Hydraulic Fracturing in the Marcellus Shale Region of the U.S.

By Kristen Coletti

Abstract: This paper reviews hydraulic fracturing in the Marcellus Shale emphasizing potential drinking water contamination via underground pathways for vertical gas and fracking fluid transport. It begins with an overview of the hydraulic fracturing process and the origins of shale gas, and then describes the regions where shale gas can be found and the composition of the fracking fluid. Potential sources of aquifer contamination are explored, with focus given to fractures as sources for vertical transport within rock layers. An overview of many contamination cases and claims across the United States is presented, followed by suggested improvements to the fracking process. Finally, federal and state legislature regarding hydraulic fracturing is reviewed.

Keywords: hydraulic fracturing, fracking, shale gas, fracking fluid, contamination, Marcellus Shale

1. Introduction

Hydraulic fracturing, better known as fracking, first began in 1949, when Halliburton Oil Well Cementing Company commercially fractured the first natural gas well [1]. Over the past 60 years, more than 600 trillion cubic feet of natural gas has been extracted from the ground via hydraulic fracturing in the United States. Half of the natural gas used today is the result of fracking done within the last three and half years. There are three types of unconventional natural gas—coalbed methane, tight gas, and shale gas—that all require hydraulic fracturing. Within the past few years, coalbed methane and tight gas production has decreased, while shale gas production has increased and is projected to continue increasing through the year 2035 (Figure 1) [8].

Although the hydraulic fracturing technology comes with potential environmental and health risks, gas companies continue to frack because this technology has positively impacted the U.S. economy by lowering natural gas prices within the last five years. For example, new advancements in fracking unconventional gas deposits lowered the price of natural gas from \$8 per thousand cubic feet to \$3.67 per thousand cubic feet in 2008 [2]. Experts postulate that with the rapid growth of shale gas production alone, natural gas prices will continue to decrease in future years [3].

Another benefit to hydraulic fracturing is a decrease in carbon dioxide emissions. The U.S. Energy Information Agency reported that this year, carbon dioxide emissions have hit an all time low since 1992 [4]. A large part of this decrease can be attributed to fracking, which collects and produces natural gas to be used in place of burning coal for fuel. Other benefits to hydraulic fracturing include decreasing the United States' dependence on foreign oil and job creation. Natural gas wells and hydraulic fracturing supported 600,000 jobs in 2010, with this number continuing to increase as more natural gas reserves are discovered. [2, 5]

Recently, hydraulic fracturing in the Marcellus Shale has been under much speculation. Concern has been raised regarding underground contamination of drinking water sources by the fracking fluid used in the process. Although no evidence has been found of contamination from shale gas fracking fluid, coalbed methane fracking has contaminated drinking water. This paper will review the hydraulic fracturing process, focusing on potential avenues for contamination and preventative measures that can be taken. Federal and state governments are continuously introducing and revising laws to better regulate hydraulic fracturing and prevent groundwater contamination [1, 6, 7].



Figure 1. U.S. Natural Gas Production in Trillion Cubic Feet Per Year [8]

2. Technical Background

Hydraulic fracturing, better known as fracking, is a process that begins when a well is drilled vertically underground to just below the deepest fresh groundwater source and a steel casing is inserted down the drilled hole. Cement is then pumped into the hole to create a steel and concrete casing protecting the groundwater from the fracking chemicals. The well is then drilled deeper into the Earth, until the vertical portion is approximately 500 feet above the rock layer containing the desired natural gas (about 1500 feet below the ground). As drilling continues, additional casing is installed to protect the surrounding earth. Directional drilling techniques are used to turn the vertical portion of the well horizontal (Figure 2). Drilling can continue horizontally anywhere from 1,000 to 6,000 feet within the rock layer.



Figure 2. Hydraulic Fracturing/Horizontal Drilling Process [9]

Over one million gallons of a high pressure water, sand, and chemical mixture, is pumped into the well. The horizontal portion of the well casing is perforated allowing the mixture to diffuse into the earth. As the mixture reaches down to almost one and half miles below the surface and the ground can no longer absorb the mixture as quickly as it is being injected, the pressure builds within the well, causing the rock layer to fracture. Sand or ceramic materials, known as proppants, are used to hold the fissures open, so that the natural gas can flow from these cracks into the well (Figure 3). The water pressure is then reduced allowing the natural gas to travel up the well for collection and storage [5, 6, 10, 11].



