




EVALUATION OF THE RELATIONSHIP BETWEEN pH AND DISSOLVED METHANE CONCENTRATIONS IN GROUNDWATER FROM DOMESTIC WATER WELLS IN NORTHEASTERN PENNSYLVANIA

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INTRODUCTION

- **Dissolved methane in northeastern Pennsylvania can be thermogenic, diagnetic, biogenic, or sourced from anthropogenic activities**
- **Dissolved methane concentrations have been found to be variable in domestic water wells on a temporal, seasonal and spatial basis**
  - Variation can be attributed to changes in atmospheric conditions, physical disturbances, anthropogenic sources, the action of water well pumping, etc.
- **The presence of dissolved methane has been associated with changes in water quality, including increases in pH**
  - Some groups have postulated that concomitant changes in pH and dissolved methane levels could be utilized as a means to identify the potential source of the methane
- **Evaluation of over 11,000 pre-drill water samples from northeastern Pennsylvania has demonstrated an association between dissolved methane and pH on a regional scale (Perry et al, 2013)**
  - It would appear that higher dissolved methane concentrations are associated with waters with higher pH values
  - The major influence on pH appears to be sodium content

STUDY OBJECTIVE

- **Evaluate the temporal changes in dissolved methane concentrations and the pH levels**
  - Determine if these changes are dependent
  - Determine if adding pH screening to methane screening would be helpful in identifying the potential source of methane in domestic water wells
- **Evaluate the differences between field pH and laboratory pH for the same sample**
  - Technical holding time for pH requires that measurement be taken in the field during sample collection
  - Even though laboratory-based pH measurements are conducted outside the technical holding time, readings are often used for decision making in lieu of field measurements because “bench” measurements are obtained under more stable conditions

STUDY DESIGN

- **Evaluated three groups of domestic water wells**
  1. Wells with no known impact from oil and natural gas drilling activities
  2. Wells with known perturbation from methane incursion
  3. Wells being investigated for complaints related to perceived changes in water quality including the presence of dissolved methane
- **All wells had multiple sampling events within the Chesapeake database**
  - No new data were collected specifically for the study
  - Some wells had sampling which spanned two to three years

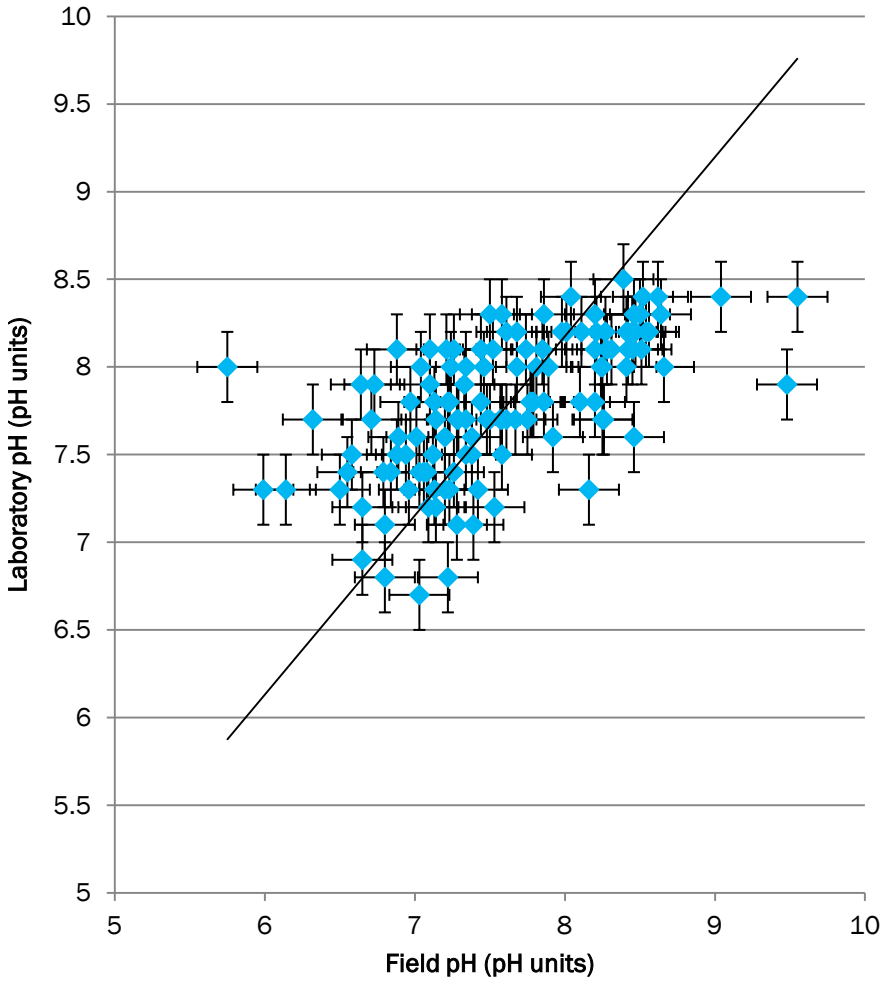
STUDY DESIGN (CONT.)

