Analysis of BTEX groundwater concentrations from surface spills associated with hydraulic fracturing operations

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Concerns have arisen among the public regarding the potential for drinking-water contamination from the migration of methane gas and hazardous chemicals associated with hydraulic fracturing and horizontal drilling. However, little attention has been paid to the potential for groundwater contamination resulting from surface spills from storage and production facilities at active well sites. We performed a search for publically available data regarding groundwater contamination from spills at U.S. drilling sites. The Colorado Oil and Gas Conservation Commission (COGCC) database was selected for further analysis because it was the most detailed. The majority of spills were in Weld County, Colorado, which has the highest density of wells that used hydraulic fracturing for completion, many producing both methane gas and crude oil. We analyzed publically available data reported by operators to the COGCC regarding surface spills that impacted groundwater. From July 2010 to July 2011, we noted 77 reported surface spills impacting the groundwater in Weld County, which resulted in surface spills associated with less than 0.5% of the active wells. The reported data included groundwater samples that were analyzed for benzene, toluene, ethylbenzene, and xylene (BTEX) components of crude oil. For groundwater samples taken both within the spill excavation area and on the first reported date of sampling, the BTEX measurements exceeded National Drinking Water maximum contaminant levels (MCLs) in 90, 30, 12, and 8% of the samples, respectively. However, actions taken to remediate the spills were effective at reducing BTEX levels, with at least 84% of the spills reportedly achieving remediation as of May 2012. Our analysis demonstrates that surface spills are an important route of potential groundwater contamination from hydraulic fracturing activities and should be a focus of programs to protect groundwater.

Implications: While benzene can occur naturally in groundwater sources, spills and migration of chemicals used for hydraulic fracturing activities have recently been thought to be a main source of benzene contamination in groundwater. However, there is little scientific literature to support that claim. Therefore, we accessed a publically available database and tracked the number of reported surface spills with potential groundwater impact over a 1-year period. Although the number of surface spills was minimal, our analysis provides scientific evidence that benzene can contaminate groundwater sources following surface spills at active well sites.

Supplemental Materials: Supplemental materials are available for this paper. Go to the publisher’s online edition of the Journal of the Air & Waste Management Association for an illustration of the average concentration of each BTEX chemical from pooled sample measurements, and various metrics from all 77 spills analyzed in this study.

Introduction

Increases in the global demand for energy are driving advances in natural gas extraction techniques such as hydraulic fracturing and horizontal drilling (Kennedy, 2007). These two technologies make it economically feasible to recover unconventional oil and gas resources from coal beds, shale formations, and tight sand reservoirs. Although hydraulic fracturing has received recent attention, the technology has been in commercial use in the United States for exploration and extraction of crude oil since the 1940s (STRONGER, 2011). Hydraulic fracturing is a technology that relies on the high-pressure injection of water mixed with a combination of chemicals and sand formulated to physically fracture subsurface reservoirs for the purpose of extracting oil and gas. Depending upon the type of geological formation and the depth associated with horizontal drilling, fracturing activities can take place anywhere from several hundred feet to several miles below the surface (ALL Consulting, 2009).

Public concerns have been expressed about drinking-water contamination from migration of chemicals used during the hydraulic fracturing process, as well as from the escape of methane from fractured rock and well casings (Dammel et al., 2011; Groat and Grimshaw, 2012; Osborn et al., 2011; Rozell and Reaven, 2012; U.S. EPA, 2011). However, strong scientific evidence to
support these concerns is lacking. To our knowledge, only one study has been published in the scientific literature evaluating the potential for groundwater contamination with methane (Osborn et al., 2011). These authors reported methane contamination of aquifers overlying the Marcellus Shale formation and noted that the contamination accompanied gas-well drilling and hydraulic fracturing activities in the area. However, the authors concluded that more research was still needed to clearly understand the mechanism of contamination (Osborn et al., 2011).

In November 2011, the U.S. EPA introduced a plan to examine methane contamination of drinking water in several drilling areas across the United States, including the Marcellus Shale; the results of this study are forthcoming (U.S. EPA, 2011). Regarding drinking water contamination from hydraulic fracturing fluids, a recent U.S. EPA study reported that two deep monitoring wells near an aquifer in Pavillion, Wyoming, tested positive for glycols, alcohols, and high levels of methane, all of which were thought to originate from hydraulic fracturing activity conducted below the aquifer. This was the first report of drinking-water contamination resulting from the migration of chemicals from a fractured formation, although, to date, confirmation of chemical migration remains in question and conclusions from this study are currently undergoing further evaluation (DiGiulio et al., 2011; McLernon, 2012).

