Important considerations in the use of carbon and hydrogen stable isotopes to determine the origin of hydrocarbons in groundwater –A case study from pre-shale gas Tioga County

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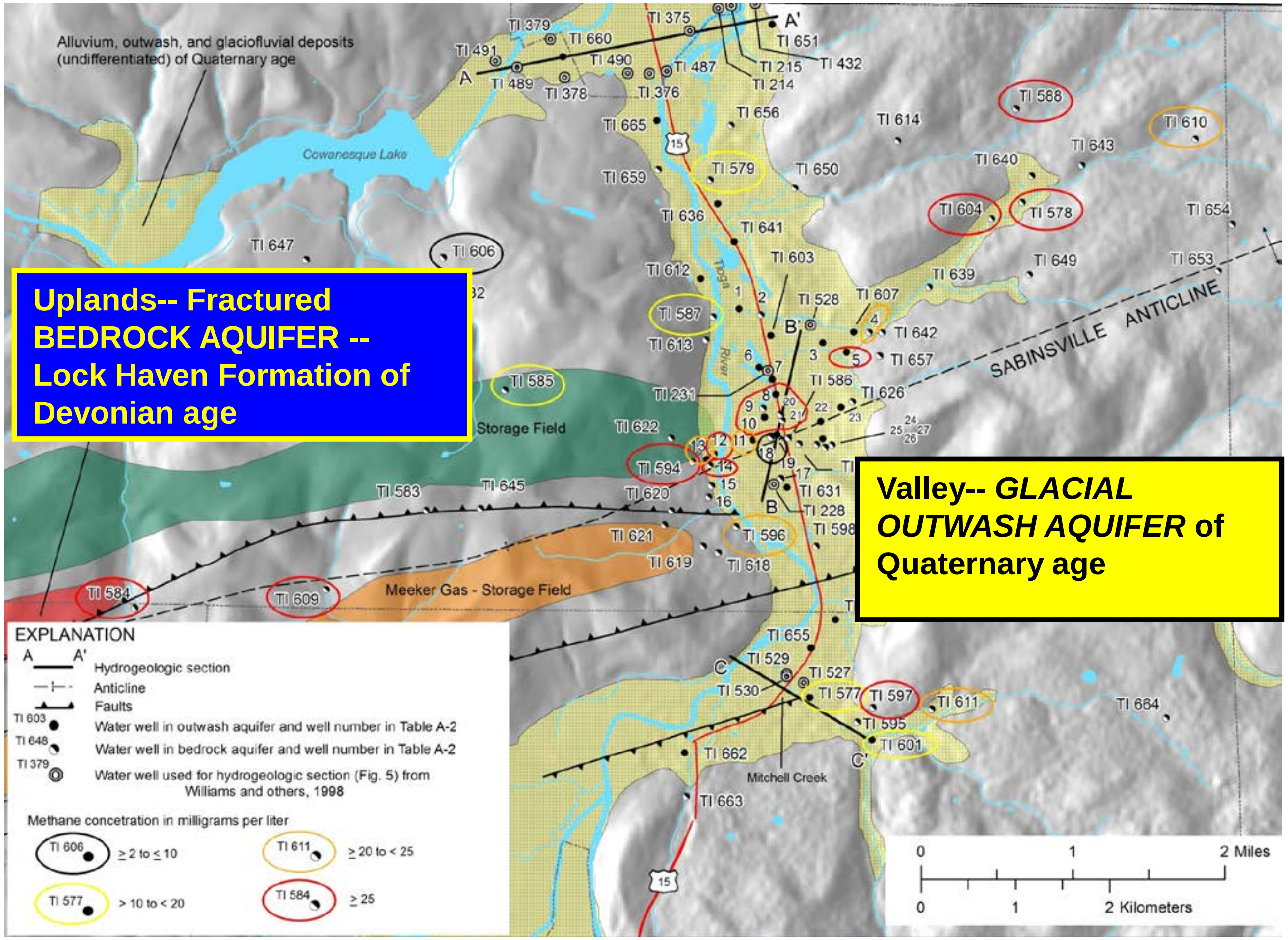
Study area; the circles indicate water wells where measurable natural gases were found



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Microbial Methane production

1. Near-surface environment, marsh etc.

CH_4 production by fermentation pathway:

$CH_3COOH = CH_4 + CO_2$

Isotope change: Intra-molecular fractionation: CH_3 = $\delta^{13}C$ in CH_3 depleted in ^{13}C; it is enriched in COOH.

