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SECRETARÍA DE INVESTIGACIÓN Y POSGRADO

VULNERABILIDAD DE UN ACUÍFERO BAJO CONDICIONES ÁRIDAS Y ESCENARIOS DE CAMBIO CLIMÁTICO: DIAGNÓSTICO Y PROSPECCIÓN

POR:

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Vulnerabilidad de un acuífero bajo condiciones áridas y escenario de cambio climático: diagnóstico y prospección. Disertación presentada por Aurora Mendieta Mendoza como requisito parcial para obtener el grado de Doctor in Philosophia, ha sido aprobado y aceptada por:

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A Dios, mi familia, compañeros, amigos y maestros .

Gracias por ser parte de esta odisea.

DEDICATORIA

A lo más sacro que tengo en el mundo:

mi familia

Al arquetipo de mujer que persigo ser:

Guadalupe Mendieta (1978-2020)

A mis abuelas:

Alicia Camarena (1935-2019) y Aurora Alvarado (1934-2020)

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GENERAL ABSTRACT

VULNERABILITY OF AN AQUIFER UNDER ARID CONDITIONS AND CLIMATE CHANGE SCENARIOS: DIAGNOSIS AND PROSPECTING

BY:

M.C. AURORA MENDIETA MENDOZA

In Chihuahua, agriculture is one of the most important economic activities which requires large amounts of water, producing a deficit and low quality of surface and ground water . The objective was to evaluate chemical vulnerability of the Jiménez-Camargo aquifer under historical and current conditions, as well as to project future scenarios of vulnerability under climate change conditions. The methodology was carried out using a) in situ and spectrometric techniques for the measurement of chemical species in water, b) use of historical data of chemical, hydrological, geological and climatic variables, c) use of tools such as statistical and SIG for spatial evaluation and description of variables, and d) modelling methodologies (DRASTIC, DRASTICL, DRSTIL) and climate change scenario tools (RCP 4.5 and 8.5) to obtain indices of aquifer vulnerability. As a result, the concentrations of TDS, Ca, Mg, S, Cl, and As in water exceeded the limit established by Mexican and international regulations. Through multivariate analysis, it was determined that the origin of the elemental composition is due to minerals in the soil and sediments that compose the aquifer geologically. Thus the wells were classified into three groups located in different areas, based on: a) alkaline earth elements, b) halogens, c) dissolved ions. Due to the high content of salts in groundwater, isotopic U concentration was obtained by comparing three

radiochemical techniques, which yielded statistically similar results. ^{238,234}U activity concentrations exceeded the limit established by Mexican regulations. However, by using DRASTIC, DRASTICL, DRSTIL models, it was determined that the south zone is the most sensitive to pollution of groundwater. The results by climate change scenarios showed that the area of highest recharge decreases while aquifer vulnerability increases. Thus, the deficit problem of replenishment from recharge to the aquifer remains from present conditions, and has the potential to increase in the future.

RESUMEN GENERAL

VULNERABILIDAD DE UN ACUÍFERO BAJO CONDICIONES ÁRIDAS Y ESCENARIOS DE CAMBIO CLIMÁTICO: DIAGNÓSTICO Y PROSPECCIÓN

POR:

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En Chihuahua, la agricultura es una de las actividades económicas más importantes que requiere grandes cantidades de agua, produciendo un déficit y baja calidad en agua superficial y subterránea. El objetivo fue evaluar la vulnerabilidad química del acuífero Jiménez-Camargo en condiciones históricas y actuales, así como proyectar escenarios futuros de vulnerabilidad ante condiciones de cambio climático. La metodología se llevó a cabo utilizando a) técnicas *in situ* y espectrométricas para la medición de especies químicas en el agua, b) uso de datos históricos de variables químicas, hidrológicas, geológicas y climáticas, c) uso de herramientas estadísticas y SIG para evaluación, así como la descripción de variables, y d) metodologías de modelado (DRASTIC, DRASTICL, DRSTIL) con herramientas de escenarios de cambio climático (RCP 4.5 y 8.5) para obtener índices de vulnerabilidad de acuíferos. Como resultado,

las concentraciones de SDT, Ca, Mg, S, Cl y As en el agua excedieron el límite establecido por las regulaciones mexicana e internacionales. Mediante análisis multivariado, se determinó que el origen de la composición elemental se debe a los minerales del suelo y sedimentos que componen geológicamente el acuífero. Así, los pozos se clasificaron en tres grupos ubicados en diferentes áreas, en base a: a) elementos alcalinotérreos, b) halógenos, c) iones disueltos. Debido al alto contenido de sales en las aguas subterráneas, la concentración de U isotópico se obtuvo mediante la comparación de tres técnicas radioquímicas, que arrojaron resultados estadísticamente similares. Las concentraciones de actividad de $238,234U$ excedieron el límite establecido por la normativa mexicana. Por otro lado, al utilizar los modelos DRASTIC, DRASTICL, DRSTIL, se determinó que la zona sur es la más sensible a la contaminación de las aguas subterráneas. Los resultados por escenarios de cambio climático mostraron que el área de mayor recarga disminuye mientras aumenta la vulnerabilidad del acuífero. Por lo tanto, el problema del déficit de la reposición de la recarga del acuífero sigue siendo de las condiciones actuales y tiene el potencial de aumentar en el futuro.

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GENERAL INTRODUCTION

Groundwater has become the main source of water in many societies around the world. It is the primary source of water for domestic, urban, agricultural and industrial use. Over the last 40 years, there has been an accelerated increase of groundwater use for irrigation along with increased groundwater pumpage (López, Arras et al. 2011). This jeopardizes the agricultural economy as well as food and water security for the region.

In this context, southeaster part of the state of Chihuahua is located in one largest semiarid ecosystem in the north of Mexico; which gives it a fragile state susceptible to droughts. The Jimenez-Camargo aquifer is located in this zone and is under increased water demand and "hardened demand" from long-term orchards that require water over decades and not just seasonal or interannual demands for irrigation. Besides, it is an important agricultural area, which is the main economic source to local inhabitants. The predominant agriculture in the region are pecans orchards (65.7%) with a total surface of 247,969 ha., and have increased owing to high export demand up to 89% since 1980 (CONAGUA 2018, CONAGUA 2020), along with increases in other seasonal crops with high water demand such as alfalfa (28.53%), grain corn (11.25%), oat (7.84%), and pepper (19.84%) (SAGARPA 2019).

Therefore, the evaluation of hydrochemistry and radioisotopes are a useful tool to governmental and private agencies, which must consider prioritizing groundwater resource and to implement sustainable management programs to provide not only drinking water but also water of good quality for food production and

maintain the health of land and water resources. The overarching goal of this research was to evaluate hydrochemistry and radioisotopes of an aquifer under arid conditions and agriculture use to assessment chemical vulnerability as well as potential vulnerability zones with DRASTIC method. Improved methods included climate change scenarios projected to the future, using RCP 4.5 and 8.5, for the assessment of potential vulnerability within this aquifer system. These results have practical relevance for decision making about the agronomic, urban, and industrial uses for upcoming and future decades in the southeast part of the state of Chihuahua.

LITERATURE REVIEW

Groundwater

Groundwater is the water that completely saturates the pores or interstices of the subsoil. In Mexico presents an average annual recharge of 91,788 hm^3 of which 38.9% supplied (33310 hm^3 $year^{-1}$) the country's total water consumption. It is used mainly for crops irrigation with 76.3%, 14.6% in public consumption with more than 71 million people (55 million in urban areas and 16 million in rural areas), 4.8% in energy generation and 4.3% in industrial facilities (at least 50% of self-supplied industrial facilities) (Martínez Austria, Díaz-Delgado et al. 2019).

Groundwater quality comprises the physical, chemical, and biological qualities of ground water. Temperature, turbidity, color, taste, and odor make up the list of physical water quality parameters. Since most ground water is colorless, odorless, and without specific taste, we are typically most concerned with its chemical and biological qualities. Naturally, groundwater contains mineral ions; that slowly dissolve from soil particles, sediments, and rocks as the water travels along mineral surfaces in the pores or fractures of the unsaturated zone of the aquifer. They are referred to as dissolved solids and can be divided into three groups: major constituents (Na, Ca, Mg, HCO_3^-, $SO4^{-2}$, and Cl^-), minor constituents (K, Fe, Sr, CO_3^{-2} and NO_3) and trace elements (Al, As, Br, Cd, Cr, Co, Cu, Mg, Ni, Se, U and Zn). At a high TDS concentration, water becomes saline and is a problem for irrigation on crops with low or medium salt tolerance.

Groundwater pollution

Human activities can alter the natural composition of ground water through the disposal or dissemination of chemicals and microbial matter at the land surface and into soils, or through injection of wastes directly into ground water.

Chemical pollution of groundwater

Currently the analysis of chemical species such as trace elements in groundwater has been increasing (Cervantes-Trejo, Pinedo-Álvarez et al. 2018). The presence of this species is mainly due to two factors. The first one is related to the leaching of the soil and rocks; transported by air and water. While the second one is related to the waste from human activities (urbanization, mining, waste generated by industries and households and agriculture) that are discharged into the environment (Gutiérrez and Carreon 2008, Chumacero, Ozuky et al. 2016). Therefore, the quality of resources has been impoverished by spreading harmful elements through the trophic chains (Gu et al. 2016). For example, the presence of As has already been reported in several studies; where its presence in the state of Chihuahua is natural (Hernández 2012, Valles-Aragón et al. 2017).

Increased salinity and nutrients have also degraded productivity, as well as the soil available for agriculture, resulting in restrictions as well as additional assessments of salt and nutrient loads in major agricultural areas (Central Valley Salinity Coalition and CVSALTS 2012). This phenomenon of high amounts of salts, result in additional pumpage and irrigation to leach salts from the root zone (Hanson, McLean et al. 1994, Cahn and Bali 2015, Boyce et al. 2019, Fries, Silva et al. 2020, Rodríguez-Huerta et al. 2020).

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Groundwater pollution by natural radioisotopes

Uranium (U) is a natural radioactive element with three isotopes: ^{238}U (99.2739%), ^{235}U (0.7205%), and ^{234}U (0.0056%). In nature, U can be found forming salts and oxides in different compositions (Colmenero Sujo et al. 2004, SGM 2016). The main effect of U over the environment is its compounds toxicity. The U geochemical cycle begins with the weathering from the earth's crust leading to U mobilization in surface and groundwater, through particles or dissolved fractions (Bonotto 2017). The oxidation-reduction conditions play an important role in the U mobilization; under reduction conditions, U is mainly in + 4 oxidation state and it is insoluble while in oxidation conditions it takes + 6 oxidation state and form soluble ions (OH^-, CO_3^{-2}, F-, SO_4^{-2}, PO_4^{-3}) (Ioannidou et al. 2011, Carvalho and Fajgelj 2013).

In the State of Chihuahua, 56 localities with uraniferous activity have been recognized. The main deposits of mineral U in the state of Chihuahua are in the municipalities of Ahumada (Moctezuma), Chihuahua (San Marcos), Aquiles Serdan (Santa Eulalia), Aldama (Peña Blanca and Placer de Guadalupe) and Lopez (Sierra de Adargas). Within one of the main uranium deposits is the Sierra Adargas in the south of the State, in the municipality of Lopez, Chihuahua (SGM 2014). A previous study examined the drinking water that they auction to the city of Jimenez, finding that its U levels are according to the norm (0.58 Bq / L) (Rentería Villalobos 2004).

Aquifer vulnerability models

The management of groundwater quality presents difficult problems. Detection of contamination and monitoring of water quality are usually difficult and

costly. Besides, groundwater contamination varies spatially; for example, not all places are equally affected or equally vulnerable. Protection strategies, therefore, need to be targeted upon those areas most threatened in order to provide the greatest benefit for a given investment. Targeting must be based upon reliable forecasts of the risk of groundwater pollution under a variety of possible future climate/socio-economic/land use scenarios (Twarakavi and Kaluarachchi 2006). In most instances, modeling and mapping of groundwater vulnerability to pollution is considered a critical first-step in implementing groundwater management programs (Li 2012).

During the past 35 years, a variety of methods for modeling and mapping groundwater vulnerability have been developed. These models typically involve the analysis of the inter-relationships between hydrogeologic characteristics (depth to water, soils, hydrogeology and recharge) and, sometimes, land use and land cover (LULC). Land uses involve application of farm chemicals that had been influenced the groundwater quality (Kozłowski and Sojka 2019, Shahab et al. 2019). Although groundwater vulnerability models generally consider similar factors, the models employ different approaches for data integration and analysis. These can be grouped into three categories: index methods (Aller 1985), statistical procedures and process-based methods (Focazio et al. 2002).

Groundwater pollution vulnerability models are usually implemented in a single point in time based on current hydrogeologic and LULC conditions (Butscher and Huggenberger 2009). However, groundwater vulnerability is strongly dependent on factors such as depth to water table, recharge and LULC conditions, all of which

are influenced by climate conditions and human activities. Climate change can potentially alter the vulnerability of shallow aquifers by affecting depth to water table and recharge (Toews and Allen 2009). And, human activities such as changes in LULC can also affect groundwater vulnerability. It has been forecast that agricultural land use, and associated application of farm chemicals, may change quite significantly as a result of global warming and/or changing socio-economic (Li 2012).

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STUDY I. RECONNESAINCE OF CHEMICALLY VULNERABLE AREAS OF AN AQUIFER UNDER ARID CONDITIONS WITH AGRICULTURAL USES

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ABSTRACT

RECONNESAINCE OF CHEMICALLY VULNERABLE AREAS OF AN AQUIFER

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Agriculture is one of most important economic activities that requires large amounts of water, which, in addition to changes in climate, presents a major impact on the water availability. Excess of salt and nutrient concentrations build up damages to soil such as reduced drainage and increase in anoxic conditions in the root zone, as well as decreasing productivity and usable farm lands. The objective of the present study was to evaluate the chemical vulnerability of an aquifer in arid conditions with a high level of extraction through the detection of risk zones and potential subregions of different risks. An evaluation of the quality of the groundwater was performed, as a reconnaissance prior to more detailed studies, in which samples of 30 wells were analyzed to determine physical-chemical parameters (recorded *in situ*), dissolved chemical species (UV-Vis spectrophotometry), and elemental content (X-ray fluorescence spectrophotometry). Concentrations of TDS, as well as Ca, Mg, S, Cl, and As determined in the water under analysis exceeded the limit established for water for consumption and irrigation. It is suggests that the origin of the elemental composition is mainly due to the mineral composition of the aquifer sediments. The wells were classified in three groups located in different zones, based on: a) alkaline earth elements, b) halogens, c) dissolved ions. Water salinity is mainly composed by sulphates and, a lesser extent, by hydrochloric salts from leaching of evaporites. Furthermore, the highest chemical vulnerability are

located from central to north zone, where the soils showed crop leaching requirement by above of threshold value for pecan crops, one of the major agricultural products of the valley. In conclusion, both the salinity and the high level of water extraction for agriculture, combined with the arid conditions, are provoking an increase in contents of some chemical species in soil of crops. The immediate consequences are related to a reduction in the agricultural production and, therefore, a decrease in the productive competitiveness.

Key words: Arid zone, chemical species, spatial distribution, groundwater

RESUMEN

RECONNESAINCE OF CHEMICALLY VULNERABLE AREAS OF AN AQUIFER

UNDER ARID CONDITIONS WITH AGRICULTURAL USES

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La agricultura es una de las actividades económicas más importantes, además requiere grandes cantidades de agua. Aunado a lo anterior, los cambios en el clima, presenta un gran impacto en la disponibilidad de agua. El exceso de concentraciones de sal y nutrientes acumula daños al suelo, como un drenaje reducido y un aumento de las condiciones anóxicas en la zona de las raíces, así como la disminución de la productividad en las tierras agrícolas. El objetivo del presente estudio fue evaluar la vulnerabilidad química de un acuífero en condiciones áridas con un alto nivel de extracción mediante la detección de zonas de riesgo y subregiones potenciales de diferentes riesgos. Se realizó una evaluación de la calidad del agua subterránea, como reconocimiento previo a estudios más detallados, en la cual se analizaron muestras de 30 pozos para determinar parámetros físico-químicos (registradas *in situ*), especies químicas disueltas (espectrofotometría UV-Vis), y contenido elemental (espectrofotometría de

fluorescencia de rayos X). Las concentraciones de SDT, así como Ca, Mg, S, Cl y As determinadas en el agua bajo análisis excedieron el límite establecido para el agua para consumo y riego. Se sugiere que el origen de la composición elemental se debe principalmente a la composición mineral de los sedimentos del acuífero. Los pozos se clasificaron en tres grupos ubicados en diferentes zonas, con base en: a) elementos alcalinotérreos, b) halógenos, c) iones disueltos. La salinidad del agua está compuesta principalmente por sulfatos y, en menor medida, por sales clorhídricas procedentes de la lixiviación de evaporitas. Además, la mayor vulnerabilidad química se encuentra desde la zona central a la norte, donde los suelos mostraron un requerimiento de lixiviación de los cultivos por encima del valor umbral para los cultivos de nuez, uno de los principales productos agrícolas de esta zona. En conclusión, tanto la salinidad como el alto nivel de extracción de agua para la agricultura, combinado con las condiciones áridas, están provocando un aumento en los contenidos de algunas especies químicas en el suelo de los cultivos. Las consecuencias inmediatas están relacionadas con una reducción de la producción agrícola y, por tanto, una disminución de la competitividad productiva.

Palabras clave: zona árida, especies químicas, distribución espacial, agua subterránea

INTRODUCTION

Worldwide there are different regions that are facing severe consequences resulting from climate change and related overexploitation of natural resources such as water and land. The Latin American region is currently facing situations of severe exposure to climate-related risks such as tropical cyclones, flooding, droughts, and heat waves (Selvakumar, Ramkumar et al. 2017). Furthermore, the climate has started to present variations, for which changes in the climate are expected to occur with higher frequency in the coming decades (Banco del Desarrollo de America Latina 2014). In addition, the close relationship between human activities and overexploitation of water and land use results in environmental pollution (Gu, Gao et al. 2016). Heavy metals (Cr, Cd, Cu, Fe, Hg) released from aquifer sediments or from human sources, some organic substances (solvents, hydrocarbons, dyes), as well as several chemical products (resulting from household, pharmaceutical, industrial, and agricultural waste, among others) are among the contaminants found most commonly in water. These can have and acute or chronic impact on the environment (Wang *et al.*, 2014; Chacon-Chumancero *et al.*, 2016). The increase in salinity and nutrients has also degraded the productivity as well as the land available for agriculture, and has resulted in the need for restrictions and additional assessment of salt and nutrient loadings in major agriculatural areas (Central Valley Salinity Coalition and CVSALTS 2012). Collectively, these deteriorating conditions threaten the sustainability of the resources as well as food and water security.

The southeastern part of the state of Chihuahua is located within one of the largest semi-arid ecosystems in the north of Mexico, which gives it a fragile state,

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susceptible to droughts. The Pecan (*Carya illinoinensis*) is native to northern Mexico and is considered one of the most profitable fruit species (SAGARPA 2011), both for its production (nuts) and for its timber (Diaz Rizo, Castillo et al. 2011). It is cultivated in the central-southern part of the state of Chihuahua, mainly in the municipalities Jimenez, Delicias, Camargo, and Saucillo (Ojeda-Barrios *et al.*, 2010), because of the ideal climatological conditions: a dry semi-arid climate, hot summers, alkaline soil, and a long period without frost (Valles-Aragón *et al.* 2017). That crop is mainly supplied by groundwater, which is not strictly regulated and, consequently, is potentially not sustainable managed. Chemical vulnerability of any medium is described by factors such as the degree of disturbance by contaminants from natural or human sources, the susceptibility to be contaminated, the detrimental effects (lack of water quality) which limits its beneficial uses, and the ability to response and recovery (to mitigate and address the risks associated with pollutants) (Belitz, Jurgens et al. 2016). This, in turn, jeopardizes the agricultural economy of the region, as well as food and water security for the region.

It is important to note that current monitoring programs do not provide a complete spectrum of measurement and analysis of toxic substances that are affecting groundwater quality and agricultural sustainability. Thus, when water conditions are less favorable, the major crops suffers from toxicity and a nutrient imbalance (Chowdhury *et al.*, 2016), commonly, salinity. In addition, factors such as high water tables, soil type changes in the profile, soil compaction, soil salinity, and soil fertility, may restrict root development. As a result, absorption of nutrients through the roots is reduced, lowering growth of the leaves, buds, and fruits (Ben Salem et al., 2014), and overall crop productivity . This also requires more irrigation

to leach the root zone and this indirectly drives further overexploitation of the groundwater resources. Because of this, studies on the current situation of the aquifers based on the availability of the resource are needed, due to the environmental conditions and overexploitation. The assessment of chemical vulnerability including emerging contaminants have to be determinted as it has been carried out in zones with intense agriculture practices such as Central Valley, CA, USA (Belitz, Dubrovsky et al. 2003, Harter, Rollins et al. 2008, Belitz, Jurgens et al. 2016). In that region, it has implemented the Sustainable Groundwater Management Act that have identified in new laws and regulations that these vulnerabilities are unacceptable and are termed undesirable results from overexploitation of the groundwater resources and conjunctive use of surface and ground water (SGMA 2014), through the detection of risk areas. Therefore, the evaluation of chemical vulnerability is a useful tool to governmental and private agencies, which must consider prioritizing groundwater resource and to implement sustainable management programs to provide not only drinking water, but also water of good quality for food production and maintain the health of land and water resources. The objective of the present reconnaissance study was to make a preliminary evaluation of the chemical vulnerability of an aquifer under arid conditions and to explore detection of risk and related risk areas with a high rate of consumption and extraction, as well as additional potential contaminants. Without a well-defined program of long-term management and related limits to uses, these deleterious effects can result in further overexploitation and degradation of the groundwater quality plus secondary adverse effects such as groundwater storage depletion and related land subsidence and capture of streamflow.

MATERIALS AND METHODS

To identify and delineate potential vulnerability and risk zones based on groundwater availability in an agricultural area the following aspects were evaluated: a) evaluation of the quality of the groundwater including diverse chemical species, and b) identification of risk areas based on statistical methods such as PCA and Cluster analysis combined with risk indicators such as SAR and CLR to help frame the potential risks to agriculture from various poor-quality waters from multiple sources.

