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Geochemical evidence for possible natural migration of Marcellus Formation brine to shallow aquifers in Pennsylvania

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Abstract

The debate surrounding the safety of shale gas development in the Appalachian Basin has generated increased awareness of drinking water quality in rural communities. Concerns include the potential for migration of stray gas, metal-rich formation brines, and hydraulic fracturing and/or flowback fluids to drinking water aquifers. A critical question common to these environmental risks is the hydraulic connectivity between the shale gas formations and the overlying shallow drinking water aquifers. We present geochemical evidence from northeastern Pennsylvania showing that pathways, unrelated to recent drilling activities, exist in some locations between deep underlying formations and shallow drinking water aquifers. Integration of chemical data (Br, Cl, Na, Ba, Sr, and Li) and isotopic ratios ($^{87}\text{Sr}/^{86}\text{Sr}$, $^2\text{H}/\text{H}$, $^{18}\text{O}/^{16}\text{O}$, and $^{228}\text{Ra}/^{226}\text{Ra}$) from this and previous studies in 426 shallow groundwater samples and 83 northern Appalachian brine samples suggest that mixing relationships between shallow ground water and a deep formation brine causes groundwater salinization in some locations. The strong geochemical fingerprint in the salinized ($\text{Cl} > 20 \text{ mg/L}$) groundwater sampled from the Alluvium, Catskill, and Lock Haven aquifers suggests possible migration of Marcellus brine through naturally occurring pathways. The occurrences of saline water do not correlate with the location of shale-gas wells and are consistent with reported data before rapid shale-gas development in the region; however, the presence of these fluids suggests conductive pathways and specific geostructural and/or hydrodynamic regimes in northeastern Pennsylvania that are at increased risk for contamination of shallow drinking water resources, particularly by fugitive gases, because of natural hydraulic connections to deeper formations.

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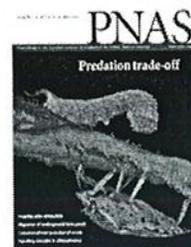
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The extraction of natural gas resources from the Marcellus Shale in the Appalachian Basin of the northeastern United States (1, 2) has increased awareness of potential contamination in shallow aquifers routinely used for drinking water. The current debate surrounding the safety of shale gas extraction (3) has focused on stray gas migration to shallow groundwater (4) and the atmosphere (5) as well as the potential for contamination from toxic substances in hydraulic fracturing fluid and/or produced brines during drilling, transport, and disposal (6 ↓ ↓–9).

The potential for shallow groundwater contamination caused by natural gas drilling is often dismissed because of the large vertical separation between the shallow drinking water wells and shale gas formations and the



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gas wells (10, 11). Recent findings in northeastern Pennsylvania (NE PA) demonstrated that shallow water wells in close proximity to natural gas wells (i.e., < 1 km) yielded, on average, higher concentrations of methane, ethane, and propane with thermogenic isotopic signature. By comparison, water wells farther away from natural gas development had lower combustible gas concentrations and an isotopic signature consistent with a mixture between thermogenic and biogenic components (4). In contrast, when inorganic water geochemistry from active drilling areas was compared to nonactive areas and historical background values, no statistically significant differences were observed (4). Increasing reports of changes in drinking water quality have nevertheless been blamed on the accelerated rate of shale gas development.

The study area in NE PA consists of six counties (Fig. 1) that lie within the Appalachian Plateau physiographic province in the structurally and tectonically complex transition between the highly deformed Valley and Ridge Province and the less deformed Appalachian Plateau (12, 13). The geologic setting and shallow aquifer characteristics are described and mapped in greater detail in multiple sources (4, 14) and in *SI Methods* (lookup/suppl/doi:10.1073/pnas.1121181109/-DCSupplemental/pnas.1121181109_SI.pdf?targetid=STXT). The study area contains a surficial cover composed of a mix of unconsolidated glacial till, outwash, alluvium and deltaic sediments, and postglacial deposits (the Alluvium aquifer) that are thicker in the valleys (17-19) (Fig. S1 (lookup/suppl/doi:10.1073/pnas.1121181109/-DCSupplemental/pnas.1121181109_SI.pdf?targetid=SF1)). These sediments are underlain by Upper Devonian through Pennsylvanian age sedimentary sequences that are gently folded and dip shallowly (1-3°) to the east and south (Fig. S2 (lookup/suppl/doi:10.1073/pnas.1121181109/-DCSupplemental/pnas.1121181109_SI.pdf?targetid=SF2)). The gentle folding creates alternating exposure of synclines and anticlines at the surface that are offset surface expressions of deeper deformation (12, 20). The two major bedrock aquifers are the Upper Devonian Catskill and the underlying Lock Haven Formations (14, 15, 18, 19). The average depth of drinking water wells in the study area is between 60 and 90 m (Table S1 (lookup/suppl/doi:10.1073/pnas.1121181109/-DCSupplemental/ST01.pdf)). The underlying geological formations, including the Marcellus Shale (at a depth of 1,200-2,500 m below the surface) are presented in Fig. 2, Fig. S2 A and B (lookup/suppl/doi:10.1073/pnas.1121181109/-DCSupplemental/pnas.1121181109_SI.pdf?targetid=SF2), and *SI Methods* (lookup/suppl/doi:10.1073/pnas.1121181109/-DCSupplemental/pnas.1121181109_SI.pdf?targetid=STXT).

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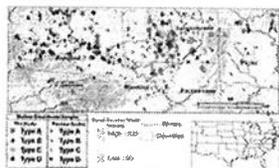


Fig. 1.

Digital elevation model (DEM) map of northeastern PA. Shaded brown areas indicate higher elevations and blue-green shaded areas indicate lower elevations (valleys). The distribution of shallow (< 90 m) groundwater samples from this study and previous studies (18, 19) are labeled based on water type. Two low salinity (Cl < 20 mg/L) water types dominated by Ca-HCO₃ (type A = green circles) or Na-HCO₃ (type B = blue triangles) were the most common, and two higher salinity (Cl > 20 mg/L) water types were also observed:

Br/Cl < 0.001 (type C = pink squares) and brine-type groundwater Br/Cl > 0.001 (type D = red diamonds). Type D groundwater samples appear associated with valleys (Table S1 (lookup/suppl/doi:10.1073/pnas.1121181109/-DCSupplemental/ST01.pdf)) and are sourced from conservative mixing between a brine and fresh meteoric water. The DEM data were obtained from NASA' Shuttle Radar Topography Mission <http://srtm.usgs.gov/> (<http://srtm.usgs.gov/>).



