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Office of Research and Development
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Extended Abstract

In response to complaints by domestic well owners regarding objectionable taste and odor problems in well water, the U.S. Environmental Protection Agency initiated a ground water investigation near the town of Pavillion, Wyoming under authority of the Comprehensive Environmental Response, Compensation, and Liability Act. The Wind River Formation is the principal source of domestic, municipal, and stock (ranch, agricultural) water in the area of Pavillion and meets the Agency's definition of an Underground Source of Drinking Water. Domestic wells in the area of investigation overlie the Pavillion gas field which consists of 169 production wells which extract gas from the lower Wind River Formation and underlying Fort Union Formation. Hydraulic fracturing in gas production wells occurred as shallow as 372 meters below ground surface with associated surface casing as shallow as 110 meters below ground surface. Domestic and stock wells in the area are screened as deep as 244 meters below ground surface. With the exception of two production wells, surface casing of gas production wells do not extend below the maximum depth of domestic wells in the area of investigation. At least 33 surface pits previously used for the storage/disposal of drilling wastes and produced and flowback waters are present in the area. The objective of the Agency's investigation was to determine the presence, not extent, of ground water contamination in the formation and if possible to differentiate shallow source terms (pits, septic systems, agricultural and domestic practices) from deeper source terms (gas production wells).

The Agency conducted four sampling events (Phase I - IV) beginning in March 2009 and ending in April, 2011. Ground water samples were collected from domestic wells and two municipal wells in the town of Pavillion in Phase I. Detection of methane and dissolved hydrocarbons in several domestic wells prompted collection of a second round of samples in January, 2010 (Phase II). During this phase, EPA collected additional ground water samples from domestic and stock wells and ground water samples from 3 shallow monitoring wells and soil samples near the perimeter of three known pit locations. Detection of elevated levels of methane and diesel range organics (DRO) in deep domestic wells prompted the Agency to install 2 deep monitoring wells screened at 233 - 239 meters (MW01) and 293 - 299 meters (MW02) below ground surface, respectively, in June 2010 to better evaluate to deeper sources of contamination. The expense of drilling deep wells while utilizing blowout prevention was the primary limiting factor in the number of monitoring wells installed. In September 2010 (Phase III), EPA collected gas samples from well casing from MW01 and MW02. In October 2010, EPA collected ground water samples from MW01 and MW02 in addition to a number of domestic wells. In April 2011 (Phase IV), EPA resampled the 2 deep monitoring wells to compare previous findings and to expand the analyte list to include glycols, alcohols, and low molecular weight acids.

Detection of high concentrations of benzene, xylenes, gasoline range organics, diesel range organics, and total purgeable hydrocarbons in ground water samples from shallow monitoring wells near pits indicates that pits are a source of shallow ground water contamination in the area of investigation. When considered separately, pits represent potential source terms for localized ground water plumes of unknown extent. When considered as whole they represent potential broader contamination of shallow ground water. A number of stock and domestic wells in the area of investigation are fairly shallow (e.g., < 30 meters below ground surface) representing potential receptor pathways.

Determination of the sources of inorganic and organic geochemical anomalies in deeper ground water was considerably more complex than determination of sources in shallow media necessitating the use of mulitiple lines of reasoning approach common to complex scientific investigations. pH values in MW01 and MW01 are highly alkaline (11.2-12.0) with up to 94% of the total alkalinity contributed by hydroxide suggesting addition of a strong base as the causative factor. Reaction path modeling indicates that sodium-sulfate composition of ground water typical of deeper portions of the Wind River Formation provides little resistance to elevation of pH with small addition of potassium hydroxide. Potassium hydroxide was used in a crosslinker and in a solvent at this site.

The inorganic geochemistry of ground water from the deep monitoring wells is distinctive from that in the domestic wells and expected composition in the Wind River formation. Potassium concentration in MW02 (43.6 milligrams per liter) and MW01 (54.9 milligrams per liter) is between 14.5 and 18.3 times values in domestic wells and expected values in the formation. Chloride concentration in monitoring well MW02 (466 milligrams per liter) is 18 times the mean chloride concentration (25.6 milligrams per liter) observed in ground water from domestic wells and expected in the formation. Chloride enrichment in this well is significant because regional anion trends show decreasing chloride concentration with depth. In addition, the monitoring wells show low calcium, sodium, and sulfate concentrations compared to the general trend observed in domestic well waters. The formulation of fracture fluid provided for carbon dioxide foam hydraulic fracturing jobs typically consisted of 6% potassium chloride. Potassium metaborate was used in crosslinkers. Potassium hydroxide was used in a crosslinker and in a solvent. Ammonium chloride was used in crosslinker.