Study site. The aquifer of Jimenez-Camargo is located in the extreme southeast of the state of Chihuahua and measures 9947.7 km^2. It is located between the coordinates 27°08" North and 104°55" West, at a height of 1,380 m above sea level (INAFED 2017). The climate is semiarid, with a mean annual temperature of 18.7 °C and an average annual precipitation of 380 mm (CONAGUA 2008). The study site is located in Hydrological Region 24, from the Rio Bravo Conchos basin to the Rio Florido basin. The region is influenced by three sub-basins: Rio Florido Camargo (RH24Ma), Rio Florido-Jimenez (RH24Mb), and Rio Parral (RH24Md) (figure 1). The aquifer is almost completely composed of alluvial material located in the lower parts of the valley from the north to the southeast. The aquifer Jimenez-Camargo is an unconfined aquifer, with some regions semiconfined. The surface is composed of sand and gravel, and can even contain accumulated clay and/or carbonate-sulphate minerals, therefore its nature generates a high content of some chemical species (Hernández 2012). Sedimentary rocks are present in the aquifer, clustered from the north to the southeast, as well as limestones, shales, and

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sandstones. Igneous rocks of the following types also outcrop in different areas, rhyolites, volcanic rocks, and basalts (CONAGUA 2018). The soil of the aquifer is mainly composed of xerosol which is characteristic of dry areas, with a clear and thin surface, with highly variable amounts of organic matter depending on the type of texture. Under this layer there is an accumulation of clay minerals and/or carbonates or sulfates; at a certain depth there are spots, lime agglomerations, and gypsum or caliche crystals (CONAGUA 2018). In the zone, there are mining districts of Pb, Fe, Zn, Mn, Cu, and Ba (Servicio Geológico Mexicano 2007, INAFED 2017, INEGI 2017). Figure 1 shows the location of the study area, as well as the locations of the wells sampled.

Evaluation of the water quality

Water sampling

The Jimenez-Camargo aquifer is placed in the municipalities of Allende, Coronado, Camargo, Jiménez, López, Matamoros, and Santa Barbara. In this aquifer, there is a total of 1326 wells, where 303 of these are inactive. The water uses of them are for agriculture (829), urban consumption (105), livestock (54), unidentified (22), diverse (12), and industry (1). In the present study, and according to the criteria established to an aquifer scale proportion (Belitz, Jurgens et al. 2010), a subset of wells was evaluated for this initial reconnaissance in the area of the most intensive agriculture production; this area has 208 wells for irrigation and it is located in the municipality of Jiménez (Figure 1).
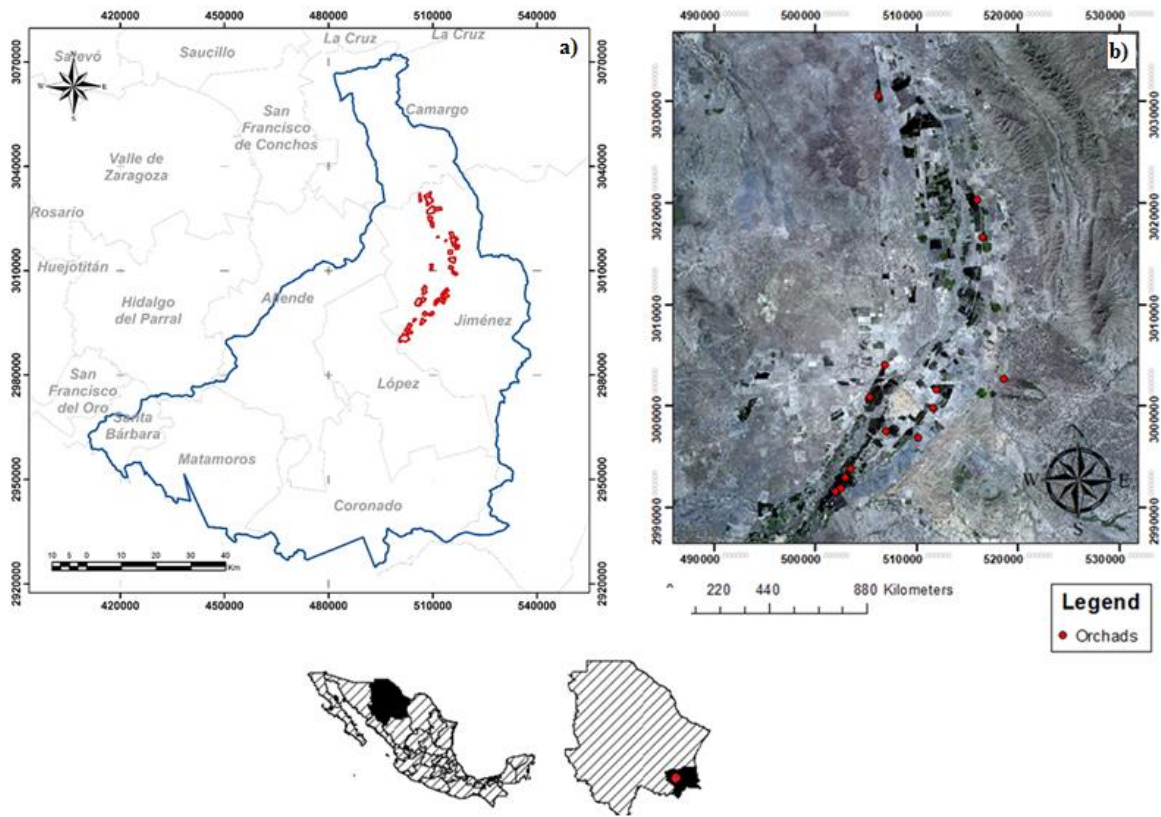
Figure 1. Location of study area: a) sub-basin Bravo-Conchos, and b) location of the sampled wells.

Thus, water samples from 30 wells used for irrigating pecan-producing orchards were analyzed for water quality and water chemistry. Samples were taken in sterile polypropylene containers of 1 L (NOM-014-SSA1-1993 1993) that were placed on ice (4°C ±1°C) until further analysis. Depth of sampled wells are between 130 to 150 m. Sample locations were determined randomly and they were located using a global positioning system (GPS).

Measurement techniques

Parameters measured *in situ* were; temperature (T), pH, turbidity (Tb), electric conductivity (EC), and total dissolved solids (TDS), using a multi-parametric equipment (Hanna, HI98130) and a portable turbidity meter (Hanna, HI, 93703). To determine anions such as sulfates, nitrates, nitrites, and chlorides a spectrophotometer was used (UV-Vis HACH d3900). The determination of the element composition was done with an X-ray fluorescent spectrophotometer (TXRF). For this, the material used in the equipment was prepared and a chemical process was performed to isolate specific elements. Prior to the analysis, the sapphire disc used in the elemental deposition process was set up using the protocol described in the manual of the equipment. Thus, sapphire discs were immersed in a 10% HNO_3 solution (Sigma-Aldrich), at 40°C for 30 min. After, these were washed with distilled water and acetone (Sigma-Aldrich), to be dried using fresh air. An aliquot of water sample of 995 μL was spiked with 5 μL of 1000 ppm Ga standard (Sigma-Aldrich) and stirring until a homogeneous mixture was achieved. From this solution, 10 μL aliquot was taken to be deposited in the sapphire discs and put under dryness at 80°C. Measurement of the inorganic chemical elements (Na, Mg, S, Cl,

Fe, Br, As, Pb, Sr, and Zn) was performed with a Bruker S2 PICOFOX spectrophotometer (USA).

Statistical analysis

To determine the origin of obtained variables, a Pearson correlation matrix was calculated using the procedure CORR in package (SAS 2000), with $P < 0.05$ and $P < 0.01$. Then, to reduce the number of variables, a Principal Component Analysis (PCA) was performed using the procedure PRINCOMP (SAS 2000), with significant values of $P < 0.05$.

Chemical vulnerability and spatial distribution maps

To estimate parameter values for areas with no information on the parameters that were quantified *in situ*, as well as for anions, cations, and metals present in the water, Kriging Interpolation was used to generate regional estimates as maps of chemical attributes. This method uses existing values surrounding the area that is to be estimated. Raster layers were generated using the program ArcGis 10.3® (Environmental Systems Research Institute 2014) with information linked to the database of the variables analyzed in the present study. The interpolations were conducted using the Geostatistical Analyst extension. Water irrigation may contain excess of salt and nutrient, as well as toxic elements leading to build up damages in soil of crops. This has been documented to limit productivity and the overall amount of usable farmland with increased salinity in the Arkansas River Valley of Colorado after decades of agriculture (Morway and Gates 2012). The chemical vulnerabilities related to salinity in water for irrigation were obtained using the sodium absorption ratio (SAR) and the crop leaching requirements (CLR). Deflocculating of clays (SAR)

is an indicator of damages such as a reduced drainage and an increase in anoxic conditions in the root zone of crops. Due to soil acts as a water reservoir, the CLR in the root zone must be known in order to determine how much irrigation water is needed. SAR and CLR were obtained by equations 1 (Minhas, Qadir et al. 2019) and 2 (Rhoades, Chanduvi et al. 1999, Laloy, Javaux et al. 2011), respectively:

$$SAR = [Na^+] / \sqrt{([Ca^{2+}] + [Mg^{2+}]) / 2} \qquad (1)$$

Where $[Na^+]$, $[Ca^{2+}]$, $[Mg^{2+}]$ are the Na, Ca, and Mg concentrations (meq/L), respectively.

$$CLR = ECw/(5*ECe-ECw) \qquad (2)$$

Where ECw is electrical conductivity of irrigation water and ECe is electrical conductivity in soil; CLR can be multiplied by 100 to obtain the fraction in percent.

RESULTS AND DISCUSSION

Evaluation of the water quality

Chemical characterization

The samples collected were compared to the Mexican regulation (NOM-127-SSA1-1994 1994, CONAGUA 2009) and the federal law on water rights, as well as to the international regulation (FAO 1976, USEPA 1996, OMS 2010). In Table 1, the results from the water quality analysis are shown. Values of pH were between 7.06 and 8.59, from neutral to slightly basic. EC showed values up to 6.25 dS m^{-1}, whereas Tb of 22.2 NTU. In addition, TDS oscillated between 386 and 3115 mg L^{-1}. Finally, T ranged from 14 to 36°C, with 15 wells above 25 °C. Furthermore, for anions, nitrate values were found from 0.50 to 32.5 mg L^{-1}; whereas nitrites presented concentrations between 0.5 and 7 mg L^{-1}. On the other hand, chlorides went up to 1760 and sulfates up to 2175 mg L^{-1}.

Element composition for elements with concentrations over 1 mgL^{-1} were observed in the following order of abundance: S>Ca>Na>Cl>Mg>K>Sr, whereas the order of abundance for elements with concentrations lower than 1 mgL^{-1} was P>Br>Zn>As>Fe>Cu>Pb.

Statistical analysis

The multivariate principal component analysis (PCA) is a factor analysis, which statistically is useful for reducing the number of variables to a few components that represent the majority of the variation (Li, Yang et al. 2017).

Table 1. Physical-chemical parameters and chemical species measured in well water.

Variables	Average	Min	Max	SD	VC	Allowed Limits				
						NOM[1]	WHO[2]	EPA[3]	FAO[4]	CONAGUA[5]
pH	7.7	7.1	8.6	0.4	6	6.5-8.5	8.5	6.5-8.5	6.5-8.4	6-9
TDS (mg L^{-1})	1095	386	3115	702	64	1000	500	500	2000	500
EC (dS m^{-1})	1.95	0.8	6.25	1288	66				3	2.02
Tb (NTU)	4.3	0.6	22.17	4.8	113	5.0	0.1	5		10
T (°C)	26.6	14	35.8	5.7	21	25				
Cl^- (mg L^{-1})	573	100	1760	356	62	250	250			250
NO_2^- (mg L^{-1})	1.3	<<1	7	2	130	1	1	1	10	0.05
NO_3^- (mg L^{-1})	7.6	0.5	32.5	10.3	137	10	10	10		5
SO_4^{2-} (mg L^{-1})	503	<<1	2175	667	133	400	400	250	960	250
Na (mg L^{-1})	53.2	9.7	153	39	74	200	75		920	
Mg (mg L^{-1})	15.5	<<1	66.2	20	127		50		60	
P (mg L^{-1})	0.5	<<1	1.7	0.48	91					0.01
S (mg L^{-1})	194	36.8	580	155	80					
Cl (mg L^{-1})	22.2	0.3	152	35	156		5			
K (mg L^{-1})	6.6	3.4	16	3.9	59	10			78	
Ca (mg L^{-1})	150	42.3	434	119	79	250			400	
Fe (mg L^{-1})	0.11	<<1	0.8	0.16	140	0.3		0.3		0.3
Cu (mg L^{-1})	0.018	<<1	0.2	0.034	192	2	2	1	0.5	1
Zn (mg L^{-1})	0.33	<<1	1.1	0.284	107	5	5	5	2	5
As (mg L^{-1})	0.15	0.01	0.8	0.194	126	0.05	0.01	0.01	0.2	0.05
Br (mg L^{-1})	0.39	0.07	2	0.426	110					
Sr (mg L^{-1})	3.62	1	11	3	79					
Pb (mg L^{-1})	0.009	<<1	0.06	0.0128	148	0.01			0.1	0.05

[1]NOM-127-SSA1-1994, (Secretaría de Salud 1994), water for human consumption.
[2]World Health Organization (WHO 2008), water for human consumption.
[3] United States Environmental Protection Agency (EPA 1996). Water Quality Standards Handbook
[4]Food and Agriculture Organization of the United Nations (FAO), Ayers (1976), water quality for agriculture.
[5]Comision Nacional Agua (CONAGUA, 2009). Federal Law on water rights. Agricultural use. Official Journal of the Federation.
SD= standard deviation, VC= coefficient of variation.

Thus, PCA is useful in reconnaissance studies because it can help to identify groups of attributes and groups of samples that have similar composition and variability (Guan, Hutson et al. 2013, Ravikumar and Somashekar 2017). In the present study, the first six components explained 81.7% of the total variation in the wells (Table 2). The first component (PC1) represented 26.45% of the total variation. It can be observed that significant variables ($P < 0.05$) were Mg, S, Sr, K, Cu and Ca. Principal Component 2 (PC2) represented 19.18% of the variation, where significant values were Tb and nitrates, Cl, Zn, and Br. PC3 was responsible for 13.28% of the variation with T, Na, and nitrites. PC4 represented 9.73%, with high representation of chlorides, TDS, EC, and As. PC5 explained 6.95% with sulphates, Fe, and Pb. Finally, PC6 explained 6.12% with variables such as pH and K.

The cluster analysis identified samples with the same location and geological origin that in turn, may indicate similar sources, chemistry, and potential contaminants (Mohapatra, Vijay et al. 2011). Three groupings were identified with an R^2 value of 0.70 (Figure 2). The first group with three wells presents a TDS of 916 $mg \ L^{-1}$, and a Tb of 11.2 NTU, indicating moderate to high presence of salts. The second group, with 18 wells, presents high levels of Ca (164 $mg \ L^{-1}$), Mg (16 $mg \ L^{-1}$), and K (7.1 $mg \ L^{-1}$), whereas group 3 with five wells presents the highest amount of TDS with 2073 $mg \ L^{-1}$, a T of 30.9 ˚C, and Cl⁻ of 705 $mg \ L^{-1}$, for which these last wells are very saline.

Table 2.Principal Component Analysis of the water samples; the highest contribution is in bold.

Variable	Components					
	CP1	**CP2**	**CP3**	**CP4**	**CP5**	**CP6**
T (°C)	0.395	-0.531	**0.561***	0.021	0.197	0.206
TDS (mg L^{-1})	-0.232	0.389	0.402	0.094	0.043	**0.605**
EC (dS m^{-1})	-0.074	0.15	0.572	**0.664***	-0.296	-0.21
Tb (NTU)	-0.128	0.332	0.446	**0.698***	-0.294	-0.233
pH	-0.312	**0.461***	-0.416	0.298	0.071	-0.166
Cl$^-$ (mg L^{-1})	0.28	-0.288	0.083	**0.537***	0.474	0.262
NO$_2^-$ (mg L^{-1})	-0.264	**0.643***	-0.372	0.068	-0.128	0.212
NO$_3^-$ (mg L^{-1})	-0.04	-0.463	**0.577***	0.018	-0.02	0.04
SO$_4^{2-}$ (mg L^{-1})	-0.299	0.34	-0.482	0.212	**0.438***	-0.135
Na (mg L^{-1})	0.215	-0.294	**0.694**	0.05	0.33	-0.296
Mg (mg L^{-1})	**0.885***	-0.062	-0.32	0.109	-0.212	0.125
P (mg L^{-1})	0.11	0.422	0.389	-0.05	-0.049	**0.607***
S (mg L^{-1})	**0.964***	-0.097	-0.056	0.148	-0.116	-0.031
Cl (mg L^{-1})	0.496	**0.797***	0.177	-0.141	0.032	0.006
K (mg L^{-1})	**0.935***	0.062	-0.191	-0.026	-0.158	-0.065
Ca (mg L^{-1})	**0.957***	0.144	-0.181	0.015	-0.145	0.016
Fe (mg L^{-1})	0.449	0.367	0.214	-0.294	**0.499***	-0.204
Cu (mg L^{-1})	**0.648***	0.156	0.164	-0.428	0.319	-0.165
Zn (mg L^{-1})	0.028	**0.765***	0.192	0.182	0.187	-0.194
As (mg L^{-1})	0.574	-0.379	-0.301	**0.524***	0.126	-0.018
Br (mg L^{-1})	0.476	**0.700***	0.421	-0.001	0.13	-0.019
Sr (mg L^{-1})	**0.895***	0.005	-0.236	0.112	-0.255	0.088
Pb (mg L^{-1})	0.035	-0.102	-0.466	0.45	**0.600***	0.229
Autocorrelation	6.082	4.41	3.055	2.239	1.598	1.407
Proportion of variance %	26.45	19.18	13.28	9.73	6.95	6.12
accumulated percent of total variance %	26.45	45.62	58.9	68.64	75.58	81.7

* Significance level = 0.05
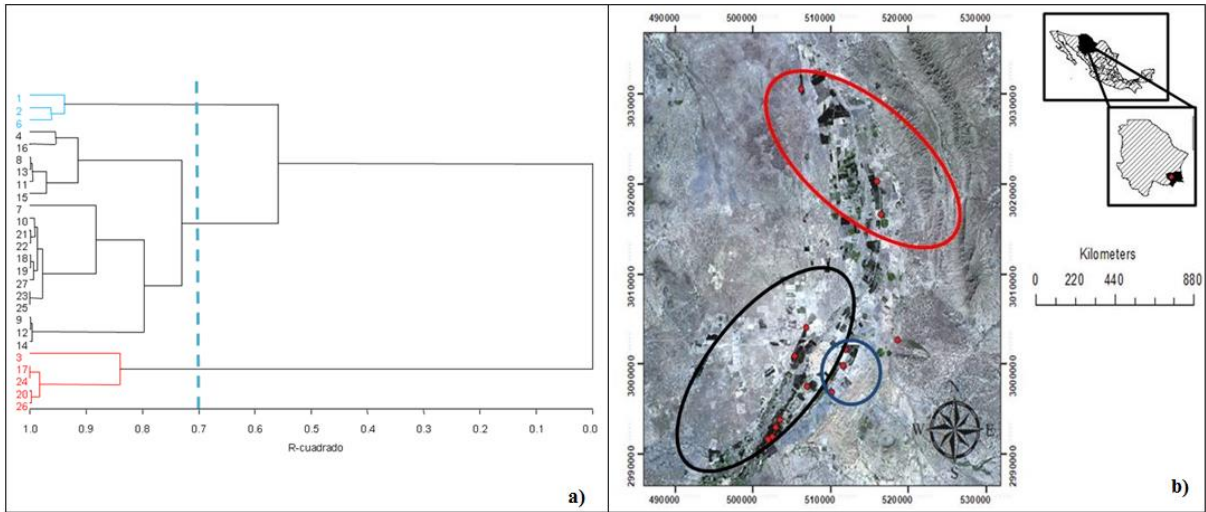
Figure 2. Grouping of the sampled wells: a) cluster analysis and b) cluster on map.

Spatial distribution of chemical species

The results on the spatial distribution of the dissolved ionic species and elements present in the water are shown in Figures 3, 4, and 5. Sulphates showed a high concentration in well-defined areas, distributed to south, central, and north parts. Likewise, nitrates are mainly concentrated within the southern part of the study area. Conversely, high contents of nitrites and chlorides are located to northern part of the area. Furthermore, high concentrations of physic-chemical parameters (Tb, TDS, EC, and pH) are located in the central part of the study area. Distribution of these attributes is not shown here. Higher temperatures were measured in the south and central parts in groundwater up to 40 °C. Furthermore, the distribution of the element content is shown. It can be seen that the highest concentrations are in the central part of the study area for Sr, Ca, K, and Mg. In the case of As and Pb it can be seen that the area with higher concentrations is much more well defined.

In the present work, the vulnerability from selected chemical species was evaluated for an aquifer in an agricultural area under arid conditions, where on average the Tmax is 30 °C, precipitation is 2.5 mm year^{-1}, relative humidity is 34%, and solar radiation is 20.5 MJ m-^{2}.