Product: CH_4 = is depleted in ^{13}C; CO_2 = is enriched in ^{13}C. (DIC)

Concentration change: CH_3COOH decreasing

CH_4 and CO_2 increasing (DIC)

2. Drift gas -old, covered by glacial drift deposit.

CH_4 production by CO_2 reduction pathway :

$CO_2 + 4H_2 = CH_4 + 2H_2O$

Isotope change: CH_4 = CH_4 = is depleted in ^{13}C; CO_2 = is enriched in ^{13}C (DIC);

Concentration change: CH_4 increasing, CO_2 decreasing (DIC)

3. Minimal C_2 and C_3 production, they are very depleted in ^{13}C.

Thermogenic Methane production

– formed by thermal break down.

1. Higher hydrocarbons (C_2; C_3; etc.) are present
2. $\delta^{13}C$ isotope of CH_4 is closer to the isotope of substrate it is produced from (more enriched than microbial).
3. C_2 and C_3 are more enriched than microbial in ^{13}C if there is any in microbial natural gas.

Methane oxidation

independent from production pathways

$$2CH_4 + 4O_2 = 2CO_2 + 4H_2O$$

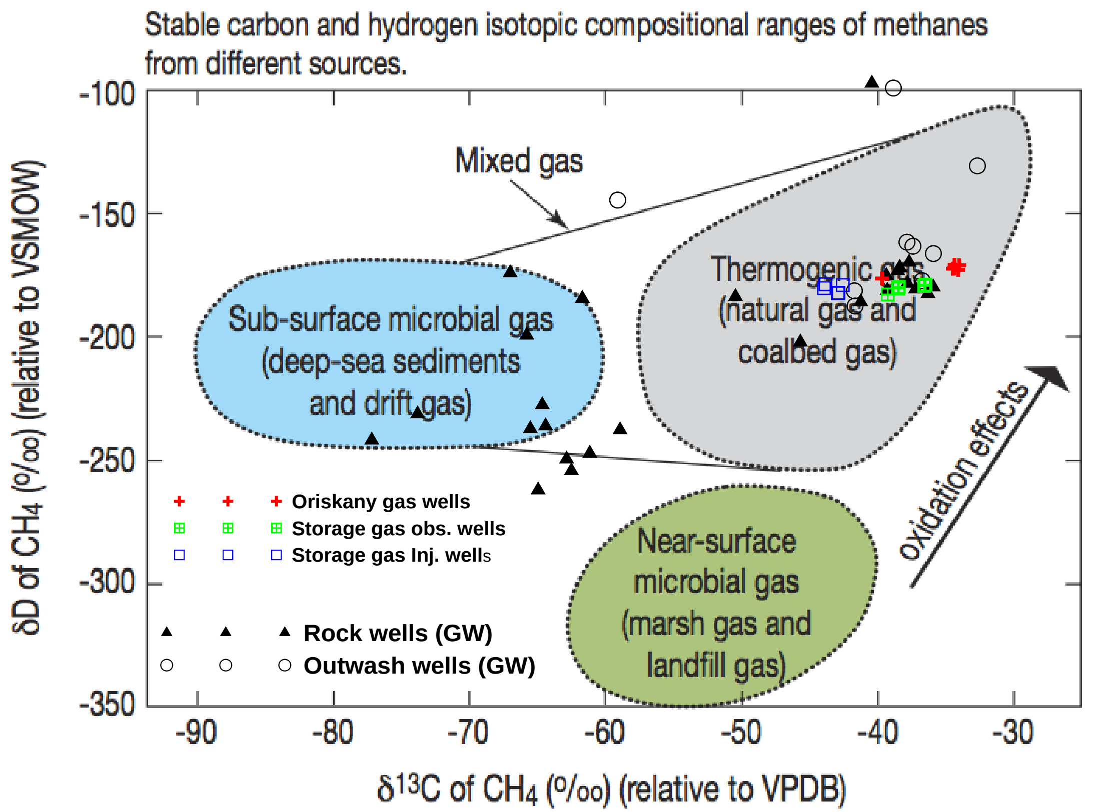
Concentration change:

CH_4 decreasing, CO_2 (DIC) increasing.

