Assessment of groundwater contamination and the role of hydraulic fracturing operation in Weld County, USA

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11 GRAPHICAL ABSTRACT

19 Abstract

In shale gas-producing countries, soil, and groundwater contamination due to surface spills 20 associated with hydraulic fracturing operations is one of the most worrying problems that arise, 21 22 since its elimination is not easy or cheap to carry out, and its effects persist for many years. Thus, 23 this study identifies the environmental and health risks associated with the extraction of 24 unconventional gas. The study was carried out based on the available data obtained from Colorado 25 Oil and Gas Conservation Commission (COGCC) regarding groundwater pollution from spills that 26 have occurred in Weld County where fracking has become a common practice. Data sources 27 related to spills were analyzed. A range of parameters that characterize the quality of the water were investigated to determine the groundwater quality and compared with the international 28 standards to evaluate its suitability for different utilizations. 29

The result showed that the groundwater is not suitable for human consumption nor irrigation purposes. The study shows that there are 33 surface water bodies, 17 wetlands, 23 livestock, and 31 occupied building are threatened with pollution. The study also indicated that about 80 % of cases of spills are due to equipment failures. It can be concluded that the most important cause of surface spills and therefore potential contamination of soil and groundwater is equipment failure. Oil surface spills are the main causes of groundwater contamination, yet the contribution of agricultural activities to the spread of this contamination should not be neglected.

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Key words: Groundwater pollution, Hydraulic fracking, Oil Spills, Agricultural activities, Water
 aquifers.

40 **1. Introduction**

The continuous rise in the population and the rising standard of living of emerging and developing countries with high population numbers have increased the demand for energy in the world, along with the constant fear of depleting oil resources, prompting an expanding search for new sources of energy supply to meet our needs. Natural gas is one of the energies that is being investigated more (Magazzino et al., 2021).

Until now, most exploited natural gas resources came from conventional accumulations of isolated 46 gas and associated gas dissolved in oil. However, natural gas is also found in reservoirs that, due 47 48 to their low porosity and permeability, have characteristics that until very recently have not been 49 economically profitable and that can only be exploited using unconventional techniques (Zhang et 50 al., 2021). The particularities of these deposits give rise to the so-called unconventional gas. 51 However, concurrent with the increased production of unconventional gas, concerns have arisen 52 about the effects of extraction processes on groundwater quality, human health, and the climate, 53 due in part to the migration of methane and other associated hydrocarbon gases and volatile organic 54 compounds (Hammond et al., 2020).

55 The exploitation of shale gas through hydraulic fracturing and like any surface industrial activity

- can affect soil, surface water, and groundwater due to accidental spills and leaks from ponds, etc.
- 57 Petroleum derivatives deserve special mention. These substances reach the phreatic surface by

infiltration from accidental spills or by ruptures of tanks or pipes. Some are less dense than water 58

59 "light non-aqueous phase liquid" (LNAPL), thus remaining on the surface of the aquifer free

60 superficial, only a part dissolve. Other hydrocarbons are denser than water "dense non-aqueous

61 phase liquid" (DNAPL) and end up in the lower part of the aquifer, although some of them can

62 dissolve.

Groundwater and surface water pollution, as well as soil contamination, are negative effects that 63 usually occur as a result of such incorrect management of spills. Pollution processes, once started, 64 65 are not easy to remove and last for many years (Qin et al., 2021). Possible technical solutions for decontamination are also costly, difficult to implement, and relatively successful on many 66 occasions (Talabi & Kayode, 2019). Groundwater is a vital resource not only for domestic use but 67 68 also for developing industrial and agricultural activities. Without forgetting its importance in sustaining the ecological balance. These possible uses will be conditioned by the quality chemical 69 and biological present in these waters, which must not exceed the values established by the quality 70 regulation. When these values are exceeded, it is said that water is contaminated by human action. 71

72 Many studies confirmed that these spills contaminated the groundwater and soils in Weld County

73 (Almaliki et al., 2022). For example, 77 surface spill reports were analyzed, it was noted that the

concentration of benzene, toluene, ethylbenzene, and xylene (BTEX) exceeded the World Health 74

Organization (WHO) permissible level(Gross et al., 2013). Oil surface spills in Weld County affect 75 the shallow groundwater aquifer, which contains more than 12,000 domestic groundwater wells

