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REGIONAL GROUNDWATER FLOW SYSTEM ANALYSIS IN THE MEXICO BASIN

TESIS

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DOCTORA EN CIENCIAS DE LA TIERRA
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PRESENTA

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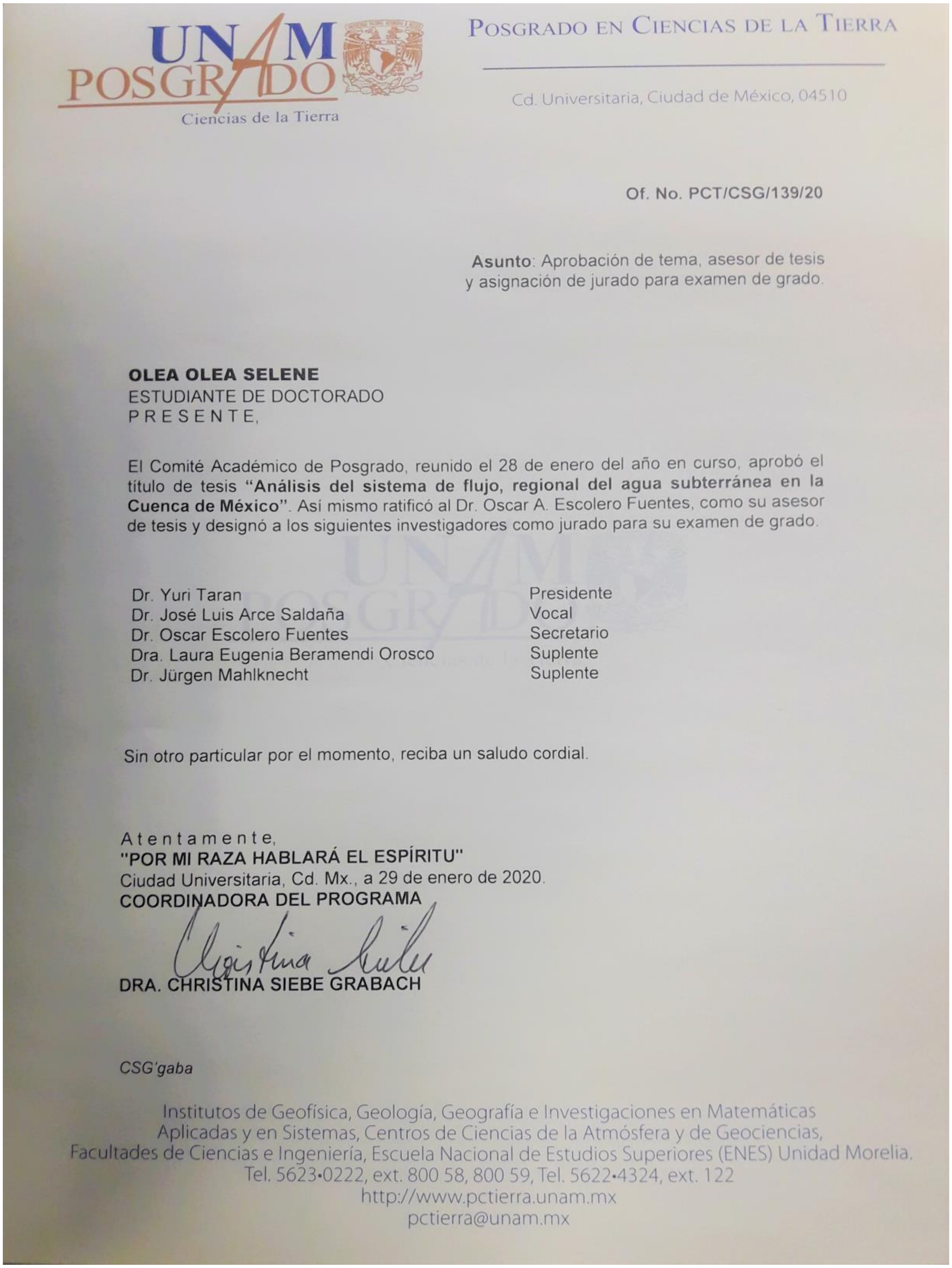

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El Comité Académico de Posgrado, reunido el 28 de enero del año en curso, aprobó el título de tesis **"Análisis del sistema de flujo, regional del agua subterránea en la Cuenca de México"**. Así mismo ratificó al Dr. Oscar A. Escolero Fuentes, como su asesor de tesis y designó a los siguientes investigadores como jurado para su examen de grado.

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SELENE OLEA OLEA

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Dedicatoria

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Abstract

The Mexico Basin is an area inhabited by more than 21 million people, where water is a highly demanding resource and which is supplied by groundwater water extraction wells and surface water from other basins. The high demand for this resource has caused extraction to be intensive and it has produced effects such as soil subsidence and poor water chemical quality in some areas. However, it is not quite understood at all how the system works furthermore, it has not been possible to generate adequate solutions for this problem.

The aim of this work is to study the system through the concept of flow systems, which is a unique and interconnected system conformed by components or flow paths that has local variations. It is necessary to identify the components of this complex system in a multilayer geological environment, so it will be necessary to develop a methodology that does not exist so far.

The work methodology consisted of collecting previous information; groundwater sampling to measure major ions, trace elements, isotopes of O, H, tritium (^{3}H), and C-14 in 406 sites (73 springs and 333 wells); laboratory analyses and cabinet work. The processing work included spatial analysis, statistical analyses, hydrogeochemical analysis and geochemical modeling with two types of modeling: inverse and mixing.

The main results of this work are: delimitation of a shallow aquifer in the immediate vicinity of Mexico City; flow components identification from two perspectives one as a whole system and two as a whole system with local variations; it was found the presence of groundwater mixture among the flow components and the mixing ratios were estimated; hydrogeochemical processes were determined in the components. The flow system components are five, four described in scientific papers and one that is not published: 1) Local is representative of recent flow, 2) Intermediate is representative of sulfate-rich flow, 3) Cold regional is representative of chemically evolved flows with long paths, 4) Hot regional is representative of more chemically evolved and deeper flows that ascend throughout faults and fractures. And an additional component that is not published yet 5) Small local is representative of very recent flow associated with spring discharges in mountain zones. These components are mixed in the groundwater extraction areas and are related to intensive extraction, complex geology, and wells design. The core hydrogeochemical processes present are water-rock interaction among minerals that form volcanic rocks (the majority), clays (lacustrine deposits), and carbonated rocks (in a single area); dissolution and precipitation; ion exchange; cold and thermal flow mixture.

The main conclusions are: components of the flow system are not static and might change over time due to extraction or climate change; the water extracted in the Valley of Mexico comes mainly from two components i.e., local and hot regional whereas in other valleys comes from local and intermediate components; relations among dissolved minerals and geology are established with geochemical modeling; with the methodology of this investigation is easy to study a complex flow system and it can be adapted for other systems with similar characteristics.

Resumen

La Cuenca de México es una zona habitada por más de 21 millones de personas, en donde el agua es un recurso altamente demando y es suministrado mediante pozos de extracción de agua subterránea y agua superficial de otras cuencas. La alta demanda de este recurso ha generado que la extracción sea intensiva y ha producido efectos como la subsidencia del terreno y mala calidad química del agua en algunas zonas, sin embargo, debido a que no se entiende como es el funcionamiento del sistema en su conjunto, no ha sido posible generar soluciones adecuadas para este problema.

El objetivo principal de este trabajo es estudiar el sistema en su conjunto a través del concepto de los sistemas de flujo, que es un sistema único e interconectado que está conformado por componentes o trayectorias de flujo y que tiene variaciones locales. Siendo necesario identificar las componentes de este sistema complejo en un medio geológico multicapas, por lo que será necesario desarrollar una metodología que hasta ahora no existe.

