The Impact of Climate Change and Soil Classification on Benzene Concentration in Groundwater Due to Surface Spills of Hydraulic Fracturing Fluids

Alaa Jasim Dakheel Almaliki 1,2,*, Mohammed J. K. Bashir 3 and Juan F. Llamas Borrajo 1

1 Escuela Técnica Superior de Ingenieros de Minas y Energía, Universidad Politécnica de Madrid, Calle de Ríos Rosas 21, 28003 Madrid, Spain; juan.llamas@upm.es
2 Aguas del Arco Mediterráneo S.A, Calle Caballero de Rodas, 22, 03181 Torrevieja, Spain
3 Department of Environmental Engineering, Faculty of Engineering and Green Technology, Universiti Tunku Abdul Rahman, Kampar 31900, Malaysia; jkbashir@utar.edu.my
* Correspondence: alaa.dalmaliki@alumnos.upm.es; Tel.: +34-606764537

Abstract: Hydraulic fracturing drilling technology can cause a high risk of surface spill accidents and thus water contamination. Climate change together with the high water demand and rapid increase in industrial and agricultural activities are valued reasons why we should all care about the availability of water resources and protect them from contamination. Hence, the purpose of this study is to estimate the risk associated with a site contaminated with benzene from oil spillage and its potential impact on groundwater. This study focused on investigating the impact of soil variability and water table depth on groundwater contamination. Temperature-dependent parameters, such as soil water content and the diffusion of pollutants, were considered as key input factors for the HYDRUS 1D numerical model to simulate benzene migration through three types of soil (loamy, sandy clay loam, and silt loam) and evaluate its concentration in the water aquifer. The results indicated that an anticipated increase in earth’s average surface temperature by 4 °C due to climate change could lead to a rise in the level of groundwater pollution in the study area by 0.017 mg/L in loamy soil, 0.00046 mg/L in sandy clay loam soil, and 0.00023 mg/L in silt loam soil. It was found that climate change can reduce the amount of benzene absorbed from 10 to 0.07% in loamy soil, 14 to 0.07% in sandy clay loam soil, and 60 to 53% in silt loam soil. The results showed that the soil properties and solute characteristics that depend on the temperature have a major and important role in determining the level of groundwater pollutants.

Keywords: groundwater contamination; hydraulic fracking; climate change; oil spillage; water aquifers

1. Introduction

The world is currently going through a moment of energy crisis where the consumption of natural gas has increased around the globe, while many countries tend to diversify their energy sources. The United States attaches great importance to extracting energy from “shale oil and gas” as an alternative to fossil fuel. California is a very important unconventional gas production field in the United States [1] Considering the reality of conventional gas fields, the boom in the exploration and extraction of shale gas reserves is due to the technical innovations that horizontal drilling and hydraulic fracturing have entailed. Advances in horizontal drilling have resulted from the improvements and innovations for downhole motors, along with drilling fluids, cutting tools, and well telemetry [2].

On the contrary, the hydraulic fracturing process has given rise in the United States to a series of accidents whose consequences have had an impact on the environment, and this has caused a great social debate about the environmental consequences of shale gas extraction [3]. Many toxins have been found in fracking fluids, such as benzene, toluene, ethylbenzene, and xylene BTEX [4]. BTEX compounds have been classified by the World
Health Organization (WHO) as dangerous compounds [5]. The exposed population may be at risk due to the potential carcinogenic effects of chronic exposure to benzene [6]. Although toluene, ethylbenzene, and xylene (TEX) are not carcinogenic, they are commonly studied together with benzene due to similarities in chemical structures and because they share the same exposure sources [4].

Simultaneously with the increase in fossil fuel production in recent years, concerns have arisen about the effects of oil and gas extraction operations on groundwater quality and climate. The main concern about the environment that arises regarding the exploitation of unconventional gas using the hydraulic fracturing technique is the contamination of the aquifers (either by the fracturing fluid used or by methane) [7].