- **Sampling and field measurements by GES and SAIC**
  - Trained sampling personnel to decrease sampling variability
  - Sampling conducted using standardized procedures and approved sampling methods
- **Laboratory analyses by NELAP-certified third-party laboratory using approved methods**
  - Third-party data verification and validation
- **Data set for each well includes general water quality parameters, metals, selected organics, and dissolved gases**
  - Water type analyses using Piper diagrams were prepared
  - Statistical evaluation conducted using ProUCL software

DESCRIPTION OF WELLS SAMPLED

- **Well depth varied**
- **Construction: typically open-hole completions in fractured bedrock**
  - Pennsylvania does not currently have well construction standards for domestic water wells
- **Completed in Catskill or Lock Haven formations or glaciated valleys**
- **Well maintenance varied**
- **Some of the wells evaluated were restricted flow zone wells which have incursions of naturally-occurring saline waters**
  - These wells typically have higher dissolved methane and sodium concentrations

EVALUATION OF FIELD AND LABORATORY pH



- Concerns had been raised on the representativeness of laboratory pH measurements since they are made beyond the technical holding time
- Compared field pH measurement with corresponding laboratory pH measurement for same sample (n = 123)
- Standard error for pH measurement is equal to 0.05 – 0.5 (median: 0.2) pH units
- Field and laboratory pH are comparable (r^2 = -1.03)
- As a result laboratory pH was utilized for all subsequent analyses

COEFFICIENT OF VARIATION EVALUTION

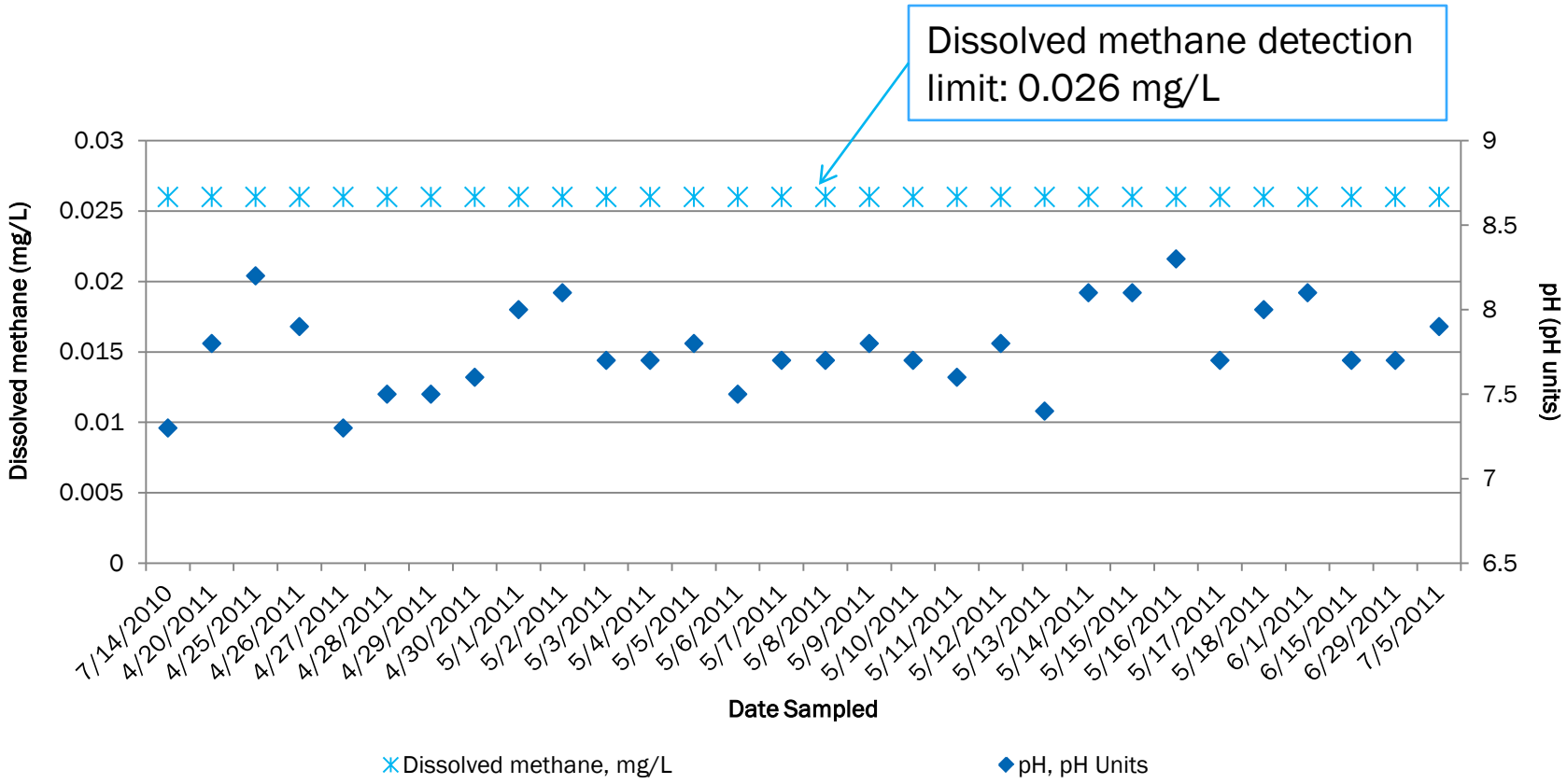
- **Coefficient of Variation (CV) for dissolved methane and pH calculated for each well in each of the three groups**
  - pH: CV ranged from 0.02 to 0.09 – indicating little variation
    - Group One wells (controls) had same range as other two study groups
  - Dissolved methane: CV ranged from 0.11 to 3.37 - more variation
- **For most wells, variation in pH is more likely to be related to sampling and laboratory measurement error**
- **Variability of dissolved methane within an individual well can be quite different**
  - Highest CV values were not necessarily in wells with known methane incursion