Figure 3. Fracturing the Rock Layer [11]

3. Origin of Shale Gas

Oil and gas originated in the prehistoric era from the remains of zooplankton and algal blooms. The zooplankton and algal blooms were found in lake bottoms or river delta environments. Remains of these species were buried under sediment, and over time, burial depth increased. As depth increased, so did temperatures and pressures, which transformed the sediment into natural gas.

Specifically, shale gas is a form of unconventional natural gas, which cannot naturally escape the shale source rock in which it was formed due to a lack of permeability. This lack of permeability is due to the tiny, poorly connected pores within the shale rock. The shale source rock forms from pressurized, flat, sheet-like sediments. As temperature and pressure increase in the source rock, organic materials, such as the zooplankton and the algal blooms, degrade anaerobically creating shale gas. Shale gas is either stored within the pores or fractures of the shale rock, or is absorbed on to the shale minerals within the shale rock. Fracturing technology must be used to release the gas from the source rock, since migration of the gas to the surface will not occur naturally. This technology is paired with horizontal drilling techniques to increase the exposed rock area, thereby increasing drainage of the reservoir and overall shale gas production. [3, 10].

4. The Shale Gas Boom

Shale gas reservoirs are located all over the U.S. Five of the major shale gas reservoirs are located in Texas alone. These reservoirs include the Barnett Shale, in north central Texas; the Haynesville Shale, along the eastern part of Texas; the Eagle Ford Shale, located in southern Texas; the Barnett-Woodford Shale in western Texas; and the Bend Shale in the Panhandle.

Another large region, which was recently discovered is the Marcellus Shale, which spans across New York, Pennsylvania, and West Virginia [6]. Although drilling in the Marcellus Shale has only been occurring for the past few years, as of 2011, 3,500 permits were issued and 1,500 wells already drilled [3]. Other smaller shale gas reservoirs are located in Alabama, Illinois, Michigan, North Dakota, Colorado, Oklahoma, Arkansas, and Louisiana (Figure 4) [6].



Figure 4. Regions of Shale Gas in the United States [12]

The implementation of horizontal drilling, along with hydraulic fracturing technology, spurred the dramatic increase in U.S. shale gas production, beginning in 2005. Shale gas production is predicted to continue to increase in the upcoming years, eventually phasing out coal production [10]. The United States Energy Information Administration (EIA) predicts that by the year 2035, half of the natural gas produced domestically will come from shale gas. In the past year alone, production of shale gas has more than doubled due to the introduction of horizontal drilling techniques. The EIA predicts that there are 616 trillion cubic feet of recoverable, unconventional natural gas resources within the United States (Table 1) [13]. If production of shale gas continues at the current rate, estimates have been made that there is enough natural gas to supply the United States for the next 90 years [14].

5. Shale Gas Fracking Fluid

Due to the increase in unconventional natural gas resources, recent claims have been made concerning groundwater, also known as aquifer, contamination. Fracking fluid is approximately 98% water and proppant, and 2% chemicals. Because the fracking sites are below aquifers and companies are not mandated to disclose the contents of their fracking fluid, the public is concerned that their drinking water will be contaminated by the use of both the fracking fluid and the hydraulic fracturing technology.

Chemicals added to the water and proppant mixture are thought to include potassium chloride, guar gum, ethylene glycol, sodium carbonate, potassium carbonate, sodium chloride, borate salts, citric acid, isopropanol, glutaraldehyde acid, benzene, toluene, xylene, kerosene, formaldehyde and petroleum distillate. These substances are used for many different reasons, including maintaining fluid viscosity, preventing pipe corrosion, minimizing friction, and preventing bacterial growth. Although useful, a handful of these substances are hazardous materials and carcinogens, which at high enough concentrations can contaminate drinking water and make it unsafe for consumption [6, 10].