^{13}C isotope change:

CH_4 becomes enriched ; CO_2 (DIC) becomes depleted in ^{13}C.

δ^{13}C and δ^{2}H (D) of methane enable us to distinguish between microbial and thermogenic origin of natural gases



After Coleman and others (1993) based on the data set of Schoell (1980)

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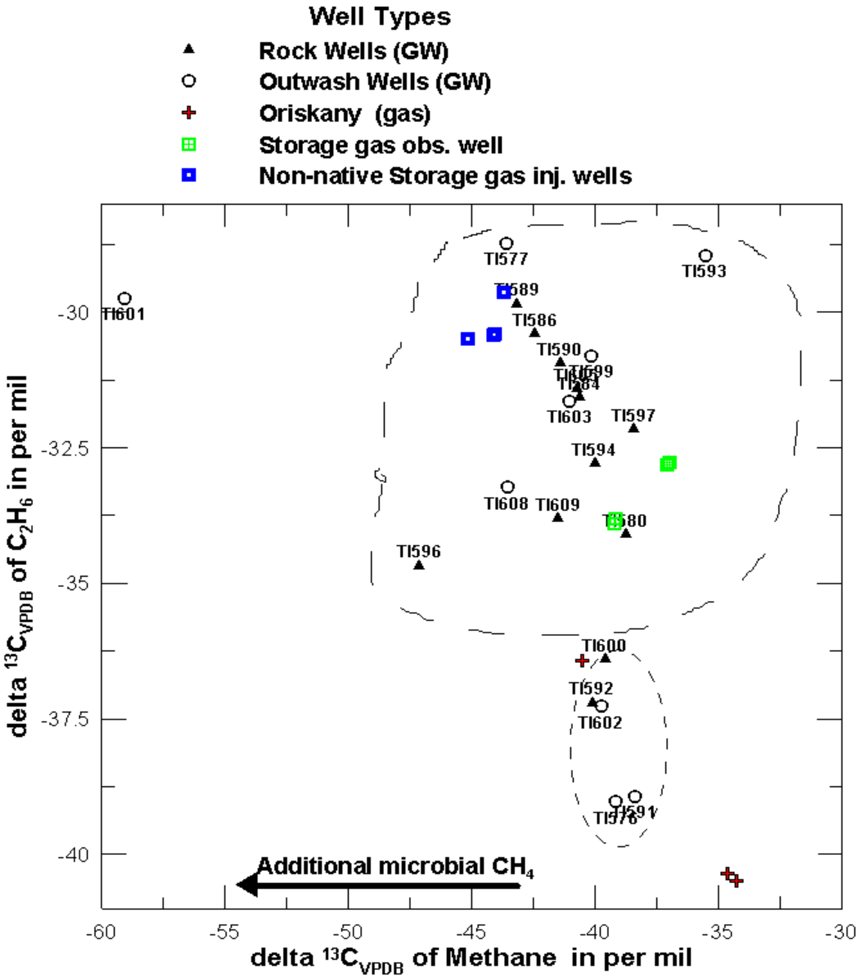
The $\delta^{13}C$ of ethane with the $\delta^{13}C$ of methane enabled us to distinguish further between different thermogenic gas origins.