- 76
- (Kanno & McCray, 2021). 77

78 Although the extraction of shale gas is the primary suspect in groundwater pollution, we should not neglect other sources of pollutants, especially those related to agricultural activity and animal 79 fecal. Where agricultural activities are one of the most widespread reasons for the deterioration of 80 the groundwater quality(Talabi & Kayode, 2019). The most significant potential pollutants in this 81 field are fertilizers and pesticides (An et al., 2021). Other pollutants of less significance are the 82 dumping of animal waste on the ground, the storage of crop residues, fertilizers, especially 83 nitrogenous compounds (Sun et al., 2021). They are the most important nutrients from the point 84 85 of view of groundwater contamination due to the mobility of nitrates (Zambito Marsala et al., 2021). Weld County is rich in agricultural activities, the probability of groundwater contamination 86 with these activities must take into consideration, and this is what will be addressed in this study. 87

Today, there is a lack of information concerning the relation between the groundwater 88 contamination in Weld County and the role of hydraulic fracturing operation related to the 89 90 extraction of unconventional gas as well as reason of spills.

Thus, the aim of this study is to analyze the groundwater quality in Weld County and compare it 91

with the international standards to demonstrate its suitability for different utilizations. In addition, 92

to determine the cause of those spills, and what actions can be taken to reduce these risks. 93

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2. Methodology 95

2.1 study area 96

Weld County is a county located in the U.S. state of Colorado, within the coordinates of (40.5632° 97 or 40° 33' 47.6" north) latitude and (-104.4835° or 104° 29' 0.7" west) longitude. Weld County is 98 the richest agricultural county in the United States with 2.5 million acres of which 75% is devoted 99 to farming and rearing livestock, the county is Colorado's main producer of beef and grain (County, 100 2021). At the same time, Weld County is one of the most important oil producers in the United 101 States (Robbins et al., 2021). Due to the intensity of unconventional oil and gas extraction using 102 fracturing technology in Weld County, many surface spills occurred (Gross et al., 2013). These 103 spills affected both the soil and groundwater. Agriculture in County Weld is highly dependent on 104 105 groundwater. Therefore, it is very important to assess the quality of groundwater and its potential to be harmful to human health. 106

107 **2.2** Spills Database Considerations

The information related to oil surface spills were obtained from Colorado Oil and Gas 108 Conservation Commission (COGCC) database. The data was analyzed with the aim to clarify the 109 110 relationship between groundwater pollution and surface spills from fracking operations, which is the focus of our study, to be able to visualize the magnitude of the resulting risks, study their 111 environmental effects, and search for ideal risk management ways. 112

- The obtained data was presented by operators from 2014 to 2021 by Form 19, which is a spill / 113 release report submitted by the party responsible for the oil and gas spill to COGCC database 114 115 (COGCC, 2019). The data includes three principal parts; spill release report that covers spill details, number of soils and groundwater impacted, and corrective actions completed. The data 116 included details of the operators, fields, and locations of spills, the number, and sizes of spills, the 117 number of impacted soil and groundwater, geology description, as well as details about what 118 surrounds those sites, cities, farms, etc. Finally, the details included active correction and other 119 details. The spill database included 4543 reports submitted by operators between 01/16/2014 to 120 121 9/17/2021. Some of the reports, indicated to the oil spill volume, but they did not indicate whether the soil and groundwater were impacted, and accordingly, only the reports that indicated that the 122 soil and groundwater impacted would be considered in assessing whether the neighboring water 123
- 124 wells being affected by pollution or not.
- 2.3 Quality parameters of groundwater 125

126 To determine the suitability of groundwater for human consumption, a series of parameters that characterize the quality of the water must be described. The quality parameters are divided into 127 physical-chemical, microbiological, and organoleptic. The total dissolved solids (TDS), which is 128 129 the mass of salts that obtained and remain unchanged when evaporating a liter of water. The 130 chemical substance that contributes most to the dry residue (TDS) are usually sodium, potassium, calcium and magnesium as cations, and bicarbonate, chloride, and sulfate as anions. Some waters, 131

- 132 silicon is also considered, an element of complex chemistry that usually occurs in anionic form,
- although its concentration is expressed as silica. 133
- 134 The ground water can contain a long list of metallic elements of different origins. For example, 135 iron and manganese are common in groundwater. Arsenic is usually of natural origin and linked

to the geological characteristics (Shaji et al., 2021). Other metals, such as mercury, cadmium,
chromium, and selenium are linked to the industrial activities. Natural water (sea, rivers, lakes,
and groundwater) is the natural habitat of many species of microorganisms. Most of these
microscopic forms do not pose a danger to humans, yet some can affect people and cause disease.