A storage tank spillage may create a large contaminated area, constituting pollutants sources that may threaten the groundwater quality. After further analysis of oil surface spill incidents reported in the United States, it was reported that most of the oil spills were caused by oil and gas facilities themselves, such as fuel tanks and pipeline ruptures [8], since the study area is located in Kern County, which sits atop large oil reserves, producing more oil than any other county in the United States [1]. The intensity of oil and gas extraction in this area has led to many accidents of surface spills. In recent years, oil spills have been frequent in Kern County; for example, between 2009 and 2014, about 575 surface oil spills occurred [5]. Yet, from 2015 to 2016, about 134 surface oil spills occurred with an estimated volume of 342 m$^3$ [5]. The Kern County in question is important apart from the extractive activity of oil and gas due to a large agricultural activity; the region contributes to its second-place rank among California counties in terms of agricultural crop value [9]. Groundwater in Kern County is considered a strategic store; it can be used for irrigation in case of scarcity of surface water [10]. These spills led to the pollution of the groundwater in the study area with benzene, and this is what was proven by Kern County Water Agency [11].

Water is essential for life and the functioning of ecosystems. Three-quarters of the earth is covered with water, but only 3% of it is fresh and not all of it is accessible. Only 1% of the planet’s water is usable by human beings [12], which is a very small proportion. The groundwater is defined as water, which occupies the pores, fissures in the rocks, and circulates through them very slowly. They represent 0.75% of all land water and 30% of the freshwater. Such statistics show the great importance of groundwater as a reserve and freshwater resource. According to the Food and Agriculture Organization (FAO), groundwater supplies drinking water to at least less than 50% of the world’s population. For example, many parts of the USA suffer from over-abstraction of groundwater resources [13]. Groundwater can be valued, exploited, and controlled like any other natural resource, and to control it, it is necessary to understand the behavior of aquifers and their relationships with other components of the hydrological cycle, rivers, lakes, atmosphere, and the unsaturated zone.

Groundwater quality parameters (pH, alkalinity, dissolved oxygen, and total dissolved solids) can change due to spills from bad practices using hydraulic fracturing [14]. For example, according to EPA, the total dissolved solids levels (TDS) can be affected by unconventional gas extraction [15]. Oil spills can affect the organisms in the soil, reduction in moisture, and nutrient retention. The toxicity of oil hydrocarbons, both aliphatic and aromatic, is variable but, in general, those of lower molecular weight are more toxic.

Many studies in recent years have indicated the existence of certain evidence of climate change and its effects on various natural systems around the planet, affecting the availability of water resources [16]. The new scenarios expected because of climate change are an increase in temperatures, a decrease in the concentration of precipitation, and a further decrease in the water recharge of the aquifers [16]. The studies have indicated that groundwater, in general, will be affected by rising temperatures at a lesser rate than surface water [17]; therefore, the demand for groundwater will be expected due to the droughts. Therefore, more attention must be paid to these few sources, and they must be protected from pollution.
Groundwater modeling is now a major part of most groundwater development and protection projects and processes. The construction of any model will depend on various assumptions, which relate to the natural system, i.e., if the hydrogeological and hydrological parameters used in the model are always approximate concerning their actual distribution in the fields. Analytical models help us in managing the polluted locations and determining the concentration of the pollutant, which is an important factor in determining the remediation program. Since such data are taken from the aquifer system, physical parameters are available from the literature.

Groundwater is a scarce commodity. It must be taken into account that, in the context of climate change, the world periodically suffering from droughts and water scarcity is a major problem in much of the world with notable decreases in rainfall. The objective is to become aware of the importance of protecting groundwater reserves, since they constitute the basis of the drinking water supply and a basic natural resource for agriculture, industry, and all natural ecosystems. Climate change, with increasingly frequent droughts, increases the danger of depletion of these underground water sources, especially in the basins most affected by global warming. The two biggest risks they face is overexploitation, and groundwater may be contaminated by human activity, forcing regeneration processes that are long and difficult.

Yet, there is a need to validate this research with a case study from the Midway-Sunset oilfield in California. It is necessary to understand the role of climate change in benzene transport in different types of soil and its impact on groundwater. Therefore, this study aims to assess the benzene concentration in shallow groundwater resulting from surface spills of hydraulic fracturing fluids, with special reference to the role of an expected rise in temperatures due to climate change and the role of soil properties, such as the water content, and the chemical substance characteristics, such as diffusion.