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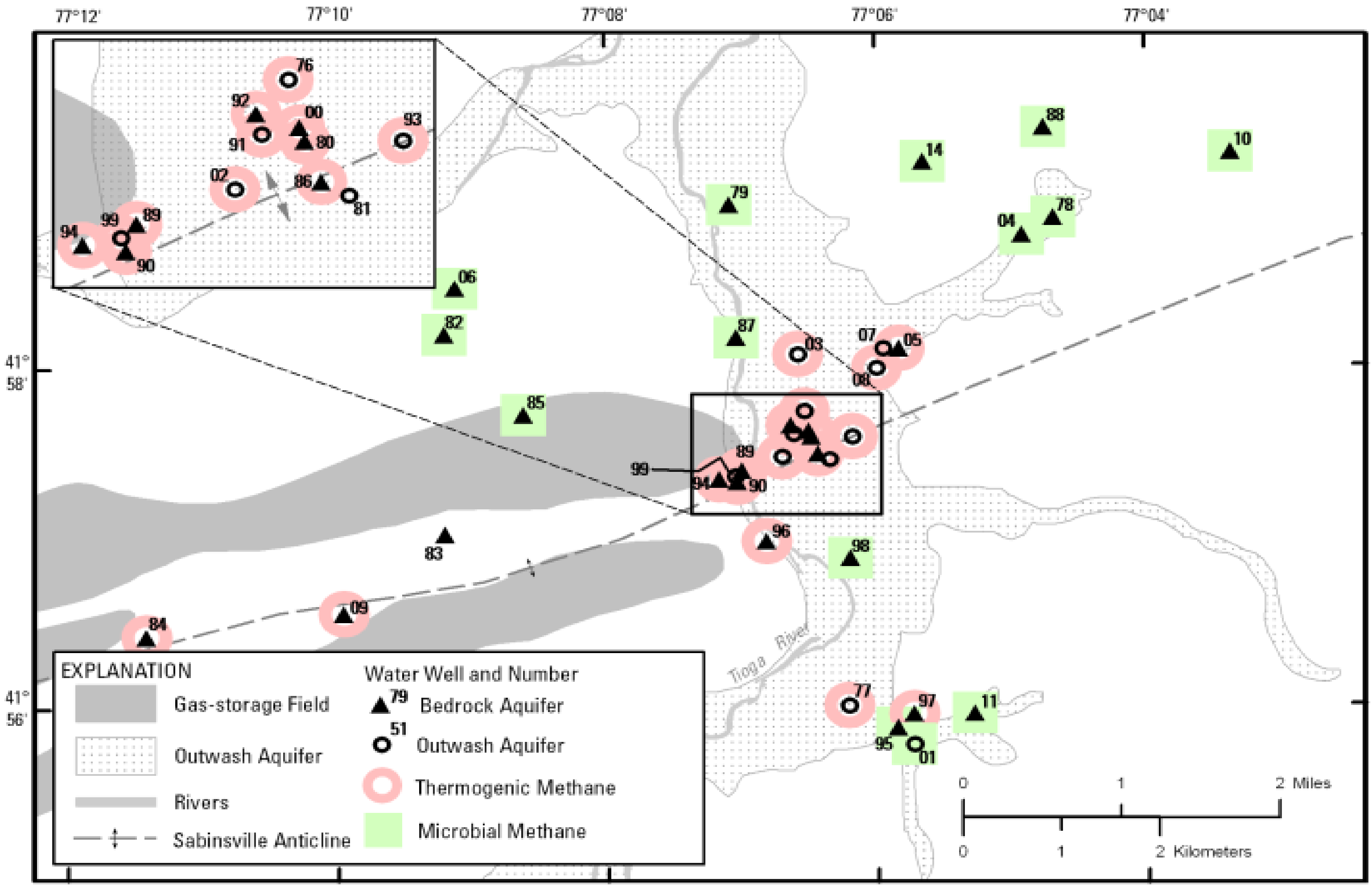
Location of thermogenic and microbial methane in the study area