La metodología de trabajo consistió en: recopilar información previa; muestreo de agua subterránea para medir iones mayoritarios, elementos traza, isotopos de O, H, tritio (^{3}H) y C-14 en 406 aprovechamientos (73 manantiales y 333 pozos); análisis de laboratorio y trabajo de gabinete. El trabajo de gabinete comprendió análisis espaciales, análisis estadísticos, análisis hidrogeoquímicos y modelación hidrogeoquímica con dos tipos de modelación: inversa y de mezcla.

Los principales resultados de este trabajo son: delimitación de un acuífero somero en las inmediaciones de la Ciudad de México; identificación de las componentes de flujo desde dos perspectivas, una como un sistema completo y dos como un sistema completo con variaciones locales; se encontró la presencia de mezcla de agua subterránea entre los componentes del flujo y se estimaron las relaciones de mezcla; se determinaron procesos hidrogeoquímicos en los componentes. Los componentes del sistema de flujo son cinco, cuatro se describen en artículos científicos y una en datos no publicados: 1) Local que es representativa de flujo reciente, 2) Intermedia que es representativa de un flujo rico en SO_4, 3) Regional fría que es representativa de flujos químicamente evolucionados con largas trayectorias de recorrido, 4) Regional caliente que es representativa de flujos químicamente más evolucionados y profundos que ascienden a través de fallas y fracturas. Y la componente adicional que aún no se publica 5) Local pequeño es representativo de caudales muy recientes asociados a manantiales que descargan en zonas de montaña. Estas componentes se mezclan en las zonas de extracción del agua subterránea y tienen relación con la extracción intensiva, la geología compleja y el diseño de los pozos. Los principales procesos hidrogeoquímicos presentes son: interacción agua roca entre minerales formadores de rocas volcánicas (en su mayoría), arcillas (en depósitos lacustres), y en una zona con rocas carbonatadas (solo en una zona); disolución y precipitación; intercambio iónico; mezcla de flujos fríos con termales.

Las principales conclusiones son: las componentes del sistema de flujo no son estáticas y pueden cambiar en el tiempo debido a la extracción o el cambio climático; el agua extraída en el Valle de México proviene principalmente de dos componentes, es decir, local y regional caliente, mientras que en otros valles proviene de componentes locales e intermedios; las relaciones entre minerales disueltos y geología se establecen con el modelado geoquímico; con la metodología de esta investigación es fácil estudiar un sistema de flujo complejo y se puede adaptar para otros sistemas con características similares.

Chapter 1.

Introduction

Chapter 1. Introduction

1.1 Introduction

The study of Mexico basin from the flow systems perspective takes us to rethink the conceptualization of flow system concept, the methodologies that can be used to study it, and the challenges involved in studying a complex flow system. This is part of the knowledge evolution, since the first groundwater studies were developed in which the flow system conceptualization was gradually given as an evolutionary topic where it was not possible to understand or manage groundwater with traditional concepts. In the same way, there are established criteria to approach the study of a flow system, but in practice, it is verified that each system and zone has its particular characteristics and it is not possible to follow them as a cooking recipe, here it is where the need arises to create new study approaches and methodologies that can be applied in non-heterogeneous and complex systems, always starting from the point of view that it is an interconnected system with components where these can present changes related to the water management.

In this work, traditional conceptualizations of groundwater study will be approached, advancing to new visions where groundwater is studied from the perspective of a flow system that later evolves to consider its local variations.

1.2 Studies of groundwater flow systems in the world

The study of groundwater in the world from the flow system perspective has been more applied since the hydrogeology specialists have understood that groundwater must be seen from a whole system that is conformed by different flow components. In this thesis section, it will be covered a review of some of the most recent works that have been developed to classify flow systems at the international level, and where the present work is placed.

The flow system works were classified according to the main methodology or data used to delimit the flow system, these are 1) chemical data, 2) isotopic data, 3) chemical and isotopic data combination, 4) geological environment data and 5) combined data of different types.

1) Chemical data

To depict the study of groundwater flow system from the water chemistry perspective, two recent works are described. The first research was carried out by Gao et al. (2020), they studied the Guanzhong basin that is located in central China, using 509 shallow groundwater samples to measuring Ca^{2+}, Mg^{2+}, HCO_3^-, SO_4^{2-}, Cl^-, F^-, Cr^{6+}, total dissolved solid (TDS) and total hardness that were evaluated by using the iterative 2-δ technique, calculated distribution function and Grubbs' test to determine the background values in the area. Their work considered of groundwater flow system continuity to evaluate the background level and to divide the basin in ten environmental groundwater units that are based on groundwater flow systems and hydrogeological structures. The second investigation was developed by Foppen and coworkers (2020), they did a study to characterize the local component of flow system to the west of Africa, in the Republic of Ghana, using a wide variety of tools such as geophysical data, groundwater samples i.e., major ions and metals, drilling cores and pumping tests. In sum, they found this is a local system in saprolite little fractured rocks (it is a weathered clay or gravel rock and you can see the original structure) not suitable for extraction.

In both works, chemical data take essential importance since these refer to properties that can be differentiated and used to outline a flow system.

2) Isotopic data

Isotope data present a reliable tool since they can be used as essential tracers in groundwater and flow system classification. In addition, the latest research on the characterization of flow systems is presented.

One of these works was carried by Babad et al. (2020) in the Hula Valley at northern Israel, sampling 41 wells to measure the major ions and isotopic composition of $\delta^{18}O$, $\delta^{2}H$, tritium (^{3}H), C-14, and ^{81}Kr; unique flow directions; and flow paths, in brief, a conceptual model of the operation of the flow system in the valley was depicted. The defined model identified two flows young and old groundwater using an isotope combination.

At the same time in Melbourne, Australia Hepburn et al. (2020) used different data in shallow groundwater to define the groundwater system such as stable isotopes ($\delta^{18}O$, $\delta^{2}H$) and carbon ($\delta^{13}C$), radioisotopes (^{3}H, C-14) and other geochemical indicators, in brief, they find the presence a modern component that recharges this flow system.

Other investigation of this topic was carried out by Shin et al. (2017) in Jeju Island in the Republic of Korea, they sampled 10 wells to estimate chemical and isotopic composition ($\delta^{18}O$, $\delta^{2}H$, and $\delta^{13}C_{DIC}$) in the zone. Flow system classification is based on $\delta^{18}O$ values and altitudinal variations, in brief, two regional flow systems were identified. These two regional systems are different by geochemical processes in soil layers and rocks, both flows were influenced by local recharges this process causing mixing of groundwater.

2. 1) Isotopic data and other data

Isotopic data can be combined with other data types to obtain more accurate tracers, for instance Elshehawi et al. (2020) investigate the Slitere national park in Latvia, they sampled 14 sites taking major ions, nutrients, stable isotopes $\delta^{18}O$, $\delta^{2}H$ and $\delta^{13}C$ and a radioactive isotope of C-14. Furthermore, they used TDS ranges and values of C-14 / $\delta^{13}C$ to identify the flow system. They found a local flow, a regional flow, and a mixing flow, then using $\delta^{18}O$ and $\delta^{2}H$ data to demonstrate that regional groundwater discharges in the dunes of the study area, moreover local system contributes and creates an intermediate mixing system.

Equally, in the same year, Ide et al. (2020) investigated the flow system in the Kyushu island in Japan and the behavior of springs before and after seismic activity. They sampled $\delta^{2}H$, $\delta^{18}O$, and chlorofluorocarbon (CFC-12) after the seismic activity, then they distinguished two flow paths one long and older and other short and young. Furthermore, they compared these measurements and found that flows are mixing.