2. Methodology
2.1. Study Area

The Midway-Sunset oil field (Figure 1) is in California, west of the United States, where it is located about 160 km east of the Pacific Ocean. The oil field runs southeast to northwest; deposits of deep-water clastic constitute the prolific; and it is one of the largest oil fields in California [18]. The field is about 30 km in length and 5 to 6 km in width. Studying the impact of pollutants is important for this field not only because of their direct impact on the groundwater but also because of its proximity to the Kern River where the field is only a few meters away from the mentioned river. The migration of pollutants toward the river or to the groundwater that feeds the river may cause risks that may affect public health. The water table in the area can be very close to the surface (within a few meters), or very deep (up to several hundred meters). According to the United States Department of Agriculture, in most California regions, the shallowest water table is between 0.9 and 1.8 m from the surface [19]. The field was selected in our study because previous studies have shown that most of the causes of surface spills are tank batteries during injection operations.

2.2. Transport Model in the Unsaturated Zone

Beneath the surface, with the pores only partially occupied by water, air and water coexist in the pores. The water is subjected to stress capillaries that make their effective pressure less than atmospheric pressure. Such areas are defined as the unsaturated zones, which can be divided into three parts:

1. The floor moisture strip: It is the upper layer of the floor surface where it is subjected to evapotranspiration. Although the thickness is determined by the climate and vegetation cover, on average, it reaches a few meters. (2) Intermediate or retention strip: the water in this area does not present any hydraulic link with the lower layers. Its average thickness range can reach 10 or 20 m. (3) Capillary strip: The thickness depends on the geological characteristics of the materials. The water can rise above the piezometric height, remaining in equilibrium in the interstices of the rock by the action of the surface tension.
In the unsaturated zone, the pollutants move vertically until the water table is found. Once reached, they are transported in the direction of the aquifer. Contaminants, before reaching the saturated zone, must pass through the unsaturated zone; after evapotranspiration, they displace downward with the water contained in the pores to accumulate above the water table. Transit times in which contaminants reach the saturated zone can vary and be very fast.

The uses of numerical models have become popular during the last 20 years due to the appearance of both public and commercial domain packages and the development of increasingly sophisticated graphical interfaces that can simplify their use. HYDRUS 1D [20] is a public domain software that simulates the movement of water, heat, and solutes in one dimension in a partially saturated medium. The software uses finite elements to solve both the flow and transport equations, using any of the conceptual models, such as 1: uniform flow; 2: mobile–immobile water; 3: dual porosity; 4: dual permeability.

In this work, 1D numerical simulations of the transport of solutes in the unsaturated zone around Kern County are presented without taking into account the infiltration and root uptake. Accordingly, the HYDRUS 1D numerical model was operated to simulate the migration of benzene from a source point on the soil toward the groundwater table. Equation (1) describes the one-dimensional transport of contaminants under steady flow in a partially saturated porous medium [20].

\[
\frac{\partial \theta c}{\partial t} + \rho \frac{\partial S}{\partial t} = \frac{\partial}{\partial z} \left( \theta D \frac{\partial c}{\partial z} \right) - \frac{\partial (qc)}{\partial z} - \varnothing
\]

where \( c \) is the concentration \([\text{ML}^{-3}]\), \( S \) is the sorbed concentration \([\text{M M}^{-1}]\), \( D \) is the dispersion coefficient \([\text{L}^2\text{T}^{-1}]\), \( q \) is the volumetric fluid flux density \([\text{L T}^{-1}]\) evaluated using the Darcy–Buckingham law, and \( \varnothing \) is the rate of change of mass per unit volume due to chemical reactions \([\text{ML}^{-3}\text{T}^{-1}]\).
According to the literature, the adsorption process is the most important factor in attenuating the migration of pollutants; HYDRUS 1D generalizes a nonlinear sorption equation that can be simplified using the Langmuir or Freundlich isotherm [20]. Therefore, linear adsorption is assumed as shown in Equation (2):

\[ S = K_d C \]  

where \( K_d \) is the distribution coefficient \([L^3 M^{-1}]\), \( S \) is the sorbed concentration \([M M^{-1}]\). Linear adsorption leads to retardation factor \( R \) [21] Equation (3):

\[ R = 1 + \frac{\rho_d K_d}{\theta} \]  

where \( \rho_d \) is the mass density in the porous medium \([ML^{-3}]\).