Fig. 2.

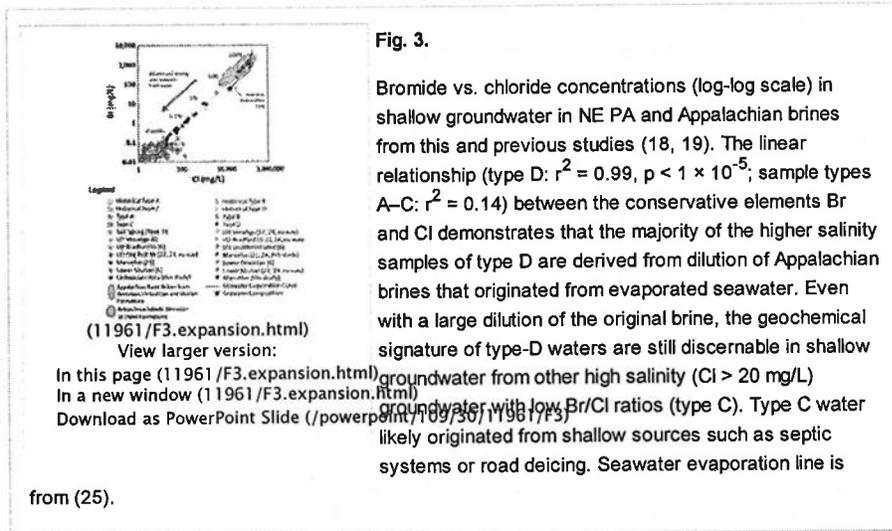
Generalized stratigraphic section in the subsurface of western and eastern PA plateau adapted from (14, 15, 18, 19) and Sr isotope data of Appalachian brines and type D saline groundwater. Variations of ⁸⁷Sr/⁸⁶Sr ratios in Appalachian Brine and type-D groundwater samples show enrichment compared to the Paleozoic secular seawater curve (dashed grey line) (49). Note the overlap in values of type-D shallow ground water with ⁸⁷Sr/⁸⁶Sr values in Marcellus brines or older formations (21, 22, 24) but no overlap with the Upper Devonian brines in stratigraphically equivalent formations (Table S2 (lookup/suppl

doi:10.1073/pnas.1121181109/-DCSupplemental/ST02.pdf)) (21, 24).

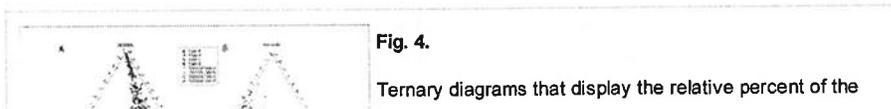
In this study, we analyze the geochemistry of 109 newly-collected water samples and 49 wells from our previous study (4) from the three principal aquifers, Alluvium (n = 11), Catskill (n = 102), and Lock Haven (n = 45), categorizing these waters into four types based on their salinity and chemical constituents (Figs. 1 and 2, and S1 Text (/lookup/suppl/doi:10.1073/pnas.1121181109/-DCSupplemental/pnas.1121181109_SI.pdf?targetid=STXT)). We combine these data with 268 previously-published data for wells in the Alluvium (n = 57), Catskill (n = 147), and Lock Haven (n = 64) aquifers (18, 19) for a total of 426 shallow groundwater samples. We analyzed major and trace element geochemistry and a broad spectrum of isotopic tracers ($\delta^{18}\text{O}$, $\delta^2\text{H}$, $^{87}\text{Sr}/^{86}\text{Sr}$, $^{228}\text{Ra}/^{226}\text{Ra}$) in shallow ground water and compared these to published (6, 21, 22) and new data of 83 samples from underlying Appalachian brines in deeper formations from the region (Table S2 (/lookup/suppl/doi:10.1073/pnas.1121181109/-DCSupplemental/ST02.pdf)) to examine the possibility of fluid migration between the hydrocarbon producing Marcellus Formation and shallow aquifers in NE PA. We hypothesize that integration of these geochemical tracers could delineate possible mixing between the Appalachian brines and shallow groundwater.

Results and Discussion

The water chemistry data from the Alluvial, Catskill, and Lock Haven shallow aquifers (Table S1 (/lookup/suppl/doi:10.1073/pnas.1121181109/-DCSupplemental/ST01.pdf)) reveal a wide range of solute concentrations from dilute groundwater with total dissolved solids (TDS) < 500 mg/L and Cl < 20 mg/L to highly saline water (e.g., a salt spring with TDS of 7,800 mg/L and Cl approximately 4,000). Based on these characteristics, we divide the water samples into four types of ground water (Fig. 1). Two groundwater types (A and B; n = 118 of 158 samples from this and our previous study (4) are characterized by low salinity and high Na/Cl and Br/Cl (all ratios reported as molar) ratios (Table S1 (/lookup/suppl/doi:10.1073/pnas.1121181109/-DCSupplemental/ST01.pdf)). The two elevated salinity (Cl > 20 mg/L) water types (C and D) were divided based on their Br/Cl ratios. Type (C) (n = 13 of 158) has a distinctive low (< 0.001) Br/Cl ratio (Fig. 3) and higher NO_3^- concentrations that we attribute to salinization from domestic sources such as wastewater and/or road salt that have typically low Br/Cl ratios. The fourth subset of shallow groundwater (type D) (n = 27 of 158) was identified with a relatively high Br/Cl ratio (> 0.001) and low Na/Cl ratio (Na/Cl < 5) with a statistically significant difference in water chemistry from types A–C (Table S3 (/lookup/suppl/doi:10.1073/pnas.1121181109/-DCSupplemental/ST03.pdf)).



A geochemical analysis of published data collected in the 1980s (18, 19) revealed similar shallow salinized groundwater with a distinctive higher Cl (> 20 mg/L) and low Na/Cl ratio. The saline groundwater mimics type D water with statistically indistinguishable (Table S3 (/lookup/suppl/doi:10.1073/pnas.1121181109/-DCSupplemental/ST03.pdf)) concentrations of major cations and anions (Fig. 4 A and B); however, bromide concentrations were not available in the historical data set. Nonetheless, we designated historical samples with high Cl (> 20 mg/L) and low Na/Cl ratio (Na/Cl < 5) as possible type D (n = 56 of 268). The remaining historical samples with Cl concentrations (> 20 mg/L) were designated as type C. All water types (A–D) were statistically indistinguishable from their respective historical types (A–D) (Table S3 (/lookup/suppl/doi:10.1073/pnas.1121181109/-DCSupplemental/ST03.pdf)).