GROUP ONE: WELLS WITH NO KNOWN IMPACT FROM NATURAL GAS ACTIVITY

- **Seven Wells – Wells 1 through 7**
  - Located in same geographic area -- served as control group
    - Two wells had no detected methane
  - Sampled daily for 24 days and subsequently sampled weekly for 4 weeks (2011)
  - At least 28 sampling events for each well which included field and laboratory measurements
  - Variation in water quality types
    - Well 2 was a restricted flow zone well with naturally occurring saline water incursion at certain depths
  - Documented temporal variability for general water quality parameters, metals, dissolved gases and radionuclides (Coleman et al, 2012)
  - Isotopic analysis of two of the seven well waters demonstrated the presence of thermogenic-type methane

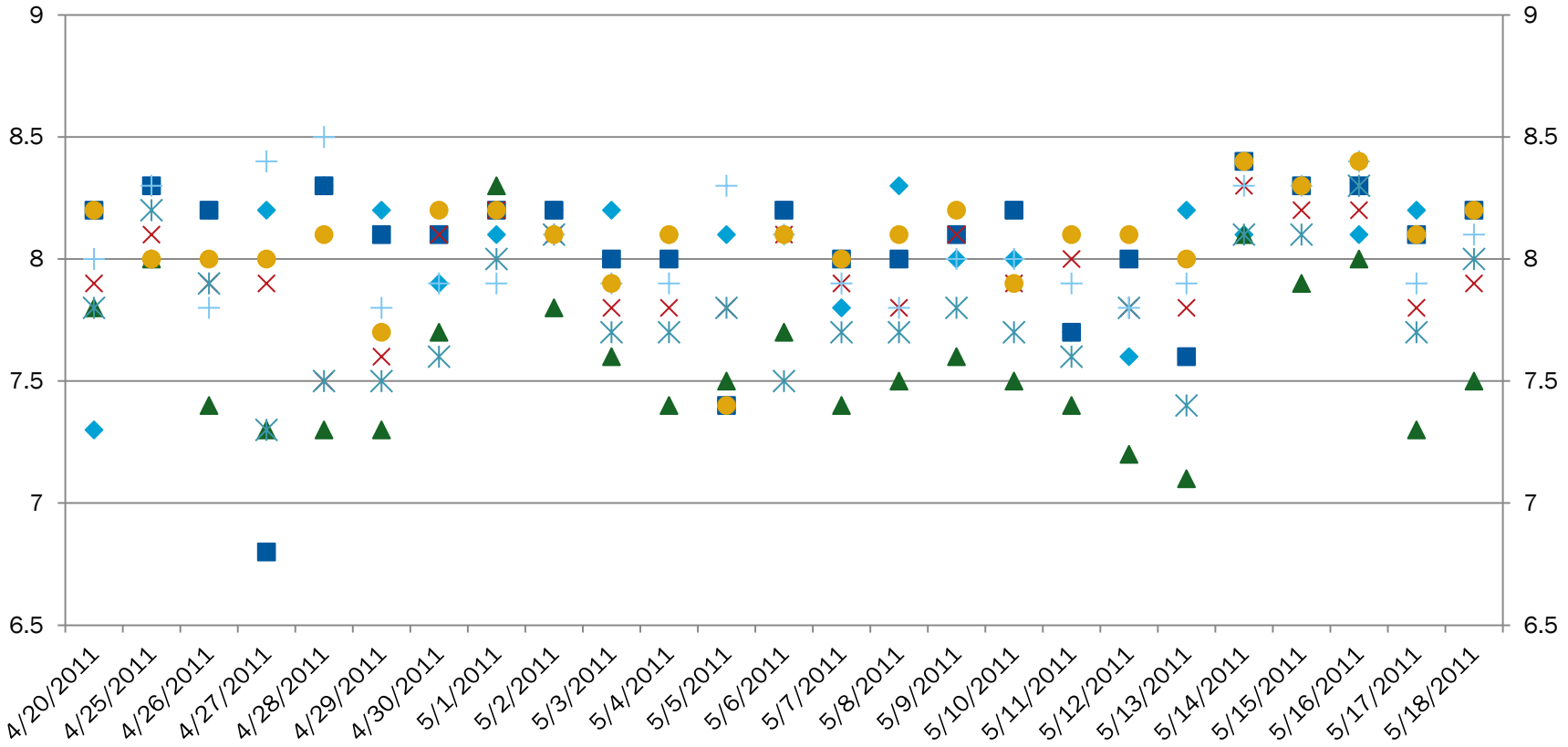
GROUP ONE – WELL 5 (DEPTH: 150')

- CV for pH – 0.033 [Range pH values - 7.3 to 8.3]
- No detected dissolved methane