The movement of solute in the unsaturated zone is simulated by using a flow model of simple porosity or uniform flow. Meanwhile, the advection-dispersion equation for inherent and unabsorbed solutes during one-dimensional water flow (Equation (4)) [22]

\[ \frac{\partial c}{\partial t} = D \frac{\partial^2 C}{\partial z^2} - v \frac{\partial c}{\partial z} \]  

where \( D \) is the longitudinal dispersion coefficient \([L]\).

Soil properties and solute characteristics play roles in pollutant transport in the unsaturated zone. For example, soil moisture is very important in contaminants’ absorption, and it is highly dependent on surface temperature. The diffusion of pollutants in the soil also depends on temperature, considering these two main parameters as key factors in solute transport in the unsaturated zone to reach the groundwater table. The model ran twice. The first time, residual soil water content established by the Carsel and Parrish [23] method was used for the first scenario. In the second scenario, a 10% decrease in these values was estimated, which is the anticipated value by the end of the 21st century due to climate change in the study area [24]. The diffusion of benzene was computed depending on the present study area’s average annual temperature, which is 18°C for the first scenario. The parameter recomputed for the second scenario depends on the average annual temperature by the end of the 21st century, considering the expected rise in surface temperature to 4°C [25] due to climate change, which is 22°C.

2.2.1. Model Parameterization

Generally, analytical models require high-precision parameters to predict contaminant transport in soil, considering external influences on these parameters. The velocity of a contaminant in the saturated zone is a very important parameter in determining the accuracy of the results, while the diversity of rock properties leads to a variable hydraulic conductivity, and therefore, velocities can be variable. Taken into consideration the variation of the hydraulic conductivity (K), the range of the saturated hydraulic conductivity of California soils (10 to 31) cm/day [26].

The starting concentrations within the region of interest are required information to solve the advection-dispersion equation. The maximum value depends on the source-loading functions used in contaminant transport models. Determining the initial concentration of pollutants is an important parameter in forecasting the level of pollution in groundwater. Accordingly, in this study, BTEX concentrations in hydraulic fracturing fluids are estimated as a portion of diesel (EPA 2004), since diesel is used as an ingredient in hydraulic fracturing fluids [27]. The partitioning coefficient (K_d) will be the most significant sorption mechanism for organic contaminants, including BTEX. The partitioning coefficient (K_d) calculated by the (K_oc) method takes into consideration the fraction of organic carbon (f_oc) equal to (0.0001). The recommended value by EPA for drilling sites where the soil is removed during well-pad construction [28]. Henry’s law constants and diffusion coefficients were computed by EPA online site assessment tool [29].
The model only considers longitudinal dispersivity, which can be estimated from the empirical equations approved in most of the analytical models. The diffusion is small in magnitude compared to mechanical dispersion [30] and is often neglected in modeling approaches. The longitudinal dispersivity in the unsaturated zone transport model is estimated to be 0.1 m based on a preliminary study [31]. Table 1 shows the parameters of the soils of the study area.

Table 1. Model parameters.