Analytical sample database obtained from 971 domestic water wells near the spill locations were
 analyzed. About 16107 samples taken from 971 domestic water wells were selected for hydro

142 chemical modeling. The samples were collected between t 1st / January /2014 to 12th /May 2021.

A wide variety of organic and inorganic parameters has been identified as potential groundwater
contaminants. These include inorganic compounds such as (Arsenic, Barium, Boron, Cadmium,
Calcium, Fluoride, Manganese, Nickel, Nitrate, and Zinc). Organic compounds such as (benzene,
toluene, ethylbenzene, and xylene (BTEX). In addition, some parameters that indicate the quality

147 of groundwater have been identified, such as (pH and conductivity) which are closely linked.

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149 3. Result and Dissection

150 3.1 Spills analysis by year

The report indicates that more than 4,539 oil spills have affected 16 cities. The vast majority were from Weld City, due to the extraction intensity in that city. About 80 % of those spills were the result of equipment failures. The report reveals that approximately 15,271 barrels were spilled between 2014 and 2021. Table 1 presents the spill analysis and causes from 2014 - 3rd Quarter 2021.

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Veen	C m:11	Oil Snilled bbl	Cause of the spill		
rear	Spin	On Spined bbi	Human error	Equipment Failure	Historical Unknown
2014	361	1940	31	87	243
2105	460	1351	41	85	334
2016	582	3155	16	172	394
2017	708	3171	30	134	544
2018	709	1024	31	111	567
2019	608	2378	30	126	452
2020	531	759	3	16	512
2021	579	3433	Not available	Not available	Not available

157 **Table 1: Spill analysis and causes**

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Table (2) shows the type of facility associated with groundwater impact in Weld County, there
were 304 spills during 2021 due to equipment failure, and the major cause of spills was tanks
battery by 56 %.

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City	Facility Type	N° of Spills	N° Soil impacted	N° Groundwater impacted	N° Data not available
Weld	Flow line system	6	5		1
Weld	Off-location flow line	51	20	1	30
Weld	Oil and Gas location	23	8	3	12
Weld	Other	22	10		12
Weld	Partially buried vessel	3	2	1	0
Weld	Pipeline	8	4	2	2
Weld	Production line	1			1
Weld	Tank battery	171	121	14	36
Weld	Well	15	12	12	3
Weld	Well site	4	4	4	0
	Total	304			

163 Table 2: Spill caused by equipment

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165 Out of the 4543 reports, only 2650 reports referred to soil and groundwater were impacted. The

reports indicated that 2145 cases of soil were impacted and only 505 cases of groundwater were

impacted. It was noticed that only 23% of soil pollution cases led to groundwater pollution. This

is due to the speedy corrective actions on the site. Figure (1) shows the number of soils cases

169 impacted compared to the number of groundwater impacted in the spill location.



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171 Fig. 1: Number of soil cases impacted vs number of groundwater impacted

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The data included information about what around spill location such as surface water near,Wetlands, Livestock near and occupied buildings. If these sites are less than one mile from the

- spill location, they considered at risk of contamination as shown in the Table 3 (based on 2021database).
- 177

178 Table 3: Number of sites near the spill location are at risk of contamination

City	Surface Water Near	Wetlands	Livestock Near	Occupied Buildings
Weld	33	17	23	31

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180 3.2 Groundwater contamination

- 181 Table 4 shows the number of samples in which the concentration of BTEX compounds exceeded
- the permissible limit.

Organia compound	No Complete and MCI	Maximum concertation µg/l		
Organic compound	N ⁻ Samples exceed WCL	Median	Range	
Benzene	603	4186	10.5 - 6.4E+4	
Toluene	133	10861	310 - 1.2E+5	
Ethylbenzene	190	5241	710 - 1.1E+5	
Xylene	228	9067	510 - 1.2E+5	

183 Table 4: Number of samples in which the concentration of BTEX exceeded the MCL

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Unusual concentrations of BTEX were detected in the analyzed water samples. One of the most common forms of BTEX contamination detected over the years is the oil spills from storage tanks, mainly located at fracturing location. These compounds are found in hydraulic fracturing fluid, forming a large part of its soluble fraction. All of them are considered toxic and dangerous compounds and are included as such in the list of elements susceptible of analysis according to WHO. Table (5) shows the number of samples in which the concentration of inorganic compounds exceeded the permissible limit.