GROUP ONE – WELLS 1 THROUGH 7

- Range CV for pH – 0.026 to 0.043
- Range pH values - 6.8 to 8.5

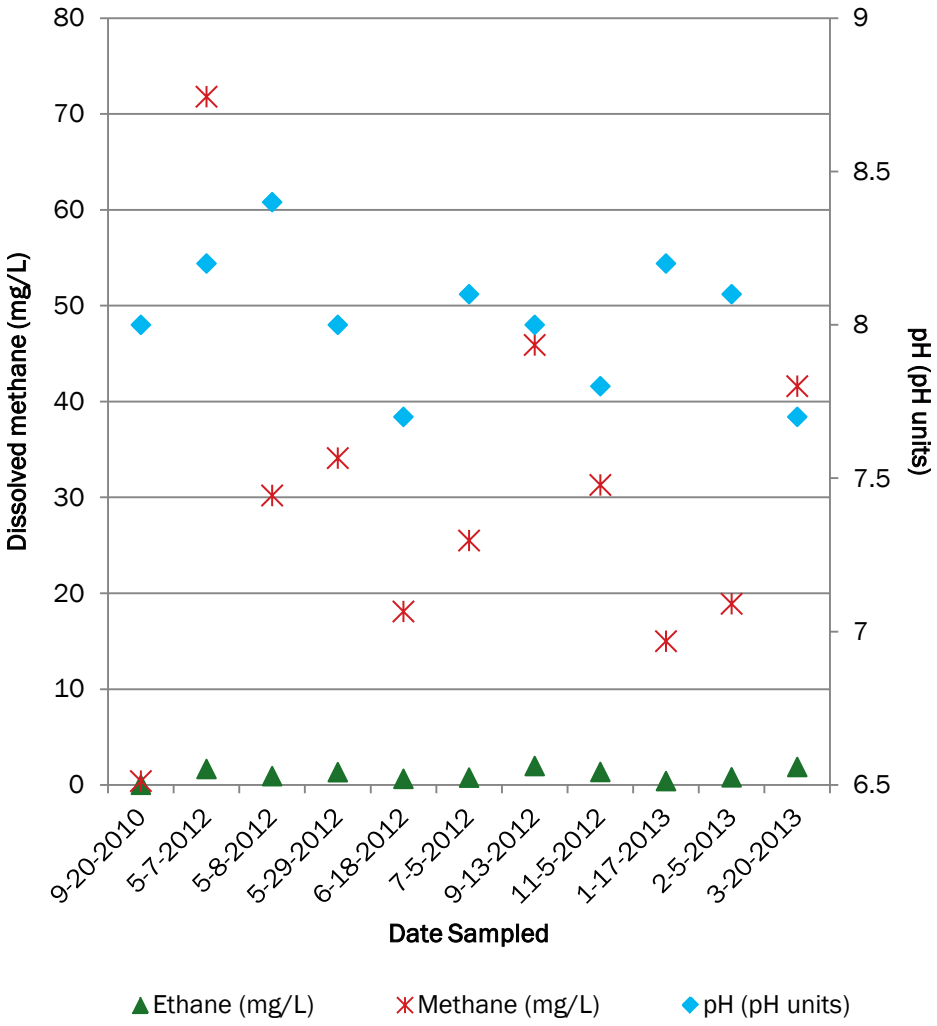


GROUP TWO: WELLS WITH KNOWN PERTURBATION FROM METHANE INCURSION INTO THE WELL

- **Seven wells – Wells 8 through 14**
  - Wells had episodes of methane incursion into the well
    - Methane detected in pre-drill samples