From a statistical point of view, the first grouping of chemical constituents (PC1) is related to cations formed from sulfur salts, mainly oxysalts. The conditions of the study site are arid, for which the presence of these elements, such as sulfur and carbonate minerals, is common (Wang, Liu et al. 2017), as well as because of the use of agrochemical fertilizers (Barranquero, Pardo et al. 2014).
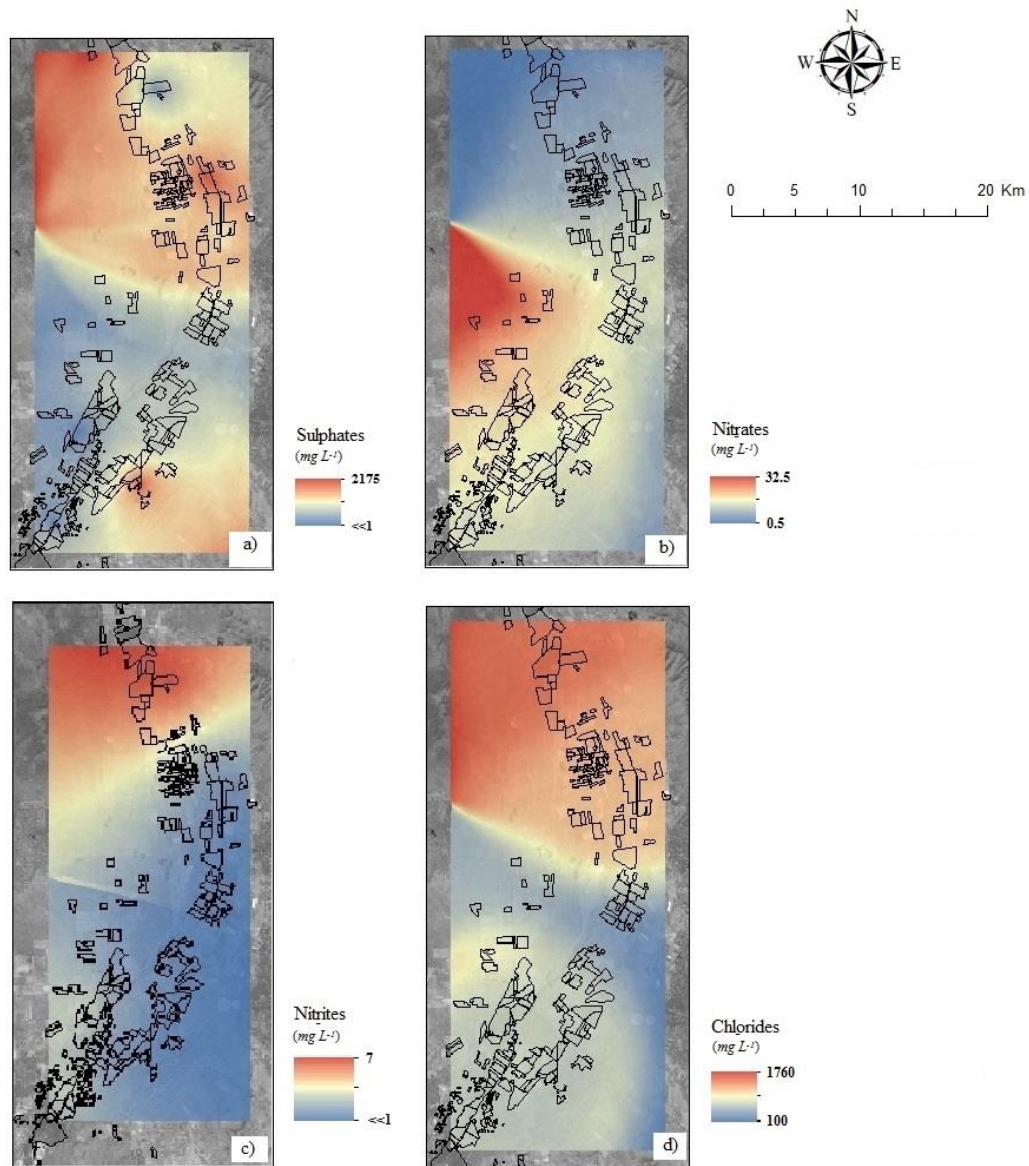
Figure 3. Distribution of the ions measured in water samples: a) Sulphates, b) Nitrates, c) Nitrites, and d) Chlorides.
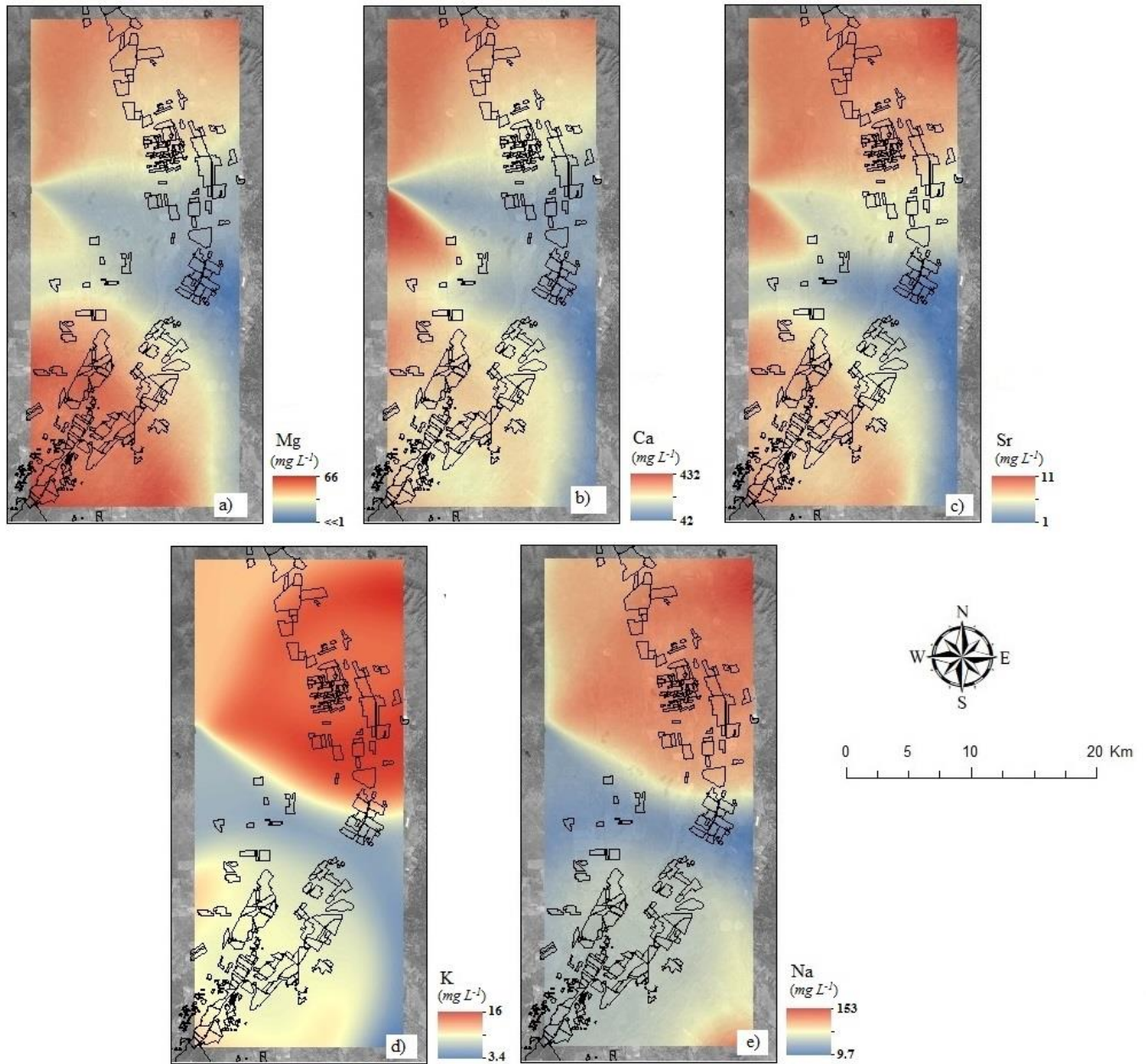
Figure 4. Distribution of selected chemical species in ground water. Alkaline earth elements a) Mg, b) Ca, and c) Sr; and Alkaline elements d) Na and e) K
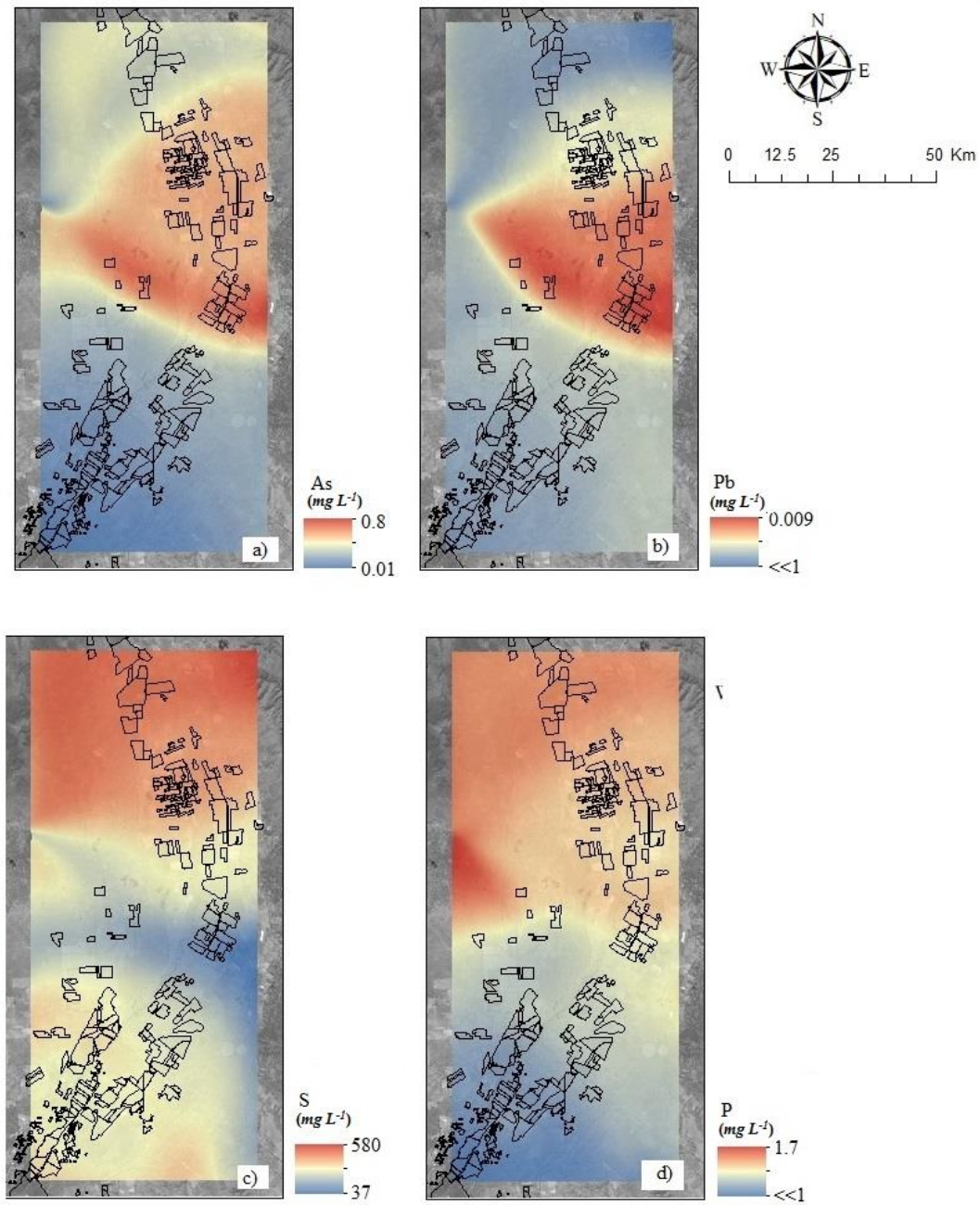
Figure 5. Distribution of selected chemical species in ground water: a) Arsenic (As), b) Lead (Pb), c) Sulfur (S), and d) Phosphorous (P).

In previous studies, the water of this aquifer was classified as Calcic-Sulfated (Hernández 2012), however, the previous study did not considered contributions from infiltration of chemical species from fertilizers. The concentrations of elements such as Mg, S, Sr, K, Cu, and Ca are those that contribute to the first statistical grouping of the water quality attributes (see Table 2). Significant correlations in agreement with the principal components were Ca with Mg (0.84 P < 0.01), S (0.93 P < 0.01), K (0.95 P < 0.01). Likewise, Sr was correlated with Mg (0.86 P < 0.01), S (0.93 P < 0.01), K (0.91 P < 0.01), and Ca (0.93 P < 0.01). The presence of alkaline earth metals such as Mg, Ca, and Sr, chemically similar with oxidation state +2, originate from dissolved rocks such as gypsum ($CaSO_4 \cdot 2H_2O$), and limestone (50% $CaCO_3$, with small amounts of clay, hematite, siderite, quartz, aragonite, iron oxide, among others). These attributes are present in the sediments that compose the underlying aquifer under analysis. Furthermore, Sr can have its origin in sulfated minerals (Bhuyan, Bakar et al. 2017), from barite ore deposits presents in study area (Servicio Geológico Mexicano 2007), as well as in weathering of rocks with a high level of silicates (Dubchak 2018). Moreover, due to its similar chemical characteristics, Sr shows a great competition or exchange with Ca, Mg, and K that originates from minerals such as calcites; this relationship can be observed in the spatial distribution (Figure 4a, b, c, and e); in which they have the same pattern (Dubchak 2018). Some of the sampled wells presented values of Ca and Mg that exceeded the maximum allowable limit for water for consumption and irrigation (Table 1). According to the Mexican regulation, 10% of the wells exceed the maximum allowable limit for Mg and Ca, and 13% for K. Furthermore, the increase in the concentrations of Ca and Mg is related to the dilution of evaporites (Hernández

2012, Valles-Aragón, Ojeda-Barrios et al. 2017). The results are similar to those reported for groundwater in India, where Ca, Mg, and Cl showed higher values (Suma, Srinivasamoorthy et al. 2015). Sulfur may come from diverse sources such as minerals of pyrite or as reduced forms of minerals going into groundwater solution. Thus, S and K can also be attributed to their presence in rocks, as well as possible lixiviation and infiltration from their contents present in fertilizers that are applied to the crops (Li, Yang et al. 2017); which is shown in the correlation of over 80% ($P < 0.01$). S and K are two of the three primary nutrients required by plants, for which they are constantly added to fertilizers (Silva-Hidalgo, Aldama et al. 2013). Because of this, the content of K is found within the allowable limits for irrigation water as established in the international regulations (FAO 1976). In contrast, in water for human consumption K exceeds the maximum allowable limit with values up to 16 mg L^{-1}. Fe, Zn, and Cu are considered essential nutrients for the optimal development of pecan orchards. The concentration of Cu in the analyzed water samples is lower compared to what was reported by other authors for groundwater used for irrigation and human consumption (Arslan and Turan 2015, Kumar, Nagdev et al. 2019). From these elements, only Fe exceeded the limit in the regulation. Although these elements are present in agricultural fertilizers or additives, Fe and Cu can be mainly attributed to their geological origin in the study area. In this analysis, Cu concentrations showed correlation only with Fe concentrations (0.66 P<0.01). Cu is an element in oxidative state +2, and tends to be present in sulfurous minerals with the presence of Fe; these elements are found in the rocks due to the hydrothermal solutions that are common in the study area, where temperatures up to 35.8 °C were measured (Table 1).

The elements that contribute most to the second grouping (PC2) are halides, Zn, pH, and NO_2^-. These chemical species, in a similar way, can have a geological origin, which can be accentuated by the arid climatic conditions present in the study area (Rajeshkumar, Liu et al. 2018). Cl is found dissolved in the water, with values up to two orders of a magnitude higher than the allowable value. In natural waters, chlorine is mainly found in the form of an ion, chloride. However, specifically for this principal component (PC2), the determined Cl is in element form. There was no correlation between chloride and the element Cl; this could be due to the presence of oxidative agents in the water (Bhunia, Keshavarzi et al. 2018, Musin, Korolev et al. 2018). Cl showed a correlation with Mg and Na ($P < 0.05$), which is directly related to the lixiviation of minerals, in addition to the excessive use of agricultural soil additives (Arslan and Turan 2015). This element was found above of permissible limits for human consumption in a 77% of sampled water (World Health Organization 2010). In addition, presence of Mg and Na chlorides can be associated to water of geothermal origin which is present in this zone. Zn is another element considered essential for pecan friut because it is present in the growth and development of the plant. Due to the arid and soil conditions there is a deficiency of Zn in the northern part of Mexico, for which this element is found in the majority of solvable fertilizers (Flores 2018). The Zn content in the water was found below the maximum allowable limit established by different regulations presented in Table 1. Br is usually found together with chlorine, especially in the form of soluble salts in saline waters; it can also be found in rocks (SGM 2016). It was correlated with Cl (0.97, $P < 0.01$), Zn (0.63, $P < 0.05$), Mg (0.47, $P < 0.05$), and Na (0.52, $P < 0.05$). The pH is one of the indicators of potable water quality because it can produce stress, mortality, and

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diseases in aquatic ecosystem (Valles-Aragón, Ojeda-Barrios et al. 2017). This parameter is strongly related to the presence of dissolved ionic species. The pH values are found within the limits of the current regulations (Table 1), and are similar (Figure 3b) to other groundwater studies (Brindha, Vaman et al. 2014, Azpilcueta Pérez, Pedroza Sandoval et al. 2017). Agriculture is the main economic activity in the study area, and fertilizers with contents of nitrates and phosphates are used to enhance crop productivity. The presence of nitrites in water samples is a reduced form of nitrates. The presence of nitrites is due to the oxidative reaction of halide salts such as NaCl that reacts with the fertilizer sodium nitrate (Sappa, Ergul et al. 2014). Ground water sampled shows nitrite contents above allowed limits in a 59% and a 52% of sampled wells, for irrigation (CONAGUA 2009) and drinking water (NOM-127-SSA1-1994 1994, USEPA 1996, World Health Organization 2010), respectively.

The third grouping (PC3) is related to the solvability of sodium and nitrates, as well as with temperature. The north of the study area has banks with material of evaporites (halite and gypsum) (SGM, 2016). Na can vary in groundwater because it is related to the dissolution of rocks and minerals rich in this element (Obiora, Chukwu et al. 2016). It was found that 30% of the wells exceed the international regulation on water for human use and consumption (World Health Organization 2010), however they do not exceed the reference values for agricultural use, see Table 1. The high concentrations of this chemical species in mineral form (NaCl) deteriorate in the soil of the agricultural fields because the constant use of water for the irrigation of the crops induces an increase of salts in the soil; this leads to a slow

or cessation of growth of the crops and intoxicates the plants (Wang, Liu et al. 2017). Nitrates increase because of human activities such as the use of sodium nitrate (NaNO$_3$) fertilizers due to their easy solubility and low cost (Mapanda, Mangwayana et al. 2005, Castañeda-Gaytán, Ortega-Escobar et al. 2008). It was found that the concentration of nitrates exceeds the limits established in the regulations (NOM-127-SSA1-1994 1994, USEPA 1996, World Health Organization 2010) for use and human consume in 33% of the evaluated wells. Moreover, these were found that 37% of sampled water exceed the Mexican regulation for irrigation (CONAGUA 2002). This indicates a contamination by nitrogen compounds in these areas. Temperature is related to the mineralization of the groundwater; therefore, an increase in temperature influences the solubility of some minerals (Garrido Schneider, García-Gil et al. 2016). Of the evaluated wells, 52% exceeds the limits in the Mexican regulation for drinking water (NOM-127-SSA1-1994 1994). The origin of the thermal water in this region is associated with the following geological characteristics; a) the southern extension of the Rio Grande rift, which stretches to the south of Chihuahua (De la Maza Benignos, Lavín-Murcio et al. 2011), and b) a local structural deformation from underground irregularities in the surrounding bedrock, and the presence of magmatic bodies still in the process of cooling (Oviedo-Padrón, Aranda-Gómez et al. 2010).

The components of the remaining three minor groupings PC4, PC5, and PC6 reiterate the presence of dissolved material in the groundwater and their direct relationship with the EC, the turbidity they confer, as well as the presence of the metal(oids) As, Fe, and Pb. The parameter turbidity (Tb) is related to the limited

penetration of light through the groundwater. In water samples analyzed, EC showed significant correlations with Na (0.47 P < 0.05), Cl (0.59 P < 0.05), and Zn (0.59 P < 0.05). This parameter is affected by the amount of dissolved solids in the groundwater (Figure 3d). Related to this, the EC content is associated with the high amount of dissolved salts, where the maximum value found was up to 6.25 dS m^{-1}. (Azpilcueta Pérez, Pedroza Sandoval et al. 2017) found EC values up to 3.74 dS m^{-1} in groundwater for agricultural use; these values are lower than those in this study. Over time, the high EC value in the water represents a risk of salinization of the agricultural soil, which impacts the crops because the accumulation of salts in the soil prevents the exchange of water and air in irrigation systems in the area (Castañeda-Gaytán, Ortega-Escobar et al. 2008). Chlorides are the inorganic ions of larger amounts in natural, residual, and treated waters (Azpilcueta Pérez, Pedroza Sandoval et al. 2017). In the analyzed groundwater, values for this ion were found that exceed in 74% both the regulation for irrigation water, as well as for human use and consumption. Additionally, chlorides are grouped with TDS and T, corroborating that the groundwater extracted from these wells has a high content of these elements. In agreement with the correlations found (P < 0.05), the salts such as Mg, Ca, Na, and Zn chlorides are those that are mainly present in the analyzed groundwater samples. This can be attributed to the ionic exchange of these elements in groundwater which are being leaching from evaporite rocks presents in the zone; (Brindha, Vaman et al. 2014) worked with irrigation water and present similar values with the relation with Cl, Ca, Mg, and Na. As and Pb exceed the limits established by national and international regulations (Table 1), and these elements showed correlation between them (0.51 P < 0.05). The presence of As has already been

reported in several studies; where its presence in the state of Chihuahua is natural (Hernández 2012, Valles-Aragón, Ojeda-Barrios et al. 2017). It was found that exceed the allowed limits in a 67% and 30% to drinking water and irrigation, respectively. The highest concentration of As has been found in areas of contact with the alluvium layer such as the mineralized parts of limestone and ignimbrites, and mineralized andesite (CONAGUA 1996). Thus, As was linked to Mg (0.49 $P <$ 0.05), K (0.52 $P < 0.05$), and Ca (0.53 $P < 0.05$). Furthermore, As also can be present because of anthropogenic contamination, such as germicides and insecticides, detergents, and fertilizers such as arsenic chloride (Bundschuh, Litter et al. 2012, Tripathee, Kang et al. 2016, Wang, Liu et al. 2017). Thus, this can occur from pumpage and/or artificial recharge (inefficient irrigation), where oxygenated waters have mobilized these metals into solution and, after, to groundwater flow from deep percolation of inefficient irrigation and natural recharge events. A prolonged exposure to elevated doses has a carcinogenic effect on humans, whereas in plants it inhibit the plant cell growth (Martínez, Manjarrez et al. 2017, Suriyagoda, Dittert et al. 2018). High concentrations of Pb are toxic for plant development, inhibiting the growth of vegetative cells. Its origin is in the wear of minerals and rocks that are rich in this element (Valles-Aragón, Ojeda-Barrios et al. 2017). It presents a sanitary risk because it substitutes Ca, complicating its elimination by damaging the cell walls (Santoni, Huneau et al. 2016). As is correlated to Pb (0.51, $P < 0.05$); their relationship can have its origin in the product of chemical reactions, minerals, as well as similarity in the transportation or deposit of both metals (Figure 5a and b) (Pérez 2004, Li, Yang et al. 2017). These correlations are stronger than those reported by

(Selvakumar, Ramkumar et al. 2017) and (Rajeshkumar, Liu et al. 2018), who worked with groundwater with a high heavy metal content.

Since 1979, an increase in the amount of TDS (1936 mg L^{-1}) and the concentration of sulfates (11.0 mg L^{-1}) has been observed; the latter is associated with evaporates such as gypsum, which forms part of the geological structure and composition of the sediments that compose the aquifer, as well as to the gypsum applied as a soil amendment to promote clay flocculation and better soil drainage for agriculture(Hernández 2012, Bhunia, Keshavarzi et al. 2018). The maximum sulfate concentration was up to 5 times the value established as the limit by the regulations. It is related to additives such as fertilizers as well as with the wear of the terrain which has an origin of alluvial sediments (CONAGUA 1996, INEGI 2017). The elevated concentrations can cause gastrointestinal effects upon consuming the water (Valles-Aragón, Ojeda-Barrios et al. 2017). The results are similar to those of (Brindha, Vaman et al. 2014) and (Selvakumar, Ramkumar et al. 2017) who also worked with saline groundwater. In the statistical analysis the presence of zinc sulfate (ZnSO$_4$) was found, which is one of the most common used fertilizers (Li, Yang et al. 2017). Furthermore, ferrous sulfate salts used for the addition of Fe to the plant and plumbic sulfate can stem from the mineral Anglesite (Brindha, Vaman et al. 2014). On the other hand, the presence of the higher TDS (Figure 3c) supports the relation between these attributes, providing a reflection of the high content of dissolved anions and cations in the water (Ben Salem, Capelli et al. 2014). According to the results, 93% of the sampled wells exceed the international regulation on water for human use and consumption, whereas 37% exceed the Mexican regulation.