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Table 5: Number of samples in which the concentration of inorganic compounds exceeded the MCL

Inorganic compounds	N° Samples exceed MCL	Maximum concertation mg/l	
8 I		Median	Range
Arsenic	1698	4.5	0.0105 - 290
Barium	4810	0.13	0.011-85.2
Boron	1708	185.8	0.502 - 2500
Cadmium	1225	1.7	0.0035 - 307
Calcium	4906	186	75.5 - 90000
Fluoride	5460	4.4	1.6 - 929

Manganese	1025	4.7	0.5 - 1000
Nickel	921	0.09	0.00728 - 20
Zinc	6	54	19 - 92

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196

197 Unusual concentrations of inorganic compounds were detected in the analyzed water samples. These elements can have different origins. In the case of groundwater, they can pass through 198 199 lithographic substrates rich in some of these metals and contaminate them. In regard, to the 200 suitability of groundwater for drinking, for example, when arsenic encounters groundwater, it can end up in drinking water if not properly treated. Due to this natural geological contamination, high 201 levels of arsenic can be found in some drinking waters that come from deep wells. Consumption 202 203 of arsenic-rich water for prolonged periods has been shown to be detrimental to health, causing skin problems and certain cancers, such as skin and lung. 204

In certain aquifers, variable amounts of boron appear because of the filtration of certain fertilizers used for some crops or due to the existence of hot springs of volcanic origin. In general, the detected concentrations are related to the geochemical background of the aquifer. Table 6 shows the number of samples in which the concentration of nitrate and phosphorus exceeded the permissible limit.

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Table 6: Number of samples in which the concentration of nitrate and phosphorus exceeded the MCL

Organia compound	Nº Samplas avaaad MCI	Maximum concertation µg/l		
	N Samples exceed WCL	Median	Range	
Nitrate (as NO ⁻ 3)	120	102	51.5 - 9999.9	
Phosphorus	802	0.51	0.11 - 71.6	

²¹³

The existence nitrate and phosphorus may be due to pollution caused by agricultural activity, where nitrogen is used as chemical fertilizer and that from nitrogen present in livestock wastewater.

Table (7) shows the results of measurements of physicochemical parameters, which consider a very useful methodology to evaluate the quality of water and establish plans for its management.

220 Table 7: The results of measurements of physicochemical parameters

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Parameter	Unit	Range
рН	-	7.28 - 8.18

Conductivity	μS / cm	558 - 5120
TDS	mg/l	122 - 5500
Dissolved Oxygen	mg/l	0.2 - 1.24
Redox	mV	71-258

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The obtained results shows that the pH indicates that in general it is water with a tendency to neutrality, oscillating between 7.28 and 8.18. The conductivity of groundwater presents values between 558 and 5120 (μ S / cm), considered within the range of freshwater (<2,000 μ S / cm).

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Regarding dissolved oxygen, values between 0.4 and 1.24 mg/L are measured, indicative of moderate to low oxygenation. The Oxidation Reduction Potential (ORP), which is indicative of anaerobic environments, which consistent with the low concentrations of oxygen that have been consumed by aerobic bacteria during degradation of the hydrocarbons present in the subsoil.

The total dissolved solids (TDS) classification is important in groundwater quality. The total dissolved solid (TDS) presents values between 122 and 5500 mg/l, TDS exceeded the WHO permissible level in five samples from seven. All groundwater samples showed that it is not potable and it is not suitable for irrigation purposes, water is suitable for irrigation when the value TDS is less than 3000 mg /l (Khwedim et al., 2017).

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237 4. Conclusion and recommendation

238 This research presents a risk assessment analysis and evaluate the potential pollution of groundwater caused by the extraction of unconventional gas. The study established the necessary 239 bases for estimating the vulnerability of water wells near spill locations to be polluted. The results 240 indicated that the surface oil spills are a real concern for groundwater pollution. In addition, other 241 242 surface water sources are also threatened by the same level of pollution, for example, there are 33 surface water, 17 wetlands, 23 livestock and 31 occupied building are threatened with pollution. 243 About 80 % of cases of spills are due to equipment failures, the major cause of equipment failures 244 was tanks battery by 56 %. Therefore, it is essential to carry out good planning and execution of 245 preventive maintenance to guarantee the correct functioning of the equipment and, therefore, avoid 246 breakdowns and unscheduled downtime. Livestock and intensive agriculture practices or the 247 burning of fossil fuels are factors that have contributed in a decisive way to the fact that nitrate 248 pollution, the negative effects of which are devastatingly felt in the environment, cease to be a 249 problem. Environmental to become a potential health risk. All groundwater samples are not 250 suitable for drinking or irrigation purposes. 251

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