    - For some wells methane concentrations temporarily showed increases following a well control problem at a nearby gas well
  - Wells are located in two different geographic areas
  - Sampled multiple times over a period of two years
  - At least 10 sampling events for each well which included field and laboratory measurements
  - Isotopic analysis demonstrated the presence of thermogenic-type methane

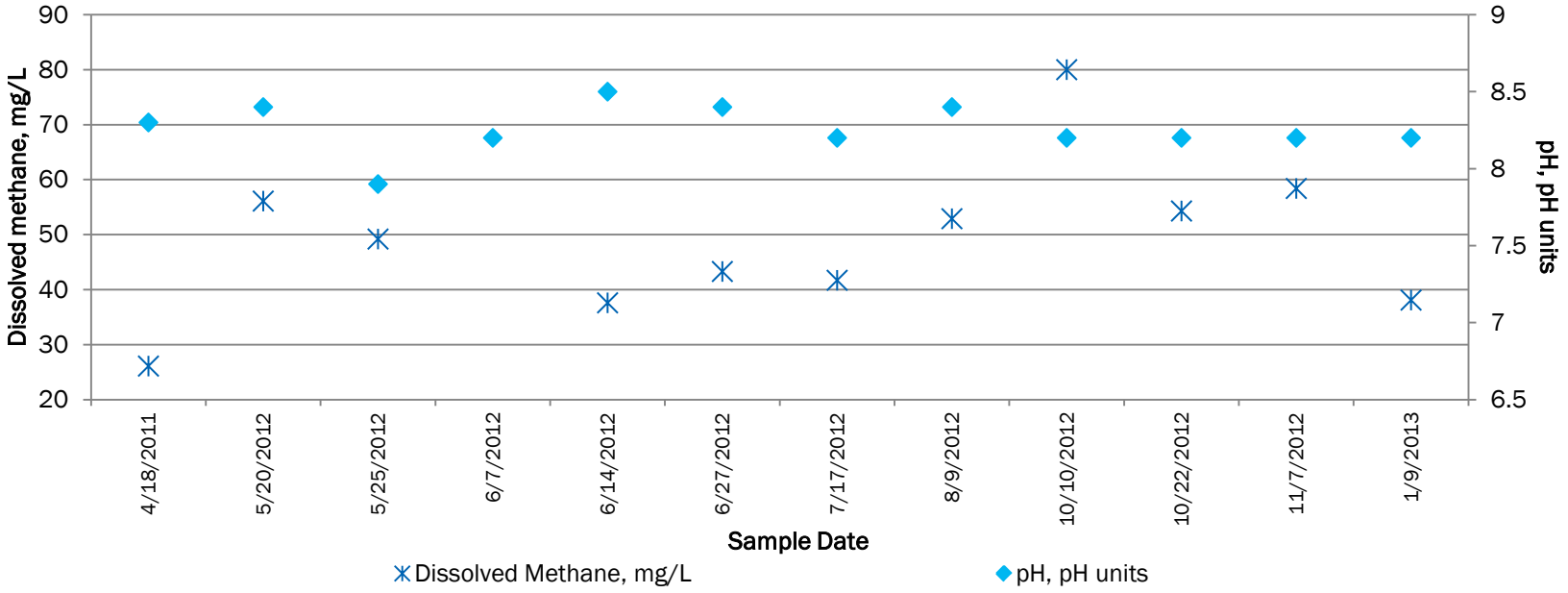
GROUP 2 – WELL 8 (DEPTH: 144')

