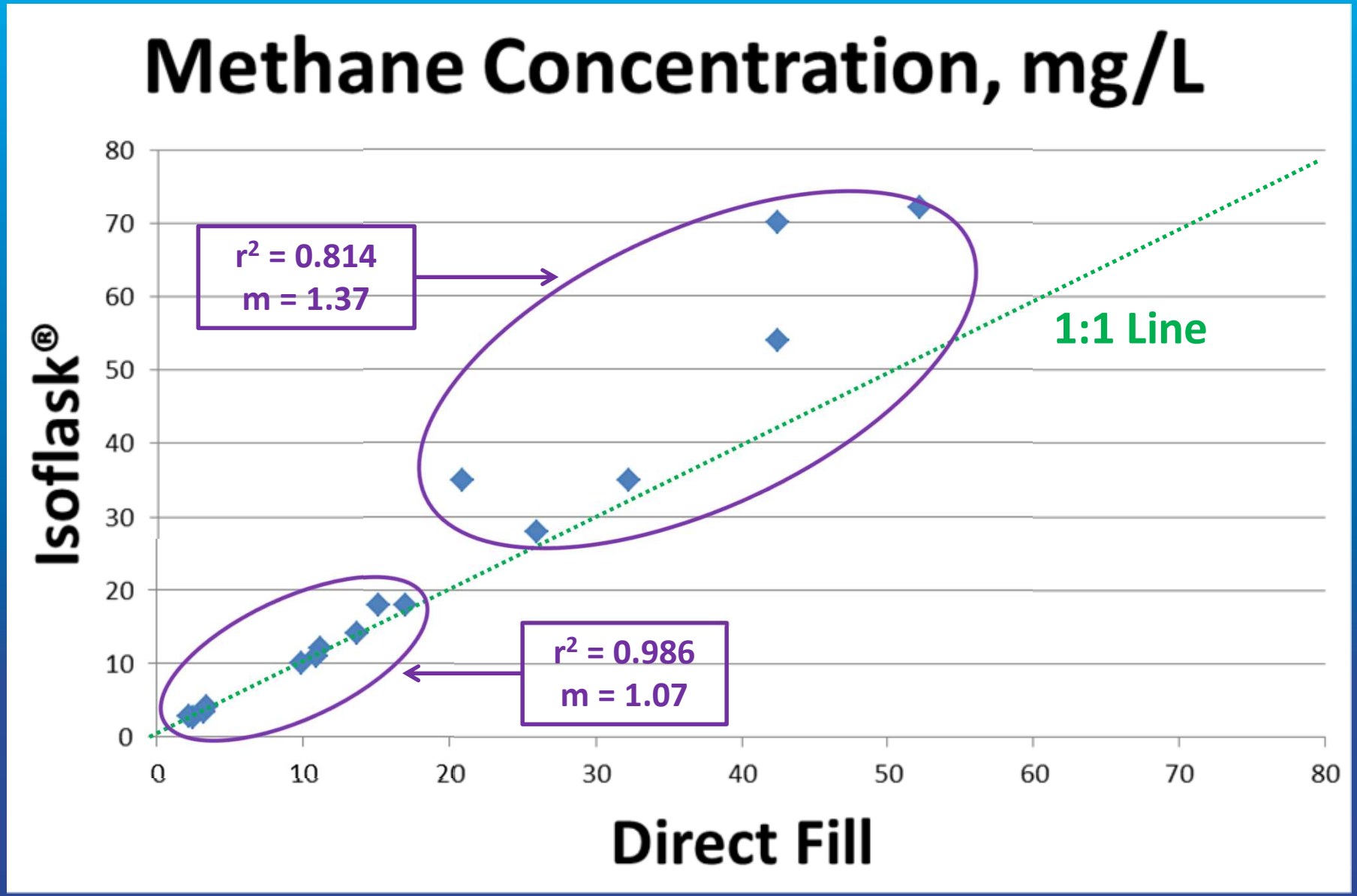
Isoflask® vs. Direct Fill



Isoflask® vs. Direct Fill

- Unlike DF vs. IF, *all* DF results were less than Isoflask® results.
- Below 20 mg/L the slope was 1.07.
  - *MAY indicate loss of analyte at time of sampling.*
  - *MAY be due to difference in analytical technique.*
- Above 20 mg/L the slope was 1.37.
  - *DEFINITELY indicates loss of analyte at time of sampling.*
  - *Loss probably due to saturation/effervescence.*

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Summary of Study Findings

	Direct Fill	Inverted Fill	Isoflask®
Applicability – Non Effervescent	(Possible) Slight negative bias	(Possible) Slight negative bias	Good
Applicability – Effervescent	Moderate negative bias	High negative bias	Good
Reproducibility	Good	Good	Good
Ease of Use	Easy	Moderate	Easy
Potential for carryover	Low	Moderate	Low
Analytical Availability	Wide	Wide	Limited
Cost	Low	Low	Moderate

Study Conclusions

1. *There is no clear advantage to using the Inverted Fill method, regardless of sample concentration.*

2. *At concentrations below 20 – 25 mg/L, the Direct Fill method is probably acceptable for most uses.*

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Study Conclusions

3. *At higher concentrations variability is increased due to the complicated relationship between saturation, effervescence, and co-dissolved gas concentration.*

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Study Conclusions

4. *At higher concentrations, use of the Isoflask® is more accurate.*

5. *The decision to use Isoflask® may depend upon budgetary and/or timeline constraints.*

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