Groundwater contamination may occur from various activities that take place at the ground surface before, during, and after a well is brought into production. In a recent article published in a nationally recognized water quality journal, it was noted that most water quality issues in the United States associated with hydraulic fracturing activities are the result of surface spills or leakage into the shallow water formations (Metzger, 2011). Only recently has the U.S. EPA announced its first proposal of a Quality Assurance Project Plan to analyze data from surface spills in states with both oil and gas production, such as Texas, Colorado, and Pennsylvania (U.S. EPA, 2012).

Based on our review, no study has been published in the peer-reviewed scientific literature that addresses the potential for groundwater contamination from surface spills associated with hydraulic fracturing activities (Groat and Grimshaw, 2012). Wells producing crude oil in addition to methane gas are a potential source of petroleum hydrocarbon release into groundwater via surface spills. Of particular interest is the release of benzene, toluene, ethylbenzene, and xylene (i.e., BTEX), which are present in low percentages in crude oil and, at sufficient doses, have been associated with adverse human health effects (ATSDR, 2000, 2007a, 2007b, 2010; Osborn et al., 2011). Opportunities for surface spills and leaks of BTEX-containing liquids include lined holding ponds, which are often constructed at well sites for temporary storage of “flowback” or “produced water,” which is the water that comes to the surface with the oil and gas following the hydraulic fracturing procedure. These ponds typically consist of a mixture of gas, oil, metals, fracturing fluids, and possibly naturally occurring radioactive materials (NORM) and can potentially leach into the groundwater through failures in the lining (Gregory et al., 2011; Smith, 1992). Tank battery systems, which are a group of tanks used for storing produced water and crude oil in various stages of separation, can contribute to leaks and spills. Moreover, production facilities are sources of hydrocarbons in the refining process. Combinations of these types of facilities are found at most well sites. Although there are many different combinations of chemicals and waste products associated with hydraulic fracturing activities and therefore potentially stored at the well site, we limited our analysis to data that were publicly available for review (i.e., BTEX) and regulated by the National Drinking Water maximum contaminant level (MCL), such as benzene (5 ppb), toluene (1000 ppb), ethylbenzene (700 ppb), and xylene (10,000 ppb), respectively (Colborn et al., 2011; HDR, 2011).

We performed a search for publicly available data regarding groundwater contamination from spills at U.S. drilling sites. The Colorado Oil and Gas Conservation Commission (COGCC) database was selected for further analysis because it was the most detailed. In addition, numerous articles have been published in the Colorado news media that suggest that surface spills at drilling sites in Weld County, Colorado were associated with the release of benzene at concentrations markedly exceeding state water quality standards (5 ppb) (Finley, 2011). Weld County is located on the eastern plains of Colorado and the county overlays part of the Niobrara Shale formation within the Denver–Julesburg Basin. The eastern plains have very little surface water and therefore groundwater is the main source of water supply for users in the area (Colorado Division of Water Resources, 2012; Pielou, 1998). We chose to focus on Weld County because nearly all active wells in Colorado have used hydraulic fracturing for completion, because it is the most densely populated county for drilling in the United States, and because some areas of Weld County may have a very shallow depth to water table (COGCC, 2012; Wockner, 2012; STRONGER, 2011). Given the increased attention to surface spills of benzene in the Colorado local news and the limited attention in the scientific literature given to surface activities, we investigated operator reports of groundwater contamination with BTEX at drilling sites in Weld County, Colorado, between July 1, 2010, and July 1, 2011.

To evaluate the potential impact to groundwater from BTEX in surface spills reported during our study period (COGCC, 2011e), we specifically focused on initial measurements taken before or early in the remediation process so that we could characterize the high end of BTEX contamination that may have occurred during the course of these spills. In addition, we analyzed various other spill metrics including spill frequency, average spill size and depth, and recorded cause of the spills, as well as the fraction of spills for which remediation had been successfully completed.

Methods

COGCC database

We analyzed publically available data reported by operators to COGCC. We considered other datasets by searching multiple websites including those associated with the Wyoming Oil & Gas Conservation Commission, Pennsylvania Independent Oil and Gas Association, Pennsylvania Department of Environmental Protection: Oil & Gas Reporting Website, Texas Oil & Gas Association, Railroad Commission of Texas, and New
Mexico Energy, Minerals and Natural Resources Department Oil Conservation Division, as well as the oil and gas conservation commissions of Oklahoma, Kansas, Montana, Arizona, Idaho, Nebraska, Iowa, Missouri, North Dakota, South Dakota, and Arkansas. We chose the COGCC database because it had the most robust data set regarding surface spills.