	Basin area (km²)	Depth (metres)	Thickness (metres)	Gas in place (bcm/km²)	Gas in place (Tcm)
Barnett	13,000	2,000–2,800	50–200	0.5–3.0	7–39
Fayetteville	23,000	300-2,100	15–100	0.5-3.0	12–69
Haynesville	23,000	3,200-4,100	60-90	1.6-2.7	37–62
Horn River	39,000	2,000-3,000	150-175	1.4-2.5	55–98
Marcellus	250,000	1,000-2,600	15–75	0.2-1.1	50-275
Montney	11,000	900-3,000	150-300	1.0-3.2	11–35
Woodford	28,000	1,800–3,300	15–70	0.4–1.3	11–36

Table 1. Scale of Leading U.S. Shale Gas Reservoirs [15]

Depending on the rock formation, different sequences of treatments and mixtures are used to optimize the fracking process. Specifically, for shale gas, the first stage consists of an acid mixture, which is pumped into the well to remove cement and debris. The second stage is made up of slickwater, which contains compounds such as potassium chloride or polyacrylamide-based compounds. These compounds are used to reduce friction in the well by 50-60%, thereby reducing the pressure needed to pump the fluid into the well. The third stage contains proppant,

which is pumped into the well to crack the shale and keep the fissures open. The final stage is a flushing stage, where fresh water is used to remove the excess proppant from the well [16].

6. Potential Sources of Aquifer Contamination

6.1 Fractures as Pathways for Gas Transport

In many recent studies, thermogenic gas, formed by heat and compression, has been found in underground drinking water that is in close proximity to fracturing sites. Osborn et al. conducted a study in 2011, which provides direct evidence of methane contamination in underground drinking water sources near hydraulic fracturing wells. This study was conducted in the Marcellus Shale in Pennsylvania and the Utica Shale in New York. The study analyzed 68 private water wells ranging from 36 to 190 meters in depth. Methane concentrations were detected in 85% of the wells and were 17 times higher on average in wells from active drilling sites. An active drilling site means there are one or more gas wells within one kilometer of each other. As neighboring gas wells were found closer together, methane concentrations in the water increased. On average, the concentration of methane in the water wells was 19.2mg/L, with a maximum concentration of 64mg/L. This average methane concentration falls within the U.S. Office of the Interior's range of methane concentration for hazard mitigation (10-28mg/L), with the maximum value exceeding this range. Although no evidence was found directly linking this methane contamination to the Marcellus Shale gas fracking fluid, it should not be eliminated as a potential source of contamination for the future [13].

Myers suggests that thermogenic gas, such as methane, found in underground drinking water sources may indicate vertical transport of the gas underground. Vertical transport occurs when a concentration gradient exists within the rock layers. If the gas can transport vertically, there is also a potential for vertical transport of the leftover fracking fluid, which could contaminate underground sources of drinking water as well [1].

6.2 Fractures as Pathways for Brine Transport

The Marcellus Shale is a primary source of brine, which is a solution of salt dissolved in water. Although not found in drinking water supplies, brine has been found more than a thousand meters above its source. Again, Myers suggests this as a second form of evidence of vertical transport where the primary upward push is due to a concentration gradient. Buoyancy is another factor which would provide an upward push for vertical transport. In the case of brine, if a density difference exists between the fracking fluid and the brine the more dense fluid (the fracking fluid) would exert an upward force on the less dense fluid (the brine) inducing vertical transport [1, 17]. The potential for aquifer contamination from fracking fluid should not be discounted because of evidence of vertical transport of both methane and brine within the rock layers as presented by both Osborn et al. and Myers.

6.3 Fracking Sites as Pathways for Vertical Transport

Myers also suggests another potential cause of vertical gas transport and contamination. He speculates it may be caused by the hydraulic fracturing process itself and the location of the

fracturing sites. Fracking increases the permeability and the pore size of the shale rock, allowing the shale gas to flow freely from the fissures. Shale wells are typically spaced 300 meters apart and up to eight wells can be drilled from a single well pad. Because of the proximity of wells, fracking can cause both natural fissures in the rock and fissures from neighboring wells to widen and connect. If sites are also located near faults, there is a greater chance of natural fractures in the rock layers and therefore, an increased chance of vertical transport. Another potential cause of vertical transport is out-of-formation fracking, which is fracking that occurs above the target shale rock layer. If out-of-formation fracking occurs, there is a potential that fractures can also reach unplugged, abandoned wells, allowing vertical transport to occur in rock layers closer to the aquifers [1].