Moreover, in irrigation water it is observed that the maximum concentration of TDS exceeds the international regulation, whereas at a national level it is up to 6 times higher. (FAO 1976) establishes guidelines for the quality of the water to be used for agriculture. These establish that irrigation water with TDS values in an interval of 400 to 2000 mg L^{-1} has a restricted use of low to moderate, and 96% of analyzed wells shows this scenario; whereas >2000 mg L^{-1} presents a severe degree of salinity (approximately 22% of wells). The presence of all these elements in the study area is supported by the cluster analysis, which indicates that there exists a grouping of wells based on the content of these elements (Figure 2). The results obtained were similar to those of (Gopal, Shanmugasundaram et al. 2018), where the majority of their water samples were clustered in one large group. Furthermore, our results are similar to those of (Wang, Liu et al. 2017), that also categorized and associated variables in groundwater. Moreover, the highest concentrations of these elements are found spatially distributed around the center-east part of the study area (Figure 4c, and 5c and d), where the spatial distribution of the parameters is very similar to other arid places in the world (Negm and Armanuos 2016, Jafarabadi, Bakhtiyari et al. 2017).

On the other hand, the water problem is not only the result of climatic variations that have impacted in a negative way on the hydrological cycle, but also a consequence from bad management practices such as increased growths of economic activities (urban, agriculture, mining, tourism/recreational, among others) and applying an intensive use of groundwater. One of the consequences of the marked increase in groundwater use is the increased salinity. In this work, the

concentrations and distribution of anionic species presents in analyzed water can help to understand the vulnerability of pecan crop. Nitrate ion is rarely present in the water by dissolution of rock containing nitrates. There are conditions to increase the water vulnerability by nitrogen: urban or agricultural activities, mainly where fertilizers are used; nitrogen fixation by vegetation (mainly legumes); soils textures with high water infiltration, low content of organic material, lack hydric conditions; high water extraction for use from ground or surface supplies; low level of natural recharge to the groundwater basin; high temperatures of evaporation and potential evapotranspiration; geological conditions of aquifer with volcanic rock with abundance of silica, promoting geochemical conditions to nitrate persistence (Cahn and Bali 2015). In this study, agriculture occupies large areas of land and is the leading activity for region, hence, the presence of nitrates can be attributed mainly to fertilization of local crops. Consequently, it is considered as an indicator of water contamination (Puig, Soler et al. 2017). Nitrite is also an indicator of a possible contamination of water; its presence is due to the oxidation of NH_4^+ or reduction of nitrates. In this study, high concentrations of nitrates are located to south of study area (Figure 3b), whereas nitrites to north of it (Figure 3c). Topographically, the surface water runoff is from south to north in the evaluated area. It can indicate that nitrites contents are due to leaching of nitrates from surface, and its consequent mobilization in the water flow both vertically and laterally, passing through to reaches of reduction areas. By composition, it can be inferred that in the aquifer the resource can be classified as old to ancient water due to presence of sulfates and chlorides with a high salt content. However, some isotope hydrology analysis and groundwater age dating should be carried out to corroborate it.

Likewise, chloride and bromide are the major soluble ions presents in water. These elements usually can help to identify sources of salinity. Thus, the Cl/Br ratio is used to determine groundwater quality (including groundwater contamination), as well as zones with sea water intrusion and its origin (Hanson 2003, Alcalá and Custodio 2008, Naily and Sudaryanto 2018). Figure 6 shows the results of chloride-bromide analysis. The origin of salinity by chloride concentrations in water can be divided in (Davis, Cecil et al. 2001, Naily and Sudaryanto 2018): a) recharge, in well number 2; b) agriculture pollution, in well number 3; c) leaching from natural halides, in wells 1, 6, and 7; and d) leaching from volcanic contribution of halite, in remaining wells. It can suggest that salinity in the present study is mainly attributed to dissolutions of alluvial sediments and bedrocks presents in the area. Geologically, the area has formations from the Precambrian with marine transgressive stages of the Upper Jurassic, gave rise to the evaporite deposit that emerge to the north of the study area (Comisión Nacional del Agua 2015, Secretaria de Gobernación 2015).

Agriculture is the main economic activity in Mexico, and for decades the majority of the groundwater in the area has been used for irrigation to support agriculture. However, soil salinity is a currently problem for crops under several natural and anthropogenic conditions. This factor may determines the productivity of farmlands, therefore, it can help to identify vulnerability areas by salts accumulation. An example of areas showing high SAR hazard were identified in the Mimbres Basin, New Mexico (Hanson, McLean et al. 1994). Currently, these regions have been abandoned for agricultural owing to high salinity accumulation in soils from irrigation with saline groundwater.
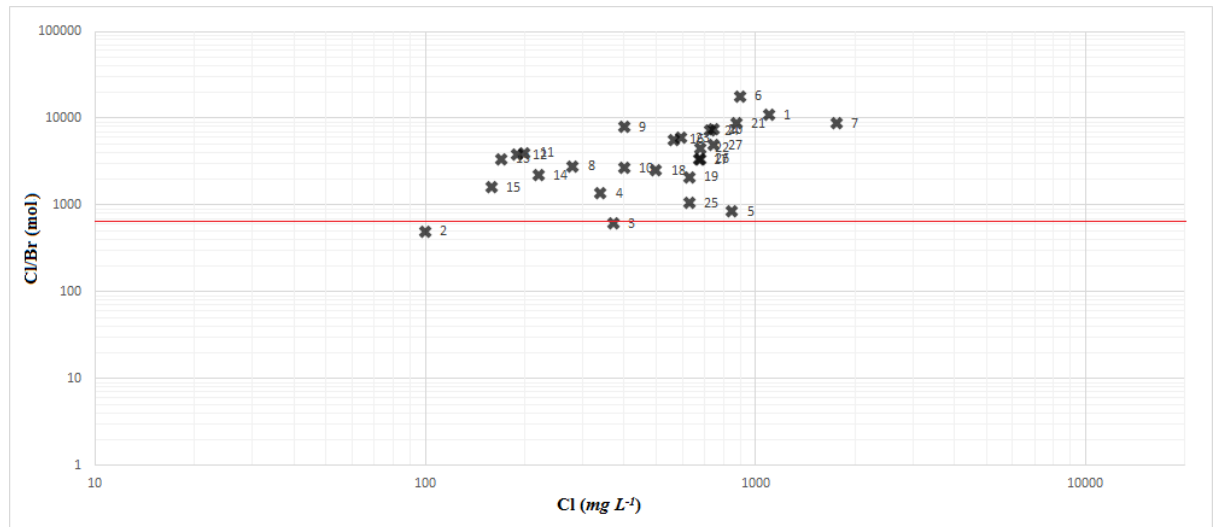
Figure 6. Type of salinity obtained using Cl/Br ratio vs Cl concentrations; red line is seawater value as salinity reference.

In the study area, water shows high EC values in groundwater, thus, distribution of SAR and CLR are showed in Figure 7. The largest values of SAR are mainly to norther part of zone, with a highpoint to south (Figure 7a). This zonation may suggest that salinity is primarily related to oxy-salts as sulfates and carbonates (see Figures 3a, 4e, and 5c) and, to a lesser extent related to the level to halides (see Figure 3d). All these salts present in water for irrigation are providing an incremental accumulation of salinity in soil and root zone. Moreover, threshold value for EC in soil (ECe) of pecan crops is 2.5 dSm^{-1} (Miyamoto, Riley et al. 1986, Miyamoto 2006); it represent the water quantity needed to support the productivity. Soils analyzed showed ECe from 0.24 to 4.9 dSm^{-1}, where 30% of orchards are above of that value.

Therefore, the CLR indicate increased leaching applications of irrigation water up to values of 58%, Figure 7b. This represent a 58% more of irrigation water to leach salts presents in the root zone to maintain the crop productivity. This is consistent with other estimates of between 22 – 60 percent estimated from model simulations (Boyce, Hanson et al. 2019), and from the Rhoades equation ranging from 1 – 88 percent depending on soil and water salinities, the salinity leaching efficiency level, and crop salinity tolerance (Cahn and Bali 2015). This leaching represents not only an additional overexploitation of the groundwater resources to maintain lower soil salinities but also an additional driver of groundwater-quality degradation that will be difficult and expensive to mitigate and reduces the sustainability of the water resources.
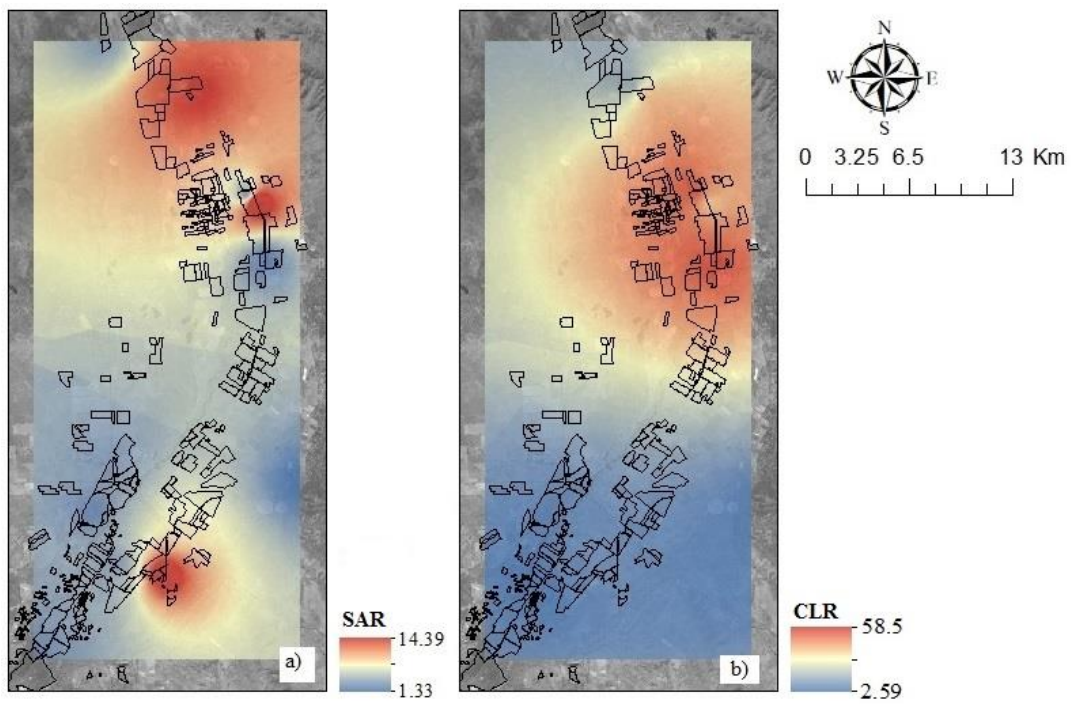
Figure 7. Chemical vulnerability evaluated by: a) Sodium Absortion Ratio and b) Crop Leaching Requirements.

In the state of Chihuahua, the extraction of groundwater through wells is deeper every time. From 1997 to 2008 the extraction of water increased from 536 to 610 Hm^3 with more than 90% of these extractions for agricultural purposes (CONAGUA 2002, Diaz Rizo, Castillo et al. 2011). As a consequence, there was a water deficit of -135.7 Hm^3 in 2002 and -142.1 Hm^3 in 2015. Therefore, the water quality in the area may decrease with an increase in the depth of extraction. The recharge of the study area is from the Rio Florido. This water body is the most important collector at surface-water runoff level and originates in the southeast of the study area. Currently, the river presents arid conditions due to prolonged droughts and the presence of two important dams along its channel that regulate surface-water flows (the dams San Gabriel and Pico de Águila) (Hernández 2012, INEGI 2017).

The coming years will face increased water demands leading to hydrologic stress if these tendencies continue. In addition, there will be an increase in the cost of extracting good quality groundwater, which will be unattainable by the majority of the habitants in the region (SOSA-RODRÍGUEZ 2012, Wang, Liu et al. 2017). Because of all these factors, there is no adequate recharge for the area, which generates environmental, economic, health, nutritional impacts, and social conflict (Silva-Hidalgo, Aldama et al. 2013), as well as jeopardizes food and water security for the region.

CONCLUSIONS AND RECOMENDATIONS

In developed hydrologic systems, with mainly agriculture, the use of water for intensive irrigation and under conditions of prolonged drought leads to overexploitation of the aquifer, which, as a consequence, produces a high salinity and an increase in the composition of toxic chemical species.

In the present reconnaissance study, a preliminary assessment of risk zones were determined based on the chemical species in an aquifer. This study will help set a better framework for more detailed studies of additional sources and constituents that will better describe and allow the understanding of the movement and mixing of these different water types and their effect on resource and agricultural sustainability. The results showed a variation in the quality of the groundwater in the area and related potential subregions of risk. Furthermore, a diverse element composition was found, which was classified in groups based on their geological and anthropic origins. Moreover, the high concentrations in this area are related to weathering of igneous and sedimentary rocks, as well as to the use of fertilizers and herbicides increases chemical species concentrations in the groundwater from the aquifer.

The initial vulnerability maps of the study area that are based on the spatial distribution of the chemical species show that, in general, the crops in the central to north part of study area show a higher vulnerability because of the water quality in that area. This suggests that in the coming years, there will be a severe problem with water quality and quantity in this area because of the environmental, geological, climatological, and chemical conditions. It is recommended to conduct periodic and

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more detailed surveys on the water quality, including chemistry of emerging, natural, and anthropogenic contaminants as well as to look for solutions on the treatment of water with a high salt content and more efficient irrigation methods that may also promote better leaching. The immediate consequence will be a further degradation of groundwater quality and increased overexploitation of the water resources and potentially a loss of arable land fit for agriculture. Thus, the sustainability of the water resources, land, and agricultural industry are all at risk. Consequently, it would be a reduction in the agricultural production and, therefore, a decrease in the productive competitiveness with other agricultural regions and/or its profit and productivity. Hence, it is essential to implement mitigation strategies such as adequate irrigation technification systems in crops, to implement procedures for recharge of aquifers, to apply efficient resource management policies. The data and analyses of the present study provide a novel approach to developing a baseline for the development of proposal and strategies for risk management related to global climate change, as well as water availability and quality. Combining additional geochemical and land and water-use surveys with integrated hydrologic modeling will further help to delineate the use and movement of various waters and help to better identify the potential risks and issues delineated within this initial reconnaissance study.

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STUDY. II HYDROCHEMISTRY AND URANIUM CONCENTRATION IN BRACKISH GROUNDWATER FROM AN ARID ZONE, CHIHUAHUA, MEXICO

BY:

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ABSTRACT

HYDROCHEMISTRY AND URANIUM CONCENTRATION IN BRACKISH GROUNDWATER FROM AN ARID ZONE, CHIHUAHUA, MEXICO

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In arid zones, the principal water supply is from groundwater, which can present a high concentration of salts, heavy metals, and radioactive elements. The aim of this study was to determine isotopic uranium concentrations in groundwater samples with a high concentration of salts and their association with other chemical species. Groundwater samples were taken from wells that show high salt contents. The ^{238,234}U radioisotope concentrations were determined by liquid scintillation and alpha-particle spectrometry. Besides, the physical-chemical parameters were recorded in situ; whereas the dissolved ions and elemental composition were measured using UV-Vis spectrophotometer and X-ray fluorescence spectrophotometry, respectively. To obtain isotopic uranium concentrations, three radiochemistry procedures were carried out. An ANOVA test was performed to compare the results from procedures, as well as an analysis of the Pearson correlation was used to obtain their associations. Statistically, the U isotopic concentrations did not show differences (0.82 p<0.5) between procedures. ^{238}U and ^{234}U showed mean concentrations of 6.7 mBq mL^{-1} and 16.6 mBq mL^{-1}, respectively, with an Activity Ratio of up 7.2. The groundwater under study showed a high concentration of TDS, calcium, sulfate, chloride, nitrate, and nitrite. Isotopic U concentrations tend to increase with NO_3>Zn>Cl>Br>SO_4>Cu>T>SDT>P; meanwhile their contents decrease with T>Cl->NO_2>Fe. These findings help to

understand the uranium behavior in groundwater with high salt contents as well as the influence of agricultural supplies on chemical species present in groundwater.

RESUMEN

HYDROCHEMISTRY AND URANIUM CONCENTRATION IN BRACKISH

GROUNDWATER FROM AN ARID ZONE, CHIHUAHUA, MEXICO

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En las zonas áridas, el principal suministro de agua proviene del agua subterránea, que puede presentar una alta concentración de sales, metales pesados y elementos radiactivos. El objetivo de este estudio fue determinar las concentraciones de uranio isotópico en muestras de aguas subterráneas con alta concentración de sales y su asociación con otras especies químicas. Se tomaron muestras de agua subterránea de pozos que presentan altos contenidos de sal. Las concentraciones de radioisótopos de $^{238,234}U$ se determinaron mediante centelleo líquido y espectrometría de partículas alfa. Además, los parámetros físico-químicos se registraron *in situ*; mientras que los iones disueltos y la composición elemental se midieron usando espectrofotómetro UV-Vis y espectrofotometría de fluorescencia de rayos X, respectivamente. Para obtener concentraciones de uranio isotópico, se llevaron a cabo tres procedimientos radioquímicos. Se realizó una prueba ANOVA para comparar los resultados de los procedimientos, así como un análisis de la correlación de Pearson para obtener sus asociaciones.

Estadísticamente, las concentraciones isotópicas de U no mostraron diferencias (0,82 p <0,5) entre procedimientos. ^{238}U y ^{234}U mostraron concentraciones medias de 6,7 mBq mL^{-1} y 16,6 mBq mL^{-1}, respectivamente, con una relación de actividad de hasta 7,2. El agua subterránea en estudio mostró una alta concentración de SDT, calcio, sulfato, cloruro, nitrato y nitrito. Las concentraciones de U isotópico tienden a aumentar con NO_3> Zn> Cl> Br> SO_4> Cu> T> SDT> P; mientras tanto, su contenido disminuye con T> Cl-> NO_2> Fe. Estos hallazgos ayudan a comprender el comportamiento del uranio en aguas subterráneas con alto contenido de sal, así como la influencia de los suministros agrícolas sobre las especies químicas presentes en las aguas subterráneas.

Palabras clave: Radioactividad, nitratos, agricultura, métodos radioquímicos

INTRODUCTION

Arid zones are those with mean annual precipitation of less than 350 mm (Méndez-García, Luna-Porres et al. 2016). These areas are characterized by water scarcity, erratic and torrential distribution of rainfall, as well as the intensive use of water for economic activities. Thus, in these regions, groundwater is the main water supply for several natural and anthropogenic activities. Therefore, the overexploitation of aquifers is a current problem that leads to the depletion of global water resources (Selvakumar, Ramkumar et al. 2017). In arid regions, groundwater tends to have a high content of dissolved salts, which represents a disadvantage for human use and consumption. Uranium (U) is a natural radioactive element with three isotopes: ^{238}U (99.2739%), ^{235}U (0.7205%), and ^{234}U (0.0056%). In nature, U can be found forming salts and oxides in different compositions (Colmenero Sujo, Montero Cabrera et al. 2004, Mexican geological service 2017). The main effect of U over the environment is its compounds toxicity. The U geochemical cycle begins with the weathering from the earth's crust leading to U mobilization in surface and groundwater, through particles or dissolved fractions (Bonotto 2017). The oxidation-reduction conditions play an important role in the U mobilization; under reduction conditions, U is mainly in + 4 oxidation state and it is insoluble while in oxidation conditions it takes + 6 oxidation state and form soluble ions (OH^-, CO_3^{-2}, F-, SO_4^{-2}, PO_4^{-3}) (Carvalho 2011, Ioannidou, Samaropoulos et al. 2011).

The detection of U in water samples has been carried out with non-radiometric techniques (e.g. ICP-MS, atomic absorption, and fluorescence spectroscopy) and radiometric techniques (e.g. liquid scintillation, alpha-particle spectrometry). The first one consists of total U determination without isotopic information meanwhile the

second one gives information about active radios of U isotopes (Jobbágy, Kávási et al. 2010).

Previous results demonstrated the presence of U in shallow and groundwater samples in Chihuahua, Mexico by radiometric techniques (Villalba, Colmenero et al. 2003). However, radiometric techniques are limited by high elements/salts concentrations resulting in low-quality spectrum and yields. Authors have proposed some improvements to the current procedures, these apply pre-concentration, separation of radionuclides by co-precipitation, and ions exchange resin (Kiliari and Pashalidis 2010, Noli, Kazakis et al. 2016). Therefore, it is important to obtain methodologies that lead the radioactive measurement of samples with high salt concentration as in groundwater from arid zones. This study aimed to determine ^{238,234}U concentrations in groundwater samples and their geochemical relationship with other chemical species. These results will be a baseline for this type of study and will provide help in water treatment studies.

MATERIALS AND METHODS

Study site. The aquifer of Jimenez-Camargo is located in the extreme southeast of the state of Chihuahua with an area of 9947.7 km^2. It is located between the coordinates 27°08" North and 104°55" West, at a height of 1,380 m above sea level. The climate is semiarid, with a mean annual temperature of 18.66 °C and average annual precipitation of 380 mm (CONAGUA 2008). The surface of the aquifer is almost completely composed of alluvial material located in the lower parts from the north to the southeast. It is an unconfined aquifer with some semiconfined zones. The surface is composed of sand and gravel, and can even contain accumulated clay and/or carbonate-sulfate minerals; therefore, its nature generates a high content of some elements (Hernández 2012). The soil of the aquifer is mainly composed of xerosol which is characteristic of dry areas, with a clear and thin surface, and highly variable amounts of organic matter depending on the type of texture. Under this layer, there is an accumulation of clay minerals and/or carbonates/sulfates; at a certain depth, there are spots, lime agglomerations, and gypsum crystals with different levels of salts (CONAGUA 2018), Pb, Fe, Zn, Mn, and Cu (INAFED 2017, INEGI 2017). Figure 8 shows the location of the study area, as well as the sampling points.

Water sampling

The groundwater from 30 wells, which are used for irrigation of pecan-producing orchards, was analyzed. Samples were taken in two types of containers: a) sterile polypropylene containers of 1 L (NOM-014-SSA1-1993 1993) for determination of dissolved ions (which were preserved on ice to 4°C ±1°C) and b) containers of 15 L for determination of isotopic U, as well as major and trace

elements. Sample locations were determined randomly; these sampling points were located using a global positioning system (GPS). Parameters such as temperature (T), pH, turbidity (TB), and total dissolved solids (TDS), were measured in situ using multi-parametric equipment (Hanna, Hl98130) and a portable turbidimeter (Hanna, HI, 93703).

