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## Forensic Isotope Hydrology: Use of Carbon and Hydrogen Isotopes to Determine the Origin of Natural Gas in Water-Supply Wells

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In 2001, residents near Tioga Junction, Tioga County, Pennsylvania, USA reported gas bubbles that were not noticeable before in their well water. The gas was identified as methane with minor concentrations of ethane in some instances. The U.S. Geological Survey, in cooperation with the Pennsylvania Department of Environmental Protection, conducted a study to determine the origin of the gas in the water wells. Potential origins of the gas include (1) a natural gas storage field for imported natural gas in sandstone of the Oriskany Group, a former native gas production zone about 1,200 m below land surface, (2) abandoned native Oriskany natural gas wells, (3) shale gas (native from  $\sim$ 300-m depth) and (4) drift gas from buried and decomposed organic material. In the present study only the first two could be sampled as end members. Two gas wells producing native gas from the Oriskany Sandstone and six gas wells with non-native gas from the gas-storage field were sampled. Samples from the gasstorage field were collected in two modes, injection mode representing the non-native pipeline gas, and observation mode representing the gas-storage field gas. Of the 91 private water-supply wells inventory, 35 samples had sufficient gas for isotopic analysis. Some of the water wells were screened to fractured siliciclastic bedrock of Upper Devonian age, and the others were screened to glacial outwash of Quaternary age in the Tioga River and tributary valleys. Gas composition measurement and measurements of stable carbon and hydrogen isotope amount ratios of methane and stable carbon isotope amount ratios of ethane were used to identify the origin of gases in water wells. The amount of carbon-14 (C-14) in dissolved methane was also analyzed in 9 selected groundwater samples from 7 outwash- and 2 bedrock-aquifer wells.

The stable isotopic data of methane and ethane from gas wells indicate that the native Oriskany gas and the non-native pipeline gas from three storage-field injection wells are thermogenic in origin, but have significantly different isotopic signatures. The storage-field gases from three observation wells are intermediate in isotopic composition, indicating a mixture of non-native gases from the storage field and Oriskany gases. The data from 21 water wells indicate that the gases were thermogenic in origin; the majority clustered at the eastern end of storage field and more closely resembled gases from the storage-field observation wells than the native Oriskany gases. The data from 14 other water-wells, chiefly bedrock-aquifer wells in non-clustered occurrence, have evidence a microbial gas isotopic signature. The C-14 analyses of gases from outwash-aquifer wells showed and AVE of 1.6 percent modern carbon (PMC) component, indicating the presence of recent microbial gas; however, the stable isotope values indicate that the gas in these 7 well samples as primarily thermogenic gas with only a small amount of microbial gas present. The C-14 analyses of gases from water wells in the bedrock aquifers showed and AVE 4.6 PMC indicating that these gases are mainly microbial origin. This is in agreement with stable isotope values that indicate a microbial origin.

In summary, two gas origins were identified in the private groundwater supply wells; one is thermogenic gas, which is the mixture of Oriskany and non-native, storage-field gas, and which occurs primarily in bedrock – and outwash- aquifer wells clustered at eastern end of the storage field; the other is a microbial gas which occurs in a dispersed pattern chiefly in bedrock-aquifer wells. Further study is needed to (1) investigate and characterize the shallow native shale gas and (2) better understand the occurrence of the microbial gas.