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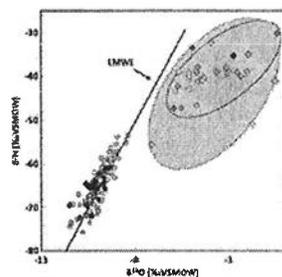
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major cations (A) and anions (B) in shallow groundwater samples from this and previous studies (18, 19). The overlap indicates that Na-Ca-Cl type saline water was present prior to the recent shale-gas development in the region and could be from natural mixing.

Type D saline waters are characterized by a Na-Ca-Cl composition with Na/Cl, Sr/Cl, Ba/Cl, Li/Cl, and Br/Cl ratios similar to brines found in deeper Appalachian formations (e.g., the Marcellus brine) (4, 6, 21, 22) (Table S2 (/lookup/suppl/doi:10.1073/pnas.1121181109/-/DCSupplemental/ST02.pdf)). This suggests mixing of shallow modern water with deep formation brines. Furthermore, the linear correlations observed for Br, Na, Sr, Li, and Ba with chloride (Fig. 3 and Fig. S3 A–F (/lookup/suppl/doi:10.1073/pnas.1121181109/-/DCSupplemental/pnas.1121181109_SI.pdf?targetid=SF3)) demonstrate the relatively conservative and nonreactive behavior of these constituents and that the salinity in these shallow aquifers is most likely derived from mixing of deeper formation brines.

The stable isotopes ($\delta^{18}\text{O} = -8$ to -11% ; $\delta^2\text{H} = -53$ to -74%) of all shallow groundwater types (A–D) are indistinguishable ($p > 0.231$) and fall along the local meteoric water line (LMWL) (23) (Fig. 5). The similarity of the stable isotopic compositions to the modern LMWL likely indicate dilution with modern (post-glacial) meteoric water. Shallow groundwater isotopic compositions do not show any positive $\delta^{18}\text{O}$ shifts towards the seawater evaporation isotopic signature (i.e., higher $\delta^{18}\text{O}$ relative to $\delta^2\text{H}$) as observed in the Appalachian brines (Fig. 5 and Table S2 (/lookup/suppl/doi:10.1073/pnas.1121181109/-/DCSupplemental/ST02.pdf)). Because of the large difference in concentrations between the brines and fresh water, very small contributions of brine have a large and measurable effect on the geochemistry and isotopes of dissolved salts (Fig. 3) but limited effect on $\delta^{18}\text{O}$ and $\delta^2\text{H}$. Mass-balance calculations indicate that only a brine fraction of higher than approximately 20% would change the $\delta^{18}\text{O}$ and $\delta^2\text{H}$ of salinized groundwater measurably. Oxygen and hydrogen isotopes are, therefore, not sensitive tracers for the mixing of the Appalachian brines and shallow groundwater because of the large percentage of the fresh water component in the mixing blend. For example, the salt spring at Salt Springs State Park with the highest salinity among shallow groundwater samples is calculated to contain $< 7\%$ brine.



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Fig. 5.

$\delta^2\text{H}$ vs. $\delta^{18}\text{O}$ in shallow groundwater from this study and Appalachian brines. The water isotope composition of the shallow groundwater samples including the Salt Spring appear indistinguishable from each other and the local meteoric water line (LMWL) (23) and do not show any apparent trends toward the stable isotope ratios of the Appalachian brines (6, 22). The data indicate that dilution of the type-D waters likely occurred on modern (post-glacial) time scales. Symbol legend is provided in Fig. 3.

The discrete areas of type D water have lower average elevations and closer distances to valley centers but do not correlate with distance to the nearest shale gas wells (Fig. 1 and Fig. S1 (/lookup/suppl/doi:10.1073/pnas.1121181109/-/DCSupplemental/pnas.1121181109_SI.pdf?targetid=SF1) and Table S1 (/lookup/suppl/doi:10.1073/pnas.1121181109/-/DCSupplemental/ST01.pdf)). The lack of geospatial association with shale-gas wells and the occurrence of this type of saline water prior to shale gas development in the study area (14, 15, 18, 19) (see distribution in Fig. 4 A and B) suggests that it is unlikely that hydraulic fracturing for shale gas caused this salinization and that it is instead a naturally occurring phenomenon that occurs over longer timescales.

Distinguishing the ultimate source of the salinized water in NE PA requires an evaluation of the geochemical signatures of underlying brines in the Appalachian Basin. The data presented in this study (Figs. 2 and 3, and Fig. S3 A–F (/lookup/suppl/doi:10.1073/pnas.1121181109/-/DCSupplemental/pnas.1121181109_SI.pdf?targetid=SF3) and Table S2 (/lookup/suppl/doi:10.1073/pnas.1121181109/-/DCSupplemental/ST01.pdf)) and previous studies (4, 6, 22, 24), suggest that the Appalachian brines evolved by evaporation from a common seawater origin but underwent varying stages of alteration. The first stage of evolution common to all of the brines is the evaporation of seawater beyond halite saturation resulting in brines with high Br/Cl and low Na/Cl ratios relative to seawater (6). The degree of evaporation that

is computed based on the Br/Cl ratio in the Appalachian brines ($4\text{--}7\cdot 10^{-3}$) (Fig. 3) as compared to the evaporated sea water curve (25) is equivalent to 20–40-fold, though mixing between brines of different evaporation stages cannot be excluded. The brines then likely underwent dolomitization with carbonate rocks that enriched Ca and depleted Mg in the brine relative to the seawater evaporation curve (6) (Fig. S3 B and C (/lookup/suppl/doi:10.1073/pnas.1121181109/-DCSupplemental/pnas.1121181109_SI.pdf?targetid=SF3)) and sulfate reduction that removed all sulfate. In addition, the composition of each respective hypersaline Ca-Cl Appalachian brine (i.e., Salina and/or Marcellus) was differentially altered by interactions with the host aquifer rocks presumably under tectonically-induced thermal conditions (26) that resulted in resolvable variations in Sr/Ca, Ba/Sr, and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios. The final stage of brine alteration that accounts for the observed brine compositions is dilution (6).