Uranium isotopic determination

Radiometric techniques are limited by high elements/salts concentrations resulting in low-quality spectrum and yields. Due to this, in radiometric methodologies, it is necessary to improve the isolation of the main element previous to its measurement. In this study, three radiometric procedures were applied to determine ^{238,234}U concentrations in groundwater with high salt concentration from 7 wells. Prior to radiochemical treatments, 3L of sample water aliquots were concentrated to 250 mL by evaporation; treatments applied were: 1) actinide extraction using tributyl phosphate (TBP) (Baik, Kang et al. 2015), which is widely used to analyze U in environmental samples using semiconductor detector PIPS, 2) the previous procedure to which a filter step is added, and 3) URAEX-extract procedure under sulfate media (Yoon, Cho et al. 2001, Caraveo-Castro 2018) using liquid scintillation (PERALS, Photon-Electron Rejecting Alpha Liquid Scintillation).
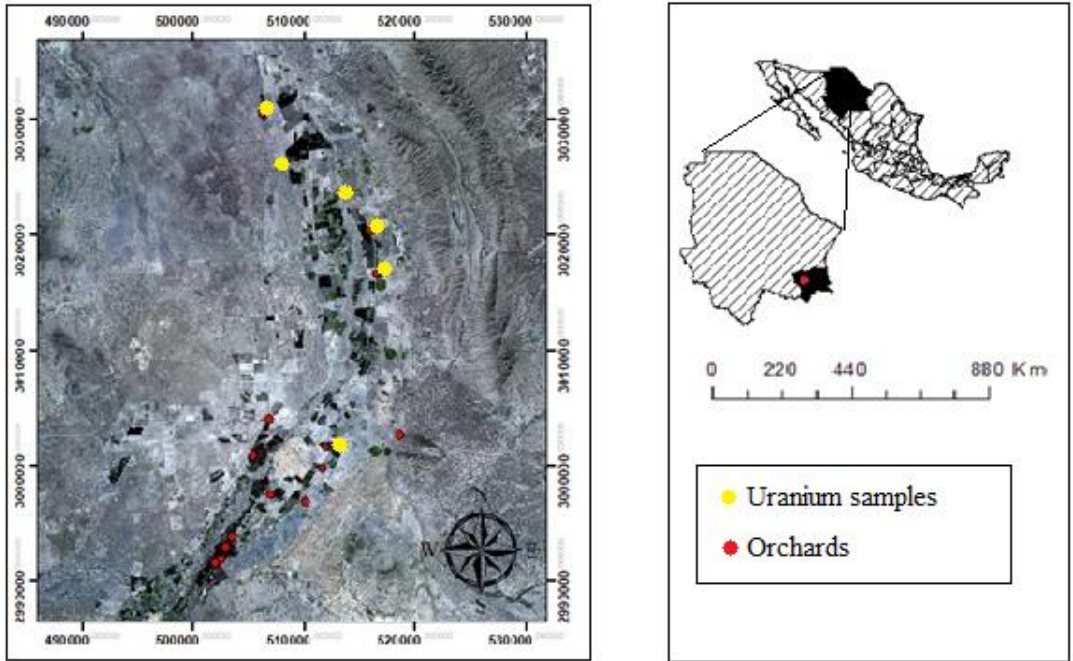
Figure 8. Location of the sampled wells.

Procedure one (P1)

50 mL of pre-concentrated samples were put under analysis; each aliquot was spiked with 0.5 mL of ^{232}U (98.12 mBq mL^{-1}) for traceability. The actinide precipitation was carried out with Fe^{+3} and, after this, the precipitate was separated from the liquid phase by centrifugation (Hettich, Rotofix 32A). ^{238,234}U extraction took place with TBP (tributyl phosphate, SIGMA-ALDRICH). Then, uranium isotopic isolation was performed by electrodeposition method, to 1.2 A during one hour. Finally, an alpha-spectrometer (Alpha analyst, CANBERRA) was used for isotopic U measurements. The uranium activity concentrations were calculated by equation (1) proposed by Kumar et al (Kumar, Yadav et al. 2009).

$$A(mBqL^{-1}) = \frac{Cps\alpha_m}{R\% * V} \quad (1)$$

where CPSα is counts per second in the alpha region, R is chemical recovery, and V is sample volume.

Procedure two (P2)

50 mL of pre-concentrated samples were filtrated by a 0.45 µm pore-diameter membrane (EMD Millipore S-Pak, HAWG047S6). Then, samples followed the same treatment that procedure one: tracer addition, actinide precipitation with Fe^{+3} solution, U extraction with TBP, electrodeposition, and alpha-spectrometry counting. Isotopic U was calculated by equation (1).

Procedure three (P3)

50 mL of pre-concentrated samples were diluted 1:4 with distilled water, reaching 250 mL of total volume. To this aliquot, 0.3 gr of 232U (High Purity Standards No. 100064-1; 128.88 mBq L^{-1}) were added as a tracer, then, this solution was carried out to dryness. This procedure was according to McKlveen, J.W. and W.J. McDowell (Yoon, Cho et al. 2001). The activity of U was counting by PERALS spectrometer (Oak Ridge TN, EUA). Isotopic U was calculated by equation (1).

Measure techniques for chemical species in groundwater

To determine anions and cations a UV-Vis HACH d3900 spectrophotometer was used; meanwhile, the determination of the elemental composition was done with TXRF, using a Bruker S2 PICOFOX. Both techniques are described in (Mendieta-Mendoza, Rentería-Villalobos et al. 2020).

Statistical analysis

To determine the origin of these variables, a Pearson correlation was carried out using the procedure CORR in the SAS package, to $P < 0.05$ and $P < 0.01$. Likewise, an ANOVA test was carried out for the three-procedure comparison using procedure PROC GLM (SAS 2000), to $P < 0.05$.

RESULTS AND DISCUSSION

Radiochemistry characterization

Water monitoring is essential in public health, automating routine as physical-chemical parameters, microbiology, among others. The high content of salts in a sample inhibits the direct extraction of certain chemical species such as radionuclides (Carvalho and Fajgelj 2013). The detection of those elements by alpha emission requires a procedure with high extraction reliability. Thus, the insolation of these alpha emitters requires an adequate radiochemistry methodology, followed by the electrodeposition process and alpha spectrometry counting.

Isotopic U activity concentrations obtained from every procedure are shown in Table 3. The averages of activity concentration were 5, 7, and 9 mBq mL^{-1} of ^{238}U in P1, P2, and P3, respectively. Whereas, ^{234}U activity concentrations were 16, 20, and 17 mBq mL^{-1} in P1, P2, and P3, respectively. The activity ratio (AR, ^{234}U/^{238}U) for the three procedures were greater than one, in an interval of 1.2 to 7.2.

Moreover, the ANOVA test showed that results obtained from procedures were similar statistically (p-value < 0.5). It is known high salt concentration in water difficulty the U detection (Noli, Kazakis et al. 2016). For actinide separation is common to use different types of resins and solvents (Tosheva, Stoyanova et al. 2004, Monroy-Guzmán 2016). However, DOWEX 1-8X and UTEVA resins have shown interferences on the insolation of U for these water samples (Caraveo-Castro 2018).

For P1 and P2, activity concentrations of isotopic uranium were similar, however, the filtering step used in P2 improved the measurement yields. This result

is similar to that found in seawater analyzed (Wood, Gill et al. 2016). Likewise, the groundwater samples analyzed by liquid scintillation (P3) showed similar yields as those obtained from alpha spectrometry. Authors have been compared some methodologies to obtain U activity concentrations, and they are found better results by alpha spectrometry than those measured by liquid scintillation (Baik, Kang et al. 2015). Aliquots volume was not interference in the modification of procedures; due to all sample volumes used were of 3L (Tosheva, Stoyanova et al. 2004, Kiliari, Pashalidis et al. 2012).

On the other hand, U activity concentrations were above the recommended limit for gross alpha emitters in drinking water (0.56 Bq/L) by Mexican regulations (NOM-127-SSA1-1994 2000), as well as the recommended limit to ^{238}U contents in drinking water of 0.37 Bq/L by EPA (Environmental Protection Agency 2000). In a previous study done in groundwater samples from Jimenez-Camargo aquifer, Ut activity concentrations were up to 0.266 mBq mL^{-1}; being below the results of this study (Rentería Villalobos 2004). This increase of Ut activity concentration may be attributed to several causes, some of those can be related to U leaching (under oxidation conditions) from aquifer material containing high U concentrations such as clay lenses and/or rocks (Alkinani, Kanoua et al. 2016). In this region, a uranium deposit is placed to the southwest (Bazán Barron 1978) which can be the main contributor of natural radioisotopes to groundwater. Moreover, this phenomenon can be exacerbated by the groundwater overexploitation, due to this water is abstracted from deeper aquifer places where dissolved material is in higher concentrations (Hernández 2012, Baik, Kang et al. 2015).

Table 3. Activity concentration of ^{234}U, ^{238}U, and Ut, as well as the activity ratio (^{234}U/^{238}U) and yield (%,) in salty water samples.

	^{238}U* mBq mL^{-1}	^{234}U** mBq mL^{-1}	AR	Ut mBq mL^{-1}	Yield (%)
Procedure one (P1)					
Minimum	1.00	2.40	1.81	3.40	34.91
Maximum	9.52	31.86	5.39	41.38	77
Mean	5.13	15.87	3.12	21.00	55.82
SD	3.07	11.00	1.32	13.75	15.95
CV	59.90	69.34	42.37	65.49	28.58
Procedure two (P2)					
Minimum	1.95	4	1.67	6.4	16.27
Maximum	20	49.2	7.24	69.16	97
Mean	6.98	20.39	3.37	27.37	41.8
SD	7.01	17.65	2.07	24.41	33.1
CV	100.41	86.57	61.33	89.21	74.24
Procedure three (P3)					
Minimum	4.81	10.5	1.19	16.24	36.26
Maximum	13.32	23.41	2.65	33.91	86.57
Mean	9.14	16.48	1.89	25.62	64.36
SD	3.28	5.59	0.50	8.18	18.19
CV	35.87	33.94	26.75	31.94	28.27

* uncertainty <30%; ** uncertainty <20%; SD, Standard deviation; CV, Coefficient of variation

Likewise, concentrations of Ut obtained in groundwater under analysis were higher than those found in aquifers with similar geological and climatic conditions (Villalba, Montero-Cabrera et al. 2006, Alkinani, Kanoua et al. 2016, Makubalo and Diamond 2020). Furthermore, AR indicated a preferential dissolution of ^{234}U over ^{238}U, generating a radioactive disequilibrium. This is the result of geochemical differentiation processes; in which the decay chain daughter (^{234}U) is more mobile than the father (^{238}U). In this process alpha energy causes recoil fragmentation between radionuclides ^{234}U and ^{238}U; mobilizing ^{234}U from the surface of water rocks resulting in disequilibrium in the solid and liquid phase (Olías, González et al. 2008). Thus, AR helps to understand the hydrological and geochemical processes in which can be groundwater markers (Chabaux, Bourdon et al. 2008, Guerrero, Vallejos et al. 2016). Therefore, low concentrations of ^{238}U and higher RA values can suggest a deeper source of water in this aquifer (Priestley, Payne et al. 2018), as well as a possible water mix with groundwater from thermal origin (Noli, Kazakis et al. 2016).

Elemental correlations

The result of trace elements and dissolve ions concentrations for these wells were published in (Mendieta-Mendoza, Rentería-Villalobos et al. 2020). Significant correlations for U are showed in Table 4. Thus, U showed positive correlations with NO_3>Zn>Cl>Br>SO_4>Cu>Tb>SDT>P; meanwhile negative correlations were for T> Cl-> NO_2>Fe.

Water chemistry plays an important role in U complex formation with different ligands. Also, 5% of the recognized minerals have U, showing ~~us~~ the great diversity of the behavior of this element (Andrews and Kay 1982). In semiarid conditions under high oxidations, water increase the U solubility (Sharma, Keesari et al. 2018).

According to results, U is highly correlated with NO_3 (0.93 $p<0.05$); this is related to agricultural activities (Yamaguchi, Kawasaki et al. 2009).

In a high oxygen environment, the nitrate concentrations are significant. Moreover, it had been found that nitrates presence may increase U mobility (Bonotto, Wijesiri et al. 2019). Furthermore, excessive irrigation and agricultural practices have been the main reasons for U leaching in groundwater. Additionally, U showed positive correlations with cations such as Zn (0.91 $p<0.5$) and Cu (0.68 $p<0.5$), due to all of them can be complexed with sulfates. In agriculture practices, zinc sulfate is widely used as a foliar additive. Due to dissolution, Zn may release from that molecule and U could be bonded with sulfate (Caraveo-Castro 2018). It can explain the U correlation with SO_4 (0.70 $p<0.5$) which can be from agricultural or geological sources from the youngest sediment layers (Jobbágy, Kávási et al. 2010, Zachara, Ilton et al. 2013, Khater 2019). This is similar to some studies where high U concentrations in groundwater were found from quaternary and tertiary sediments regions that exhibited U detectable concentrations (Thivya, Chidambaram et al. 2016). Likewise, Cu had a geological origin by sulfate minerals that facilitate U complex, releasing Cu (Charles, Markich et al. 2006). Groundwater from this zone was classified as calcic-sulfated due to the calcite rocks in the zone (Hernández 2012). Also, sulfate, Ca, and Mg concentration increase by evaporites dissolutions reflected in dissolve ions by parameters like TDS (Arslan and Turan 2015).

In addition, U also showed correlation with TB (0.62 $p<0.5$) and TDS (0.44 $p<0.5$), indicating a geological complex zone. U showed a positive correlation with Cl (0.76 $p<0.5$) and Br (0.75 $p<0.5$) from minerals, corroborating zones with high

Table 4.Uranium correlations with water quality variables.

	TB	T	TDS	Cl⁻	SO$_4$	NO$_3$	NO$_2$	P	Cl	Fe	Cu	Zn	Br
^{238}U	0.66*	-0.82*	0.43*	-0.50*	0.68*	0.94*	-0.50*	0.35	0.74*	-0.35	0.69*	0.92*	0.73*
^{234}U	0.56*	-0.76*	0.46*	-0.44*	0.73*	0.92*	-0.48*	0.42*	0.78*	-0.42*	0.67*	0.89*	0.77*
Ut	0.64*	-0.81*	0.44*	-0.49*	0.70*	0.94*	-0.50*	0.37	0.75*	-0.37	0.69*	0.92*	0.74*

* Significant level 0.05

dissolved ions (Andrews and Kay 1982). Finally, P (0.38 p<0.5) can be associated with phosphate fertilizers that increase U concentration (Michikuni, Yuka et al. 2008).

On the other hand, U shows a negative correlation with T (-0.80 p<0.5). A previous study show similarity in groundwater (Sharma, Keesari et al. 2018); corroborating the influence of T to kinetic reactions for different U complex (mainly with carbonates) more than its distribution (Alkinani, Kanoua et al. 2016). Likewise, U concentrations decrease in presence of Cl^- (-0.48 p<0.5) and NO_2 concentration (-0.5 p<0.5); it can suggest the presence of reduced zones in which U takes +4 oxidation state and is precipitated (Bonotto 2017). Finally, U showed a significate negative correlation with Fe (-0.38 p<0.5) which is attributed to the dissolution and formation of some U complex (Ioannidou, Samaropoulos et al. 2011).

CONCLUSIONS AND RECOMENDATIONS

In this study, isotopic uranium concentration was obtained from salty groundwater samples. From a statistical point of view, uranium contents from groundwater analyzed by the three procedures were similar. Furthermore, the isotopic uranium concentrations in groundwater under study are attributed to a geological source, from deeper aquifer zones. The agriculture practices in that region can be increasing the isotopic uranium concentrations due to the intensive use of water for irrigation..

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STUDY III. POTENTIAL ADVERSE IMPACTS ON VULNERABILITY AND AVAILABILITY OF GROUNDWATER FROM CLIMATE-CHANGE AND LAND USE

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ABSTRACT

POTENTIAL ADVERSE IMPACTS ON VULNERABILITY AND AVAILABILITY OF

GROUNDWATER FROM CLIMATE-CHANGE AND LAND USE

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Groundwater is an important water source for economic activities and human consumption. Currently, this resource is being affected by intensive abstraction, pollution, and climatic change. This study assessed the vulnerability and recharge of groundwater by weighted indices of an aquifer used for agricultural water supply in Chihuahua, Mexico, for current and future conditions. The efficacy of the DRASTIC model and modified versions were compared and were used to assess the vulnerability of a semi-arid aquifer. Furthermore, scenarios of vulnerability and recharge indices were projected to the nearest future (2015-2040) and distant future (2045-2069), through climate-change and land use projections using RCP 4.5 and 8.5. Three vulnerability zones were observed for every index with a common high vulnerability in the regions of agricultural land use. Vulnerability maps were also compared with groundwater-quality (K^+, Na^+, and NO_3^-), indicating the southern regions of the aquifer are the most sensitive to pollution of groundwater. Indices with the highest accuracy of vulnerable zones were identified with the new DRASTICL and DRSTIL methods. The results obtained by the application of climate change scenarios show that the area of highest recharge decreases while aquifer vulnerability increases. Thus, the deficit problem of replenishment from recharge to the aquifer remains from present conditions, and has the potential to increase in the future. In turn, these consequences will also cause vulnerability of economic

activities from the region and finally, of social and economic security of the local populations that depend on the resource for agricultural water supply as well as for water, land, and food security.

RESUMEN

POTENTIAL ADVERSE IMPACTS ON VULNERABILITY AND AVAILABILITY OF

GROUNDWATER FROM CLIMATE-CHANGE AND LAND USE

POR:

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El agua subterránea es una fuente de agua importante para las actividades económicas y el consumo humano. Actualmente, este recurso se ve afectado por la extracción intensiva, la contaminación y el cambio climático. Este estudio evaluó la vulnerabilidad y recarga de las aguas subterráneas mediante índices ponderados de un acuífero utilizado para el suministro de agua agrícola en Chihuahua, México, para las condiciones actuales y futuras. Se comparó la eficacia del modelo DRASTIC y las versiones modificadas y se utilizaron para evaluar la vulnerabilidad de un acuífero semiárido. Además, se proyectaron escenarios de índices de vulnerabilidad y recarga al futuro más cercano (2015-2040) y futuro lejano (2045-2069), a través de proyecciones de cambio climático y uso del suelo utilizando RCP 4.5 y 8.5. Se observaron tres zonas de vulnerabilidad para cada índice con una alta vulnerabilidad común en las regiones de uso de suelo agrícola. Los mapas de vulnerabilidad también se compararon con la calidad del agua subterránea (K +, Na + y NO3-), lo que indica que las regiones del sur del acuífero son las más sensibles

a la contaminación del agua subterránea. Los índices con la mayor precisión de las zonas vulnerables se identificaron con los nuevos métodos DRASTICL y DRSTIL. Los resultados obtenidos por la aplicación de escenarios de cambio climático muestran que el área de mayor recarga disminuye mientras aumenta la vulnerabilidad del acuífero. Por lo tanto, el problema del déficit de la reposición de la recarga del acuífero sigue siendo de las condiciones actuales y tiene el potencial de aumentar en el futuro. A su vez, estas consecuencias también generarán vulnerabilidad de las actividades económicas de la región y finalmente, de la seguridad social y económica de las poblaciones locales que dependen del recurso para el abastecimiento de agua agrícola, así como para la seguridad hídrica, territorial y alimentaria.

INTRODUCTION

Regional depletion of groundwater is a worldwide problem, where many groundwater systems are not depleted at rates way beyond replenishment and will jeopardize continued use by society and ecosystems. Since the 1950s, groundwater irrigation has increased by a factor of ten in the whole world; because of its easy access using well technology and a secure source of water in arid areas (Shah et al. 2007). Human activities on the land's surface, have increased the intensive use of this resource, contributing to degradation of groundwater quantity and quality (Antonakos and Lambrakis 2007).

In hydrogeology, groundwater vulnerability is defined as the susceptibility of the aquifer to be polluted (Thapa et al. 2018). Beyond simple application of pollutants on the land surface, the potential for aquifer water-quality degradation can also include 1) the mobilization of natural contaminants such as trace metals (Hanson 2015; Everett et al. 2013), 2) accumulation of organic attributes such as total-dissolved carbon and nitrates from riparian habitats (Edmonds and Gellenbeck 2002; Long, Brown, and Gellenbeck 1997), and 3) inter-aquifer flow through short circuiting of contaminants to deeper aquifers through wellbore flow in wells screened over multiple aquifers (Konikow and Hornberger 2006; Hanson 2015).

Moreover, climate change can further exacerbate these concerns with temperature increases that will increase evapotranspiration combined with reduced precipitation, causing a reduction in ground water recharge as well as increased consumption of water and reduced sustainability (Harding et al. 2014). Combined with increased human demands for urban supply and agriculture climate change and

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increased human use are the two major threats to sustainability of water resources (Vörösmarty et al. 2000; Cooney 2012). There are few studies about the future vulnerability and availability of groundwater combined with the effects of climate change scenarios, with almost all studies focused on historical and current conditions (Lu et al. 2017). Vulnerability index maps have been a tool for decision making concerning the protection and management of groundwater resources relative to pollution. Both statistical and numerical models are techniques for developing mapping schemes of aquifers vulnerability index (Focazio et al. 2002). The most known and widely used methods are: GOD (Foster and Hirata 1988), AVI (Stempvoort, Ewert, and Wassenaar 1993), DRASTIC (Aller 1985), SINTACS (Civita and De Maio 1997).

The DRASTIC method uses statistical inference to focus on the potential vulnerability of aquifers to anthropogenic sources applied at the land surface that might infiltrate vertically to an unconfined shallow aquifer. This method does not account for the geohydrologic framework and related layering of aquifer systems that could also control or prevent vertical migration of any potential contaminants (Vengosh et al. 2002; Russo 2012). However, they help to identify areas that are susceptible to pollution as well as informative and educative plans about the need to protect the aquifers (Al-Abadi, Al-Shamma'a, and Aljabbari 2017). The objective of this study is an initial assessment of the vulnerability and recharge of Jimenez-Camargo aquifer using the DRASTIC method along with development and evaluation of improvements to this method. The assessment of these improved methods included climate change scenarios projected to the future, using RCP 4.5

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and 8.5, for the assessment of potential vulnerability within this aquifer system. These results have practical relevance for water-resource planning as well as decision making about the agronomic, urban, and industrial uses for upcoming and future decades in the southeast part of the state of Chihuahua. Thus, the DRASTIC method and improved versions used in this study provide indicators of vulnerability to some of these surface sources and helps to further evaluate how additional factors can further refine the assessment of vulnerability from anthropogenic sources applied at the land surface. To address process, ultimately the water-quality data and DRASTIC factors can also be evaluated within an integrated hydrologic model combined with transport or particle tracking (Plummer et al. 2004; Hanson et al. 2013).

MATERIALS AND METHODS

To develop vulnerability indices of the aquifer and improved vulnerability tools, the following components were evaluated: a) Computation of five vulnerability indices (DRASTIC model and improved versions), b) Efficacy of DRASTIC modified versions, and c) Projection of precipitation, temperature, and land use through selected climate-change scenarios for the analysis of potential future effects on recharge and vulnerability groundwater.

Study Area. The area used to evaluate these improved DRASTIC methods is located in the subbasin of the Florido River that includes the municipalities of Camargo, Jiménez, Allende, López, Coronado, and Matamoros (**Figure. 9**).