7. Contamination Cases across the U.S.

Although contamination from fracking fluid has not been documented in the Marcellus Shale as of yet, there have been many contamination cases from fracking fluid in other natural gas reservoirs across the U.S. The EPA found contamination of drinking water wells by hydraulic fracturing fluid in Wyoming in 2009. Residents of this area had been complaining about miscarriages, rare cancers, and central nervous system disorders in residents. Suspicions were raised concerning if these cases had anything to do with the contaminated drinking water [6].

In 2010, urine and blood from residents living in Texas near the Barnett Shale were tested for harmful chemicals. Of the samples tested, 65% had high levels of toluene and 53% had high levels of xylene. Other contamination cases have involved improper handling of surface materials. In Louisiana in 2009, fracking fluid leaked from a well pad to a nearby pasture killing seventeen cattle. [6]. These cases, although not all necessary linked to the Marcellus Shale, prove the hazardous nature of the hydraulic fracturing fluids currently used.

In the San Juan Basin of Colorado and New Mexico, dangerous levels of methane and hydrogen sulfide were found in homes of residents living near coalbed methane wells. High methane concentrations were also found in many of the water wells and residents observed water to be cloudy with gray sediments a few days after nearby wells were fracked. This contamination was likely due to the removal of wastewater in the fracking process and hundreds of wells were found to be affected [1].

7.1 Contamination Claims in the Marcellus Shale

Although there is not any documented evidence of groundwater contamination in the Marcellus Shale thus far, many claims and have arisen within the past few years in Pennsylvania. These claims have led to much controversy surrounding whether or not contamination does exist. Multiple plaintiffs, in November 2009, filed suit against Cabot Oil & Gas Corporation and Gas Search Drilling Services Corporation claiming the fracking activities were releasing harmful chemicals and pollutants into the drinking water supply. The plaintiffs claim that the fracking fluids contain carcinogenic and toxic chemicals, including diesel fuel and lubricating agents, which raised the levels of 1, 2, 4-trimethylbenzene, aluminum, iron, N-propylbenzene, and P-isopropyl toluene in the water supply.

Another lawsuit was filed in Pennsylvania against Southwest Energy Production Company and Southwestern Energy Company for elevated levels of methane, ethane, barium, and other harmful substances in the drinking water. Similar claims were raised against Chesapeake Appalachia, L.L.C., Chesapeake Energy Corporation, and Nomac Drilling, L.L.C., in October 2010 and against Atlas Energy, Inc, in September 2009. To prove whether any of these claims are true and that fracking in the Marcellus Shale is indeed contaminating underground drinking water, reliable scientific evidence must be presented by qualified experts in the field [7].

8. Improvements on the Fracking Process

In order to prevent aquifer contamination, Myers offers improvements that can be made to the fracking process. When choosing a fracking location, the subsurface should be mapped to determine if there are any faults nearby. A standard distance between faults and fracking locations should be set and based on a risk analysis determining the effect fracking has on increasing the pressure within the fault. Properties of the shale rock should be tested after fracking, to determine ways in which the rock formation changes as a result of fracking. Finally, a system of monitoring wells at varying depths should be installed in areas of high volume development before the hydraulic fracturing process begins [1].

Other ways to improve upon the fracturing process include using more environmentally friend chemicals in the fracking fluid. Some companies have been substituting diesel with mineral oil or plant-based oils. Other companies have stopped using fluorocarbons or other known environmental pollutants in the fracking fluid altogether.

GASFRAC Energy Services is conducting studies using liquefied petroleum gas (LPG) as the fracking fluid. The LPG can transport the proppants into the fractures and can be 100% recaptured back up the well. This eliminates leftover wastewater as a source of potential underground contamination [10].

9. Regulations & Legislature on Hydraulic Fracturing in the Marcellus Shale

9.1 Regulations & Legislature at the Federal Level

In 1997, after the first claim of contaminated drinking water was made involving coalbed methane fracking, the Environmental Protection Agency (EPA) conducted a study, which was completed in 2004. The investigation involved interviews with state and local government agencies, comments from residents who expressed concerns about contamination, and peer-review publications. The EPA concluded that there was no evidence suggesting that drinking water was contaminated from coalbed methane fracking. Upon completion, this study was highly scrutinized, many believing the study was politically motivated and scientifically unsound [1, 3, 6, 7, 14].