The net results of these processes generated large variations in brine salinity (TDS of 10–343 g/L), relatively homogeneous elevated Br/Cl ratios (range of $2.4\cdot 10^{-3}$ to $7.6\cdot 10^{-3}$) and enriched $\delta^{18}\text{O}$ (0‰ to -7‰) and $\delta^2\text{H}$ (-33‰ to -45‰) in all Appalachian brines. The remnant geochemical signatures (i.e., Sr/Ca, Ba/Sr, and $^{87}\text{Sr}/^{86}\text{Sr}$) of formation specific brine-rock interactions provide the most suitable basis for differentiating the Appalachian brines. The Sr/Ca ratios (0.03–0.17) of the produced waters from Marcellus wells are significantly higher than brines evolved through calcite ($0.4\text{--}1.6\cdot 10^{-3}$) or aragonite ($1.5\text{--}2.2\cdot 10^{-2}$) dolomitization but are consistent with equilibrium with other minerals such as gypsum or celestite (27). Similarly, the Ba/Sr (0.01–1.78) ratios range up to values observed for typical upper continental crust (Ba/Sr = 1.3–1.7) (28).

New and compiled data presented in Table S2 (/lookup/suppl/doi:10.1073/pnas.1121181109/-DCSupplemental/ST02.pdf) show distinctive geochemical fingerprints (Sr/Ca, Ba/Sr, Sr/Cl, Ba/Cl, Li/Cl, and $^{87}\text{Sr}/^{86}\text{Sr}$) among the Appalachian brines in the different formations. We, therefore, used these variables as independent tracers to differentiate possible brine sources for the shallow type D groundwater. Brines from the Marcellus Formation show systematically low (less radiogenic) $^{87}\text{Sr}/^{86}\text{Sr}$ (0.71000–0.71212; $n = 50$) and high Sr/Ca (0.03–0.17) ratios compared to the more radiogenic Upper Devonian brines ($^{87}\text{Sr}/^{86}\text{Sr}$ ratio = 0.71580–0.72200; $n = 12$; Fig. 6) and low Sr/Ca (0.002–0.08) (Fig. S4 (/lookup/suppl/doi:10.1073/pnas.1121181109/-DCSupplemental/pnas.1121181109_SI.pdf?targetid=SF4)). Because of the relatively high Sr concentration and diagnostic Sr/Ca, Ba/Sr, and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios, this geochemical proxy has the potential to elucidate regional flow paths, salinity sources, and the specific source of the Appalachian brines (21, 24) (Fig. 6). The $^{87}\text{Sr}/^{86}\text{Sr}$ ratios ($0.71030\text{--}0.71725 \pm 0.000003$ SE) of low-saline groundwater (type A and B) vary widely in the shallow aquifers, but the overwhelming majority are distinctly different from values of produced water brines from Upper Devonian (0.71580–0.72200) (24) (Table S2 (/lookup/suppl/doi:10.1073/pnas.1121181109/-DCSupplemental/ST02.pdf)) and Middle Devonian Marcellus Formation (0.71000–0.71212) (21) (Fig. 6). Conversely, the type D shallow groundwater data show a linear correlation between Sr and Cl (i.e., conservative behavior of Sr) (Fig. S3D (/lookup/suppl/doi:10.1073/pnas.1121181109/-DCSupplemental/pnas.1121181109_SI.pdf?targetid=SF3)) and a decrease of $^{87}\text{Sr}/^{86}\text{Sr}$ from 0.71453–0.70960 with increasing Sr concentrations and salinity confirming that the resulting salinity is likely derived from mixing with Marcellus Formation brine (Fig. 6). Our data also display a strong association between $^{87}\text{Sr}/^{86}\text{Sr}$ and Sr/Ca ratios (Fig. S4 (/lookup/suppl/doi:10.1073/pnas.1121181109/-DCSupplemental/pnas.1121181109_SI.pdf?targetid=SF4)), a relationship suggested as a sensitive indicator of Marcellus brines because of the unique combination of low $^{87}\text{Sr}/^{86}\text{Sr}$ ratios and high Sr/Ca ratios reported for brines from the Marcellus Formation (21).

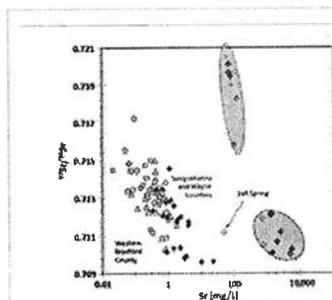


Fig. 6.

$^{87}\text{Sr}/^{86}\text{Sr}$ vs. Sr concentrations (log scale) of Appalachian Brines (21, 24) and shallow groundwater samples in the study area. The shallow groundwater samples are divided in the figure based on water types. Increased concentrations of Sr in the shallow aquifers are likely derived from two component mixing: (i) A low salinity, radiogenic $^{87}\text{Sr}/^{86}\text{Sr}$ groundwater sourced from local aquifer reactions; and (ii) A high salinity, less radiogenic $^{87}\text{Sr}/^{86}\text{Sr}$ water consistent with Marcellus Formation brine. The Marcellus Formation $^{87}\text{Sr}/^{86}\text{Sr}$ appears lower in Western Bradford than in Susquehanna and Wayne counties. Other brine sources such as the Upper Devonian formations have a more radiogenic $^{87}\text{Sr}/^{86}\text{Sr}$

ratio that does not appear to show any relationship to the salinized shallow groundwater. Symbol legend is provided in Fig. 3.

The saline waters in the eastern portion of the study area follow the expected Sr-isotope mixing trend

hypothesized from new and published data on produced water from the Marcellus Formation (Fig. 6). In contrast, the saline waters from the western portion of our study area show systematic mixing with an end member of a slightly lower $^{87}\text{Sr}/^{86}\text{Sr}$ ratio (0.70960). This lower ratio could reflect provenance variations within the formation (e.g., lower siliclastic detrital component away from the Acadian clastic source) in the region (21). In sum, whereas the high Br/Cl ratio in type D saline groundwater reflects mixing with underlying Appalachian brines from a common evaporated seawater origin, the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios indicate mixing with brines with lower $^{87}\text{Sr}/^{86}\text{Sr}$ fingerprints of approximately 0.7096–0.7110 that cannot be accounted for by Upper Devonian formations but are similar to the underlying Marcellus Formation brines.