| Parameter       | Description                                      | Unit      | Value |
|-----------------|--------------------------------------------------|-----------|-------|
| $K_{oc}$        | Liquid–solid partitioning coefficient for soil   | mL/g      | 67    |
| $f_{oc\,\text{max}}$ | Fraction organic content                          |           | 0.0001|
| $C_0$           | Initial concentration                             | mg/L      | 0.28  |
| $K_h$           | Henry’s constant at 18 °C                         |           | 0.167 |
| $K_h$           | Henry’s constant at 22 °C                         |           | 0.23  |
| $Q_r$           | Residual water content loamy soil 1st scenario    |           | 0.078 |
| $Q_r$           | Residual water content loamy soil 2nd scenario    |           | 0.0702|
| $Q_r$           | Residual water content sandy clay loam soil 1st scenario |           | 0.1   |
| $Q_r$           | Residual water content sandy clay loam soil 2nd scenario |           | 0.09  |
| $Q_r$           | Residual water content silt loam soil 1st scenario |           | 0.067 |
| $Q_r$           | Residual water content silt loam soil 2nd scenario |           | 0.0603|
| $i$             | Hydraulic gradient                                | cm/cm     | 0.001 |
| $a_x$           | Longitudinal dispersivity                         | cm        | 10    |
| $D_{uw}$        | Diffusion coefficient in free water at 18 °C      | cm$^2$/day| 0.747 |
| $D_{uw}$        | Diffusion coefficient in free water at 22 °C      | cm$^2$/day| 0.847 |
| $D_a$           | Diffusion coefficient in soil air at 18 °C        | cm$^2$/day| 7439  |
| $D_a$           | Diffusion coefficient in soil air at 22 °C        | cm$^2$/day| 7629  |
| $\rho$          | Bulk density                                      | g/cm$^3$  | 1.6   |

2.2.2. Model Validation

Model validity check was performed by comparing HYDRUS 1D simulation outputs by available data obtained from designated US governmental bodies monitoring groundwater quality [35]. It is a database regarding groundwater pollution obtained from domestic water wells near the spill location.

3. Results and Discussions

3.1. The Effect of Soil Properties and Solute Characteristics on Contaminant Transport

The results show that the soil properties and solute characteristics that depend on the temperature have a major and important role in determining the level of groundwater pollutants with benzene. A rise in temperature and, consequently, soil loss of part of the water content due to evaporation may threaten shallow groundwater aquifers with benzene. As shown in Table 2, the maximum concentration ($C_{\text{max}}$) in the loam and sandy clay loam soils is somewhat close to the initial concentration ratio, which is (0.28 mg/L), and this is due to the low fraction of organic carbon in the soil because of soil removal to prepare and construct well pads. As for silt loam soil, the result showed that it has a higher ability to absorb benzene.

Table 2. The maximum concentration mg/L into the water table set at a depth of 100 cm.

| Type of Soil   | $C_{\text{max}}$ of Benzene at 18 °C | $C_{\text{max}}$ of Benzene at 22 °C |
|----------------|-------------------------------------|-------------------------------------|
| Loam           | 0.25108                             | 0.26469                             |
| Sandy clay loam | 0.24335                             | 0.26265                             |
| Silt loam      | 0.11666                             | 0.13243                             |
The anticipated increase in earth’s average surface temperature by 4 °C could increase the $C_{\text{max}}$ of benzene in the aquifers a few centimeters below the surface due to a supposed oil spill by (0.01361 mg/L) in loamy soil, (0.0193 mg/L) in sandy clay loam soil, and (0.01577 mg/L) in silt loam soil.

Figures 2–4 show the results of the maximum concentrations concerning water table depth at 100 cm. The tables show an increase in the $C_{\text{max}}$ of benzene in groundwater in the second scenario due to a rise in surface temperatures.

**Figure 2.** $C_{\text{max}}$ of benzene at depth 100 cm—Loam soil.

**Figure 3.** $C_{\text{max}}$ of benzene at depth 100 cm—Sandy clay loam soil.
As shown in Figures 2–4, the \( C_{\text{max}} \) of benzene was registered in a water table at 100 cm depth after 200 days. Loam soil may reduce the maximum concentration by 10%; this value may reduce to 0.07% due to a rise in temperature because of climate change. While sandy clay loam soil may reduce the maximum concentration by 14%, this value may reduce to 0.07%, and while silt loam soil may reduce the maximum concentration by 60%, this value may reduce to 53% due to the same reason mentioned before.