We analyzed surface spills in Weld County between July 1, 2010, and July 1, 2011, using data reported to COGCC (COGCC, 2011d). The COGCC data were not in a tabulated or compiled format; rather, the information for each spill was found on one or more separate documents. Thus, as a first step, it was necessary to manually extract all of the relevant data and compile them in a format that was useful for analysis. The study period was selected to provide a snapshot of surface spills that were reported to have groundwater impact. According to the rules outlined by the COGCC, surface spills that are greater than five barrels in size or that impact state water sources must be self-reported by the operators. Operators are required to map the area affected by the spill, including the directional flow of the groundwater, to describe how the spill was excavated, and to submit a groundwater sampling plan to determine the extent of the groundwater contamination (COGCC, 2011a). According to the COGCC Rule 900 Series, “samples shall be collected from areas most likely to have been impacted, downgradient or in the middle of excavated areas. The number and location of samples shall be appropriate to determine the horizontal and vertical extent of the impact.” Groundwater samples were collected by various methods, including bore holes or excavation of the soil at the spill site.

Once collected, groundwater samples were analyzed for BTEX concentrations by an independent laboratory using U.S. EPA Method 8260B (COGCC, 2011d). Information regarding the spill volume, the area and depth of the spill, the type of facility from which the spill originated, and the reported cause of the spill was also extracted from the COGCC database.

BTEX concentrations

We sought to characterize BTEX groundwater concentrations during the course of the spill and the remediation, (i.e., groundwater samples that were taken early in each spill, either before or shortly after remediation began). Seventy-seven spills impacting groundwater were reported to COGCC by operators in Weld County during the study period. Sixty-two of the spill reports were accompanied by analytical BTEX concentrations from initial groundwater sampling. For 10 of the remaining spills, groundwater monitoring data were not collected during the initial stages of the spill and therefore were not used in our analysis. For the remaining five reported spills, there were no BTEX measurements available for review.

Statistical analysis

Among the 62 spills for which groundwater sampling data were available, there were in total 218 groundwater samples collected. Descriptive statistics were performed for all 218 samples pooled together and for various subsets of these data. Because there were a high number of samples below the reporting limit, PROUCL 4.0 was used to estimate means using the Kaplan–Meier (KM) method, which is useful for analyzing left-censored data sets with multiple reporting limits and is not based on an underlying distribution of the data set (Helssel, 2005). Also using PROUCL 4.0, the 97.5% upper confidence limits (UCL) on the means were calculated using the Chebyshev inequality with KM. The 97.5% UCL was calculated rather than a 95% UCL because of the sample size, skewness of the data, and percent of samples below the reporting limit (Singh et al., 2006). Pairwise comparisons between means were evaluated using the Gehan method, a nonparametric test that is useful for censored data sets with multiple reporting limits (Millard and Deverel, 1988; Palachek et al., 1993). For the data shown in Supplemental Figure S1, nondetect values were treated as one-half the reporting limit because there were frequently too few samples per spill to permit use of the Kaplan–Meier method when estimating the mean for each spill.

Disposition of spills

We performed a follow-up survey of the remediation status of the 77 spills with groundwater impact by reviewing publically available documents on the COGCC website and noting which spills were deemed “resolved” by COGCC such that no additional remediation was required (see Supplemental Table S1) (COGCC, Form 19A).

Results

Frequency of spills

Between July 1, 2010, and July 1, 2011, operators drilling for gas and oil in Weld County reported 77 surface spills with groundwater impact. During this time period, there were nearly 18,000 active wells in Weld County (COGCC, 2012). These findings indicated that less than 0.5% of these active wells experienced a spill that impacted groundwater. Analysis of surface spills without groundwater impact was outside the scope of the current study.

Adherence to Colorado regulations may be a contributing factor to the low percentage of surface spills with groundwater impact at active well sites. There are a number of regulations and contingency plans in place that operators must follow in order to control fluids used and stored at the surface, as well as to manage risk of groundwater contamination from surface spills should they occur. For example, the COGCC site selection criteria take into account operating near surface water supply areas, equipment to be used, secondary containment, baseline groundwater sampling, and an emergency plan (COGCC, 2011b). Placement and protection of tanks as well as industry standards for tank construction, maintenance, operation, and labeling are also regulated under Colorado guidelines. Colorado rules dictate the operating standards for permitting requirements, and for the construction and protection of holding ponds (COGCC, 2011c, 2011d; STRONGER, 2011).