Other features that characterize the produced waters from the Marcellus Formation are the high activities of naturally occurring nuclides of ^{226}Ra and ^{228}Ra and low $^{228}\text{Ra}/^{226}\text{Ra}$ ratios (7). ^{226}Ra and ^{228}Ra are the disintegration products of ^{238}U and ^{232}Th , respectively, and are generated in groundwater from alpha recoil, desorption from sediments, and dissolution of aquifer material (7, 29). In most of the shallow groundwater we sampled (Table S1 ([lookup/suppl/doi:10.1073/pnas.1121181109/-DCSupplemental/ST01.pdf](#))), combined Ra activities were low (< 5 pCi/L). In contrast, reported activities of Ra in Marcellus brines from the study area were high (1,500–3,100 pCi/L) (Fig. S5 ([lookup/suppl/doi:10.1073/pnas.1121181109/-DCSupplemental/pnas.1121181109_SI.pdf?targetid=SF5](#))) with low $^{228}\text{Ra}/^{226}\text{Ra}$ ratios (0.12–0.73) (7). The highest Ra activities that we measured were in type D waters, and the range (0.4 to 28 pCi/L) is consistent with our calculated mixing range of approximately 0.01–7% based on chloride and bromide mass-balance calculations (Fig. 3), though some interaction such as adsorption with the aquifer rocks (29) is likely. In addition, the $^{228}\text{Ra}/^{226}\text{Ra}$ ratio in the salinized groundwater (mean = 0.56) is higher than that of the majority of the Marcellus produced waters from the study area (mean = 0.33) (7) (Table S2 ([lookup/suppl/doi:10.1073/pnas.1121181109/-DCSupplemental/ST02.pdf](#))) indicating that the dissolved Ra in the shallow groundwater is likely derived from a combination of local water-rock interactions and conservative mixing.

Methane data from our previous studies (4, 30) can be examined based on the four water types (A–D) we found in this study. The highest average methane concentrations were observed in type D waters throughout the dataset, followed by type B and A. In locations > 1 km away from shale gas drilling sites only one sample, a type B water, out of total of 41 samples contained elevated methane concentrations (> 10 mg/L). One newly sampled type D water from the spring at Salt Springs State Park (30) also had concentrations > 10 mg/L. Within 1 km of a natural gas well, three type A, three type B, and five type D samples had methane concentrations > 10 mg/L. In three type D groundwater samples that were located in the lowland valleys > 1 km from shale gas drilling sites, methane concentrations were 2–4 mg/L for the two previously sampled shallow ground waters and 26 mg/L for the newly sampled salt spring. In contrast, type A groundwater > 1 km away from drilling sites had methane concentrations < 0.01 mg/L in all samples ($n = 14$). This could suggest that methane in type D water > 1 km away from drilling sites could be derived from natural seepage (31) but at concentrations much lower than those observed near drilling (4).

Cross-formational pathways allowing deeper saline water to migrate into shallower, fresher aquifers have been documented in numerous study areas including western Texas (32, 33), Michigan Basin (34, 35), Jordan Rift Valley (36), Appalachian Basin (26), and Alberta, Canada (37). In the Michigan Basin, upward migration of saline fluid into the overlying glacial sediments (34, 35) was interpreted to reflect isostatic rebound following the retreat of glaciers, leading to fracture intensification and increased permeability (34). Alternatively, vertical migration of over-pressured hydrocarbons has been proposed for the Appalachian Basin in response to tectonic deformation and catagenesis (i.e., natural gas induced fracturing) during the Alleghenian Orogeny (38–40). This deformation resulted in joints that cut across formations (J₂) in Middle and Upper Devonian formations (39). In addition, the lithostatic and isostatic rebound following glacial retreat significantly increased fracture intensification and permeability in the Upper Devonian aquifers within our study area.

We hypothesize that regions with the combination of deep high hydrodynamic pressure and enhanced natural flow paths (i.e., fracture zones) (39, 41, 42) could induce steep hydraulic gradients and allow the flow of deeper fluids to zones of lower hydrodynamic pressure (43, 44). The higher frequency of the saline type D water occurrence in valleys (Table S1 ([lookup/suppl/doi:10.1073/pnas.1121181109/-DCSupplemental/ST01.pdf](#))) is consistent with hydrogeological modeling of regional discharge to lower hydrodynamic pressure in the valleys with greater connectivity to the deep subsurface (43–45).

The possibility of drilling and hydraulic fracturing causing rapid flow of brine to shallow groundwater in lower hydrodynamic pressure zones is unlikely but still unknown. By contrast, the time scale for fugitive gas contamination of shallow aquifers can be decoupled from natural brine movement specifically when gas concentrations exceed solubility (approximately 30 cc/kg) and forms mobile free phase gases (i.e., bubbles). In western PA, on the Appalachian Plateau, contamination of shallow aquifers has been described as leakage of highly pressurized gas through the over-pressurized annulus of gas wells and into the overlying freshwater aquifers via fractures and faults (43, 44). The faults are often connected to local and regional discharge areas (i.e., valleys) where the methane contamination is observed (43). Buoyant flow of methane gas bubbles through these fractures is far more rapid than head-driven flow of dense brine, occurring on time scales of

less than a year (46).

This study shows that some areas of elevated salinity with type D composition in NE PA were present prior to shale-gas development and most likely are unrelated to the most recent shale gas drilling; however, the coincidence of elevated salinity in shallow groundwater with a geochemical signature similar to produced water from the Marcellus Formation suggests that these areas could be at greater risk of contamination from shale gas development because of a preexisting network of cross-formational pathways that has enhanced hydraulic connectivity to deeper geological formations (43). Future research should focus on systematically monitoring these areas to test potential mechanisms of enhanced hydraulic connectivity to deeper formations, confirm the brine source, and determine the timescales for possible brine migration.