3.2. The Distribution Coefficient Role in Controlling Contaminant Transport

Generally, there are processes of a chemical or biochemical nature that affect the fate of pollutants transported in the unsaturated zone. The retardation factor \( (R) \) is a consequence of the processes that prevent the transfer of polluting substances. The retardation factor is defined as the ratio between the transport velocities of the pollutant concerning the groundwater flow. The most widely used method to estimate the retardation of pollutants due to absorption is based on the distribution coefficient \( (K_d) \).

The distribution coefficient \( (K_d) \) plays a key role in controlling the solute migration in the unsaturated zone. The estimated \( (K_d) \) values show a very wide range in the literature, and this makes finding its generic value more difficult [36]. In addition to the organic carbon partition coefficient \( (K_{oc}) \), the distribution coefficient \( (K_d) \) depends on the organic carbon in the soil \( (F_{oc}) \). Soil organic carbon is diverse in its composition and components that differ in particle size and rate of decomposition. Organic carbon is the main energy source for soil microbes, which plays a major role in organic pollutants absorption. In this study, \( (K_d) \) was computed with a very small low fraction of organic carbon, as mentioned earlier, because the soil was removed. However, if we re-stimulate the benzene migration through the soils by using the value found in the literature (0.002 g/g) and recommended by EPA [36] the role of \( (K_d) \) was noticed as shown in Figures 5–7.

In Figures 5–7, the role of the \( K_d \) appears especially in loam and sandy clay loam soils. The value of \( K_d \) proposed in the literature reduced the maximum concentration by (0.00097 mg/L) in loamy soil and (0.00085 mg/L) in sandy clay loam soil, while a lower reduced value was noticed in a silt loam soil (0.00018 mg/L) because the steady state is reached in all cases.
Figure 5. The effect of the distribution coefficient ($K_d$)—Loam soil.

Figure 6. The effect of the distribution coefficient ($K_d$)—Sandy clay loam.
4. Conclusions

In this work, the risk of benzene contamination in groundwater was evaluated in one of the oil fields, California, US. The effect of different factors was investigated, including climate change, soil classification, and water table depth. The study was conducted to analyze the impact of climate change on benzene concentration in the groundwater due to surface spills of hydraulic fracturing fluids. Two temperature-dependent parameters were used as a key factor; soil moisture and diffusion of benzene were calculated, taking into consideration the present average annual surface temperature and that by the end of the current century in California, USA. By using the HYDRUS 1D transport model, two scenarios were simulated. The following conclusions can be drawn from this research:

- The expected rise in temperature due to climate change can appreciably affect the soil moisture, which considers the first barrier to protect the groundwater from surface sources of contaminants.
- Diffusion coefficient of benzene in the soil is an important characteristic that is directly proportional to the temperature; therefore, it is a factor that led to increasing groundwater contamination.
- Sorption processes cause a delay in the benzene movement concerning water velocity, which is generally quantified by the coefficient of partition (or distribution), especially in loamy and sandy clay loam soils.
- An anticipated increase in earth’s average surface temperature by 4 °C due to climate change could lead to a rise in the level of groundwater pollution in the study area by 0.017 mg/L in loamy soil, 0.00046 mg/L in sandy clay loam soil, and 0.00023 mg/L in silt loam soil.
- Climate change may reduce the amount of benzene absorbed from (10 to 0.07)% in loamy soil, from (14 to 0.07)% in sandy clay loam soil, and from (60 to 53)% in silt loam soil.
- The impact of benzene in shallow groundwater aquifers is slight, demonstrating that any impact would take more than 200 days to be considerable.
- Groundwater aquifers that are only 100 cm away from the spill source are more threatened by contamination. As the depth of the groundwater increases, it is safe from surface sources pollutants.

Figure 7. The effect of the distribution coefficient ($K_d$)—Silt loam soil.
• Construction of the well pad can substantially reduce the organic carbon in the soils, therefore, reducing its role in controlling the movement of pollutants.

**Author Contributions:** Conceptualization and methodology, A.J.D.A. and J.F.L.B.; investigation and analysis, A.J.D.A. and M.J.K.B.; writing—original draft preparation A.J.D.A. and M.J.K.B.; writing—review and editing, A.J.D.A. and M.J.K.B.; supervision and project administration, J.F.L.B. and M.J.K.B. All authors have read and agreed to the published version of the manuscript.