- Impacted by incursion of methane into domestic water well and into the structure
  - Source appears to be abandoned Oriskany well based on comparison of isotopic gas signature
- Downhole camera inspection revealed rapid bubbling at one fracture and bubbles entering from two other fractures; at least seven other fractures with no bubbling occurring
- Isotopic results demonstrated presence of post-mature thermogenic gas
- CV for pH = 0.027 [Range: 7.7 to 8.4]
  CV for methane = 0.622
  [Range: 0.4 to 71.8 mg/L]
- Regression analysis showed no relationship between methane and pH (R^2 = 0.0079)



GROUP TWO – WELL 9 (DEPTH: UNKNOWN)

- Restricted flow zone well – sodium-bicarbonate type water
- Isotopic analysis revealed change in gas type from baseline sample (early thermogenic) to mixed early thermogenic/post-mature thermogenic gas after onset of incident
- CV for pH = 0.019 [Range: 7.9 to 8.5]
  CV for methane = 0.344 [Range: 19.3 to 80 mg/L]
- Regression analysis showed no relationship between methane and pH (R^2 = 0.011)
- Trends analysis show weak trend of decreasing pH with increasing methane concentrations (α = 0.05)

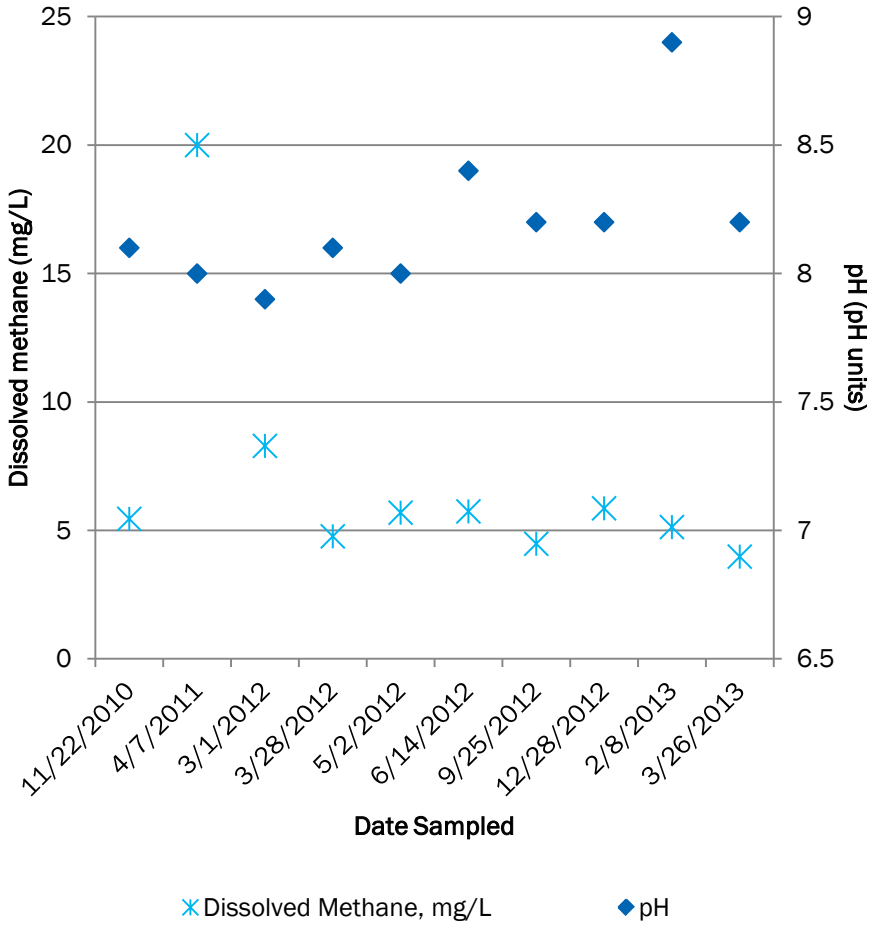


GROUP THREE: WELLS UNDER INVESTIGATION FOR COMPLAINTS RELATED TO PERCEIVED CHANGES IN WATER QUALITY

- **16 wells – Wells A through R**
  - Domestic wells with homeowner complaints regarding perceived changes in water quality
  - Located in several geographic areas
  - Sampled multiple times over a period of two years
  - At least 6 sampling events for each well which included field and laboratory measurements
  - Isotopic analysis demonstrated the presence of thermogenic-type methane