Isotopic data can be combined with statistical methods in the delineation of flow systems, for instance in the Geum River basin, Korea Jung et al. (2019) collected 195 samples of rain and snowfall every week, 67 samples of wells and 67 samples of perennial streams to measure field parameters, stable isotopes ($\delta^{18}O$ and $\delta^{2}H$) and radioactive isotope (tritium ^{3}H). They applied a statistical method called End Member Mixing Analysis (EMMA) using the groundwater isotopes to clarify the groundwater flow contributions in mountainous areas and the interaction of surface groundwater in the zone moreover they assigned three end-members relating to precipitation in summer and winter, and water that evaporates in the plains. The areas using in EMMA were related to ^{3}H value where they found local (lower zone), intermediate (between the upper and middle zones), and regional (upper zone) flows. This study did not take in account previous data from fracture and fault zones, therefore, the authors suggest that more research is needed to understand the groundwater flow system in the basin, particularly the regional flow.

Isotopes are powerful tracers that when combined with noble gases enhance their capacity in the study of the flow system, for instance in Arizona, USA Beisner et al. (2018) sampled 24 sites in the river and 6 samples from springs measuring physicochemical data, majority ions, trace elements, stable isotopes ($\delta^{18}O$ and $\delta^{2}H$), noble gases (He, Ne, Ar, Kr, and Xe), radon (^{222}Rn) in groundwater, additionally, isotopes of strontium (^{87}Sr / ^{86}Sr), C-14, $\delta^{13}C$, and tritium were determined. The authors modeled the discharge in the stream and its concentration furthermore they identified two flows; regional and local flows using a combination of isotopic data.

Similarly, the combination of isotopic data with other types of tracers was used in Kumamoto Japan by Kagabu et al. (2017), they sampled 41 sites consisting of 9 sites with shallow groundwater, 22 locations of deep groundwater, and 10 springs. They took physicochemical parameters; stable isotopes of $\delta^{18}O$ and $\delta^{2}H$, radioactive isotopes tritium (^{3}H), and ^{85}Kr; chlorofluorocarbons (CFCs) and sulfur hexafluoride (SF6). This research found that correlating data of ^{85}Kr and ^{3}H in recharge areas can help to identify a local system. In addition, the authors found that water age increases from the recharge to discharge areas, finding waters of approximately 55 years old called old groundwaters.

Equally, the isotopic data and other data combination were used to study the groundwater flow system in the North China basin by Cao et al. (2016), the authors used a previous conceptual model to adjust it using groundwater flow simulations, groundwater age and heat transport in a three-dimensional model. This research developed a new alternative conceptual model based on geological, thermal, isotopic (^{18}O, ^{2}H, ^{14}C, ^{36}Cl or ^{4}He) and historical data. Thus two flows are identified: one is shallow or local flow and the other is deep or stagnant flow moreover the transition zone between both components is caused by long-term transient behavior and/or mixing due to hydrodynamic dispersion.

The investigations display how the isotopic data can be efficiently used in the flow system classification, the application of these data are increasingly known in the field of flow systems and thus they could be a more powerful tool in combination with other tracers.

3) Chemical and isotopic data combination

The previous sections about chemical and isotopic data describe the latest research in the world and their application in flow systems, in turn, considering that both are strong options to apply in this research area, their combination generates an application field that it will be addressed in the following paragraphs.

In the central part of China, Li et al. (2019) sampled 36 hot springs and 6 shallow cold waters to estimate flow system components. They used the combination of chemistry, stable isotopes of $\delta^{18}O$ and $\delta^{2}H$, geochemical characteristics, and geothermometers to establish two components: 1) short flow paths, fast flow rates and low ionic concentrations in a local component, 2) deep flow pathways and longtime residence with high ionic concentrations in a regional thermal component. Furthermore, with the use of stable isotopes, the recharge of both components was estimated in different areas founding mixing in pumping wells, this mixing is produced by the rise of the regional component through faults, the mixing ratio was estimated with the use of geothermometers, having 84.9% of cold water and 15.1%. of deep thermal water.

The use of chemical data in the first part of an investigation and the incorporation of isotopic data in a new study display an example of dataset combinations, for instance in the Selva Basin, Spain Folch et al. (2011) sampled 60 water wells and they used nitrate and fluoride as tracers. Thus the authors found two flow components: a local flow with short residence time and regional flow with high residence time. Two years after Puig et al. (2013) studied the same zone choosing 37 water wells of the 60 previous wells to measure hydrochemical data along with $d^{15}N$, $d^{18}ONO_3$, $d^{34}S$, $d^{18}OSO_4$ and $d^{13}CHCO_3$, the isotope tracers confirmed mixing between regional and local flow systems.

In all groundwater studies it is common to obtain data on water chemistry, nonetheless, the research described above were selected taking the main character of chemical data in combination with isotopic data, both data can form a pair of tracers very useful in the study of the groundwater flow system.

4) Geological environment data

The physical and geological environment data can be used to characterize the flow systems, for instance in Nigeria Akinwumiju and Olorunfemi (2019) used the integrated adoption of 2D (ArcGIS) and 3D (RockWorks and Suffer) software; Vertical Electric Sounding (VES) data, well soundings and geological data to develop a conceptual model of the groundwater system. They found three components; 1) the local flow controlled by horizontal and vertical hydraulic gradients, 2 and 3) regional and transregional flows that are controlled by fault networks.

5) Combined data of different types

In the same way, all data sets can be used to classify a flow system, using different combinations such as data from the physical environment, isotopic, chemical, and so on, to generate a tool that can be correlated among a wide variety of parameters.

For example in the northeast of Switzerland Epting et al. (2018) investigated the groundwater interaction with the river, they used high-resolution groundwater flow models using physicochemical parameters, electrical resistivity in geological materials, hydraulic head, groundwater penetration estimated by radar, $\delta^{18}O$ and $\delta^{2}H$ isotopes, organic and microbiological indicators. The researchers quantified the transitory nature of the local and regional components at different times and areas, estimating percentages of influence of both in the river.

1.3 Hypothesis

The Mexico Basin is a complex flow system with related manifestations to components in the groundwater flow system. Where discharges and wells of fresh and cold water correspond to the intermediate and local components, while discharges and wells of hot water correspond to the regional component. This can be demonstrated through the hydrogeochemical behavior in extraction wells and natural groundwater discharges. Based on hydrogeochemical it is expected that the local component will have a less chemically evolution with low ionic values and cold water temperature; the intermediate component will have an intermediate chemical evolution with sulfate-rich water; the regional component will have more chemically evolution with chlorine-rich water, deep circulation, and hot water temperature.

1.4 Justification

The Mexico Basin is an area inhabited by more than 21 million people, where water is a highly demanding resource and is supplied by groundwater water extraction wells and surface water from other basins. The high demand for this resource has caused extraction to be intensive and has produced effects such as soil subsidence and poor water chemical quality in some areas. However, it is not quite understood at all how the system works, furthermore it has not been possible to generate adequate solutions for this problem.

The aim of this work is to study the system through the concept of flow system, which is a unique and interconnected system that is conformed by components or flow paths. It is necessary to identify the components of this complex system in a multilayer geological environment, so it will be necessary to develop a methodology which does not exist today.

1.5 Objective

To analyze the behavior of components in a complex groundwater flow system in the Mexico basin, having the vision of a flow system as a whole that presents local variations, establishing its relationship with wells and natural discharges (hot and cold) through the creation of hydrogeological and geochemical models in the region.