In 2005, the National Energy Policy Act was passed by Congress, which exempted hydraulic fracturing from the regulations defined in the Safe Drinking Water Act, except where it involved the injection of diesel fuel [4, 8]. In 2009, the Fracturing Responsibility and Awareness of Chemicals (FRAC) Act was introduced to Congress to modify the 2005 Energy Policy Act. Not

only would fracking fluid now be subject to safe drinking water laws, but companies would also have to disclose chemical constituents of the fracking fluid. The FRAC Act is still under review in Congress [1, 3, 6, 14].

In 2010, the EPA issued an endangerment order against a company fracking in the Barnett Shale of Texas after finding flammable and bubbling tap water in homes nearby. The EPA conducted tests on this water supply and found elevated levels of methane, which posed an immediate risk of either explosion or fire. They also found benzene in the drinking water, which is a known carcinogen [6]. After this finding, Congress prompted the EPA to conduct a study to assess the potential risks to drinking water, including both coalbed methane and shale gas reservoirs. This study will also include further investigation into the possible connection between hydraulic fracturing and contaminated drinking water. Initial results from this study are due to be released sometime this year [1, 6].

9.2 Regulations & Legislature at the State Level

As the fear of contamination heightens over the years, more and more states are beginning to regulate hydraulic fracturing. Specifically, states involved in the shale gas boom have started to take action regarding hydraulic fracturing and horizontal drilling legislation, since the federal government has not [6]. In 2010, New York State placed a moratorium on horizontal drilling and hydraulic fracturing in the Marcellus Shale region, but continued to allow vertical drilling. This moratorium was placed for one year giving the state time to conduct an environmental review studying drinking water contamination [3, 6, 7, 14].

In May 2009, the Delaware River Basin Commission (DRBC) announced that natural gas companies may not begin projects in shale formations that lie within the Delaware River Basin without first applying for and obtaining DRBC approval. [7] In 2011, hydraulic fracturing in the Delaware River watershed, which spans southern New York and northeastern Pennsylvania, was banned due to fear of contamination. This watershed provides 17 million people with drinking water [3].

Regulators in Pennsylvania have made many changes regarding oversight and enhanced drilling and production operations. The Pennsylvania Department of Environmental Protection (PA DEP) has made many changes since 2008, including doubling the number of oil and gas inspection staff and implementing new water quality standards. In 2010, amendments to Pennsylvania law regarding casing and cementing requirements for wells were revised and routine inspections of existing wells are now required. Gas companies are also required to submit pre-drilling water test results to the PA DEP and to water supply owners under these new amendments. Also in 2010, the Pennsylvania Environmental Quality Board revised regulations regarding wastewater treatment and disposal. Only wastewater that is treated at a centralized wastewater treatment facility and that meets certain quality standards can be disposed of in surface waters [7].

10. Conclusions

This paper examined hydraulic fracturing in the Marcellus Shale, emphasizing the potential sources for aquifer contamination via vertical transport and suggesting improvements that should be made to the fracking process. Experts, government officials, and the general public disagree about whether contamination from fracking fluid has occurred in the Marcellus Shale. Claims have been made, although no hard evidence has yet been found by experts in the field. Experts do agree that a potential for contamination does exist and that more research needs to be conducted surrounding the hydraulic fracturing process.

Gas companies should take caution when hydraulic fracturing because contamination in the Marcellus Shale is possible. Both Myers and Osborn et al. provide evidence that groundwater has been contaminated with methane and brine, even in the Marcellus Shale. This proves that vertical transport pathways exist and it is only a matter of time before fracking fluid travels vertically and also contaminates water wells.

Other sources provide cases of groundwater contamination in the U.S. from other types of unconventional natural gas reservoirs and shale gas reservoirs in other areas of the country, such as Texas. If contamination can readily occur in these areas, it can occur in the Marcellus Shale, too. Because the Marcellus Shale is a recent development, it is too soon to determine without doubt that contamination will not occur in these reservoirs as well.

Government officials should continue to amend legislature to better regulate hydraulic fracturing and prevent contamination from occurring. Companies should also continue researching ways to use environmentally friendly fracking fluids and improve the process to lessen the chances of vertical transport via fracturing pathways. Because hydraulic fracturing supplies a significant portion of the United States' domestic natural gas, this process should not be eliminated all together. More strict regulations and a better understanding of the process will allow fracking to continue in a non hazardous manner, without aquifer contamination.