Size and depth of surface spills

If known, operators reported the volume of oil or produced water spilled at a well site. Only 13 of 77 reported spills indicated a
Origin of spills

The types of facilities from which surface spills were reported to occur and the number of spills associated with each facility type are summarized in Table 1. The tank battery systems (34/77 spills) and production facilities (29/77 spills) were by far the largest sources of surface spills with groundwater impact. The remaining facilities and equipment were each reported for 5 or fewer of the 77 spills. Four of these remaining facility types, with one spill attributed to each, were associated with the tank batteries, and thus might be more appropriately counted as part of that category.

A tank battery usually provides storage for the collected oil and equipment for separating the oil from produced water (COGCC, 2011a). The tanks are commonly connected by manifolds and other piping to permit transfer of liquids from one tank to another. Production facilities are used to remove water, gases, and other impurities from the oil and natural gas. The U.S. EPA requires that secondary containment structures for tank batteries and production facilities such as dikes, berms, and other barriers be used around these two systems to help prevent migration of leaks or spills (U.S. EPA, 2009). In total, 26 of 77 spills in Weld County were retained within a constructed containment, although the spill report still indicated an impact to the groundwater. For the remaining 51 spills, the spilled fluid was not contained. The reason for failure of a required secondary containment system around tank batteries and production facilities

Table 1. Type of facility associated with groundwater impact in Weld County, Colorado, between July 1, 2010, and July 1, 2011

| Facility type                  | BTEX data not available | BTEX data available | Total |
|-------------------------------|-------------------------|---------------------|-------|
| Tank battery                  | 5                       | 29                  | 34    |
| Production facility           | 2                       | 27                  | 29    |
| Flow line                     | 1                       | 4                   | 5     |
| Compressor station            | 2                       | 0                   | 2     |
| Tank battery, flow line       | 0                       | 1                   | 1     |
| Tank battery, cement water pit| 1                       | 0                   | 1     |
| Tank battery, water tank      | 1                       | 0                   | 1     |
| Tank battery, dump line       | 1                       | 0                   | 1     |
| Gathering line                | 0                       | 1                   | 1     |
| Oil dump line                 | 1                       | 0                   | 1     |
| No facility type reported     | 1                       | 0                   | 1     |
| Total                         | 15                      | 62                  | 77    |

Causes of spills

Operators are also required to indicate the cause of the spill. Therefore, we categorized the surface spills with groundwater impact according to reported cause of the spill (Table 2). Equipment failure (47/77 spills) was the most common cause of groundwater impact, whereas 10 of 77 spills reportedly resulted from corrosion/equipment failure. Historical impact (i.e., discovery of a spill during inspection) was cited as the
cause of the spill in 15 of 77 reported spills. Only 3 of 77 spills were associated with human error.

**BTEX measurements**

Although BTEX measurements were taken throughout the spill remediation process, we focused on analysis of BTEX measurements from groundwater samples that were taken either before or shortly after remediation began, as opposed to during the monitoring stages of a Remediation Work Plan. This allowed us to characterize the high end of BTEX contamination that occurred during the course of the spill and the ensuing remediation. BTEX data were available for 62 of 77 spills, constituting a total of 218 total samples per chemical. Summary statistics for these data are presented in Table 3. In addition, the average, minimum, and maximum concentrations of each BTEX chemical for each reported spill are illustrated in Figure S1 of the supplemental material.

As noted in Table 3, BTEX measurements for 78 of 218 groundwater samples were taken for a single spill (#2608769); thus, we considered this spill separately so that the analysis would not be overly influenced by the results of a single spill. It was not clear from the information available why so many groundwater samples were collected for this single spill.

Since we expected that the groundwater samples taken from inside of the spill excavation areas would have higher BTEX concentrations than the samples taken outside of the excavation areas, these groups of groundwater samples were analyzed separately (Table 3). In accordance with our expectations, groundwater samples collected within the excavation area had reported mean BTEX measurements that were 2.2-, 3.3-, 1.8-, and 3.5-fold higher, respectively, than groundwater samples collected just outside the excavation area. The difference in KM means from these data are presented in Table 3. In addition, the average, minimum, and maximum concentrations of each BTEX chemical for each reported spill are illustrated in Figure S1 of the supplemental material.