1.5.1 Specific objectives

- To establish the flow system components in the Mexico Basin.
- To explain the presence of thermal wells and springs that could be associated with faults and/or fractures of the regional flow component.
- To understand the presence of the different natural discharges of groundwater in the Mexico Basin and their relationship with the flow system.
- To model the hydrogeochemical functioning of the groundwater flow in the Mexico Basin.
- To develop a scientific methodology that allows to characterize complex flow systems and to relate the wells and springs with the different components of this complex flow system.

1.6 Thesis organization

This research is divided in nine sections, five of them depict an introduction of the thesis theme for instance the introduction, theoretical framework, study area description, methodology and finally discussion and conclusions. The other four sections correspond to four scientific publications where different contributions are evolved in the subject of delineation and understanding of the groundwater flow system.

Chapter 2 presents a theoretical framework that served as reference of the methodology used in this investigation. This chapter explains the groundwater system conceptualization and the known criteria for studying them moreover the water-rock interaction that includes all the chemical reactions that can occur between water and rocks, as well as the groundwater in each rock type, moreover is described geochemical modeling, model types that exist as well as its delimitation and applications.

Chapter 3 depicts a studying area of this investigation, for instance, its geographic location, climate, water table, geology and tectonic features.

Chapter 4 describes the methodology applied in this work to indicate all the steps developed and its importance in the study of the flow system.

Chapter 5 depicts the paper "Relationships between urban aquifers and preserved areas south of Mexico City". This explains the presence of shallow groundwater and deeper groundwater in the south of Mexico City using geologic sections, hydrogeochemical and isotope data. It is a previous work before the groundwater flow system methodology application since this shows the presence of two flows that need to be studied from the flow system perspective for its understanding.

Chapter 6 displays the research "Geochemical characterization of components of the groundwater flow system in the basin of Mexico". This work analyzes the flow system in the Mexico Basin using a statistical cluster method correlating with literature definitions and hydrogeochemical data. In this paper the entire basin is taken as a heterogeneous unit and applied the same analysis criteria without local variations considerations. The results show four flow components that are not clearly delimited among them.

Chapter 7 portrays the investigation "Identification of the components of a complex groundwater flow system subjected to intensive exploitation". This research applied the concept of the groundwater flow system as a unit that is conformed of components interconnected among them and they have local variations. The methodology applied in this work is a new approach to combine different tools for understanding a complex flow system. This methodology consists of using the hydrogeochemical data, geological data, tectonic data, well depth and construction design to select representative parameters to apply in an end-member mixing analysis (EMMA) statistical method. In this work, four end-members were used (which delimited using major ions, and temperature) representing four flow components (i.e., local, intermedia, and two regionals), these were used to delineate the flow system components in combination with regional features i.e., faults and fractures.

However, Jung et al. (2019) and this work used EMMA method with different sources, objectives, and data types. The main contrast in both works is associated with model conception, Jung et al. (2019) used isotopic data to delimit sources related to precipitation and evaporation; and in the present research, major ions and temperature were used to delimited sources related to flow components. Furthermore, Jung et al. (2019) related their sources with ^3H values to delimit flow components and did not take in account data from fracture and fault zones; and in this work, delimited components were associated with faults and fractures in the area. Therefore, this work is the first to use the EMMA analysis to delineate flow system components from the conceptual model creation in combination with regional features i.e., faults and fractures.

Chapter 8 depicts the paper "Water-rock interaction and mixing processes of complex urban groundwater flow system subject to intensive exploitation: The case of Mexico City". This document explains the hydrogeochemical relations among the flow components taking account of the main process such as water-rock interaction, ion exchange, and mixing flows. The geochemical model was used to present the processes that control the behavior in every component and it is used to understand the natural processes in the flow system.

Chapter 9 gives the discussion and conclusions of this thesis boarding the importance of applying the groundwater flow system study from the single system interconnected with local variations. This section explains the flow component relations found in all the basin, and they are not described in these chapters. Furthermore, this chapter explains the importance to take this methodology in the study of complex groundwater systems in the world.

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Chapter 2.

Theoretical framework

Chapter 2. Theoretical framework

2.1 Groundwater flow systems

2.1.1 First concepts

The groundwater flow system is a single system, and it is conformed by components or flow paths. For understanding, this definition is necessary to see the evolution of the concept over the time. Therefore, this section looks at the first researches and their concepts that were subsequently used to develop all knowledge of groundwater flow systems.

1. Delesse (1862) was the first to consider groundwater as a flow system using a map with piezometric levels.

2. Dupuit (1863) explained the groundwater concept from the regional perspective and he did not take the vertical flow in his analysis. Afterwards Forchheimer (1886) presented a differential equation for the elevation of the water table in free aquifers, referring to the Dupuit approach. The concept has been known as the Dupuit-Forchheimer approach, and it argues that groundwater flows horizontally in a free aquifer, and that its discharge is proportional to the saturated thickness of the aquifer, for which they simplified the equations of groundwater flow in analytical solutions.

3. Posepny (1889) explained the difference between superficial and deep groundwater flow systems.

4.Subsequently, Kring (1899) recognized the close relationship that exists between the water table and topography. This relation was described by other studies like Meinzer (1923), who found that water table contour is a line where all points have the same altitude, and he used water table profiles. Other scholars showed the Kring and Meinzer concept in their studies such as Farvolden (1961); Meyboom (1961); Jones (1962); Tóth (1962, 1963); Freeze and Witherspoon (1966, 1967) among many others.

5. Lichkov (1933) defined zones to classify groundwater.

6. In 1940, Hubbert published "The theory of groundwater movement", in this article he presented the physical laws of groundwater flow governance in an comprehensive theoretical framework, using the construction of flow water table map, besides he was the first to develop a conceptual model groundwater flow for flow between parallel flows which includes resistance to vertical flow.

7. Lange (1947) suggested a groundwater flow component distribution in different areas.

8. Makarenko (1948) was the first to introduce a division of the groundwater flow system into three components or flow paths, depending on climate influence and base level discharge of groundwater flow.

9. Koudelin (1949) developed a method to establish groundwater flow system components.

10. Raspopov (1950), in Russia, elaborated regional flow system maps and related the zones with different climatic conditions.

11 Norvatov and Popov (1961) resumed Makarenko's idea and divided the flow system into four components.

12. Nonetheless, Tóth (1963) revised the Makarenko, Norvatov and Popov works, and distinguished among the three flow system components, namely local, intermediate, and regional. He used mathematical models in a theoretical case and discriminated the flow system components using flow water table maps and hydraulic potential.

13. Mifflin (1968) applied the Tóth theory to a practical case in Nevada, USA. He established that detailed information about the three-dimensional variations of hydraulic

potential would be necessary to apply the approach with an adequate level of accuracy. Hence, he proposed to define groundwater flow system components using hydrogeochemistry, based on the water evolution concept of Chebotarev (1955), and he combined it with groundwater temperature and residence times. He was the first to outline the idea that there could be more components than the three proposed by Tóth.

14. Haitjema and Mitchell-Bruker (2005) analyzed the water table and the mechanisms that control the presence of local and regional components, thus, they found that recharge-controlled water tables tend to have mostly regional flow cells, while topography-controlled water tables tend to form local flow cells.

2.1.2 Components of the Groundwater flow systems

After establishing the groundwater flow system concept, many approaches were developed in which this system was delimited by components or zones. The first works were developed by Lichkov (1933) and Lange (1947), how suggested a groundwater flow classification; after them, Makarenko (1948) proposed to divide the flow system into three zones:

1. Upper or active flow zone, strongly influenced by weather conditions, their lower edge coincides with the local discharge base level of rivers and streams.
2. Intermediate or delayed flow zone, little climatic influence, their lower border matches with the discharge base level of large rivers.
3. Lower zone with slow water flow, their level discharge is below great rivers.