It comprises an area of approximately 9,947 Km^2 (Figure. 9a) that is still predominantly native vegetation (86.3%) with some intensive agricultural land use (13.4%), and other minor uses (0.3%). The major economic activities include ranching and agriculture. Land ownership of the 761,676 hectares is mostly private. The 55.4% of land use corresponds to continuous mechanized agriculture and 11.2% for traditional agriculture that uses industrial agricultural methods such as cultivation with plows (INEGI 2005). The land surface is covered by soil of alluvial origin that are derived from surrounding bedrock. Other rock types that form parts of the regional aquifer system include limestones, igneous, and sedimentary rocks, with igneous rocks composing the largest portion of the aquifer system (CONAGUA 2018), (Figure 9b).
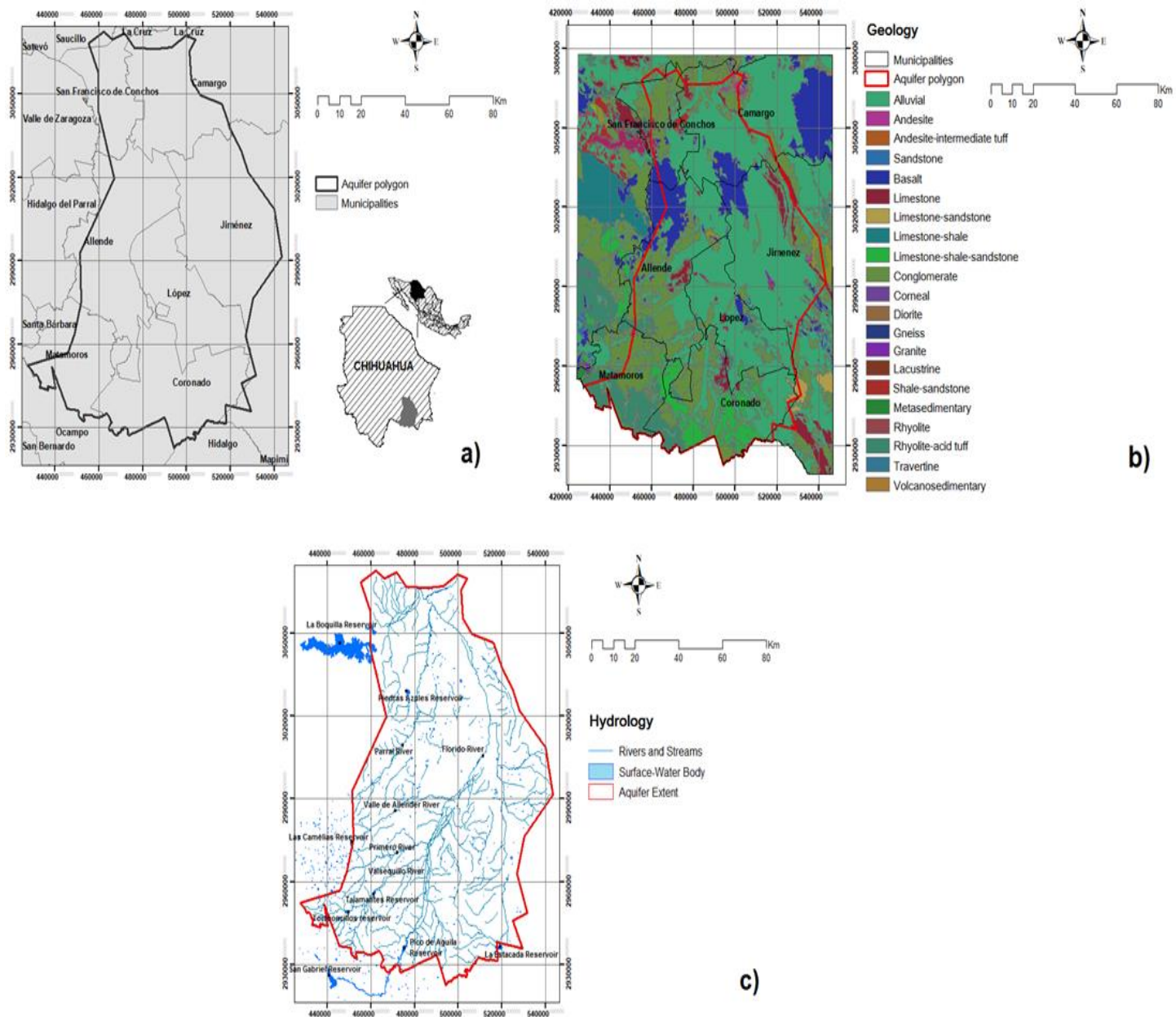
Figure 9.Study area description: a) aquifer location, b) geology, and c) surface hydrology.

The water from the main rivers that cross the valley, the Florido and the Parral rivers, also is used in combination with groundwater for irrigation, through diversion channels and direct diversions along the river channels (Figure 9c). Two storage reservoirs, Parral and Pico de Aguila dams capture, store, and supply surface water for irrigation.

Development of the new DRASTIC Indices

The DRASTIC model was originally developed by the Environmental Protection Agency of the U.S.A., EPA (Aller 1985). This model is based on geological and hydrological parameters that could affect vertical groundwater movement from the land surface. It assumes that pollution produced on the land surface can potentially vertically transport to the saturated zone of the underlying aquifers (Aller 1985). DRASTIC provides a numerical index obtained from ratings and weights assigned to the modelled parameters. Each parameter class is given by a range from low (1) to high (10) vulnerability, and are based on their relative effect on the vulnerability of the aquifer. These model parameters are also weighted to reflect their relative importance, from 1 (less important) to 5 (most important). In addition, the model presents a classification system according to the impact on the soil (general texture distribution) and to the impact of conditions from agriculture and others anthropogenic activities (ex. pesticides and herbicides). This addition to the original DRASTIC uses the same parameters as DRASTIC but with different weights. The values scale was grouped into three categories: low (50-100), medium (100-130), and high (>130). In this study, the models that were used were DRASTIC for general conditions, and the new versions of DRASTIC called DRASTIC-pesticide (-p) for intense agriculture conditions, DRASTICL with the addition of the land use,

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DRASTICL-pesticide (-p) as a version for intense agriculture conditions, and DRSTIL version with the parameters representing the layers of the aquifer and hydraulic conductivity removed from the model.

The vulnerability index by DRASTIC, uses equation (1):

$$DRASTIC = D_rD_w + R_rRw + A_rA_w + S_rS_w + T_rT_w + I_rI_w + C_rC_w \qquad (1)$$

Where **D** is the depth to the unconfined groundwater, **R** is the annual natural recharge, **A** is the aquifer material (lithology of the aquifer), **S** is soil media (the texture of soil), **T** is the topography slope, **I** is the impact of the vadose zone, and **C** is the rock type vertical hydraulic conductivity. The sub-indices **r** and **w** represent the rating of the parameter, and an assigned weight for the parameters, respectively. Additional pesticide conditions are summarized in supplementary material.

For the new DRASTICL model, the additional layer of the land use was added (L) and related term in the analysis. The application results are advantageous because it reflects the impact of diverse activities developed over the land surface (Sahoo, Dhar, et al. 2016). DRASTICL uses equation (2):

$$\mathbf{DRASTICL = D_rD_w + R_rRw + A_rA_w + S_rS_w + T_rT_w + I_rI_w + C_rC_w + L_rL_w} \quad (2)$$

Finally, the simplified version of DRASTIC, DRSTIL, has the factors of the aquifer media (**A**) and hydraulic conductivity (**C**) omitted. This approach omits the flow, length, and dispersion of the pollutants considered throughout the aquifer system (Li and Merchant 2013; González Herrera et al. 2018). However, this method was modified to include the additional attribute of land use (L) to estimate the impact

of agriculture as a potential source of artificial recharge and related pollutants. This version of the DRASTIC model uses equation (3):

$DRSTIL = D_rD_w + R_rRw + S_rS_w + T_rT_w + I_rI_w + L_rL_w$ (3)

Description and Estimation of DRASTIC layers

The description and estimation of every layer used in this work are summarized in Table 5. The complete information of DRASTIC layers is described in the appendage.

For the D and R layers, an interpolation was made with ordinary kriging from the Geostatistical Analyst extension of Arc-Gis (ESRI, 2014). While for the T layer, a slope was estimated with the Slope method of the Surface extension of Arc-Gis (ESRI, 2014).

Sensitive analysis

To evaluate the sensitivity of DRASTIC methods, two analyses were applied: single parameter sensitivity and map removal sensitivity measure (Al-Abadi, Al-Shamma'a, and Aljabbari 2017; Pacheco et al. 2015; Tomer, Katyal, and Joshi 2019; Zhao et al. 2019). The map removal sensitivity method identifies the sensitivity of the vulnerability map towards removing one or more layers from vulnerability analysis. The sensitivity is estimated with equation (4):

$$S_i = \left| \frac{v}{N} - \frac{v*}{n} \right|$$ (4)

Table 5. Data sources of index layers

Layer/Attribute	Source
D	Estimates for depth to the unconfined groundwater (D) were derived from groundwater-level data from National Water Commission from Mexico (CONAGUA) survey (CONAGUA 2002).
R	Net annual recharge (R) of the aquifer was calculated using historical data (1920-2010) of precipitation, evaporation, and surface water runoff, using Thornthwaite formula (Zair, Chaab, and Bertrand 2017)
A	Aquifer media (A) was derived from a lithology classification using the geological map (SGM 2014).
S	Soil texture (S) data was estimated from the edaphology layer (INEGI 2014).
T	The slope percentages (%) from topographic data (T) were estimated from MDE (INEGI 2017), using Spatial Analyst tool in ArcGis 10.3 for interpolation (ESRI, 2014)
I	Impact of the Vadose zone (I) was inferred from the geological map (SGM 2014).
C	Vertical hydraulic conductivity (C) was estimated from data using the Soil Contamination Assessment manual: Reference Manual (ONU-FAO 2000), where according to the type of rock it is related to ranges of vertical hydraulic conductivity K_v (m/day) (Hernández 2012).
L	Land Use (L) data was compiled from vegetation and the land use maps of CONABIO (INEGI 2017).

Where S_i is the sensitivity, v and v* are the unperturbed and the perturbed vulnerability indices, respectively; N and n are the number of data layers used to compute v and v*. The calculated vulnerability index obtained by using all factors is considered as an unperturbed parameter while the vulnerability computed using a lower number of data layers was considered as a perturbed parameter.

The single-parameter sensitivity measure evaluates the impact of each of the DRASTIC factors on the vulnerability index. This analysis compares the effective weight of each input factor for a polygon with the 'theoretical' weight assigned by the analytic DRASTIC model. The effective weight of each polygon is obtained with equation (5):

$$W_{pi} = \frac{P_r - P_w}{v} * 100 \qquad (5)$$

Where w refers to 'effective' weight for each factor, Pr and Pw are the rating and weighting values of each factor, and v was defined previously.

Comparison of the Vulnerability Index by Water Quality Values

An evaluation and comparison of the vulnerability indices were estimated with Pearson and Spearman correlations. These correlations were performed between vulnerability areas with chemical species such as total dissolved solids (TDS), sulfates (SO_4^{2-}), calcium (Ca), Magnesium (Mg), Chloride (Cl), potassium (K), and sodium (Na), as well as nitrates, an agricultural byproduct from chemical fertilization. Chemical species concentrations from selected wells from CONAGUA surveys between 2002 and 2019 (CONAGUA 2002, 2019). A Pearson correlation matrix de (SAS 2006) allowed comparison across all attributes of indices and groundwater sample chemical attributes. A Spearman correlation (rho) also was used to remove

the restriction caused by the general distribution form of two variables and the sample size (Lake, Lovett et al. 2003, Zhao, Zhang et al. 2018) with equation (6).

$$\rho = 1 - \frac{6 \sum_{i=1}^{N} d_i^2}{N(N^2 - 1)} \qquad (6)$$

where N is sample size, and d is the rank difference between groundwater vulnerability and nitrate concentration level.

Model Discrimination analysis

ANOVA was used to analyze for potential of a statistical differences between models (DRASTIC and new versions) to 95% reliability. All of the DRASTIC versions were normalized using the BOX-COX method (SAS 2006) and a Tukey test to compare multiple means of factors analyzed (SAS 2006).

Vulnerability Indices on Climate Change Scenarios

To obtain the vulnerability indices on projected scenarios of climate change, the recharge of the aquifer was computed according to projected future temperature variation and precipitation, as well as the projection to potential changes in land use. The scenarios were projected into two future periods representing the nearest future (2015-2040) and the distant future (2045-2069).

Climate Change Scenarios

Climate scenarios used the Atlas Climático Digital de México (ACDM) (Fernández-Eguiarte, Zavala-Hidalgo, and Romero-Centeno 2012; Centro de ciencias de la Atmosfera 2012), and the model of the National Centre of Meteorological Research (CNRM-CM5) (National Centre for Meteorological Research 2014). Each climatic scenario was structured for two radiative forcings of

greenhouse gas emissions (RCP; Representative Concentration Paths) by the year 2069: 4.5 and 8.5. These prescribed pathways, for CO_2 concentrations joined to land use change, are widely used to model the climatic future scenarios (San José et al. 2016). These climatic scenarios represent an increase of 29% and 125% by the end of the 21st century, respectively, over current CO_2 emission (416.2 ppm).

Projected Recharge of the Aquifer

The annual potential recharge under these scenarios was obtained by the difference between annual projected precipitation and evapotranspiration (ET) (Li and Merchant 2013). The projected ET was computed from the empirical TURC equation (González Herrera et al. 2018; Rodríguez-Huerta, Rosas-Casals, and Hernández-Terrones 2020). This was obtained from equation (7) and (8):

$$ET = P \bigg/ \sqrt{0.9 + \frac{P^2}{L^2}} \qquad (7)$$

$$L = 300 + 25T + 0.005T\text{^}3 \qquad (8)$$

Where P is precipitation (mm/yr) and T is temperature (degrees Celsius).

Statistical analysis

A paired two-tailed t-test was applied to analyze the significance of the statistical differences between climatic parameters such as precipitation, actual evapotranspiration, and recharge projected to RCP 4.5 and 8.5 scenarios, in the nearest and the distant future periods.

Projection of land use

For a greater consistency with the climate-change model, the land-use layer was also modified to reflect the potential conditions for the nearest future (2015-2039) and distant future (2045-2069). Two satellite images were used for years 1997 (Landsat 5 Thematic Mapper (TM)) and for 2017 (Landsat 8 Operational Land Imager (OLI)) from the U. S. Geological Survey (USGS)(GLOVIS 2016). The land-use classification was developed with CLUSTER analysis from the IDRISI Selva program (Eastman 2012). Prediction of land-use change was estimated with the CA-MARKOV model (Hamad, Balzter, and Kolo 2018). the projected land-use maps were validated by VALIDATE module of IDRISI Selva, where the estimated statistic Kappa (K) with values greater or equal to 0.6 are considered acceptable (Escandón Calderón et al. 2018).

RESULTS AND DISCUSSION

Classification of Layers

The reclassified layers obtained by DRASTIC are shown in Figure 10. Depth to groundwater varies widely from 9 m to more than 30 m (Figure 10a). Likewise, the aquifer is widely composed of alluvial material (54%) that fills the lower parts of valley (Figure 10b and c). Slopes for the study area range from 6 to 12 degrees, whereas in the upper parts of the valley and mountains with igneous and sedimentary rocks show steeper slopes (>18°) (Figure 10d).

These bedrocks formations delineate the surface boundaries of the aquifer with sedimentary rocks composing the northeast limit of the aquifer. These higher elevations also are composed of calcareous and conglomeritic rocks, which is formed by Las Pampas, Las Margaritas, El Mimbre, and Los Acebuches mountain ranges (INEGI 2005). The southeastern bedrock area also includes an "open area" filled by alluvial material (Figure. 10e). The 14% of aquifer area showed low permeability due to extrusive igneous rocks outcrop (10^{-6} cm/s) located to the northern and the southwester (Figure 10d and e).

The surface soils and sedimentary alluvium are composed of medium and fine-grained texture alluvium (Figure 10f), 78% and 19%, respectively. Thus, medium-grained texture soils supporting most of native vegetation while fine-grained texture areas are coincident with riparian and agricultural areas (Figure 10g). The recharge layer showed three ranges of values for recharge, with the highest values ranging from 102 to 178 mm/y.
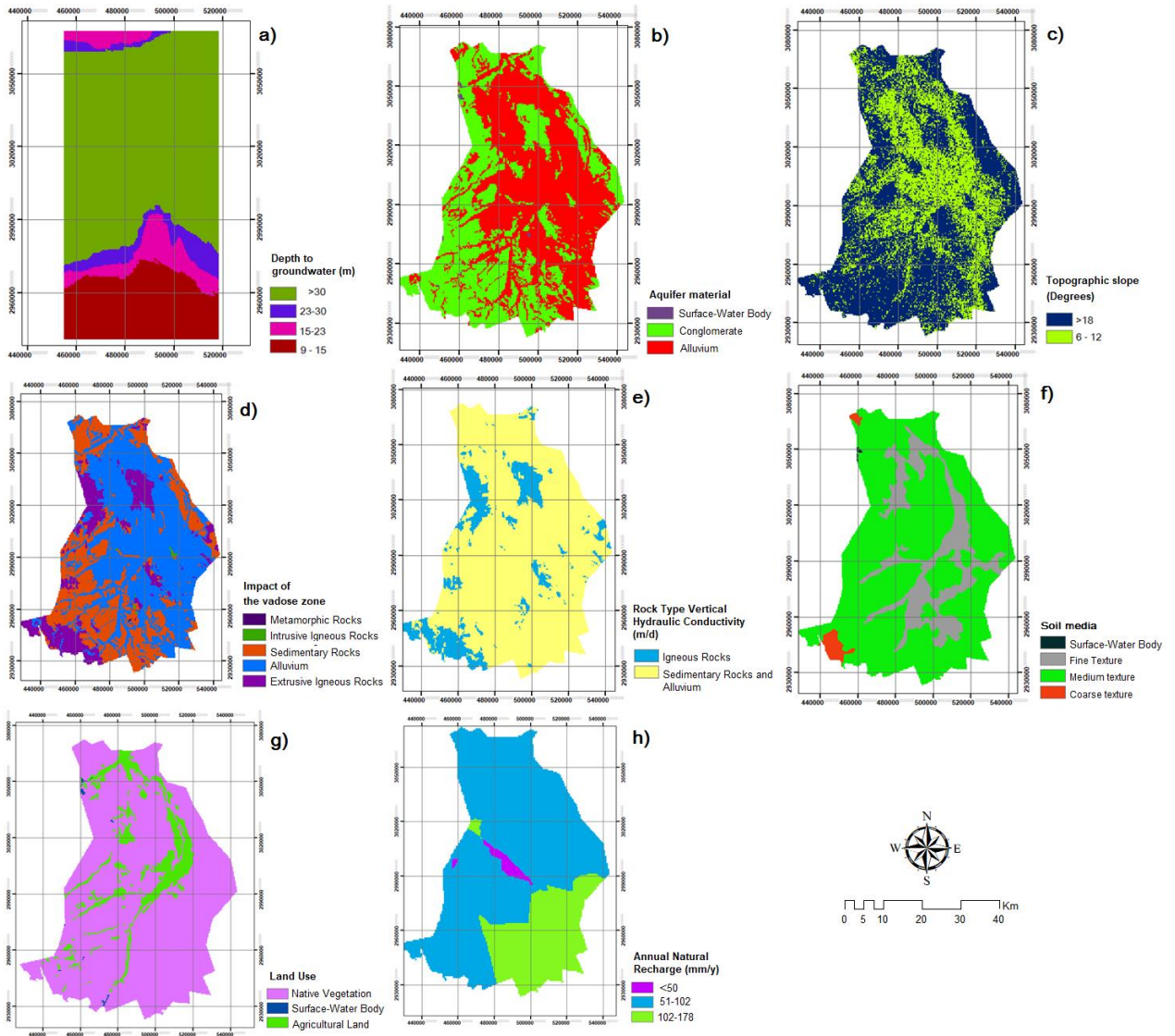
Figure 10.Layers used to build the indices: a) Depth to groundwater, b) Aquifer Material, c) Topographic Slope, d) Impact of the Vadose Zone by rock type, e) Rock Type Vertical Hydraulic Conductivity, f) Soil Media (Grain-Size texture distribution), g) Land Use, and h) Annual Natural Recharge.

This high recharge zone occurs at the southeast part of the aquifer (Figure 10h), according with the highest precipitation and lowest evapotranspiration conditions (see results in appendix, Figure 1a,b), as well as medium-grained soil texture, and native vegetation. To the southeast of the aquifer, the San Gabriel and Pico de Aguila reservoirs (CONAGUA 2020), as well as La Estacada lagoon and the Florido River are within these recharge zones (Secretaría General de Gobierno 2019).

Sensitivity analysis

The aquifer media (mean=7) and soil texture (mean=5) layer are the main contributors to pollution risk in the aquifer based on the DRASTIC Vulnerability Indices. Depth to the water table, recharge, topography, and vertical hydraulic conductivity also showed moderate risk contribution to the aquifer. However, contributions of every layer to the different versions of the DRASTIC models used, sensitivity was estimated from single parameters and map removal analysis. The layer contribution to the DRASTIC Vulnerability Index, as well as sensitivity analysis results are summarized in supplementary material.

The single-parameter sensitivity analysis, revealed that impact of the vadose zone, aquifer media, and soil texture layers tend to be the most sensitive parameters in the vulnerability assessment to DRASTIC and DRASTICL. This is due to their mean effective weights are higher than their respective theoretical weights. In DRSTIL index, impact of the vadose zone and soil texture layers were the most sensitive. The map-removal sensitivity analysis also showed that the impact of the vadose zone was the layer with highest mean rating for DRASTIC (4.2), DRASTICL

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(3.4), and DRSTIL (4.7). Thus, the impact of vadose zone (mean=6.8) is the major contributor to the high contamination risk in Jimenez-Camargo aquifer.

Impact of the vadose zone, aquifer media, and soil texture are intimately related. Due to water-rock/soil interactions, several contaminants can be leached. Hence, their transport to deeper groundwater depends on parameters such as porosity (including capillary fringe and rock fractures) and permeability. On the other hand, the topography, recharge and land-use layers are highly variable in the analysis of vulnerability index by DRASTIC, with variation coefficients of 94%, 75.5%, and 74.2%, respectively. The variability of these layers also will be the main parameters to predict the behavior of vulnerability index in future scenarios.

Vulnerability Indices

The spatial distribution of vulnerability indices of low, moderate, and high categories according to weighted value assigned and obtained from the analysis of DRASTIC and modified DRASTIC methods (Figure 11).