**Funding:** This research received no external funding.

**Institutional Review Board Statement:** Not applicable.

**Informed Consent Statement:** Not applicable.

**Data Availability Statement:** The datasets generated during and/or analyzed during the current study are available from the corresponding author on reasonable request.

**Conflicts of Interest:** The authors declare that they have no conflict of interest.

**References**

1. U.S. Energy Information Administration. *Proved Reserves of Crude Oil and Natural Gas in the United States, Year-End 2019*; U.S. Energy Information Administration: Washington, DC, USA, 2021.

2. Mojid, M.R.; Negash, B.M.; Abdulaleah, H.; Jufar, S.R.; Adewumi, B.K. A state-of–art review on waterless gas shale fracturing technologies. *J. Pet. Sci. Eng.* 2021, 196, 108048. [CrossRef]

3. U.S. Department of Energy. *Economic and National Security Impacts under a Hydraulic Fracturing Ban*; U.S. Department of Energy: Washington, DC, USA, 2021.

4. De Voogt, P. *Reviews of Environmental Contamination and Toxicology*; Springer: Berlin/Heidelberg, Germany, 2015; Volume 236.

5. Almaliki, A.J.D.; Bashir, M.J.K.; Borrajo, J.F.L. Appraisal of groundwater contamination from surface spills of fluids associated with hydraulic fracturing operations. *Sci. Total Environ.* 2022, 815, 152949. [CrossRef] [PubMed]

6. Fayemiwo, O.M.; Daramola, M.O.; Moothi, K. BTEX compounds in water–future trends and directions for water treatment. *Water SA* 2017, 43, 602. [CrossRef]

7. Rosecrans, C.Z.; Landon, M.K.; McMahon, P.B.; Gillespie, J.M.; Kulongoski, J.T.; Stephens, M.J.; Hunt, A.G.; Shimabukuro, D.H.; Davis, T.A. Groundwater Quality of Aquifers Overlying the Oxnard Oil Field, Ventura County, California. *Sci. Total Environ.* 2021, 771, 144822. [CrossRef] [PubMed]

8. Clancy, S.A.; Worrall, F.; Davies, R.J.; Gluyas, J.G. The potential for spills and leaks of contaminated liquids from shale gas developments. *Sci. Total Environ.* 2018, 626, 1463–1473. [CrossRef] [PubMed]

9. USDA_NASS. *California Agricultural Overview*; USDA_NASS: Athens, GA, USA, 2016.

10. Azar, M.; Han, S.; Davis, S.; Ayers, A. Example the impact of hydraulic fracturing on groundwater quality in the perim Basin, West Texas, USA. *Water 2020,* 12, 796. [CrossRef]

11. Taylor, R.G.; Scanlon, B.; Stadler, B.; Rodell, M.; Van Beek, R.; Wada, Y.; Longuevergne, L.; Leblanc, M.; Famiglietti, J.S.; Edmunds, M.; et al. Ground water and climate change. *Nat. Clim. Chang.* 2013, 3, 322–329. [CrossRef]

12. Catna, M.O.; Gleeson, T.; Moosdorf, N.; Befus, K.M.; Schneider, A.; Hartmann, J.; Lehner, B. Global patterns and dynamics of climate–groundwater interactions. *Nat. Clim. Chang.* 2019, 9, 137–141. [CrossRef]

13. Olabisi, O. Integrated Reservoir Characterization of a Miocene Submarine Fan System, Midway-Sunset Oil Field, San Joaquin Basin, California, USA. In Proceedings of the 2018 AAPG Pacific Section Meeting, Bakersfield, CA, USA, 22–25 April 2018; Volume 20431.

14. Natural Resources Conservation Service; United States Department of Agriculture. Soil Survey of Kern County, California, Southwest Part. California, 2009. Available online: http://soils.usda.gov/survey/printed_surveys/ (accessed on 24 March 2022).