After the Makarenko zoning, other researchers using their concepts such as Koudelin (1949) developed a method to establish groundwater flow system components; Raspopov (1950) stated that the upper or active flow component reflects the climatic conditions of annual variations, while the two deeper components respond to long-term climatic variations.

Subsequently, Norvatov and Popov (1961) proposed to divide the groundwater flow systems in components based on river discharges and considering their geographical distribution, in four zones:

1. Prevailing drainage zone of the upper groundwater by the rivers, marked by excessive humidity conditions.
2. Abundant drainage zone of surface and deep groundwater, marked by sufficient but variable humidity conditions.
3. Groundwater drainage zone predominantly deep and marked by unstable and insufficient humidity conditions.
4. The zone without a flow of groundwater to the streams, coinciding with areas of extreme aridity and where groundwater drains deep.

Tóth (1962, 1963) relied on Makarenko, Norvatov and Popovop zoning to classify in three the components of the groundwater flow system:

1. A local system of groundwater flow has its recharge area at a topographic high and its discharge area at a topographic low that are located adjacent to each other.
2. An intermediate flow system is where the recharge and discharge areas do not occupy the highest or lowest elevated places respectively, in the basin, one or more highs or lows may be located between them.
3. A regional flow system is when the recharge area occupies the main watershed and its discharge area is at the bottom of the basin.

After, Mifflin (1968) showed the possibility to have more than three components as defined by Tóth (local, intermediate, and regional). He found other subdivisions such as small local, local, and regional. This study was the first to indicate the possible variations in the flow components.

2.1.3 Factors that control the groundwater flow system

Agricola (1533) studied the factors that influence groundwater flow system behavior and demonstrated that groundwater is scarcer in arid regions than in regions with high rainfall, which was observed in groundwater discharge levels of springs that function as communicating vessels with movement from the highest points to the lowest points, the factors are:

- Geology, in terms of the hydraulic conductivity of subsoil materials; stratification and variability of its hydraulic properties; strata fracture; regional tectonics and geological faults presence, and thickness and extension of the subsoil strata.
- Weather, depending on water availability for recharge, temporal and spatial water variability for recharge, environmental temperature, evapotranspiration, and climate changes.
- Geomorphology, due to terrain relief variations, topographic slopes and geoforms historical evolution in the terrain.
- Heat flow, by geothermal gradients; shallow heat sources presence and the subsoil materials thermal conductivity.

Factors combination causes the greater or lesser presence of groundwater in an area or region and groundwater flow movement dynamics, thus generating large groundwater flow systems in some regions, while that in others the flow systems are of very limited extension or very slow dynamics.

2.1.4 Main interactions between groundwater and the environment

Chemical processes

Dissolution is a general process and should be considered in the groundwater chemistry evolution. The groundwater typical dissolution zones of gases are soil, unsaturated zone, and vadose zone, as well as areas with oil and gas accumulation. The gases N_2, Ar, O_2, H_2, He, CO_2, NH_3, CH_4, and H_2S commonly interact with groundwater.

Gases dissolution can give water an acidic character; dissolution degree depends on the solubility of mineral, the water previous concentration, and pressure and temperature present in a locality. Higher solubility rocks include limestones ($CaCO_3$), dolomites ($CaMgCO_3$), gypsum ($CaSO_4$), halite (NaCl) and silvite (KCl); these rocks serve as the main source of Ca^{2+}, Mg^{2+}, Na^+, K^+, CO_3^{2-}, SO_4^{2-} and Cl^- in the groundwater. Silicates and other rocks called insoluble which are soluble under certain chemical and/or thermal conditions and also provide trace constituents in groundwater (Tóth, 1999).

Mineral matter chemical precipitation what is dissolved in the groundwater can occur for several reasons: 1) the reaction with solid ions of non-soluble forms with precipitating characteristics, due to the fluorine (CaF_2) formation by the reaction of the fluorite in the water with calcium from the encasing rock; 2) pressure and temperature changes affect the solubility of certain constituents in water, such as precipitation of calcareous rocks ($CaCO_3$) around the holes in the springs due to the release of dissolved CO_2 by the decrease in pressure, or the silica (SiO_2) deposit from the thermal springs due to the temperature decrease; 3) dissolved matter oxidation that is exposed to air components as result of solubility decrease, such as iron hydroxide ($Fe(OH)$) precipitation of three waters containing ferric iron ($Fe(OH)_2$) in solution (Tóth, 1999) (Fig. 1).

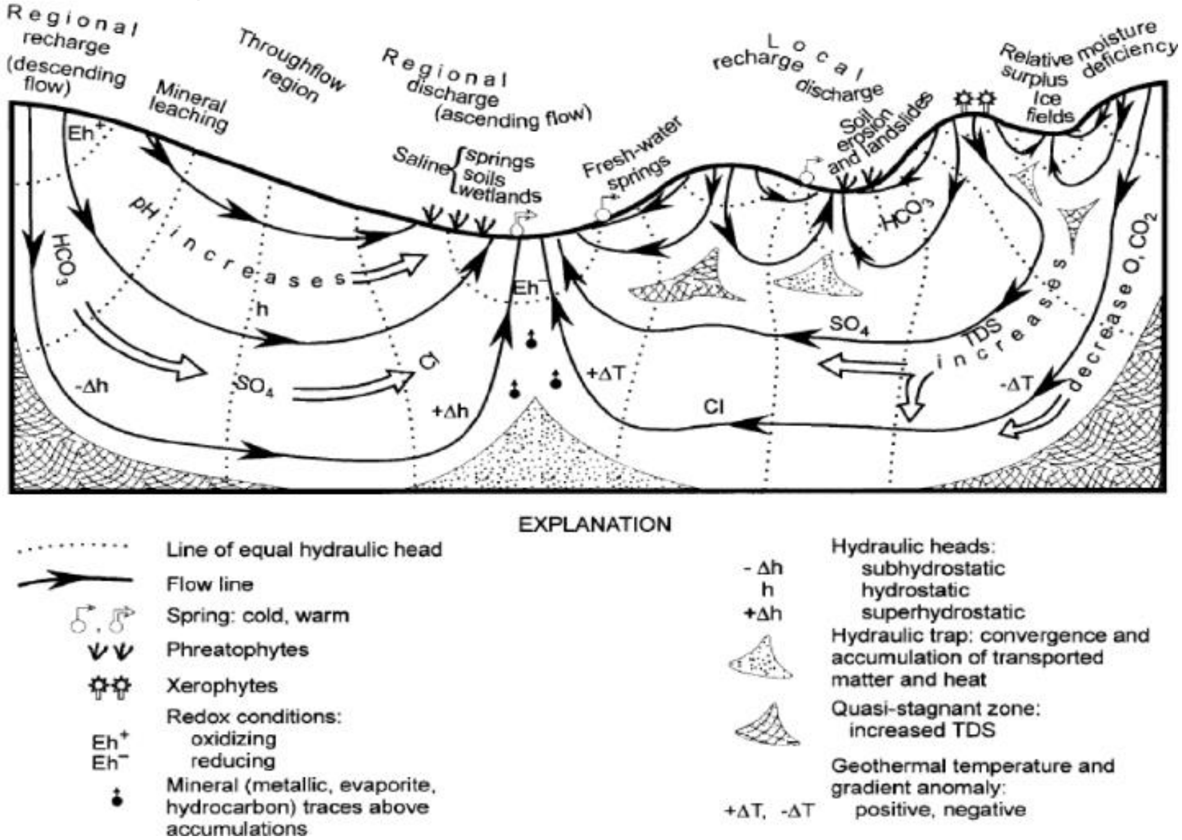

Figure. 1. Chemical changes in the groundwater flow system from Tóth (1999).