Comparing these 60 BTEX measurements to their respective MCLs, 90, 30, 12, and 8% of the BTEX samples, respectively, were above their MCLs. These data indicate that benzene and toluene are of greater concern than ethylbenzene and xylene when considering BTEX groundwater concentrations from these surface spills. In fact, the 97.5% UCL of the mean for these 60 samples was below the MCL for ethylbenzene and xylene, and the 95th percentile measurements exceeded the MCL by only 1.3-fold for ethylbenzene and 1.2-fold for xylene.

Although the mean benzene and toluene measurements for the 60 groundwater samples taken inside the excavation areas during the first sampling date exceeded the MCL by 280- and 2.2-fold respectively, the benzene and toluene mean concentrations decreased significantly for later sampling dates and for groundwater samples collected just outside the excavation area. This suggests that actions taken by the operators to stop and remediate the spill were effective for reducing groundwater BTEX contamination. The 95th percentile toluene concentration from the 25 groundwater samples collected during the second sampling date was below the MCL, and for the third or later sampling date, none of the toluene measurements exceeded the MCL.

Air monitoring for BTEX has been conducted during various stages of well development and production at some well sites in Colorado (McKenzie et al., 2012). In the environment, BTEX can volatilize from soil or the water's surface, and once volatilized, BTEX disperse and readily biodegrade (e.g., benzene degrades in days, and toluene degrades in the atmosphere within hours); BTEX can also pass through soil into the groundwater. Since BTEX are only slightly soluble in water, BTEX tend to collect at the top of the water table where they degrade more slowly than in the soil (ATSDR, 2007a). It is likely that the observed decrease in mean BTEX concentrations over the course of multiple sampling dates is, at least in part, attributable to evaporation and degradation of the BTEX chemicals.

Of the 218 measurements taken for each BTEX chemical, 60 samples per chemical were taken inside of the excavation areas during the first sampling date (Table 3). The KM mean of the 60 measurements were 1400, 2200, 190, and 2600 ppb for BTEX, respectively. These means constitute 280-, 2.2-, 0.27-, and 0.26-fold of the National Drinking Water MCLs for BTEX, respectively (HDR, 2011). Thus, the KM means for benzene and toluene in these samples were above their respective MCLs (benzene 5 ppb and toluene 1000 ppb), whereas the KM means for ethylbenzene and xylene were below their respective MCLs (ethylbenzene 700 ppb and xylene 10,000 ppb). It should be noted that the distributions of these data are highly skewed, as evidenced by the fact that the median values are much lower than the estimated means, in some cases several hundred-fold lower.

None of the median values for toluene, ethylbenzene, or xylene exceed their respective MCLs.

Although the mean benzene and toluene measurements for the 60 groundwater samples taken inside the excavation areas during the first sampling date exceeded the MCL by 280- and 2.2-fold respectively, the benzene and toluene mean concentrations decreased significantly for later sampling dates and for groundwater samples collected just outside the excavation area. This suggests that actions taken by the operators to stop and remediate the spill were effective for reducing groundwater BTEX contamination. The 95th percentile toluene concentration from the 25 groundwater samples collected during the second sampling date was below the MCL, and for the third or later sampling date, none of the toluene measurements exceeded the MCL. Regarding benzene, the mean concentration decreased 41-fold in groundwater samples collected during the first sampling date compared to samples collected on the third or later sampling date. Although 59% of the benzene measurements in groundwater samples collected on the third or later sampling date still exceeded the MCL for benzene, it would be expected that benzene concentrations in groundwater samples would continue to decrease with time and as additional remediation is carried out. Likewise, the mean benzene concentration decreased two-fold in groundwater samples taken inside versus just outside of the excavation area, with only 37% of samples outside of the excavation area exceeding their respective MCLs.
Table 3. BTEX concentrations (ppb) from groundwater samples taken before or early during the remediation process of Weld County surface spills involving groundwater contamination. Samples ($n = 218$) were pooled from spills that occurred between July 1, 2010, to July 1, 2011.