Methods

Drinking water wells were purged until pH, electrical conductance, and temperature were stabilized. Samples were collected prior to any treatment systems and filtered/preserved following USGS protocols (47). All major element and isotopic chemistry analyses were conducted at Duke University. Major anions were determined by ion chromatography, major cations by direct current plasma optical emission spectrometry, and trace metals by VG PlasmaQuad-3 inductively coupled plasma mass-spectrometry. Alkalinity was determined by titration with HCl to pH 4.5. Stable isotopes were determined by continuous flow isotope ratio mass spectrometry using a ThermoFinnigan TCEA and Delta + XL mass spectrometer at the Duke Environmental Isotope Laboratory (DEVIL). Analytical precisions for $\delta^{18}\text{O}$ and $\delta^2\text{H}$ were estimated as $\pm 0.1\%$ and $\pm 1.5\%$, respectively. Radium isotope analyses (^{226}Ra and ^{228}Ra) were measured at the Laboratory for Environmental Analysis of RadioNuclides (LEARN) using a DurrIDGE RAD7 radon-in-air monitor (^{226}Ra) and Canberra DSA2000BEGe gamma detector (^{228}Ra) following methods described in (29) and (48). Strontium isotopes were analyzed by a thermal ionization mass spectrometer on a ThermoFisher Triton. The mean $^{87}\text{Sr}/^{86}\text{Sr}$ of the Standard Reference Material-987 standard was 0.710266 ± 0.000005 (SD).

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Footnotes

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Fracking-Earthquake Report Suggests Low Risk For Large Tremors

AP | By SETH BORENSTEIN Posted: 06/15/2012 1:05 pm

WASHINGTON (AP) — The controversial practice of hydraulic fracturing to extract natural gas does not pose a high risk for triggering earthquakes large enough to feel, but other types of energy-related drilling can make the ground noticeably shake, a major government science report concludes.

Even those man-made tremors large enough to be an issue are very rare, says a special report by the National Research Council. In more than 90 years of monitoring, human activity has been shown to trigger only 154 quakes, most of them moderate or small, and only 60 of them in the United States. That's compared to a global average of about 14,450 earthquakes of magnitude 4.0 or greater every year, said the report, released Friday.

Most of those are caused by gas and oil drilling the conventional way, damming rivers, deep injections of wastewater and purposeful flooding. Only two worldwide instances of shaking — a magnitude 2.8 tremor in Oklahoma and a 2.3 magnitude shaking in England— can be attributed to hydraulic fracturing, a specific method of extracting gas by injection of fluids sometimes called "fracking," the report said. Both were last year.

"There's a whole bunch of wells that have been drilled, let's say for wastewater and the number of events have been pretty small," said report chairman Murray Hitzman, a professor of economic geology at the Colorado School of Mines. "Is it a huge problem? The report says basically no. Is it something we should look at and think about? Yes."

With increased drilling to satisfy the country's thirst for energy, it is important to watch injection and other wells better and consider potential repercussions before starting, the report said. No one has been killed, nor has there been major damage, from man-made quakes in the United States, said the report by the council, which is part of the National Academy of Sciences, a private nonprofit institution that provides expert advice to the government.

"There is potential to produce significant seismic events that can be felt and cause damage and public concern," the report said.

The research council report shows that most of the tremors that can be blamed on humans occurred in California, Texas, Colorado, Oklahoma, and Ohio. California and Oklahoma had the biggest man-made shakes as byproducts of conventional oil and gas drilling. Colorado has one of the most documented cases of three 5.0 to 5.5 man-induced quakes because of an injection well. Northern California also has 300 to 400 tiny quakes a year since 2005 because of geothermal energy extraction.

Man-made drilling — usually injections of fluids deep and at high pressure — can trigger shaking because it changes the crucial balance of fluid into and out of the subsurface. That can then affect the pore pressure of the soil and that's what helps keep faults from moving, Hitzman said.

The report makes sense as far as it goes, said U.S. Geological Survey seismologist William Ellsworth, but since the research council started its study, government geologists have noticed a strange increase in earthquakes that seem man-made. At a professional seismology conference in April, Ellsworth presented a USGS report on a six-fold increase in man-made quakes. He pointed to induced quakes of magnitude 4 or larger in the past year in Texas, Oklahoma, Arkansas, Colorado, New Mexico, and Ohio, but said much of this happened too late for the research council to include in its study.

Hitzman said it's still too early to tell whether those recent quakes would have changed the report's conclusions.

Another study — also too recent for the research council report — says a 4.7 magnitude quake in central Arkansas in 2011 was man-made and scientists are still looking at a 2011 quake in Oklahoma that measured 5.6 as a potential but not proven induced tremor, Ellsworth said.

The man-made quakes that Ellsworth has been seeing are almost all related to wastewater injection, he said. Ellsworth said he agreed with the research council that "hydraulic fracturing does not seem to pose much risk for earthquake activity."

If the country starts capturing the global warming gas carbon dioxide from coal power plants and injecting it underground, there is a potential for a larger quakes given the amount of the heat-trapping gas that would have to be buried, the council's report said. That's an issue that needs more study, it said.

Congress and the Department of Energy requested the 240-page report.

Online:

The National Research Council report: http://www.nap.edu/catalog.php?record_id=13355

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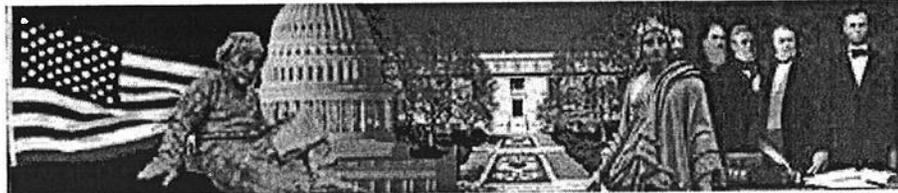
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For Congress

Date: 06/19/2012
Session: 112th Congress (Second Session)
Witness(es): Murray W. Hitzman
Credentials: Charles Fogarty Professor of Economic Geology, Department of Geology and Geological Engineering, Colorado School of Mines and Chair, Committee on Induced Seismicity Potential in Energy Technologies, Division on Earth and Life Sciences, National Research Council, The National Academies
Chamber: Senate
Committee: Energy and Natural Resources Committee, U.S. Senate
Subject: Induced Seismicity Potential in Energy Technologies

Testimony of

Dr. Murray W. Hitzman

Charles Fogarty Professor of Economic Geology
 Department of Geology and Geological Engineering
 Colorado School of Mines
 and

Chair, Committee on Induced Seismicity Potential in Energy Technologies
 Division on Earth and Life Sciences
 National Research Council
 The National Academies

before the

Energy and Natural Resources Committee
 U.S. Senate

June 19, 2012

Chairman Bingaman, Ranking Member Murkowski, and members of the Committee, I would like to thank you for the invitation to address you on the subject of induced seismicity potential in energy technologies. My name is Murray Hitzman. I am a professor of geology at the Colorado School of Mines in Golden, Colorado and served as the chair of the National Research Council Committee on Induced Seismicity Potential in Energy Technologies. The Research Council is the operating arm of the National Academy of Sciences, National Academy of Engineering, and the Institute of Medicine of the National Academies, chartered by Congress in 1863 to advise the government on matters of science and technology. I would

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like to thank the Committee for the invitation to address it on the subject of induced seismicity potential in energy technologies.