Ion exchange

Ion exchange is the process where ions and molecules absorb the surface of solid substances by physical or chemical forces (which are attraction of Van der Waals and chemical sorption respectively) in water ion exchange. Clay minerals are substances with the highest ion exchange capacity, such as kaolinite, montmorillonite, illite, chlorite, vermiculite and zeolite, ferric oxide, and organic matter, mainly due to its colloidal forms of large surface areas. An important example is the replacement of Na^+ with Ca^{2+} and/or Mg^{2+} in the bentonite that results in a natural softening of water due to the enrichment in Na^+, on the other hand, the increase in the porosity and permeability of the newly formed base clay mining of Ca^{2+} and/or Mg^{2+}, or others (Tóth, 1999).

Physical processes

The lubrication is a physic process where the water provided lubrication to rocks discontinuity bodies, which occur because the sediments have irregular surfaces in their grains, or that the sediments are not consolidated, or that they have fractures and flaws in the rocks, reduce friction and improve the effectiveness of shear stress, possibly acting on discontinuities. This is a consequence of soil and rocky material cut movement that can be induced along discontinuities, where their magnitudes are ordered from the minor importance of the grains, such as compaction, to large landslides and tremors (Tóth, 1999).

Transport or kinetic processes

Groundwater movement heat transport is one of the most visible and better-understood subsurface geological processes (Schoeller, 1965; Anderson, 2005; Tóth, 1999, 2009). Water can contain heat and transport it because the heat is a specific capacity. For example, a thermal imbalance is the presence of different temperatures between water and the environment, heat to flow in the direction of the lowest temperature. The heat transfer rate depends on numerous factors, including the thermodynamic properties of the saturated rocks and water characteristics, the difference in temperatures between water and the environment, speed of water flow. The highest heat exchange rate is the difference in temperatures (the anomaly temperature) that it is reduced between water and the environment (Tóth, 1999).

2.1.5 Criteria for characterizing a flow system

For understanding the groundwater flow system operation, it is proposed to divide them into components based on different concepts and proposals.

The first formal proposal to divide them was made by Makarenko (1948) based on two criteria (1, 2):

1. Relating with climatic influence on the internal dynamics of the flow system**,** the upper component is influenced by seasonal changes in climate; the intermediate component is only affected by medium-term changes in the climate, such as prolonged droughts or periods of several years with heavy rainfall; the deep component is only affected by long-term variations in the climate, such as climate change.
2. Relating with the flow system discharge base level, the upper component has its discharge base level in local rivers and streams; the intermediate component has its discharge base level in large rivers; the lower component has its discharge base level below the large rivers.

Tóth (1963) proposed groundwater flow systems subdivision based on two hydraulic criteria (3, 4):

3. From water table maps and hydraulic potential.
4. Groundwater flow among basins.

Mifflin (1968) proposed and developed the application of three criteria (5, 6 and 7) and found that criteria 1, 5, 6, and 7 are observable or directly measurable in practice, he deepened its analysis and application.

5. Water temperature at the point of extraction or discharge.
6. Groundwater age or residence time.
7. Groundwater chemical composition.

8. Groundwater flow path length. For example, Walker et al. (2003) considered regional flow when the route is more than 160 km in length.
9. Impact of the balance of surface basins.

10. Other authors proposed using the groundwater flow penetration depth.

11. Based on the time response to different efforts, dividing into three categories that correspond to regional, local and site components (Back, 1994; Kazemi et al., 2006).

1. Response in the range of hundreds to thousands of years.
2. Response in the range of tens to hundreds of years.3. Response in the range of one to tens of years.

2.2 Water-rock interaction processes

Groundwater is subject to diagenetic changes during its passage through the aquifer, these changes occur due to dissolution, hydrolysis, precipitation, adsorption, ion exchange, and oxidation-reduction reactions. When the more soluble minerals compound the rocks, their composition is more easily released (Matthess et al., 1982).

The complete dissolution of rock minerals or the partial mineral alteration due to mineral components leaching is called chemical weathering. This reaction occurs because the rainwater takes in contact with the rock, minerals are not in chemical equilibrium with the water. Rock's primary minerals may have formed under pressure conditions, temperature, and water vapor different from those present on earth's surface. These minerals (especially olivine, pyroxene, and hornblende classes) will never be in equilibrium with groundwater at the temperature and pressure of normal regimes. These minerals can dissolve irreversibly, releasing their chemical constituents in the water. Depending on the specific site conditions, the minerals complete dissolution can take hundreds or millions of years. Primary minerals in some rocks types (example, calcite in limestone and gypsum in salt deposits) can form under the groundwater flow system conditions; they have a reversible dissolution reaction and can balance with groundwater.

In groundwater, the relative concentrations of the dissolution constituents are determined by the available solid phases contribution of secondary minerals solubility formed by the weathering processes. If an element is present in small concentrations in the solids that come from the minerals in the flow system, this amount can increase as the residence time increases. An example is chlorine which is generally not present in high concentrations on flow system solids, but which could be found relatively in high concentrations in deep flow system components with a residence time that can be in the order of hundreds of years. Major elements concentration of rock dissolved silicates (silicon, aluminum, iron) is limited in groundwater due to the formation of reactive minerals of low solubility. The main cations (Ca^{2+}, Mg^{2+}, Na^{+}, and K^{+}) and anions (HCO_3^- / CO_3^{2-}, SO_4^{2-}, Cl^-) are present in moderate concentrations in typical storage rocks and that they form relatively soluble minerals (carbonates and sulfates) (Deustch, 1997).

These and other processes of rock-water interaction will be described in the following sections.

2.2.1 Water-rock-gas reactions

Chemical and physical water-rock-gas reactions were described by several authors; their diversity is reflected in the next lines.

Appelo and Postma (2005) described the most important reactions which are dissolution and precipitation of minerals and solids, redox reactions with organic matter, cation exchange and mineral clay sorption and organic matter. Alley (1993) explained the number of chemical reactions that can control the water general chemical composition which are relatively small, moreover dominant inorganic reactions in groundwater are generally categorized as solution-precipitation, acid-base reactions, substitution-hydrolysis, oxidation-reduction, ionic filtration and osmosis, dissolution and ex-solution of gases, and sorption-desorption.

Saturation Index

Thermodynamically, dissolution or precipitation potential of solid phases can be expressed as the saturation index (SI):

$$SI= \log IAP/Ksp$$

Where IAP is the empirical ionic activity product of a given mineral in water, and Ksp is the equilibrium constant of the mineral's solubility at the same temperature and pressure in water (Freeze and Cherry, 1979; Alley, 1993).

If the saturation index is > 1, water contains an excess of ionic constituents and mineral precipitation will occur. If the saturation index is <1, the mineral will dissolve. If the saturation index is = 1, the reaction is in equilibrium. If saturation index is = 0 indicates that there is no thermodynamic tendency for dissolution or mineral precipitation. Using a saturation index reaction, it is possible to compare the current water samples state with the computerized equilibrium conditions for specific water-mineral reactions. The mineral does not need to be present in the groundwater zone, however, it is necessary to know the mineralogical composition whereas it is desired to obtain a detailed understanding of geochemical behavior and its water controls (Freeze and Cherry, 1979).