|          | Count | Percent below RL<sup>a</sup> | 50th percentile | 95th percentile | KM mean<sup>f</sup> | 97.5% UCL | Percent above MCL |
|----------|-------|------------------------------|-----------------|-----------------|-----------------|-----------|------------------|
| Benzene  |
| Spill #2608769 | 78    | 88%                          | <1.0<sup>b</sup> | 14.6            | 6.6<sup>d</sup>  | 24<sup>d</sup> | 8%               |
| Other spills | 140   | 27%                          | 22              | 5900            | 920            | 2100      | 66%              |
| -Inside excavated area | 102  | 16%                          | 38              | 6100            | 1100           | 2600      | 77%              |
| -1st sampling date | 60   | 8%                           | 100             | 6100            | 1400           | 3400      | 90%              |
| -2nd sampling date | 25   | 20%                          | 13              | 8900            | 970            | 5000      | 60%              |
| -3rd or later sampling date | 17   | 35%                          | 5.5             | 140             | 34             | 160       | 59%              |
| -Outside excavated area | 38   | 58%                          | <1.0<sup>b</sup> | 3300            | 510            | 1900      | 37%              |
| All data | 218   | 49%                          | 1.5             | 4800            | 590            | 1400      | 45%              |
| Toluene  |
| Spill #2608769 | 78    | 100%                         | <1.0<sup>b</sup> | <1.0<sup>c</sup> | na<sup>e</sup> | na<sup>e</sup> | 0%               |
| Other spills | 140   | 42%                          | 2.4             | 8800            | 1200           | 3000      | 17%              |
| -Inside excavated area | 102  | 31%                          | 10              | 10,000          | 1400           | 3800      | 19%              |
| -1st sampling date | 60   | 25%                          | 64              | 10,000          | 2200           | 5800      | 30%              |
| -2nd sampling date | 25   | 36%                          | 7.0             | 630             | 680            | 4700      | 4%               |
| -3rd or later sampling date | 17   | 47%                          | 1.3             | 120             | 34<sup>d</sup>  | 240<sup>d</sup> | 0%               |
| -Outside excavated area | 38   | 71%                          | <1.0<sup>b</sup> | 3200            | 430            | 1700      | 13%              |
| All data | 218   | 63%                          | <1.0<sup>b</sup> | 4100            | 750            | 1900      | 11%              |
| Ethylbenzene |
| Spill #2608769 | 78    | 91%                          | <1.0<sup>b</sup> | 49              | 8.2<sup>d</sup>  | 36<sup>d</sup>  | 0%               |
| Other spills | 140   | 41%                          | 3.0             | 720             | 100            | 230       | 6%               |
| -Inside excavated area | 102  | 32%                          | 4.3             | 780             | 120            | 290       | 7%               |
| -1st sampling date | 60   | 18%                          | 47              | 900             | 190            | 460       | 12%              |
| -2nd sampling date | 25   | 32%                          | 2.3             | 150             | 20             | 88        | 0%               |
| -3rd or later sampling date | 17   | 82%                          | <1.0<sup>b</sup> | 26              | 5.3<sup>d</sup>  | 28<sup>d</sup>  | 0%               |
| -Outside excavated area | 38   | 66%                          | <1.0<sup>b</sup> | 420             | 65             | 220       | 3%               |
| All data | 218   | 59%                          | <1.0<sup>b</sup> | 420             | 67             | 150       | 4%               |
| Xylene   |
| Spill #2608769 | 78    | 86%                          | 3.0             | 1700            | 230            | 810       | 0%               |
| Other spills | 140   | 25%                          | 66              | 8400            | 1500           | 3900      | 4%               |
| -Inside excavated area | 102  | 15%                          | 130             | 12,000          | 1800           | 5000      | 6%               |
| -1st sampling date | 60   | 7%                           | 320             | 12,000          | 2600           | 7600      | 8%               |
| -2nd sampling date | 25   | 20%                          | 41              | 6900            | 1100           | 6000      | 4%               |
| -3rd or later sampling date | 17   | 35%                          | 7.6             | 390             | 62             | 310       | 0%               |
| -Outside excavated area | 38   | 53%                          | <1.0<sup>b</sup> | 2200            | 520            | 2000      | 0%               |
| All data | 218   | 47%                          | 4.4             | 5600            | 1000           | 2600      | 3%               |