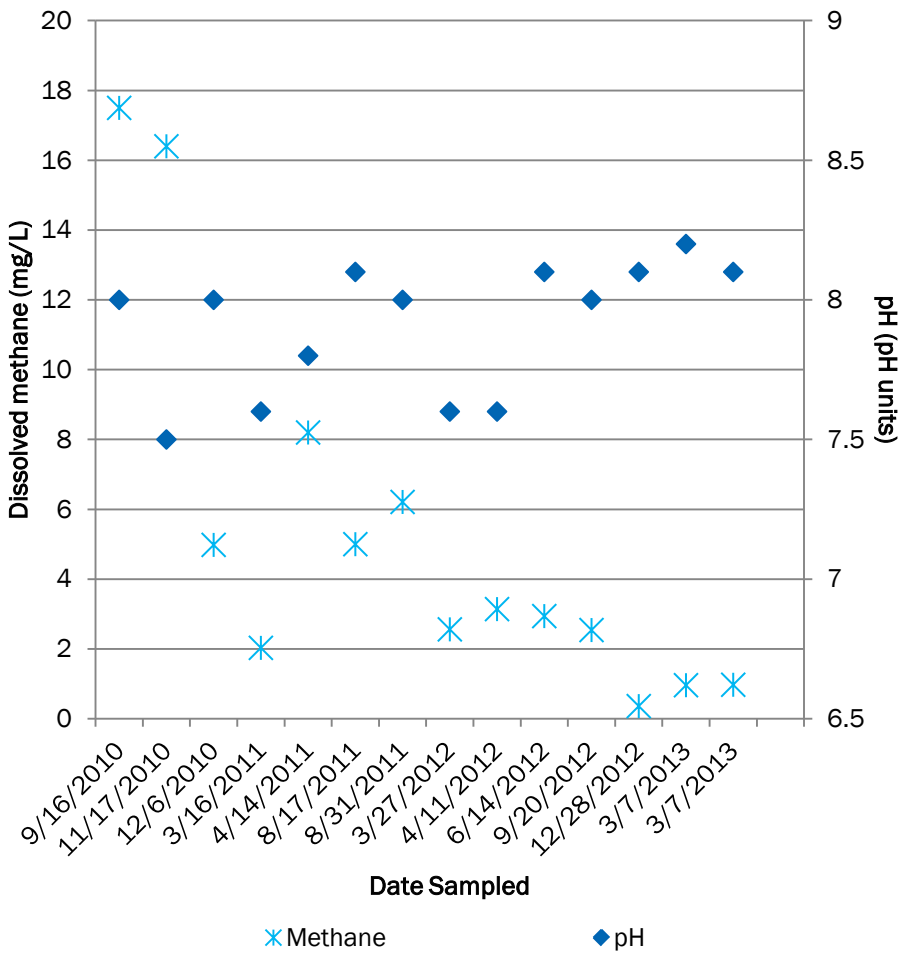
GROUP THREE – WELL D (DEPTH: 125')

- Calcium-bicarbonate type water
- CV for pH – 0.0345
  [Range: 7.9 to 8.9]
  CV for methane – 0.682
  [Range: 3.98 to 20 mg/L]
- Regression analysis revealed no correlation between pH and dissolved methane ($R^2 = 0.105$)
- Trend analysis indicated a weak trend for pH to increase with decreasing methane concentration ($\alpha = 0.05$)