A number of synthetic organic compounds were detected in MW01 and MW02. Isopropanol was detected in MW01 and MW02 at 212 and 581 micrograms per liter, respectively. Diethylene glycol was detected in MW01 and MW02 at 226 and 1570 micrograms per liter, respectively. Triethylene glycol was detected in MW01 and MW02 at 46 and 310 micrograms per liter, respectively. Another synthetic compound, *tert*-butyl alcohol, was detected in MW02 at a concentration of 4470 micrograms per liter. Isopropanol was used in a biocide, in a surfactant, in breakers, and in foaming agents. Diethylene glycol was used in a foaming agent and in a solvent. Triethylene glycol was used in a solvent. *Tert*-butyl alcohol is a known breakdown product of methyl *tert*-butyl ether (a fuel additive) and *tert*-butyl hydroperoxide (a gel breaker used in hydraulic fracturing). Material Safety Data Sheets do not indicate that fuel or tert-butyl hydroperoxide were used in the Pavillion gas field. However, Material Safety Data Sheets do not contain proprietary information and the chemical ingredients of many additives. The source of *tert*-butyl alcohol remains unresolved. However, *tert*-butyl alcohol is not expected to occur naturally in ground water.

Benzene, toluene, ethylbenzene, and xylenes (BTEX) were detected in MW02 at concentrations of 246, 617, 67, and 750 micrograms per liter, respectively. Trimethylbenzenes were detected in MW02 at 105 micrograms per liter. Gasoline range organics were detected in MW01 and MW02 at 592 and 3710 micrograms per liter. Diesel range organics were detected in MW01 and MW02 at 924 and 4050 micrograms per liter, respectively. Aromatic solvent (typically BTEX mixture) was used in a breaker. Diesel oil (mixture of saturated and aromatic hydrocarbons including naphthalenes and alkylbenzenes) was used in a guar polymer slurry/liquid gel concentrate and in a solvent. Petroleum raffinates (mixture of paraffinic, cycloparaffinic, olefinic, and aromatic hydrocarbons) were used in a breaker. Heavy aromatic petroleum naphtha (mixture of paraffinic, cycloparaffinic and aromatic hydrocarbons) was used in surfactants and in a solvent. Toluene and xylene were used in flow enhancers and a breaker.

Detections of organic chemicals were more numerous and exhibited higher concentrations in the deeper of the two monitoring wells. Natural breakdown products of organic contaminants like BTEX and glycols include acetate and benzoic acid. These breakdown products are more enriched in the shallower of the two monitoring wells, suggesting upward/lateral migration with natural degradation and accumulation of daughter products. Hydraulic gradients are currently undefined in the area of investigation. However, there are flowing conditions in a number of deep stock wells suggesting that upward gradients exist in the area of investigation.

Alternative explanations were carefully considered to explain individual sets of data. However, when considered together with other lines of evidence, the data indicates likely impact to ground water that can be explained by hydraulic fracturing. A review of well completion reports and cement bond/variable density logs in the area around MW01 and MW02 indicates instances of sporadic bonding outside production casing directly above intervals of hydraulic fracturing. Also, there is little lateral and vertical continuity of hydraulically fractured tight sandstones and no lithologic barrier (laterally continuous shale units) to stop upward vertical migration of aqueous constituents of hydraulic fracturing in the event of excursion from fractures. In the event of excursion from sandstone units, vertical migration of fluids could also occur via nearby wellbores. For instance, at one production well, the cement bond/variable density log indicates no cement until 671 m below ground surface. Hydraulic fracturing occurred above this depth at nearby production wells.

A similar lines of reasoning approach was utilized to evaluate the presence of gas in monitoring and domestic wells. A comparison of gas composition and stable carbon isotope values indicate that gas in production and monitoring wells is of similar thermogenic origin and has undergone little or no degradation. A similar evaluation in domestic wells suggests the presence of gas of thermogenic origin undergoing biodegradation. This observation is consistent with a pattern of dispersion and degradation with upward migration observed for organic compounds.

Elevated levels of dissolved methane in domestic wells generally increase in those wells in proximity to gas production wells. Near surface concentrations of methane appear highest in the area encompassing MW01. Ground water is saturated with methane at MW01 which is screened at a depth (239 meters below ground surface) typical of deeper domestic wells in the area. A blowout occurred during drilling of a domestic well at a depth of only 159 meters below ground surface close to MW01. A mud-gas log conducted in 1980 (prior to intensive gas production well installation) located only 300 m from the location of the blowout does not indicate a gas show (distinctive peaks on a gas chromatograph) within 300 meters of the surface. Again, with the exception of two production wells, surface casing of gas production wells do not extend below the maximum depth of domestic wells in the area of investigation. A number of production wells in the vicinity of MW01 have sporadic bonding or no cement over large vertical instances. Again, alternate explanations of data have been considered. Although some natural migration of gas would be expected above a gas field such as Pavillion, data suggest that enhanced migration of gas has occurred within ground water at depths used for domestic water supply and to domestic wells. Further investigation would be needed to determine the extent of gas migration and the fate and transport processes influencing migration to domestic wells.