<sup>a</sup>The reporting limit was 1 ppb for all benzene, toluene, and ethylbenzene samples that were below the reporting limit. The average reporting limit and standard deviation for the xylene samples that were below the reporting limit was 2.3 ± 0.9 ppb. <sup>b</sup>More than 50% of the data were below the reporting limit (RL), and therefore the reported 50th percentiles are based on nondetect values. <sup>c</sup>More than 95% of the data were below the reporting limit (RL), and therefore the reported 95th percentile is based on nondetect values. <sup>d</sup>These values were calculated based on fewer than 10 values above the reporting limit (9 for benzene and toluene, 7 for ethylbenzene spill #2608769, and 3 for ethylbenzene day 3 or later), and thus may not be as reliable as the other reported values. <sup>e</sup>It was not possible to calculate a value because there were no measurements above the reporting limit. <sup>f</sup>The Gehan test was used to test for significant differences between the following measurements: 1st sampling date vs. 2nd sampling date, 1st sampling date vs. 3rd or later sampling date, 2nd sampling date vs. 3rd or later sampling date, and inside vs. outside the excavation area. All pairwise comparisons were found to be significant ($p < 0.05$) except for benzene 2nd sampling date vs. 3rd or later sampling date.
area exceeding the MCL for benzene. This highlights the fact that benzene groundwater concentrations decrease rapidly for locations further away from the spill site.

Disposition of spills

In addition to BTEX measurements in groundwater, we also assessed the remediation status of the spills. The remediation or “resolution” process outlined in the COGCC database appeared to vary as a function of the initial BTEX concentrations. When the initial sampling was below the National Drinking Water MCLs, the spill was considered “resolved” according to the COGCC and no further remediation was required. Alternatively, if the BTEX concentrations in the groundwater from the initial sampling exceeded the applicable National Drinking Water MCLs, operators are required to remove the contaminated soil and groundwater, to dispose of the contaminated waste in a state authorized hazardous waste disposal site, and to complete a Remediation Work Plan (COGCC, 2011f). As part of the remediation plan, groundwater monitoring is carried out by an independent reclamation company under the guidance of the operator. Specifically, the monitoring guidelines set forth by COGCC for remediation of groundwater indicate that a spill may be considered resolved when the measured groundwater contaminant concentrations fall below the respective MCLs for four consecutive sampling periods following excavation of the spill (COGCC, 2009). The COGCC’s use of the term “resolved” refers to this specific metric and does not refer to evaluation or resolution of other spill metrics.

For each of the 77 reported spills in Weld County with impact to groundwater, we determined whether the spill had been labeled “resolved” by COGCC as of May 2012 by accessing publically available data on the COGCC website. For 54 of 77 reported spills, resolution acceptable to COGCC was achieved after the initial excavation was performed and the operator completed a remediation plan for the spill. Alternatively, for 11 of 77 spills, resolution was achieved when a COGCC agent determined that the initial excavation of the spill and the respective BTEX analysis indicated that no further action was necessary. For all of these 11 spills, the reported initial BTEX concentrations in the associated groundwater samples were below the reporting limit following excavation of the spill. Regarding the remaining 12 reported spills, three spills were still in the process of remediation and remained unresolved per COGCC. Finally, for 9 of 77 spills no information regarding spill resolution was available for review.

To our knowledge, our analysis is the first attempt to quantitatively analyze the potential impact to groundwater from surface spills containing BTEX concentration at drilling sites where hydraulic fracturing occurs. However, there are several limitations to our analysis.

Limitations of analysis

First, our analysis was constrained by the availability and accuracy of the information on the COGCC website. All data were obtained from operator-reported spills, and therefore it is possible that additional spills may have occurred which went unreported. In addition, BTEX measurements from groundwater samples were not available for all reported spills. However, since BTEX data were available for over 80% of the spills, and remediation status could be determined for 88% of the spills, we do not anticipate that our conclusions would change markedly if the missing data were made available. In turn, it is important to note that our findings are specific to Weld County, Colorado, and do not necessarily represent other geographical areas where hydraulic fracturing activities are conducted. Regional differences including different regulations and average depth to water table would likely impact that rate of groundwater BTEX contamination from surface spills. Since depth to the water table in some parts of Weld County is shallow, groundwater contamination from spills in this county may be more likely should a spill occur.

Another important piece of information that was not available for our analysis was baseline sampling measurements of BTEX in the groundwater. Although such sampling may have occurred, we were unable to locate it in the COGCC database. BTEX are found at low levels in crude oil and are also natural compounds found in coal and gas deposits. As such, BTEX may naturally be present at low concentrations in groundwater located in the vicinity of these types of deposits. Without baseline water quality analysis performed prior to development of the drilling site and/or prior to the spill, the background BTEX concentrations in the groundwater are uncertain.

It is possible that BTEX groundwater concentrations prior to the first sampling date may have exceeded the reported measurements because there was often a delay between the reported spill date and the first day of sampling. In addition, 15 of the spills were noted to be historical, which indicates that they were leaking for some time before the spill was discovered.