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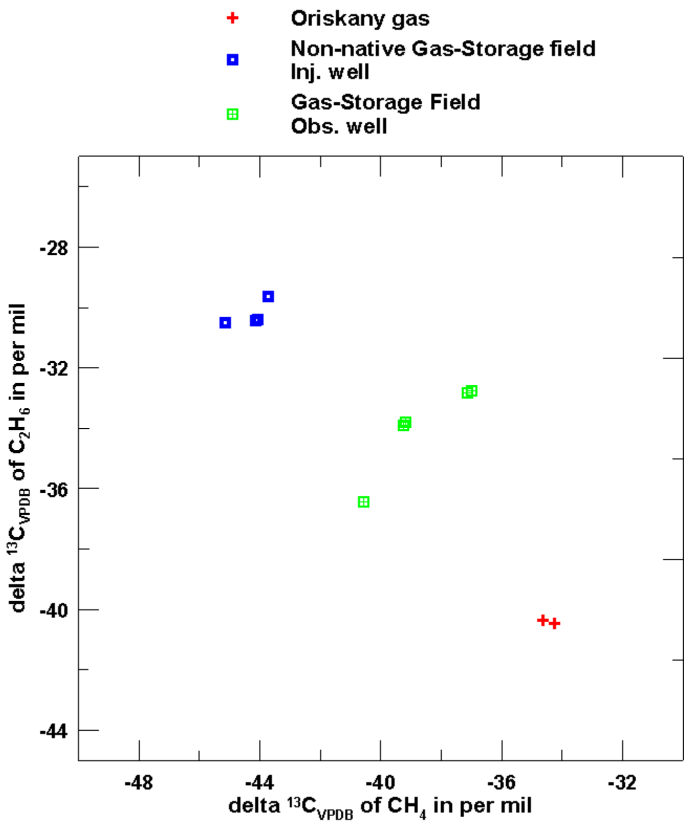
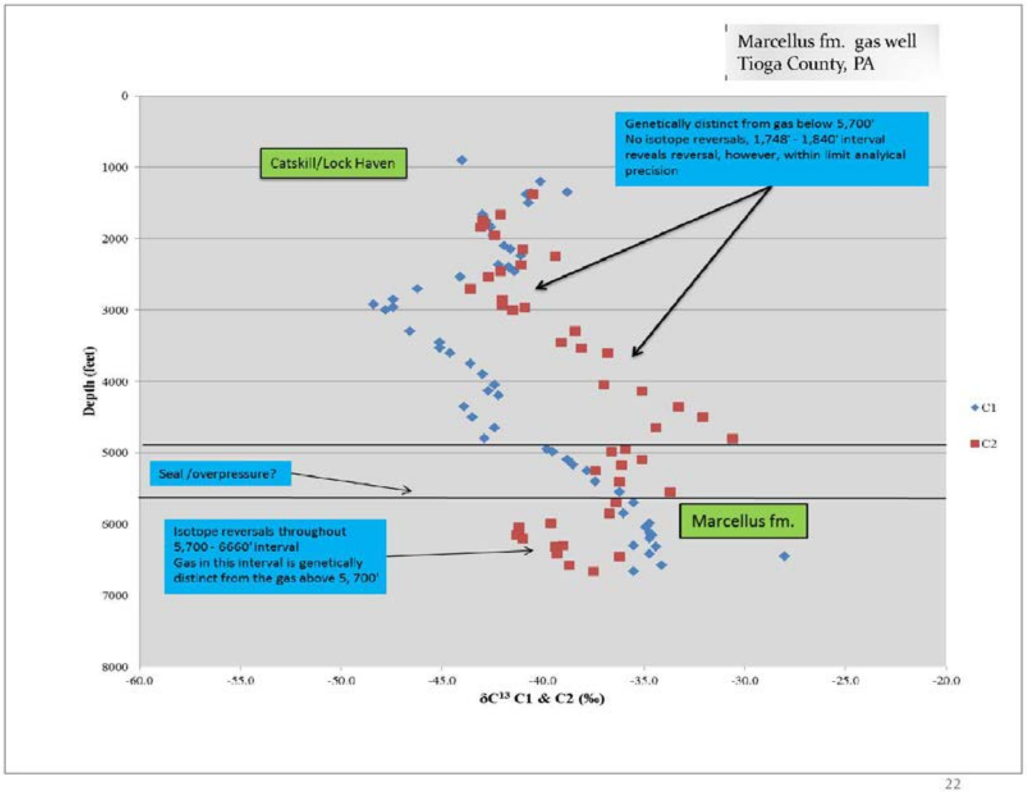
Essential data to identify stray gas origins

1. **Identify possible gas sources.**
2. **Create a baseline gas signature library.** Determine concentrations and $\delta^{13}C$ - $\delta^{2}H$ of CH_4; and $\delta^{13}C$ of higher hydrocarbons across the play from various source units.
3. **Carry out site specific monitoring of natural gas and dissolved inorganic carbon DIC) in groundwater before (baseline), during and after drilling.** (Concentrations and $\delta^{13}C$ - $\delta^{2}H$ of CH_4; and $\delta^{13}C$ of higher hydrocarbons $\delta^{13}C$ of DIC). Determine the source(s) of stray gas in domestic-supply wells and identify gases from major and minor gas production zones across the play.
4. **Monitor longer-term changes** in methane presence/concentration as play develops (well density), and as the play ages (leakage from casing/grout seals) **during and following gas production (decades).**