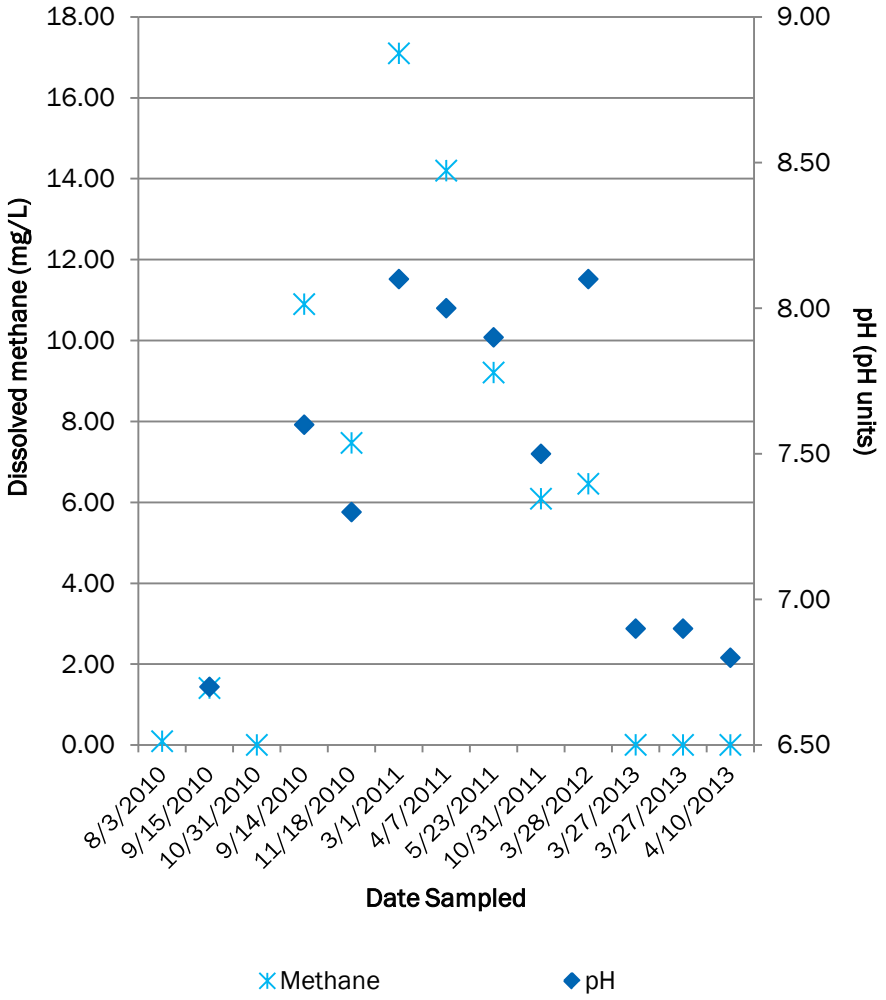
GROUP THREE – WELL P (DEPTH: 200')

- Calcium/sodium-bicarbonate type water
- CV for pH – 0.03
  [Range: 7.5 to 8.2]
  CV for methane – 1.025
  [Range: 0.36 to 17.5 mg/L]
- Regression analysis revealed no correlation between pH and dissolved methane ($R^2 = 0.09$)
- Trend analysis indicated a statistically significant trend for pH to increase with decreasing methane concentration ($\alpha = 0.05$)



GROUP THREE – WELL Q (DEPTH: 142')

- Calcium-bicarbonate type water
- CV for pH = 0.087
  [Range: 6.4 to 8.1]
  CV for methane = 1.06
  [Range: <0.005 to 17.1 mg/L]
- Regression analysis revealed a correlation between pH and dissolved methane (R^2 = 0.766)
- Trend analysis show apparent increase in pH with increasing methane concentration
  (α = 0.05)



SUMMARY OF DATA ANALYSIS

- **Inconsistent relationship between pH and methane regardless of which study group**

Number of Wells	pH Increasing	pH Decreasing
Methane Increasing	7	11
Methane Decreasing	5	1

  - 4 wells with no observable change

SUMMARY OF INDIVIDUAL WATER WELL EVALUATION

- **Group One – No Known Impact Group**
  - No correlation between pH and methane using regression analysis (R^2 = 0.001 to 0.102)
  - No statistically consistent trends for pH and methane

- **Group Two – Known Perturbation from Methane Incursion**
  - No correlation between pH and methane (R^2 = 0.002 to 0.095)
  - No statistically significant trends for increasing pH and methane

SUMMARY OF INDIVIDUAL WATER WELL EVALUATION (CONT.)

- **Group Three – Perceived Changes in Water Quality**
  - No consistent correlation between pH and methane (R^2 = 0.0091 to 0.766)
  - No consistent statistically significant trends for pH and methane (α = 0.05)
    - Well P: Statistically significant trend for increasing pH and decreasing methane with time (α = 0.05), correlation very weak (R^2 = 0.09)
    - Well Q: R^2 = 0.766, pH increasing and methane increasing with time
    - Well L: R^2 = 0.330; pH increasing and methane increasing with time
    - Well I: R^2 = 0.237; pH decreasing and methane increasing with time

CONCLUSIONS

- **For this study, field and laboratory pH values were comparable**
  - Use of laboratory pH values does not affect trend results
- **pH and dissolved methane vary naturally in domestic well water**
- **There is no relationship on a individual well basis between pH and dissolved methane**
  - Changes in pH cannot be utilized with changes in dissolved methane to draw any conclusions on the potential source of the dissolved methane
- **Observed changes in pH results for an individual well are generally within the range of error for the analytical test for pH**
  - No apparent pattern between individual wells by sample date
- **Dissolved methane is more variable within an individual well than pH**

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