Acknowledgements: I would like to thank my revision club partners, Jennifer Judge and Michael Duffy, as well as my professor, Tom Akbari, for their constructive criticism, which was used to strengthen this paper. I would also like to thank my fellow employees at Shaw Energy & Chemicals, for inspiring me to pursue a career in the energy industry.

References

[1] Myers, Tom, "Potential Contaminant Pathways from Hydraulically Fractured Shale to Aquifers," *Ground Water 50*, no. 6, pp. 872–882, 2012.

[2] Millican, Robin, "Hydraulic Fracturing – Is It Safe?," *Institute for Energy Research*, 2011. http://www.instituteforenergyresearch.org/2011/05/03/hydraulic-fracturing-is-it-safe/ [3] Rogers, Howard, "Shale Gas – The Unfolding Story," *Oxford Review of Economic Policy*, vol. 27, no. 1, pp. 117-143, 2011.

[4] "Fracking Leads to Cleaner Air," *Investors.com*, 2012. <u>http://news.investors.com/ibd-editorials/082012-622858-fracking-drops-carbon-emissions-to-new-low.htm?p=full</u>

[5] "Hydraulic Fracturing 101," *Halliburton*, 2012. http://www.halliburton.com/public/projects/pubsdata/hydraulic_fracturing/fracturing_101.html

[6] Rahm, Dianne, "Regulating Hydraulic Fraturing Shale Gas Plays: The Case of Texas," *Energy Policy*, vol. 39, pp. 2974-2981, 2011.

[7] McKay, Lynn Kerr, Johnson, Ralph H., Salita, Laurie Alberts, "Science and the Reasonable Development of Marcellus Shale Natural Gas Resources in Pennsylvania and New York," *Energy Law Journal*, vol. 32:125, pp. 125-143, 2011.

[8] Brendenberg, Al, "The Damage Done, Part 4 — Natural Gas, Green or Dirty?," *ThomasNet.com/news*, 2011. <u>http://news.thomasnet.com/green_clean/2011/12/27/the-damage-done-part-4-natural-gas-green-or-dirty/</u>

[9] "Freeing Up Energy, Hydraulic Fracturing, Unlocking America's Natural Gas Resources," *American Petroleum Institute*, pp. 1-14, 2010. <u>http://www.api.org/policy/exploration/hydraulicfracturing/upload/HYDRAULIC_FRACTURIN</u> <u>G_PRIMER.pdf</u>

[10] Campbell, David J., Kargbo, David M., Wilhelm, Rong, "Natural Gas Plays in the Marcellus Shale: Challenges and Potential Opportunities," *Environmental Science & Technology*, vol. 44, pp. 5679-5684, 2010.

[11] "What is Hydraulic Fracturing?," *ProPublica*, 2012. http://www.propublica.org/special/hydraulic-fracturing-national

[12] "Hydraulic Fracturing Stimulating Reservoirs to Increase Natural Gas Production," *Baker Hughes*, 2011. http://public.bakerhughes.com/shalegas/fracturing.html

[13] Osborn, Stephen G., Vengosh, Avner, Warner, Nathaniel R., Jackson, Robert B., "Methane Contamination of Drinking Water Accompanying Gas-well Drilling and Hydraulic Fracturing," *PNAS*, vol. 108, pp. 8172-8176, 2011.

[14] Wiseman, Hannah, "Untested Waters: The Rise of Hydraulic Fracturing in Oil and Gas Production and the Need to Revisit Regulation," *FORDHAMENVTL*, pp. 1-55, 2009.

[15] "EPA Takes New Look at Gas Drilling, Water Issues," *IEA World Energy Outlook, Paris, International Energy Agency*, 2009. http://www.investors.com/NewsAndAnalysis/Article.aspx?id5162927&source5APOnline [16] "Hydraulic Fracturing: The Process," *FracFocus Chemical Disclosure Registry*, 2010. http://fracfocus.org/hydraulic-fracturing-how-it-works/hydraulic-fracturing-process

[17] Warner, Nathaniel, R., Jackson, Robert B., Darrah, Thomas H., Osborn, Stephen G., Down, Adrian, Kaiguang, Zhao, White, Alissa, Vengosh, Avner, "Geochemical Evidence for Possible Natural Migration of Marcellus Formation Brine to Shallow Aquifers in Pennsylvania," *PNAS*, vol. 109, no. 30, pp. 11961-11966, 2012.