The effect of the common ion

In many situations, ions addition for mineral dissolution can influence other minerals solubility to a greater degree than the effect exerted by activity coefficients change. If an electrolyte does not have Ca^{2+} or CO_3^{2-} and adheres to the calcite aqueous solution saturated, calcite solubility may increase because of ionic strength. However, if an electrolyte adheres and contains some Ca^{2+} or CO_3^{2-}, eventually calcite will precipitate because the product $[Ca^{2+}]$ $[CO_3^{2-}]$ must be adjusted to reach a value equal to the equilibrium constant. This process is known as the effect of the common ion (Freeze and Cherry, 1979).

Dissolution-precipitation reactions

Mineral dissolution begins when water comes in contact with minerals, and continues until a balance water concentration is reached or until minerals are consumed. Mineral solubility is defined as mineral mass that can be dissolved in a unit volume of an under specific conditions solution along flow patterns of several orders of magnitude. These depend on minerals and water that come in contact with them during their flow history, dissolved solid values may be higher in groundwater than rainwater, or to be saltier than seawater (Freeze and Cherry, 1979).

In the dissolution process, solids are dissolved in the groundwater and precipitate as solid phases, many components of groundwater are derived from rock-forming minerals dissolution in the subsoil. Generally, the high content of water dissolved materials is due to the long contact time between groundwater and rocks that contain it, groundwater dissolved components can be removed by water through precipitation processes (Alley, 1993).

Dissolution and precipitation processes among groundwater, solids, gases and organic matter can be added in the following general reaction (Thorstenson, 1990):

Initial water composition + "reactant phases" final water composition + "phase products"

The dissolution of rock-forming reactant minerals increases the porosity and permeability in the flow system, while the precipitation of new phase products decreases porosity and permeability. Reactions that involve groundwater and solid phase minerals are classified as diagenetic alterations, with many well-known examples of solution and precipitation in calcite, dolomite, clay minerals, pyrite, quartz, and feldspar phases (Alley, 1993).

Mineral dissolution could be incongruous or congruent; a congruent dissolution is when the mineral simply dissolves in the water, without any change in the residual portion composition of the solid that it has not yet been dissolved; an incongruous dissolution occurs when some of the aqueous solution mineral components are a different rate, or to a different extent, they leave a solid residue or form a new precipitate that it has a different composition than the original mineral. The incongruous solution is well-known for Mg-carrying calcites or for many clay minerals. The solubility of elements and other components in groundwater is increased by the formation of ionic complexes (Alley, 1993).

Dissolution and precipitation processes are controlled by ion concentrations (pH) and redox potential. The temperature of the contact surface between rock and groundwater is a strong factor in mineral solution processes because that dissolution is a surface phenomenon. Dissolution processes are promoted by the temperature increase in the surface area exposed in the solution (Matthess et al., 1982).

Dissolution and precipitation processes during the mixture

Groundwater has several qualities that can be mixed among different groundwater flow system components or in boundaries among different compositions groundwater. Mixing processes can take place during the water extraction that if different water types are mixing in the well at pumping time or that if surface waters are mixing with the groundwater in recharge areas and percolated by the river's course (Matthess et al., 1982).

The mixture of different water types can lead to dissolution and precipitation processes that can impart new properties to the water. When waters are in a carbonated hydrogen system, a carbonate equilibrium mixture can occur; in other cases, the mixture or dissolution of a carbonate deposit occurs; when waters of different temperatures are mixing with each other, a displacement of the carbonate-hydrogen-carbonate equilibrium can occur when it is dependent of temperature. Temperature increase in mixture water can lead to a partial loss of dissolved gases, particularly the CO_2 that can be incorporated into the $CaCO_3$ deposit. Changes in the pH value are a mixture consequence of basic groundwater with strongly acidic waters also condition the deposition of pH solution substances sensitive. Substances may precipitate during the mixing waters of different redox potentials when the solubility depends on the redox potential (Matthess et al., 1982).

Coprecipitation

Matthess and Harvey (1982) showed that in the precipitation of the particular substance the strange ions usually leave the solution. These ions are incorporated by the isomorphic substitution with an ion of similar size within the mineral structure which is forming it (coprecipitation) or within one of the ones that it has formed (replacement). The replacement of an element in the lattice of a crystal by another is common in the creation of new minerals.

Effect of ionic strength

A comparison of mineral solubility in pure water with high salt content water indicates that salinity increases the solubility, this is known as the ionic force effect due to salinity increase is caused by the decrease in activity coefficients as a result of the increase in ionic forces (Freeze and Cherry, 1979).

Hydrolysis

Minerals breakdown under H^+ and OH^- ions influence in water which is known as hydrolysis. Silicate minerals decomposition, particularly feldspars, is the best example of this process. Hydrolysis attacks minerals surface, which is otherwise insoluble, and causes new minerals formation at the same time that Ca^{2+}, Mg^{2+}, Na^+ and K^+ ions are removed in the solution (Matthess et al., 1982).

Solutes transport process

Bundschuh and Zilberbrand (2012) described three processes that occur in the solutes transport:

1. Advection governs solutes transfer along paths aligned with the fluid flow direction.
2. The solute molecular diffusion (which is called simple diffusion) reflects the random movement of solute molecules with the fluid.
3. Dispersion is the solute transport in porous media, this causes a mixing zone that it develops between the fluid and composition that it is adjacent or it is deployed by some other composition.

Sorption and desorption reactions

Solids and aquifers contain abundant materials that can be chemically sipped by water. Sorption is, in abstract terms, the chemical concentration changes of solid matter as a result of mass transfer between a solid and solution, this process can be subdivided into adsorption, absorption, and exchange. Adsorption indicates that it chemically adheres to the solid surface, absorption suggests that chemical solution is absorbed by the soil, and exchange involves a replacement of one chemical with another on the solid surface (Appelo et al., 2005).

Surface complexation processes

The surface complexation process is a union species to functional groups present on the solid surfaces of amorphous aluminosilicates, metal oxides/hydroxides, and organic matter. The ion exchange is a surface complexation type but is generally restricted by cation exchange associated with permanent loading of aluminosilicate mineral surfaces. Ion exchange reactions occur primarily in response to the electrostatic attraction that it is characterized by the exchange coefficient, while surface complexation reactions occur in response to both chemical and electrostatic components. Superficial complexation is the mechanism by which trace elements are removed from the solution.

The superficial complexation is analogous to aqueous complexation, which is the close association of a central solute molecule surrounded by other dissolved solutes, such as the carbonate complexation with hydrogen ions that form the bicarbonate species (HCO_3^-) and carbonic acid (H_2CO_3). In surface complexation, functional groups on the surface soil attract solutes, which are complexed with the functional group union. Solid surfaces will have some attraction to all dissolved species, the surface complexation degree by certain species will depend on the surface chemical affinity of the species and the electrostatic (physical) attraction or repulsion of the species with the solid surface charged (Deustch, 1997).

Acid-base reactions

Acid-base reactions involving hydronium ion (H_3O^+) transfer between dissolved aqueous species, moreover acids are substances that can give a hydronium ion, while bases accept the hydronium ion (Alley, 1993). The behavior of groundwater dissolved substances is deeply influenced by H_3O^+ transfer. For example, to pH of about 7, the As oxidizing form in normal groundwater dominates is $H_2ASO_4^-$, while to pH above 7 the As oxidizing form in most water occurs as $HASO_4^{2-}$ (Masscheleyn et al., 1991); this aqueous species difference is an important controlling factor in As absorption or dissolution degree on the surface of minerals. Other example of the H_3O^+ dominant order is when carbonate minerals dissolution and solubility reactions strongly increase with pH decrease, due to an increase in the degree of $H_3SiO_4^-$ (aqueous) formation in the solution (Hem, 1985; McSween et al., 1989).