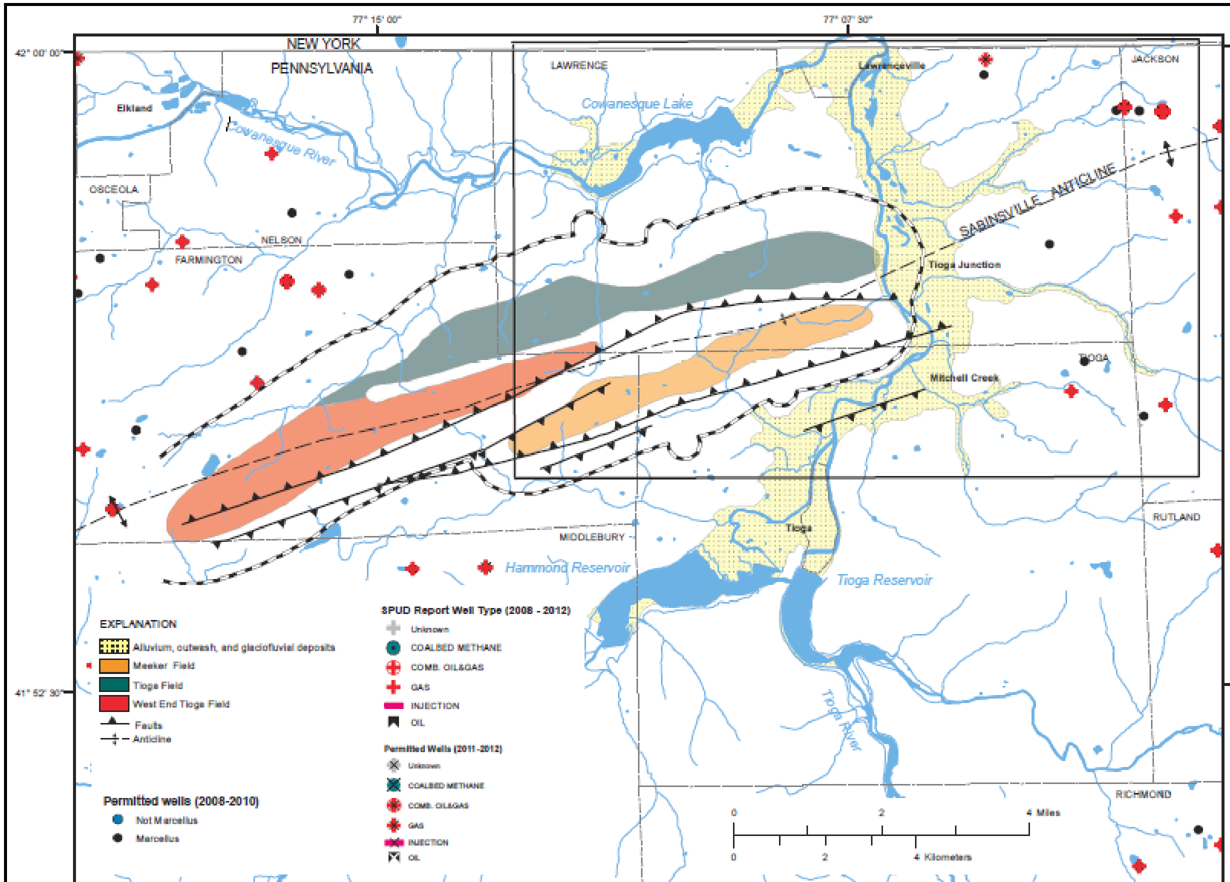


Révész, and Others, 2012 in Applied Geochemistry



Fred Baldassare and others, GWPC, Atlanta, GA, September 2011

Map showing the 2005 study area (square in the map), and the hydraulic fracturing drilling sites (red symbols).



Source of SPUD and permitted wells: PA Dept of Environmental Protection, Office of Oil and Gas Management
Oil and Gas Report URL: http://www.portal.state.pa.us/portal/server.pt/community/oil_and_gas_reports/20297