The DRASTIC index was found in a range from 67 to 141, and it showed moderate vulnerability (57%) and 23% of high vulnerability. Vulnerability was highest mainly in the southern part of the aquifer (Figure 11a), where the high recharge, alluvial material and sedimentary rock outcrops, and some surface-water bodies are located. Precipitation and applied water also can be leaching some chemical species from these rocks and transporting them down to the groundwater. The water-table depth is also relatively less in this bedrock area than the alluvial areas (Figure 10a).
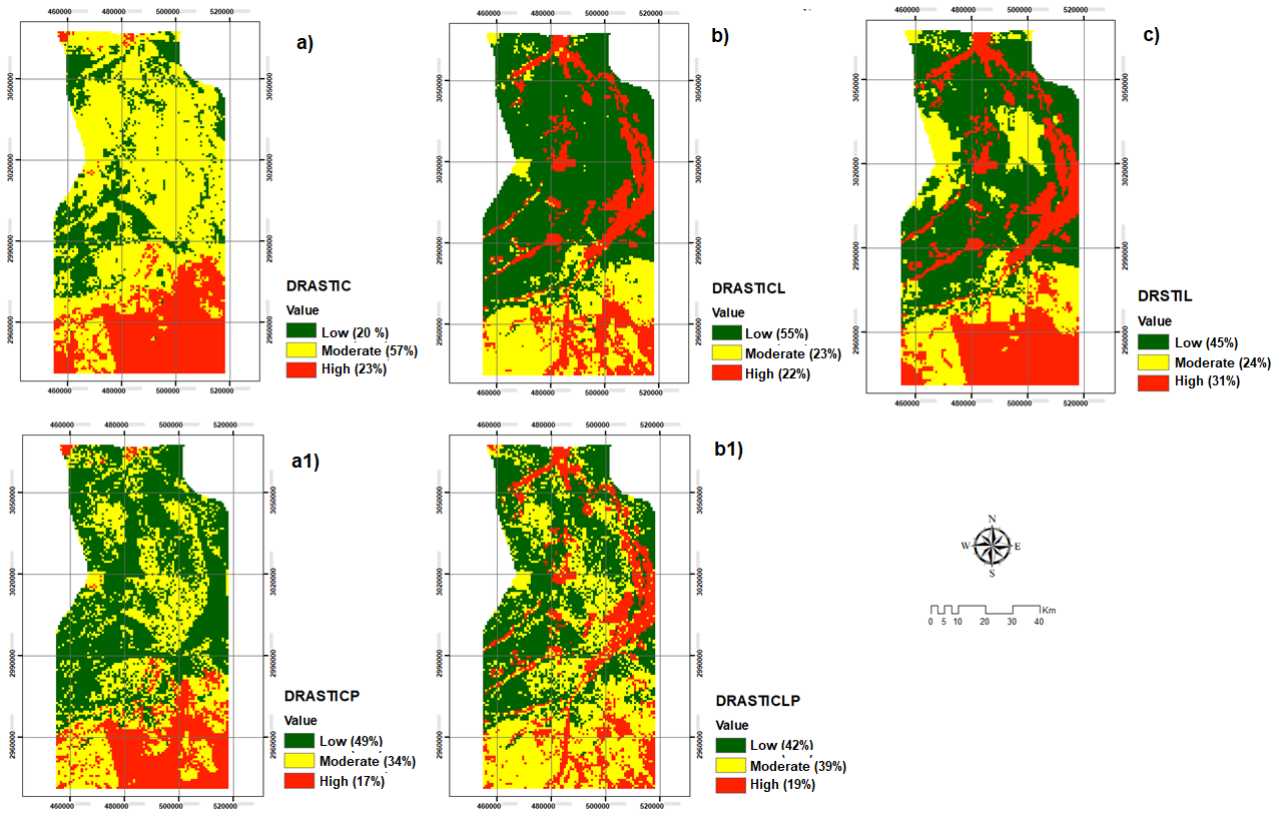
Figure 11.Current scenarios of vulnerability index (with percent of aquifer area) to Jim´enez-Camargo aquifer according to: a) DRASTIC, a1) DRASTIC-p, b) DRASTICL, b1) DRASTICL-p, and c) DRSTIL.

Even though, the range for the DRASTIC-p index values ranged from 58 to 161, similar to DRASTIC, the high and moderate vulnerabilities zones reduced their area in 6% and 23%, respectively (Figure 11a1), where, the low vulnerability zone increased to cover half the area of aquifer. The vulnerability index is predominantly low is in zones where the fine-grained soils are present (Figure 10f). This is due to, in this version (DRASTIC-p), the soil texture layer has a higher weight. These particles on the surface produce low permeability reducing water infiltration. Much of the soil has developed a "desert crust" that is smooth and hardened surface, from continuous processes of wetting and drying climatic condition and related accumulation of fine-grained particles. In addition, moderate vulnerability zone spreads where the alluvial material, moderate recharge, and native vegetation are present (Figure e,g, and h); the aquifer area is mainly covered by scrub and grassland, 88% of the total aquifer area. As with DRASTIC, the highest vulnerability was found to the south. The higher vulnerability areas are in zones where the sedimentary rocks and alluvial material are located (Figure 10e), with vertical hydraulic conductivity of 10^{-4} cm/s. The DRASTICL index range of values (82 to 181) were higher than those results from DRASTIC version. This vulnerability index includes the land-use layer (Figure 10), obtaining low vulnerability for more than a half of the aquifer area. The main contributor parameters to uncertainty were the land use (L) and topography (T), with variances of 10 and 8, respectively. Nevertheless, high vulnerability is well delineated in areas with agricultural and urban land use (Figure 10g). Thus, additional and relatively higher vulnerability can be attributed to the anthropogenic activities associated with agricultural and urban land use. Both activities can modify the soil structure and composition, producing a higher

exposure to potential pollutants. Similarly, in DRASTICL-p the vulnerability ranged from 73 to 201, where moderate vulnerability increased to cover 39% of the aquifer area. The vulnerability areas delineated with DRASTICL-p are located in similar zones than those obtained by DRASTICL. However, it is now also taking into account the soil texture. Finally, when lithology layer of the aquifer was removed to the DRASTIC, using DRSTIL, the vulnerability ranged from 59 to 148 with the high vulnerability area of 31%. This increase is mainly attributed to land use, topography, recharge, and unconfined water-table depth.

The ANOVA analysis showed significant differences between DRASTIC and their versions (<0.0001); these differences are mainly due to land-use layer. Thus, two groups were identified: the first group is integrated by DRASTICL and DRISTIL while the second group includes DRASTIC and DRASTIC-p. This highlights the importance of tracking land use as well as the application of pesticides and herbicides. For example, in California, USA there is a requirement to report all applications and amounts along with crop type, application date, and location. This information is integrated into a publicly available database called California Pesticide Inventory Program (CALPIP) (California Department of Pesticide Regulation 2019).

Comparison of the Vulnerability Indices

The maps of vulnerability were compared using correlations with parameters of groundwater quality (CONAGUA 2002). Significant correlations of Na, K, and NO_3^- were found for DRASTICL and DRSTIL (p<0.05). The mean concentrations of Na, K, and NO_3^- from aquifer well samples were 164 mg L^{-1}, 26 mg L^{-1}, and 4.12 mg L^{-1}, respectively. The Pearson correlation, DRASTICL showed correlations of 0.6 and

0.5 with Na and K, respectively, while DRSTIL just had a significant correlation with K (0.5), and none of the parameters showed correlation with NO_3^-. Moreover, the Spearman Correlation, for the three chemical species Na, K, and NO3- showed significant correlation with DRSTIL of 0.5. These results suggest that the original form of DRASTIC did not reflect actual groundwater vulnerability (Huan, Wang et al. 2012). Conversely, DRASTICL and DRSTIL vulnerability maps are reasonable for this study area. These results suggest that the addition or subtraction of layers and the weight changes improved the correlation value. Similar improved relations were obtained from published studies (Sahoo, Dhar et al. 2016).

Assessment of the Vulnerability Indices for Climate Change Scenarios

The evapotranspiration, precipitation, and recharge parameters were analyzed using RCP 4.5 and 8.5 scenarios, for both the nearest future (2015-2040) and distant future (2045-2069) periods (Figure 12 and 13). The vulnerability index assessment included statistical analysis of the parameters precipitation, evapotranspiration, recharge, Tmax, and Tmin, (Table 6).

The evapotranspiration, precipitation, and recharge have similar spatial distribution but different magnitudes for RCP's 4.5 (Figure 12) and 8.5 (Figure 13) in both future periods.

The highest evapotranspiration and precipitation values tend to be present in the southern parts of the aquifer for both RCP (4.5 and 8.5) scenarios and future periods. These two parameters showed similar values in the nearest future for the RCP's (4.5 and 8.5), but increased in the distant future for RCP4.5 while decreasing

Figure 12.Climatic parameters analyzed applied in RCP 4.5: a) Evapotranspiration, mm/y (2015–2040); b) Evapotranspiration, mm/y (2045–2069); c) Precipitation, mm/y (2015–2040); d) Precipitation, mm/y (2045–2069); e) Natural Recharge, mm/y (2015–2040); and f) natural Recharge, mm/y (2045–2069); and g) Land use (2045–2069) and (2045–2069).
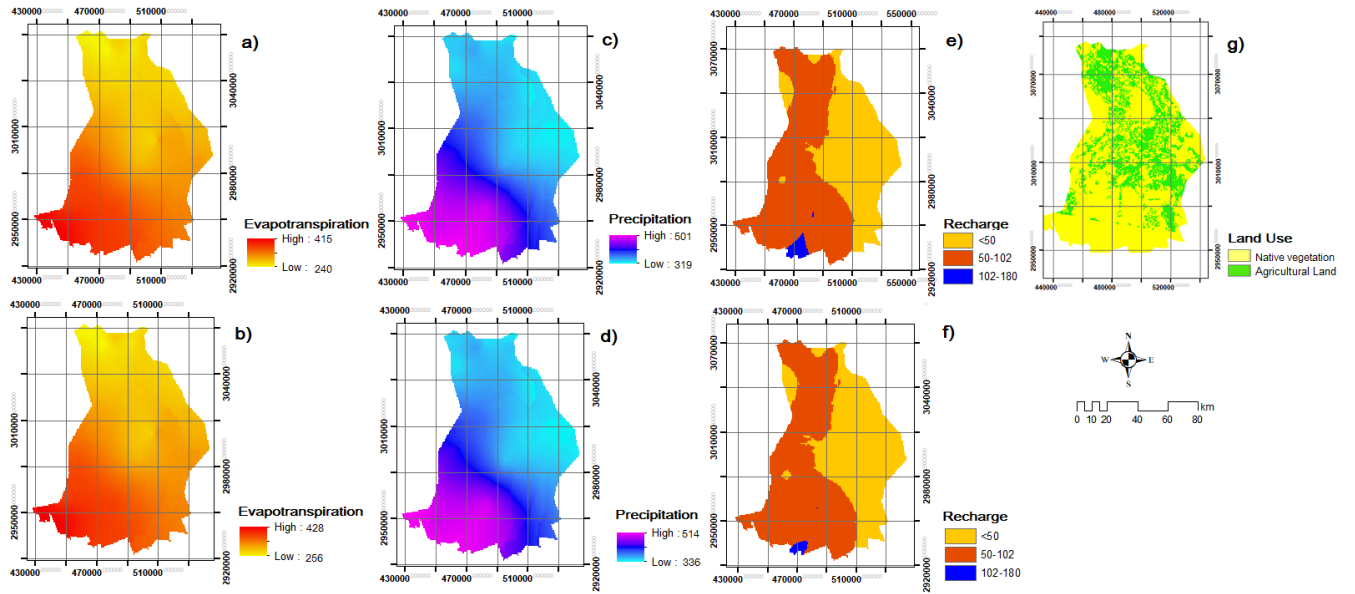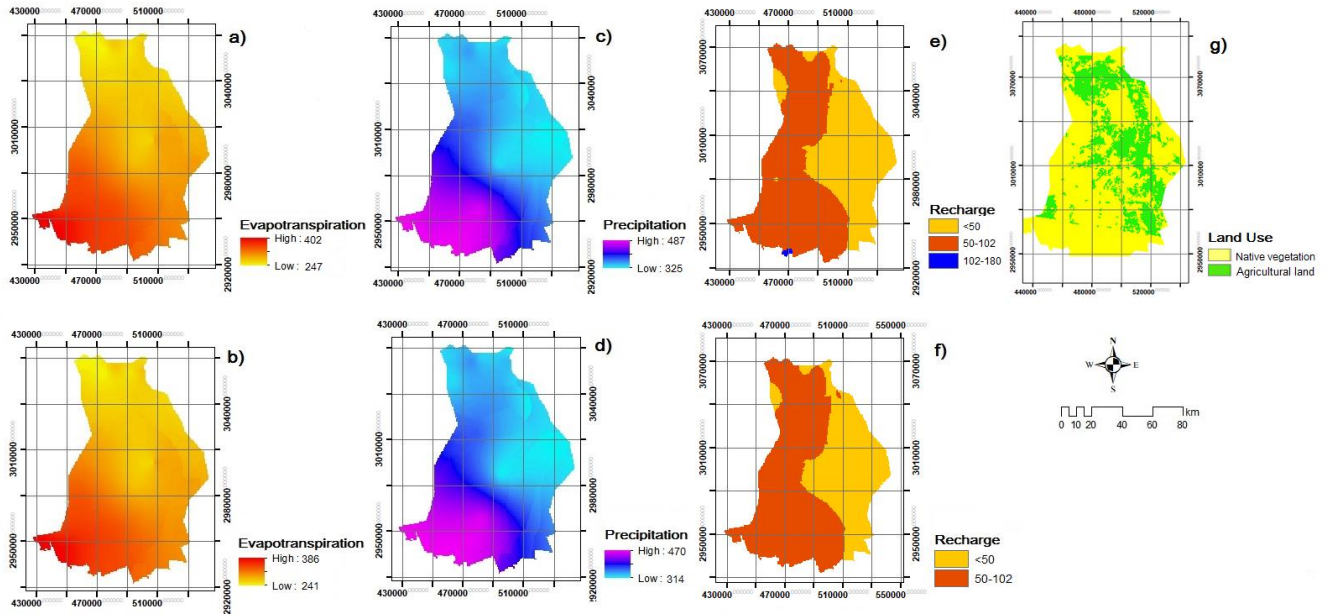
Figure 13.Climatic parameters analyzed applied in RCP 8.5: a) Evapotranspiration, mm/y (2015–2040); b) Evapotranspiration, mm/y (2045–2069); c) Precipitation, mm/y (2015–2040); d) Precipitation, mm/y (2045–2069); e) Natural Recharge, mm/y (2015–2040); f) Natural Recharge, mm/y (2045–2069); and g) Land use (2045–2069) and (2045–2069).

for RCP8.5. Higher evapotranspiration (64 – 82%) and precipitation (27 – 115%) increase relative to historical values for both future periods and both RCP scenarios. The highest values of evapotranspiration and precipitation are expected in the southern part of the aquifer (Figure 12a,b; 13a,b), for an R=0.9 (p<0.05) for both scenarios and future periods. Sedimentary rocks compose the southeastern part of aquifer, combined with shallow unconfined water-table depths (Figure 11a) where the groundwater will be more exposed to high temperature. With surface water the main source of irrigation for cultivated areas in that region, the increased evaporation and evapotranspiration also will increase the irrigation demand from both groundwater and surface water.

Similarly, under scenarios of increased CO_2 emissions, the agriculture irrigation demand in the Central Valley, California, drove additional undesirable effects such as land subsidence and reduced streamflow (Hanson et al. 2012; Hanson et al. 2010; Zhu et al. 2020).   The projections from analysis with IDRISI SELVA on the land use layer, showed an increase in the estimated size of future agricultural land use. The reliability of this projection was acceptable with a Kappa index value of 0.68. This analysis showed an increase from the current agricultural land use of 13.4% to 24.8% for the period 2015-2040. This potential land-use expansion is located in areas with favorable alluvial soils and smooth topographic slopes. Conversely, the future urban land use is projected to decrease by 3% from 2015-2040 to 2045-2069.

The highest potential recharge is expected in the southern regions of the aquifer, for both RCP scenarios and future periods. However, recharge is projected to be slightly larger in the nearest future (2015-2040) than in the subsequent future period (2045-2069) (Figures 12 and 13). With precipitation and ET projected to increase (Table 6), demand and consumption at the land surface will be greater that will result in a net reduction of water availability for recharge (<100 mm/y). Much of this larger recharge zone in both future periods can be attributed to vertical infiltrations from surface reservoirs such as Pico de Aguila dam and other reservoir (dams and lakes) located in the southern aquifer region (Figures 12e and f). A decrease in the high recharge area was estimated for both RCP scenarios and future period.

In RCP 4.5, the high recharge area in the nearest future is 157 km^2 but dramatically decreases to 0.7 km^2 in the distant future. The high recharge area decreases even more in the RCP 8.5 than in future periods of the RCP4.5 (Table 6, Figures 13e and f). For RCP8.5, the high recharge area decreases to 0.3 km^2 in 2015-2040 and is projected to potentially disappear completely in 2045-2069. The recharge parameter showed correlations with precipitation (R=0.55, p<0.05) and Tmin (R=-0.53, p<0.05), even though precipitation values are not less in futures periods relative to the current period, and recharge is also affected by Tmin (R=0.75, p<0.05).

Temperature is one of the most important parameters when climatic change is assessed. The projected range of temperatures is similar for both RCP scenarios within both future periods (Table 6). However, the range of temperature between

Table 6. Average (range) of physical parameters evaluated in three different scenarios.

	Historical data (1920-2010)	RCP 4.5 (2015-2040)	(2045-2069)	RCP 8.5 (2015-2040)	(2045-2069)
Precipitation	295	390[a]	404[§]	385[a]	374[§]
(mm/y)	(193-382)	(305-525)	(322-535)	(313-503)	(307-480)
Evapotranspiration	183	318[a]	333[§]	313[a]	300[§]
(mm/y)	(98-313)	(238-443)	(254-455)	(245-426)	(239-407)
Recharge	97	52[a]	51[b]	52[a]	53[b]
(mm/y)	(34-170)	(0-111)	(0-107.17)	(0-105.52)	(6.57-99.57)
Tmax	27.3	28.3[a]	29.1[b]	28.2[a]	29.8[b]
(°C)	(24.3-28.3)	(26.9-29.3)	(27.7-30.1)	(26.8-29.2)	(28.4-30.7)
Tmin	9.0	9.9[a]	10.8[b]	10.0[a]	11.4[b]
(°C)	(6.3-10.6)	(8.1-10.9)	(9.1-11.9)	(8.3-11.0)	(9.5-12.5)

[a] no significate difference between 4.5 and 8.5 RCP˙s to nearest future ($p<0.05$)
[b] no significate difference between 4.5 and 8.5 RCP˙s to distant future ($p<0.05$)
[§] significate difference for RCP˙s and scenarios ($p<0.05$)

2015-2040 and 2045-2069 is significantly different for RCP4.5; both with a temperature increase of 0.8°C. Similarly, Tmax and Tmin averages increase more by approximately 1.5°C from 2015-2040 to 2045-2069 in RCP8.5. This suggests that aquifer recharge will be affected by T, especially with the Tmin, which is correlated with precipitation. In agricultural areas where the evapotranspiration is projected to increase dramatically, this will require larger amounts of irrigation. Even though this could drive increased artificial recharge from inefficient irrigation, there is also increased pumpage that can results in a larger and more rapid declines of groundwater levels and a potential initiation of land subsidence (Hanson et al. 2010; Zhu et al. 2020).

Based on the future values of recharge and the land use, as well as the statistical analysis, the vulnerability maps were developed with the DRSTIL and DRASTICL indices using RCP4.5 and RCP8.5 scenarios for both future periods (Figure 14). DRASTICL shows greater areas with high vulnerability, ranging from 35% (RCP 4.5, distant future) to 37% (RCP 8.5, nearest future) of the total aquifer area. These areas are located in the south (area of greatest recharge) and are coincident with the alluvial parts of the aquifer coincident with agricultural land use.

Overall the DRSTIL showed a lower range of vulnerability than DRASTICL, and was similar for each RCP scenario and future period. The higher vulnerability zones from DRSTIL range from 17% (RCP4.5, distant future) to 25% (RCP4.5, nearest future) of the total aquifer area. For RCP8.5, the percentage of the vulnerability areas is very similar between nearest and distant future. The areas of highest vulnerability are coincident with the agricultural land-use areas (medium
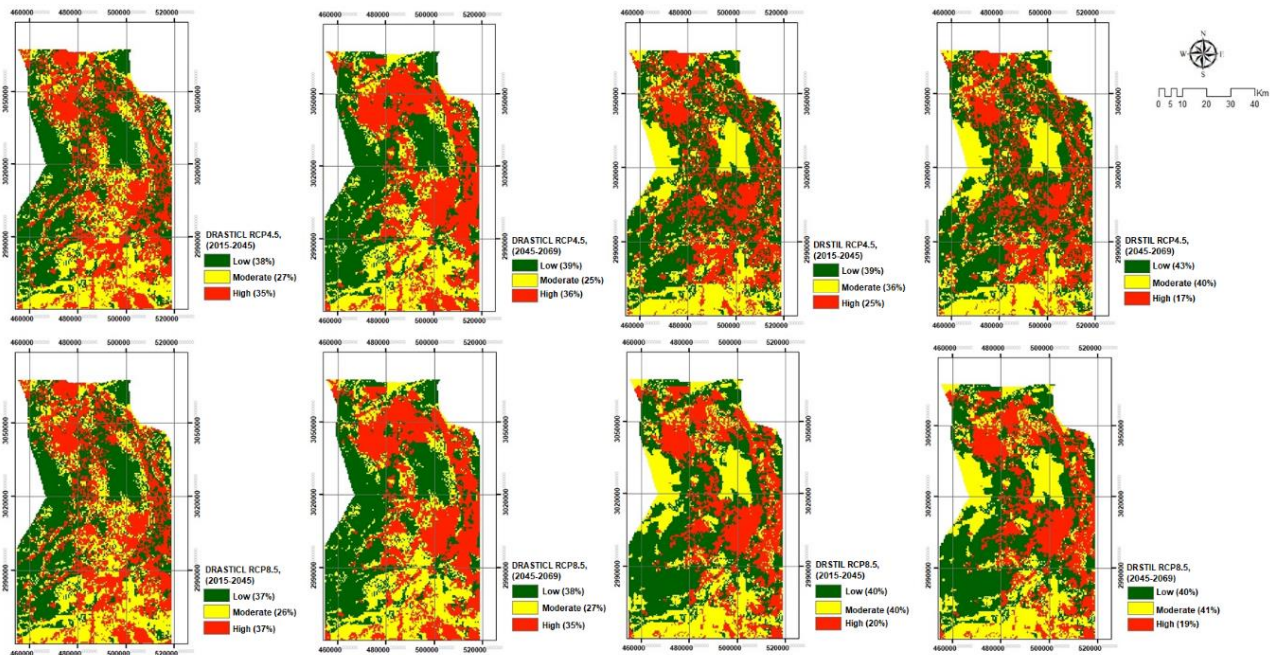
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Figure 14.Vulnerability indices (percent of aquifer area) from original DRASTIC and modified DRASTIC versions for RCP 4.5 and 8.5, for nearest and distant futures: a) DRASTICL (2015–2045), b) DRASTICL (2045–2069), c) DRSTIL (2015–2045), d) DRSTIL (2045–2069), e) DRASTICL (2015–2045), f) DRASTICL (2045–2069), g) DRSTIL (2015–2045), and h) DRSTIL (2045–2069).

recharge areas) (figs.12 and 13 -e, f, g), and mainly accentuated to the east and north (Figures 14e-h). Finally, DRASTICL showed increased high vulnerability areas of the aquifer from current to futures scenarios, from 22% to >34 %, (Figure 14).

This can be attributed to the potential increase of areas agricultural areas for future periods. Conversely, DRSTIL results showed a potential decrease in high vulnerability areas in futures periods relative to current conditions. This may be related to the projected reduction of high recharge zones, however, the leaching and transport of pollutants from aquifer media is not part of this method's evaluation, and its effect remains uncertain within the DRASTIC evaluations.