15. Šimunek, J.; Genuchten, M.T. Modeling Nonequilibrium Flow and Transport Processes Using HYDRUS. *Vadose Zone J.* 2008, 7, 782–797. [CrossRef]
21. Rassam, D.; Šimůnek, J.; Mallants, D.; van Genuchten, M.T. The HYDRUS-1D Software Package for Simulating the Movement of Water, Heat, and Multiple Solutes in Variably-Saturated Media: Tutorial, version 1.00; No. July. 2018: CSIRO Land and Water University of California Riverside, Riverside, CA, USA. Available online: https://www.pc-progress.com/Downloads/Public_Lib_H1D/HYDRUS-1D_Tutorial_V1.00_2018.pdf (accessed on 2 January 2022).

22. Šimůnek, J.; Šejna, M.; Saito, H.; Sakai, M.; van Genuchten, M.T. Version 4.08 January 2009. Department of Environmental Sciences/University of California Riverside, Riverside, CA, USA. Available online: https://www.pc-progress.com/Downloads/Pgm_hydrus1D/HYDRUS1D-4.08.pdf (accessed on 2 January 2022).

23. Parrish, C. Developing joint probability distributions of soil water retention characteristics. Water Resour. Res. 1988, 24, 755–769.

24. Cheng, L.; Hoerling, M.; Aghakouchak, A.; Livneh, B.; Quan, X.W.; Eischeid, J. How has human-induced climate change affected California drought risk? J. Clim. 2016, 29, 111–120. [CrossRef]

25. Goertler, P.; Mahardja, B.; Sommer, T. Striped bass (Morone saxatilis) migration timing driven by estuary outflow and sea surface temperature in the San Francisco Bay-Delta, California. Sci. Rep. 2021, 11, 1510. [CrossRef] [PubMed]

26. Harter, T. Basic Concepts of Groundwater Hydrology; UCANR Publications: Davis, CA, USA, 2003; Volume 8083, pp. 1–6. [CrossRef]

27. US Environmental Protection Agency. Evaluation of Impacts to Underground Sources of Drinking Water by Hydraulic Fracturing of Coalbed Methane Reservoirs Final. In Ground Water; US Environmental Protection Agency: Washington, DC, USA, 2004; p. 463. [CrossRef]

28. Kanno, C.M.; McCray, J.E. Evaluating potential for groundwater contamination from surface spills associated with unconventional oil and gas production: Methodology and application to the south platte alluvial aquifer. Water 2021, 13, 353. [CrossRef]

29. EPA. EPA On-line Tools for Site Assessment Calculation | Ecosystems Research | US EPA. 2022. Available online: https://www3.epa.gov/ceampubl/learn2model/part-two/onsite/estdiffusion.html (accessed on 2 January 2022).

30. Jha, R.K.; Bryant, S.L.; Lake, L.W. Effect of diffusion on dispersion. SPE J. 2011, 16, 65–77. [CrossRef]

31. Troldborg, M.; Binning, P.J.; Nielsen, S.; Kjeldsen, P.; Christensen, A.G. Unsaturated zone leaching models for assessing risk to groundwater of contaminated sites. J. Contam. Hydrol. 2009, 105, 28–37. [CrossRef] [PubMed]

32. Ahn, J.; Rao, G.; Mamun, M.; Vejerano, E.P. Soil–air partitioning of volatile organic compounds into soils with high water content. Environ. Chem. 2020, 17, 545. [CrossRef]

33. Thomas, H. Sampling and Analysis of Water Streams Associated with the Development of Marcellus Shale Gas; Final Report; Marcellus Shale Coalition: Pittsburgh, PA, USA, 2009.

34. Bear, S.J.; Prince, F.E.; Toth, A.L. Effect of Increasing Fertilizer Concentration on Exchangeable Cation Status of Soi. Soil Sci. Soc. Am. J. 1973, 37. [CrossRef]

35. COGCC. COGCC Data. 2022. Available online: https://cogcc.state.co.us/documents/data/downloads/environmental/WaterWellDownload.html (accessed on 2 January 2022).

36. USEPA. Understanding variation in partition coefficient, Kd, values. Volume I: The Kd Model, Methods of Measurement, and Application of Chemical Reaction Codes. Environ. Prot. Agency 1999, 1, 212.