Although the vast majority of earthquakes that occur in the world each year have natural causes, some of these earthquakes and a number of lesser magnitude seismic events are related to human activities and are called “induced seismic events” or “induced earthquakes.”

Induced seismic activity has been attributed to a range of human activities including the impoundment of large reservoirs behind dams, controlled explosions related to mining or construction, and underground nuclear tests. Energy technologies that involve injection or withdrawal of fluids from the subsurface can also create induced seismic events that can be measured and felt.

Since the 1920s we have recognized that pumping fluids into or out of the Earth has the potential to cause seismic events that can be felt. Only a very small fraction of injection and extraction activities at hundreds of thousands of energy development sites in the United States have induced seismicity at levels that are noticeable to the public. However, seismic events caused by or likely related to energy development have been measured and felt in Alabama, Arkansas, California, Colorado, Illinois, Louisiana, Mississippi, Nebraska, Nevada, New Mexico, Ohio, Oklahoma, and Texas. Although none of these events resulted in loss of life or significant structural damage, their effects were felt by local residents, some of whom also experienced minor property damage. Particularly in areas where natural seismic activity is uncommon and energy development is ongoing, these induced seismic events, though small in scale, can be disturbing to the public and raise concern about increased seismic activity and its potential consequences.

Anticipating public concern about the potential for induced seismicity related to energy development, the Chairman of this Committee, Senator Bingaman, requested that the Department of Energy conduct a study of this issue through the National Research Council. The Chairman requested that this study examine the scale, scope, and consequences of seismicity induced during the injection of fluids related to energy production. The energy technologies to be considered included geothermal energy development, oil and gas production, including enhanced oil recovery and shale gas, and carbon capture and storage or CCS. The study was also to identify gaps in knowledge and research needed to advance the understanding of induced seismicity; to identify gaps in induced seismic hazard assessment methodologies and the research needed to close those gaps; and to assess options for interim steps toward best practices with regard to energy development and induced seismicity potential. The National Research Council (NRC) released the report ***Induced Seismicity Potential in Energy Technologies*** on June 15.

The committee that wrote this NRC report consisted of eleven experts in various aspects of seismicity and energy technologies from academia and industry. The committee examined peer-reviewed literature, documents produced by federal and state agencies, online databases and resources, and information requested from and submitted by external sources. We heard from government and industry representatives. We also talked with members of the public familiar with the world’s largest geothermal operation at The Geysers at a public meeting in Berkeley, California. We also spoke to people familiar with shale gas development, enhanced oil recovery, waste water disposal from energy development, and CCS at meetings in Dallas, Texas and Irvine, California. Meetings were also held in Washington, D.C. and Denver, Colorado to explore induced seismicity in theory and in practice.

This study took place during a period in which a number of small, felt seismic events occurred that were likely related to fluid injection for energy development. Because of their recent occurrence, peer-reviewed publications about most of these events were generally not available. However, knowing that these events and information about them would be anticipated in this report, the committee attempted to identify and seek information from as many sources as possible to gain a sense of the common factual points involved in each instance, as well as the remaining, unanswered questions about these cases. Through this process, the committee has engaged scientists and engineers from academia, industry, and government because each has credible information to add to better understanding of induced

seismicity.

The committee found that induced seismicity associated with fluid injection or withdrawal associated with energy development is caused in most cases by change in pore fluid pressure and/or change in stress in the subsurface in the presence of faults with specific properties and orientations and a critical state of stress in the rocks. The factor that appears to have the most direct consequence in regard to induced seismicity is the net fluid balance or put more simply, the total balance of fluid introduced into or removed from the subsurface. Additional factors may also influence the way fluids affect the subsurface. The committee concluded that while the general mechanisms that create induced seismic events are well understood, we are currently unable to accurately predict the magnitude or occurrence of such events due to the lack of comprehensive data on complex natural rock systems and the lack of validated predictive models.

The committee found that the largest induced seismic events associated with energy projects reported in the technical literature are associated with projects that did not balance the large volumes of fluids injected into, or extracted from, the Earth. We emphasize that this is a statistical observation. It suggests, however, that the net volume of fluid that is injected and/or extracted may serve as a proxy for changes in subsurface stress conditions and pore pressure. The committee recognizes that coupled thermo-mechanical and chemo-mechanical effects may also play a role in changing subsurface stress conditions.

I will briefly discuss the potential for induced seismicity with each of the energy technologies that the committee considered, beginning with geothermal energy.

Geothermal Energy

The three different types of geothermal energy resources are: (1) "vapor-dominated", where primarily steam is contained in the pores or fractures of hot rock, (2) "liquid-dominated", where primarily hot water is contained in the rock, and (3) "Enhanced Geothermal Systems" (EGS), where the resource is hot, dry rock that requires engineered stimulation to allow fluid movement for commercial development. Although felt induced seismicity has been documented with all three types of geothermal resources, geothermal development usually attempts to keep a mass balance between fluid volumes produced and fluids replaced by injection to extend the longevity of the energy resource. This fluid balance helps to maintain fairly constant reservoir pressure—close to the initial, pre-production value—and aids in reducing the potential for induced seismicity.

Seismic monitoring at liquid-dominated geothermal fields in the western United States has demonstrated relatively few occurrences of felt induced seismicity. However, in vapor or steam dominated geothermal system at The Geysers in northern California, the large temperature difference between the injected fluid and the geothermal reservoir results in significant cooling of the hot subsurface reservoir rocks. This has resulted in a significant amount of observed induced seismicity. EGS technology is in the early stages of development. Many countries including the United States have pilot projects to test the potential for commercial production. In each case of active EGS development, at least some, generally minor levels of felt induced seismicity have been recorded.

Conventional Oil & Gas

Oil and gas extraction from a reservoir may cause induced seismic events. These events are rare relative to the large number of oil and gas fields around the world and appear to be related to decrease in pore pressure as fluid is withdrawn.