Although our study demonstrated that groundwater BTEX concentrations decreased rapidly with distance from spill site and with time after remediation began, it was beyond the scope of our analysis to estimate BTEX concentrations at any downstream receptor location for any time during the course of these spills or during the remediation process. Such an analysis may be useful in some circumstances depending on the proximity of downstream receptors of concern and the BTEX concentrations in groundwater samples taken at the spill site. In addition to potential groundwater impacts, spills of crude oil and produced water also pose potential impacts from BTEX inhalation or dermal absorption by workers or others in the vicinity of the spills. Analysis of potential BTEX exposures via these routes was also beyond the scope of this study.

Conclusions and Recommendations

Our analysis indicates that surface spills of produced water from the fracturing process or crude oil from fractured wells could pose the potential for release of BTEX chemicals in excess of the national MCLs for each compound. However, the spill reports posted on the COGCC website for Weld County, Colorado, appear to indicate that the remediation process set forth by COGCC Rule 900 Series and implemented by operators has been effective at resolving spills according to these
requirements. While there are limitations to the approach we used in our analysis, these data are nonetheless valuable in beginning to obtain a quantitative characterization of the presence and fate of BTEX in surface spills at drill sites where hydraulic fracturing activities are conducted. It also appears possible that some members of the public may hold a negative view of hydraulic fracturing activities in their community because of the lack of information regarding processes such as this one to address surface spills. It is also unclear how the determination of spill "resolution" as defined by COGCC affected any actual impacts to groundwater. As a result, we offer the following recommendations going forward in order to help address any potential impact of BTEX chemicals in surface spills to the groundwater in Weld County and elsewhere.

Recommendations going forward

It has been estimated that over the next 20 to 30 years, the density of well sites will increase in the most productive areas of oil and gas recovery (Kennedy, 2007; Pelley, 2003). The current expansion has already introduced oil and gas recovery operations to suburban and urban populations, and concerns have arisen regarding potential adverse health impacts, property damage, and ecological damage. Based on our analysis, we suggest the following recommendations, some of which are specific to the potential for BTEX groundwater contamination from surface spills, and many of which are more general and apply to multiple facets of hydraulic fracturing activities.

(1) A comprehensive chemical risk analysis should be conducted by well operators in order to provide a formalized method for objectively identifying and evaluating the hazard and exposure potential posed by specific chemicals and chemical mixtures that are used in the hydraulic fracturing process (Panko and Hitchcock, 2011). This process, which has been referred to as chemical footprinting, can provide operators with an evaluation of positive and negative environmental characteristics including biopersistence, bioaccumulation potential, mobility, and exposure potential by multiple routes. With this knowledge, operators may better identify areas for improvement and safeguard against current and future regulatory compliance and public perception issues.

(2) After identifying which chemicals may pose a greater risk, operators may choose to employ alternative chemicals or to implement enhanced safety measures such as additional or increased monitoring for certain chemicals on a regular basis.

(3) Any environmental sampling plan should take into account spatial and temporal variability of chemical concentrations, achieve adequate detection limits, and properly characterize baseline or background levels of chemicals of interest. According to the COGCC website, a water sampling plan is currently under review.

(4) Important factors such as variations in the depth of the water table on the eastern plains of Colorado should be carefully considered when evaluating the location of drilling site operations. As such, consideration should be made regarding placement of storage tanks and production facilities since our data indicated that these facilities were the most common sources of high concentrations of BTEX in surface spills with groundwater impact.

(5) Given the finding that many spills reported to COGCC were the result of equipment failure rather than operator error, equipment safety systems on the surface at drilling site should be carefully considered and enhanced where needed. With the remote location of many of the drilling sites in Weld County and the absence of on-site personnel to continuously monitor each well, the improvement of remote monitoring capabilities and an increase in the redundancy of spill prevention measures may be warranted at some drilling locations.

(6) Well operators or third parties should actively engage in public education in local communities regarding the procedures used in hydraulic fracturing and horizontal drilling. Expanding and improving the public sharing of such information would be helpful in assisting workers and community members in the evaluation of personal risk versus community benefit.

(7) Well operators should more effectively communicate the health and environmental protection procedures that they have in place prior to production so that workers and local communities are aware of the extent to which hydraulic fracturing activities may or may not pose a risk.

While our recommendations may already be fully implemented by some well operations, based on the concerns voiced in Colorado by the media and the public, it appears that the procedures for prevention and mitigation of risks associated with surface spills at active well sites are not yet fully and clearly communicated.

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