The methods developed here provide a broader approach to DRASTIC analysis and indicates that land use layer gave the high vulnerability for the aquifer in this study. High and moderate vulnerability found in this work is consistent with places of arid climate and agricultural land use (Li and Merchant 2013; Neshat et al. 2014; Zair, Chaab, and Bertrand 2017; Bhaskar et al. 2018; Rodríguez-Huerta, Rosas-Casals, and Hernández-Terrones 2020; Kløve et al. 2014). Groundwater with high concentrations of Na, K, and NO_3^- may be related to leaching from aquifer geology, as well as from soils in cultivated lands (Hernández 2012). The presence of these chemical species in groundwater samples confirmed the vulnerability areas found by DRASTIC. Similar correlation using nitrates (R=0.5, p<0.05) from agricultural practices have also been documented as vulnerabilities in aquifers from Greece, India, Pakistan, and Poland (Khan et al. 2019; Kozłowski and Sojka 2019; Sahoo et al. 2016; Panagopoulos, Antonakos, and Lambrakis 2006). In addition, these pollutants have not been directly related to hydraulic conductivity and soil in

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the aquifer vulnerability assessments (Panagopoulos, Antonakos, and Lambrakis 2006).

The high vulnerability zones are coincident with agricultural land use, as well as areas with the higher elevations and related greater precipitation, and in southern parts of the aquifer, where there are also reservoirs, which also can contribute to the leaching and transport to the shallow groundwater tables. The relief and related slope of the land surface favors a greater runoff through some rivers, which transport water to low zones in the valley. Thus, greater slope areas disfavors the aquifer recharge and favor greater runoff, that yield low or moderate groundwater recharge (Cazanescu and Cazanescu). The new modified versions of DRASTIC also are more efficient, by including the land use layer, which in turn, helps to identify the importance of sub-regional forcing related to land use. For example, the impact of agricultural land use on aquifer recharge, results in the larger volumes of water used for irrigation that cause larger artificial recharge to the aquifer due to inefficient irrigation (Saida et al. 2017; Bhaskar et al. 2018; González Herrera et al. 2018; Hosseini-Moghari et al. 2019).

The study region used for comparison of the DRASTIC methods and estimation of climate change has dry conditions and is an important agricultural area, which is the main economic source to local inhabitants. Over the last 40 years, there has been an accelerated increase of groundwater use for irrigation along with increased groundwater pumpage (López et al. 2011). The predominant agriculture in the region are pecans orchards (65.7%) with a total surface of 247,969 ha., and have increased owing to high export demand up to 89% since 1980 (CONAGUA 2018, 2002), along with increases in other seasonal crops with high water demand

such as alfalfa (32.8%), grain corn (0.6%), oat (0.4%), and sorghum (0.4%) (SAGARPA 2011). Thus, Jimenez-Camargo aquifer is under increased water demand and "hardened demand" from long-term orchards that require water over decades and not just seasonal or interannual demands for irrigation. The Jimenez-Camargo aquifer is in overexploited status with a groundwater deficit of -135.3 hm3/y (CONAGUA 2018; Hernández 2012), yet the Mexican authorities have granted 284 hm^3/y of groundwater to agriculture, with about 20% artificial recharge from inefficient irrigation (56.9 hm3/y). Here, the estimation of natural vertical recharge is 116.4 hm^3/y producing a total recharge of 173.3 hm^3/y. However, the water abstraction measured is 303.1 hm^3/y with 5.5 hm^3/y of natural discharge by springs; showing a depletion in the groundwater storage, streamflow capture, and reduced discharge inflow budgets, which is not sustainable.

Even with an increase in precipitation (>100 mm), projections of climate-change scenarios, for both RCP scenarios, this analysis shows a reduction of area in the highest potential recharge areas (Figures 12 and 13). In the future scenarios, the aquifer area shows an overall decrease in recharge relative to historical conditions. This suggests that reduced recharge is due to the sum of two main causes: a) precipitation increase in the same area where evapotranspiration is also larger, and b) minimum temperature is increasing into future, which also drives larger evapotranspiration and potential increased demand for irrigation with overall hotter temperatures and longer growing seasons. In the historical scenario, the recharge average is about 33% from precipitation (Table 2), but in the projected scenarios the average water recharged from precipitations will be about 13.5%. Higher temperatures produce an increase in evaporation from surface-water bodies present

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in that area, which reduces the contact area for infiltration and the amount of surface water available for irrigation. In addition, the change in temperature patterns force the biota to modify its biochemical activity, resulting in an increase of water demand (Bhaskar et al. 2018; Kløve et al. 2014).

These projections under climate change show a decrease in the area of agricultural land use into the future. This difference can be attributed to aquifer storage depletion related to increased irrigation demands of perennial and seasonal crops in the study area. In addition, the overexploitation of aquifers from agricultural demands will also result in a loss of water quality, causing even higher vulnerability. Under this condition, the irrigated soils can present high amounts of salts, which result in additional pumpage and irrigation to leach salts from the root zone (Hanson, McLean, and Miller 1994; Cahn and Bali 2015; Boyce et al. 2019; Rodríguez-Huerta, Rosas-Casals, and Hernández-Terrones 2020; Fries et al. 2020; Mendieta-Mendoza et al. 2020). Consequently, farmlands will need major quantities of irrigation under climate change scenarios that will also include salinity issues.

The vulnerability maps show an approximation of how future changes to vulnerability will affect the potential distribution of usable groundwater (Li and Merchant 2013; Albornoz-Euán and González-Herrera 2017; Lu et al. 2017). In this study, the DRASTIC approach has helped to understand the potential vulnerability of aquifer under the effects of recharge and the land use, that, when combined with climate variations can drive increasing vulnerability for both indices as well as increased water infiltration that can transport pollutants to shallow unconfined groundwater with further water-quality degradation. Therefore, it is necessary to consider the impacts of these pollutants on its destination and paths of infiltration,

because they are highly variable and can be very hard to predict, as they can by trapped in soil strata that make up the layers of the aquifer. Within these water cycles of supply and demand, the groundwater levels continue to decrease with the decreased recharge, increased vegetation covering, and increased rate of groundwater pumpage (Fries et al. 2020; Chen et al. 2018). In a similar study of an aquifer in Yucatan, Mexico, where precipitation values are >1,050 mm, and temperature was estimated to increase by 0.62°C and 0.72°C, were coincident with estimates of reduced groundwater recharge of 23% and 20%, for RCP 4.5 and 8.5, respectively, (Rodríguez-Huerta, Rosas-Casals, and Hernández-Terrones 2020). In this study area with dry conditions, the Jimenez-Chihuahua aquifer there is an estimated groundwater recharge reduction of about 47 % for both RCP's. This is a lower estimate than the current estimate of groundwater use and must be taken into account for the sustainability of the resource.

It is important to point out the semi-arid regions includes developed agricultural areas, while seasonal rains can contribute to natural groundwater recharge; it is also necessary to assess the artificial recharge from inefficient irrigation. Artificial recharge depends on when and where the precipitation, evapotranspiration, and increment of cultivated zones are occurring and this was not part of any of these DRASTIC methods used in this study. For instance, in the Central Valley of California the evapotranspiration is higher annually than precipitation, but precipitation exceeds evapotranspiration in winter season and artificial recharge from inefficient irrigation exceeds spring-summer evapotranspiration on a monthly basis (Faunt, Belitz, and Hanson 2009). The related climate change analysis performed with an integrated hydrologic model (Hanson et

al. 2012), showed the importance of evaluating local climatic variability and climate change, as this will help to improve water budgets and supply-and-demand dynamics within climatic change and its impacts on surface water and groundwater use and movement. Moreover, these kind of studies must also include the simulation of flow and related analysis of fate and transport of contaminants, which represents many decades of model simulation though to get long enough travel paths to assess any potential change in water quality relative to nearby well and surface-water return-flow samples (Central Valley Salinity Coalition 2012).

The comparison of the DRASTIC methods and the efficacy of this analysis with related vulnerability maps provides a baseline for developing policies and decisions concerning the protection and management of water resources. Some strategies that could contribute to more sustainable groundwater budgets may include: a) efficient measuring and monitoring of groundwater pumpage. b) irrigation management/irrigation scheduling methods, c) parcel planning as well as to limit the opening of new agricultural lands, c) mapping land use on an annual or seasonal basis, d) implementation of crops with less water requirements and use of more efficient irrigation methods, and e) raising promoting the governance of conjunctive use of groundwater and surface water by the social sectors (government, population, private industry) through environmental education and modernized governance.

CONCLUSIONS AND RECOMENDATIONS

In this study, the potential effects on vulnerability and availability of groundwater from the Jimenez-Camargo aquifer was obtained by the development of modified DRASTIC methods. This study shows that DRASTICL and DRSTIL have better skill than other forms of DRASTIC to detect the vulnerability areas, where the impact of the vadose zone and land use attributes are the main contributors to the aquifer vulnerability. This study also showed that the current higher vulnerability is located in the southern part of this aquifer, and the groundwater pollution may also be related to nitrates, sodium, and potassium from agricultural activities.

Furthermore, DRASTIC versions were applied for climate change assessments on the study area. These methodologies also showed that, topography, recharge, and land use variables are useful to predict changes in projected future climate-change scenarios and related future changes in vulnerability and availability for groundwater. The climate-change scenarios projected a negative effect in the areal extent of recharge zones, as well as an increase of high vulnerability for the aquifer. In future scenarios evaluated, high vulnerability showed a spatial increment towards to the east and north of the aquifer area, according to the projected expansion of agricultural land-use zones. Therefore, with higher CO_2 emissions, there could be more significant reductions for the recharge replenishment to the underlying aquifers. Combined with an expected increase of land use for nearest future, these agricultural land-use areas will show a decrease in land use for distant future period. This is related to the reduction of water for irrigation driving a potential reduction in agricultural land use. This will, in turn, generate higher

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vulnerability within the agricultural land use, which may further exacerbate the problem of groundwater depletion and overexploitation of the aquifers.

While this initial assessment outlines the potential vulnerability and relations of vulnerability, a more comprehensive evaluation also is needed, that includes a holistic assessment of the environmental, social, and economic components of supply and demand for conjunctive use of all water, to achieve a more complete water management system. It will require a complete frameworks of monitoring systems, integrated hydrologic modeling of alternate climate change scenarios, and modeling the initial components from a broader conjunctive use and sustainability framework (Boyce et al, 2020). This will help to develop relevant strategies aimed at sustainability through potential reductions and increased efficiencies in use of water and land resources. Additionally, it will demand outreach to the general population, water purveyors, agricultural producers, as well as state and federal agencies that oversee water management are stewarding the resources and are better informed about these conditions, trends, and vulnerabilities. Without an integral approach to management and growth such as additional agricultural land use could result in potential threats to water and food security, and higher risk of pollution combined with reduced sustainability of water resources. Thus, monitoring, modeling and informed management will help to further identify and mitigate the vulnerabilities identified in this initial study and guide the governance, development, and mitigation of water uses that includes the sustainable use of surface water combined with groundwater and land use subject to climate change and climate variability.

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APPENDIX

This document shows the information of DRASTIC layers used to obtain the models proposed.

Methodology section

Description of the Vulnerability Index

Calculation of DRASTIC layers

Depth to the unconfined groundwater (D). It is considered an important factor because it is the distance from the land surface to the current water table within the aquifer. Inclusion of this parameter into the DRASTIC methodology was originally suggested for an aquifer in Japan (Babiker, Mohamed et al. 2005). The values were obtained from groundwater-level data of the well survey made by National Water Commission from Mexico (CONAGUA) in 2002 throughout this aquifer zone (CONAGUA 2002).

Aquifer material (A). This layer is composed by structures of geogenic origin. The classifications of lithology of the area of this aquifer uses the geological map from the SGM (SGM 2014).

Soil media (S). Defined here as the uppermost weathered part of the unsaturated zone at the land surface, and controls the recharge amount that can infiltrate. This layer data was taken from the edaphology layer published by INEGI (INEGI 2014).

Table 1. Factor weights in the DRASTIC method.

Factor	Range	Rating	Weight General	Pesticide (p)
D (Depth to water table for unconfined aquifer; m)	0-2	10	5	5
	2 - 5	9		
	5 - 9	7		
	9 - 15	5		
	15-23	3		
	23-30	2		
	>30	1		
R (net recharge; mm/y)	<50	1	4	4
	51-102	3		
	102-178	6		
	178-254	8		
	>254	9		
A (aquifer media)	Reservoir	0	3	3
	Conglomerate	6		
	Alluvial	8		
S (soil texture)	Reservoir	0	2	5
	Fine texture	5		
	Medium texture	7		
	Coarse texture	9		
T (topography; slope°)	0 - 2	10	1	3
	2 - 6	9		
	6 - 12	5		
	12 - 18	3		
	>18	1		
I (vadose-zone impact)	Metamorphic rocks	4	5	4
	intrusive igneous rocks	5		
	sedimentary rocks	7		
	soil (medium texture)	8		
	extrusive igneous rocks	10		
C (vertical hydraulic conductivity; m/day)	Metamorphic rocks	1	3	2
	intrusive igneous rocks	1		
	extrusive igneous rocks	1		
	sedimentary rocks	3		
	soil (medium texture)	3		
L (land use)	Urban zone	8	5	5
	agriculture	8		

scrub	2
grassland	2
forest	2
vegetation	2
Body water	3

Topography slope (T). Defined here as the variability of the land-surface slope. The percentages (%) were obtained from the study area's MDE (INEGI 2017), with the Spatial Analyst tool of ArcGis 10.3.

Impact of the vadose zone (I). Defined as the top layer as the unconfined zone between the land surface and the water table. Data was taken from the geological map of the SGM (SGM 2014). The surface of the aquifer is mostly alluvial material, also there are sedimentary rocks with limestone conglomerates, mudstone, and sandstone in some parts of the valley .

Rock type vertical hydraulic conductivity (C). This parameter was estimated from data using the Soil Contamination Assessment manual: Reference Manual (ONU-FAO 2000), where according to the type of rock it is related to ranges of vertical hydraulic conductivity Kv (m/day) (Hernández 2012).

Land use (L). Defines the natural and anthropogenic use of land at the land surface. Data was taken from the map of vegetation and the land use of CONABIO (INEGI 2017). The main land use is natural vegetation above the aquifer. The main urban areas are the cities of Camargo and Jiménez, where its principal economic activity the agriculture.

Annual natural recharge (R). The aquifer is recharged through the upper parts of the study area and the vertical infiltration by natural rainwater and runoff and artificial recharge from return flows from inefficient irrigation. Since most precipitation and evapotranspiration do not occur at the same part of a year, this becomes a non-conservative estimate of recharge. Nevertheless, in this work, the net recharge of

the aquifer was calculated using historical data using a simple annual budget formula from Thornthwaite (Zair, Chaab et al. 2017) by the following equation:

Net Recharge (mm/y) = Precipitation – Evapotranspiration – Surface Water Runoff

The average of historical annual data to precipitation, evapotranspiration, and temperature for the period from 1920 to 2010 were gathered with the climate information program ERIC III (IMTA 2009) from data recorded by CONAGUA. Likewise, the evapotranspiration data were acquired using Thornthwaite Water Balance model (1.1.0 version) from the United States Geological Survey (USGS) (McCabe and Markstrom 2007). Whereas, surface-water runoff were calculated using the equation (5) proposed by Mexican regulation (NOM-011-CONAGUA-2015 2015):

Surface-water runoff (mm/y) = Water-runoff coefficient * Annual Precipitation

Thus, to obtain the water runoff coefficient was used the equation

$$Ce = K (P - 250) / 2000 + (K – 0.15) / 1.5$$

where P is the annual precipitation (mm), and the parameter K is given according to type and use land (NOM-011-CONAGUA-2015 2015); this parameter was obtained by weighted average from K values of 0.16 and 0.27 to native vegetation and cultivated/urban zones, respectively.

The aquifer recharge was obtained by the spatial interpolation of the precipitation, evapotranspiration, and water runoff parameters. Finally, this layer was reclassified by DRASTIC categories.

Results section

Classification of Layers

The net recharge was obtained from precipitation, water runoff, and evapotranspiration; these classified layers are showed in the Fig. CD1.

Sensitivity analysis

The descriptive statistics are summarized for the eight layers that were used to compute the DRASTIC, DRASTICL, and DRSTIL indices in Table CD2. The descriptive statistics were performed for the eight layers that were used to compute the DRASTIC, DRASTICL, and DRSTIL indices.
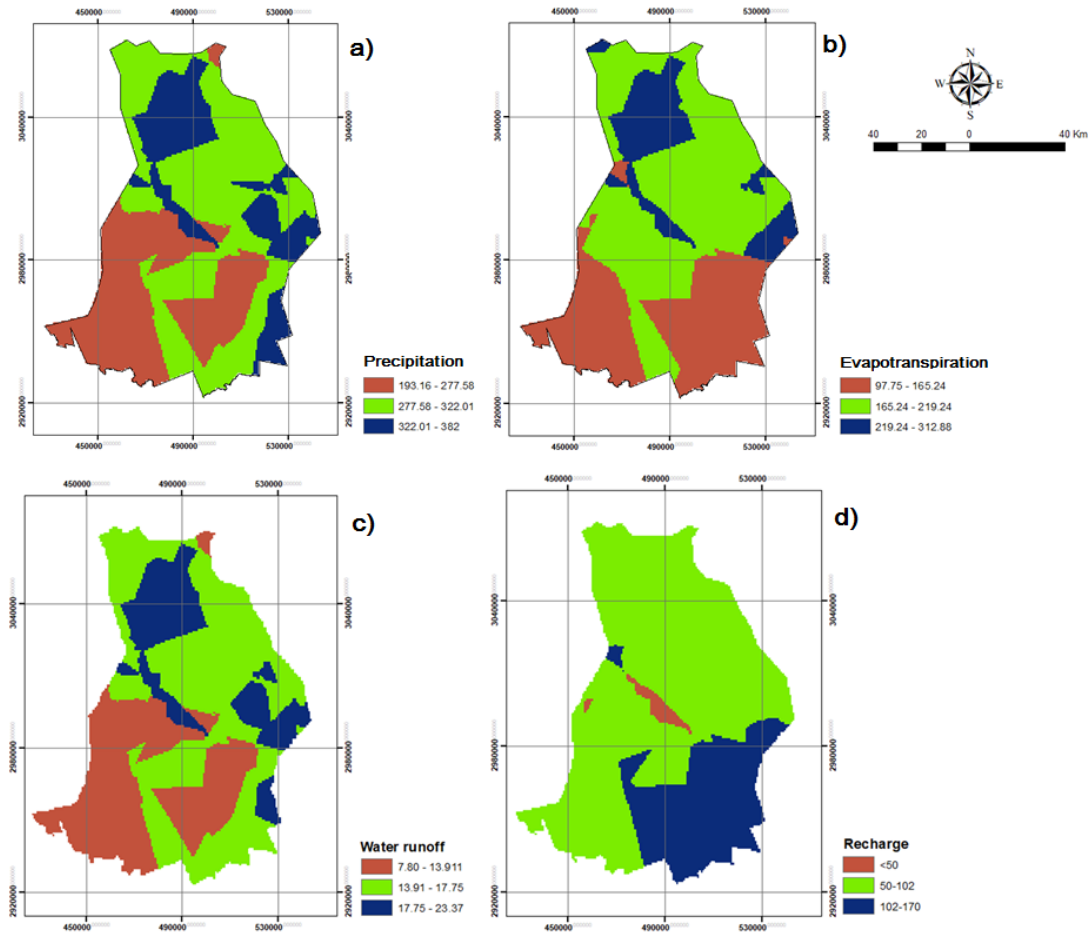
Figure 1. Layers of historical data: a) precipitation (mm/y), b) evapotranspiration (mm/y), c) water runoff, and d) aquifer recharge calculated (mm/y).

Table 2. Layer contribution to DRASTIC Vulnerability Index, as well as sensitivity analysis.

Layer	Layer Contribution			Single Parameter Sensitivity				Map Removal Sensitivity Measure		
	Rating			Theoretical Weight (%)	Effective weight (%)			Rating		
	Mean (max-min)	SD†	VC* (%)		Mean (max-min)	Median	SD	Mean (max-min)	Median	SD
D	2.8 (1-5)	1.7	62.1	21.7	8.8 (4-26)	5	6.3	1.3 (0-5)	1	0.7
R	3.3 (1-6)	2.5	75.5	17.4	12.2 (3-23)	11	3.3	0.7 (0-6)	1	0.6
A	7.0 (6-8)	1.4	20.2	**13**	**19.1** (0-31)	19	3.0	1.0 (0-2)	1	0.71
S	5.0 (3-7)	2.0	40.0	8.7	11.5 (80-18)	12	2.0	0.3 (0-2)	0	0.5
T	3.0 (1-5)	2.8	94.3	4.3	1.8 (0-7)	1	1.9	2.1 (1-3)	2	0.62
I	6.8 (4-10)	2.4	35.1	**21.7**	**35.9** (19-59)	36	5.2	**4.2** (1-7)	4	0.91
C	2.0 (1-3)	1.4	70.7	13	7.1 (2-13)	8	2.0	1.2 (0-3)	1	0.51
D	2.8 (1-5)	1.7	62.1	17.9	8.0 (3-24)	4	5.9	1.3 (0-7)	1	0.94
R	3.3 (1-6)	2.5	75.5	14.3	10.8 (2-21)	10	3.3	0.7 (0-6)	1	0.84
A	7.0 (6-8)	1.4	20.2	**10.7**	**16.8** (0-27)	16	2.6	0.8 (0-2)	1	0.45
S	5.0 (3-7)	2.0	40.0	7.1	10.1 (0-16)	11	2.1	0.6 (0-3)	1	0.54
T	3.0 (1-5)	2.8	94.3	3.6	1.5 (80-5)	0	1.8	1.9 (1-3)	2	0.5
I	6.8 (4-10)	2.4	35.1	**17.9**	**31.7** (17-50)	32	5.1	**3.4** (0-5)	3	0.74
C	2.0 (1-3)	1.4	70.7	10.7	6.2 (1-10)	7	1.7	1.0 (0-3)	1	0.5
L	4.3 (2-8)	3.2	74.2	17.9	10.9 (5-48)	8	7.3	1.1 (0-4)	1	0.91
D	2.8 (1-5)	1.7	62.1	22.7	10.5 (3-30)	6	7.3	1.9 (0-9)	2	1.2
R	3.3 (1-6)	2.5	75.5	18.2	14.2 (3-29)	13	4.2	1.0 (0-9)	1	1.0
S	5.0 (3-7)	2.0	40.0	**9.1**	**13.7** (0-23)	14	3.0	0.5 (0-3)	0	0.7
T	3.0 (1-5)	2.8	94.3	4.5	2.4 (0-7)	1	2.1	2.7 (1-5)	3	0.6
I	6.8 (4-10)	2.4	35.1	**22.7**	**42.1** (21-58)	43	6.8	**4.7** (1-7)	5	1
L	4.3 (2-8)	3.2	74.2	22.7	14.5 (6-63)	11	9.5	1.5 (0-5)	1	1.2

D is the depth to the unconfined groundwater, R is the annual natural recharge, A is the aquifer material (lithology of the aquifer), S is soil media (the texture of soil), T is the topography slope, I is the impact of the vadose zone, and C is the rock type vertical hydraulic conductivity, and L (land use) † Standard deviation * Variation coefficient