Oil or gas reservoirs often reach a point when insufficient pressure exists to allow sufficient hydrocarbon recovery. Various technologies, including secondary recovery and tertiary recovery - also called enhanced oil recovery or EOR - can be used to extract some of the remaining oil and gas. Secondary recovery and EOR technologies both involve injection of fluids into the subsurface to push more of the trapped hydrocarbons out of the pore spaces in the reservoir and to maintain reservoir pore pressure. Secondary recovery often uses water

injection or “waterflooding” and EOR technologies often inject carbon dioxide. Approximately 151,000 injection wells are currently permitted in the United States for a combination secondary recovery, EOR, and waste water disposal with only very few documented incidents where the injection caused or was likely related to felt seismic events. Secondary recovery—through waterflooding—has been associated with very few felt induced seismic events. Among the tens of thousands of wells used for EOR in the United States, the committee did not find any documentation in the published literature of felt induced seismicity.

Shale Gas

Shale formations can also contain hydrocarbons—gas and/or oil. The extremely low permeability of these rocks has trapped the hydrocarbons and largely prevented them from migrating out of the rock. The low permeability also prevents the hydrocarbons from easily flowing into a well bore without production stimulation by the operator. These types of “unconventional” reservoirs are developed by drilling wells horizontally through the reservoir rock and using hydraulic fracturing techniques to create new fractures in the reservoir to allow the hydrocarbons to migrate up the well bore. This process is now commonly referred to as “fracking.” About 35,000 hydraulically fractured shale gas wells exist in the United States. Only one case of felt seismicity in the United States has been described in which hydraulic fracturing for shale gas development is suspected, but not confirmed. Globally only one case of felt induced seismicity at Blackpool, England has been confirmed as being caused by hydraulic fracturing for shale gas development. The very low number of felt events relative to the large number of hydraulically fractured wells for shale gas is likely due to the short duration of injection of fluids and the limited fluid volumes used in a small spatial area.

Waste Water Disposal

In addition to fluid injection directly related to energy development, injection wells drilled to dispose of waste water generated during oil and gas production, including during hydraulic fracturing, are very common in the United States. Tens of thousands of waste water disposal wells are currently active throughout the country. Although only a few induced seismic events have been linked to these disposal wells, the occurrence of these events has generated considerable public concern. Examination of these cases suggests causal links between the injection zones and previously unrecognized faults in the subsurface.

In contrast to wells for EOR which are sited and drilled for precise injection into well-characterized oil and gas reservoirs, injection wells used only for the purpose of waste water disposal normally do not have a detailed geologic review performed prior to injection and the data are often not available to make such a detailed review. Thus, the location of possible nearby faults is often not a standard part of siting and drilling these disposal wells. In addition, the presence of a fault does not necessarily imply an increased potential for induced seismicity. This creates challenges for the evaluation of potential sites for disposal injection wells that will minimize the possibility for induced seismic activity.

Most waste water disposal wells typically involve injection at relatively low pressures into large porous aquifers that have high natural permeability, and are specifically targeted to accommodate large volumes of fluid. Of the well-documented cases of induced seismicity related to waste water fluid injection, many are associated with operations involving large amounts of fluid injection over significant periods of time. Thus, although a few occurrences of induced seismic activity associated with waste water injection have been documented, the majority of the hazardous and nonhazardous waste water disposal wells do not pose a hazard for induced seismicity. However, the long-term effects of any significant increases in the number of waste water disposal wells in particular areas on induced seismicity are unknown.

Carbon capture and sequestration

Carbon capture and sequestration – or CCS - is also a means of disposing of fluid in the subsurface. The committee found that the risk of induced seismicity from CCS is currently difficult to accurately assess. With only a few small-scale commercial projects overseas and

several small-scale demonstration projects underway in the United States, there are few data available to evaluate the induced seismicity potential of this technology. The existing projects have involved very small injection volumes. CCS differs from other energy technologies in that it involves continuous injection of carbon dioxide fluid at high rates under pressure for long periods of time. It is purposely intended for permanent storage – meaning that there is no fluid withdrawal. Given that the potential magnitude of an induced seismic event correlates strongly with the fault rupture area, which in turn relates to the magnitude of pore pressure change and the rock volume in which it exists, the committee determined that large-scale CCS may have the potential for causing significant induced seismicity.

The committee's findings suggest that energy projects with large net volumes of injected or extracted fluids over long periods of time, such as long-term waste water disposal wells and CCS, appear to have a higher potential for larger induced seismic events. The magnitude and intensity of possible induced events would be dependent upon the physical conditions in the subsurface—state of stress in the rocks, presence of existing faults, fault properties, and pore pressure.

The committee also investigated governmental responses to induced seismic events. Responses have been undertaken by a number of federal and state agencies in a variety of ways. Four federal agencies—the Environmental Protection Agency (EPA) the Bureau of Land Management (BLM), the U.S. Department of Agriculture Forest Service (USFS), and the U.S. Geological Survey (USGS)—and different state agencies have regulatory oversight, research roles and/or responsibilities related to different aspects of the underground injection activities that are associated with energy technologies. Currently EPA has primary regulatory responsibility for fluid injection under the Safe Drinking Water Act. It is important to note that the Safe Drinking Water Act does not explicitly address induced seismicity.

To date, federal and state agencies have dealt with induced seismic events with different and localized actions. These actions have been successful but have been ad hoc in nature. With the potential for increased numbers of induced seismic events due to expanding energy development, government agencies and research institutions may not have sufficient resources to address unexpected events. The committee concluded that forward-looking interagency cooperation to address potential induced seismicity is warranted.

Methodologies can be developed for quantitative, probabilistic hazard assessments of induced seismicity risk. The committee determined that such assessments should be undertaken before operations begin in areas with a known history of felt seismicity and updated in response to observed, potentially induced seismicity. The committee suggested that practices that consider induced seismicity both before and during the actual operation of an energy project should be employed to develop a “best practices” protocol specific to each energy technology and site location. The committee's meetings with individuals from Anderson Springs and Cobb, California, who live with induced seismicity continuously generated by geothermal energy production at The Geysers were invaluable in understanding how such a best practices protocol works.

Although induced seismic events have not resulted in loss of life or major damage in the United States, their effects have been felt locally, and they raise some concern about additional seismic activity and its consequences in areas where energy development is ongoing or planned. Further research is required to better understand and address the potential risks associated with induced seismicity.

I would like to thank the Committee for its time and interest in this subject and I look forward to questions.



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