Solids tendency to form solid or dissolved precipitates may be influenced by H_3O^+ transfer. The solubility of Fe, Mn, Al and other metals in groundwater is strongly pH-dependent, due to the control-solubility precipitation of oxyhydroxides that occurs with a pH increase (Stumm and Morgan, 1981).

Substitution-hydrolysis reactions involve organic and inorganic contaminant transformation dissolved in groundwater. These reactions should be taken to consider the acid or base reaction type. The solubility of many metals such as As, Fe and Mn is strongly dependent on hydrolysis reactions and water pH (Alley, 1993).

Oxidation-reduction reactions

Many groundwater reactions involve electrons transfer among dissolved, solid and gaseous constituents. Electrons transference has oxidation state changes of reactants and products. The oxidation state sometimes refers to an oxidation number, which represents a hypothetical charge that an atom can have that if the ion or molecule is dissociated.

Oxidation-reduction reactions are called redox reactions and they have no free electrons: each oxidation is accompanied by a reduction and vice versa. Electrons balance is always maintained, while oxidation is electron loss and the reduction is electron gain (Freeze and Cherry, 1979).

The redox potential is measured as Eh with reference to the standard hydrogen electrode, since redox potentials cannot be used directly in thermodynamic programs (for example PHREEQC), pE value is introduced as a convenient mathematical form. Analogous to the pH value, pE value is the common negative logarithm of electron activity, this is calculated using the hypothetical activity, with respect to electrons concentration, which is currently present in water (Merkel and Planer-Friedrich, 2008).

The redox reactions involve one or more electrons transfer between the chemical elements, furthermore the natural organic matter oxidation is a particular redox reaction in groundwater, which involves elements such as N, S, H and C. The dissolved species what result for inorganic matter oxidation include, NO_3^-, NH_4^+, NO_2^-, SO_4^{2-}, S^{2-}, CO_3^{2-}, CH_4, CO_2 among others. Oxide-reduction reactions also have profound effects on the speciation of dissolved elements and their solubilities (Alley, 1993).

The solubility of some elements (e.g. iron, manganese, copper, vanadium, and uranium) depends on their oxidation state, which is controlled by the redox potential and environmental pH. These solubility controls can be represented by stability diagrams (Matthess et al., 1982).

Dissolved gases

When water is exposed to the gas phase, a balance between gas and liquid is established through molecules exchange along with the liquid-gas interface. If the gas phase is a mixture of more than one gas, a balance is established for each of the gases. Groundwater contains dissolved gases as a result of (1) earth atmosphere water exposure prior to infiltration in the subsurface environment; (2) water in contact with solid gases during infiltration through the non-zone saturated; (3) gas production below water table by chemical and biochemical reactions that involve groundwater, minerals, organic matter, and bacterial activity (Freeze and Cherry, 1979).

Exchange constituents between water and gas phases is an important process that affects groundwater composition in the unsaturated area and water table. Water on surface is filtered in soil containing gases that they dissolve in water by the air atmospheric contact. In the soil zone, gases are produced and consumed by interactions with organic matter and minerals. Due these processes, soil vapor gases are usually very different from atmospheric air composition, soil water, and unsaturated zone that will have dissolved gases of different compositions and concentrations than in the surface water. Groundwater moves throughout water table and loses contact with the vapor phase separated, it cannot be balanced with this phase, but initially, it will contain dissolved gases resulting from the last contact with the water vapor. Below water table, the dissolved gas concentration may increase or decrease depending on water-rock interaction types that occur (Deustch, 1997).

2.2.2 Main ions evolution sequence

Groundwater moves through flow patterns of the saturated zone, increasing total dissolved solids and where many of the dissolved ions occur. In recharge zones, shallow groundwater has less dissolved solids than deep water areas in the same system (Freeze and Cherry, 1979).

An article based on more than 10,000 chemical analysis data from wells in Australia, Chebotarev (1955) concluded that groundwater chemical evolution tendency occurs toward the seawater composition. This work noted that this evolution is normally accompanied by the following regional changes in dominant anion species:

Travel through the flow path $\longrightarrow$

$$HCO_3^- \longrightarrow HCO_3^- + SO_4^{2-} \longrightarrow SO_4^{2-} + HCO_3^- \longrightarrow SO_4^{2-} + Cl^- \longrightarrow Cl^- + SO_4^{2-} \longrightarrow Cl^-$$

Age increasing $\longrightarrow$

These changes occur when water moves from shallow areas of active discharge throughout intermediate zones in areas where the flow is very slow and high residence time of water.

For large sedimentary basins, the Chebotarev sequence can be described in terms of three main zones, which correlate in general with depth (Domenico, 1972):

1. The upper zone is characterized by active groundwater flow that discharges through relatively leached rocks. Dominant anion is HCO_3^- and has a total dissolved solids low content.

2. The intermediate zone has less active groundwater and high total dissolved solids content. Sulfate is normally the predominant anion.

3. The lower zone has a very slow groundwater flow. Highly soluble minerals are commonly present in this zone because very little groundwater: flushing has occurred. High concentrations of Cl^- and high total dissolved solids contents are presents.

These three zones cannot be correlated specifically with travel distance or time. Travel distance and time tend to increase from the upper to the lower zone. In some sedimentary basins, groundwater in the upper zone may be years or tens of years old, while in other basins the common ages are hundreds to thousands of years. Chlorine-rich saline water in the lower zone is usually older, but current ages can vary from hundreds to millions of years (Freeze and Cherry, 1979).

The anionic evolution can be explained in terms of two main variables, mineral availability and mineral solubility. The HCO_3^- contained in groundwater is normally derived from soil area of CO_2 and calcite and dolomite solution. The partial pressure of CO_2 generates that soil zone and solubility of calcite are normally the limiting restrictions on the level of total dissolved solids reached. Many soluble sedimentary minerals release SO_4^{2-} or Cl^- after dissolution. The most common sulfate-containing minerals are gypsum $CaSO_4 . 2H_2O$ and the anhydrite $CaSO_4$. These minerals dissolve rapidly when enter in contact with water. Gypsum and anhydrite are considered more soluble than calcite and dolomite, but less soluble than chloride minerals such as halite (NaCl) and silvite (KCl). Given sufficient time, the dissolution and discharge of groundwater will eventually cause soluble minerals such as calcite, gypsum, and anhydrite to be completely removed from the active flow in the groundwater system area. The sequence of anionic evolution and dissolve total solids tendency increases along the groundwater flow path, when these generalizations are used in the context of rigorous geochemistry can provide considerable information on the history of water flow (Freeze and Cherry, 1979).

2.2.3 Main water-rock interaction processes in different geologic environmental

2.2.3.1 Igneous and metamorphic rocks

Many igneous and metamorphic rocks are impermeable in dense masses except when groundwater flows throughout fractures (faults). Volcanic rocks have high porosity particularly. Generally, groundwater contains only small amounts of dissolved solids when it is in crystalline rocks because silicate weathering is slow (Matthess et al., 1982).

Groundwater in granites, rhyolites, gneiss, and similar rocks

These rocks contain quartz, orthoclase, and feldspars rich in sodium, biotite and muscovite as the main minerals. The slow decomposition of these rocks leads to low concentrations in the solute. Granites of hornblende, diorite, and similar rocks are rich in calcium, hornblende and plagioclases. Groundwater in these rocks characteristically contains more Ca^{2+} and more dissolved silica (Matthess et al., 1982).

Groundwater in gabbro, basalt and similar crystalline rocks

These rocks contain more calcium and magnesium minerals, groundwater contain more silica than granites, rhyolites and gneiss. Alkaline earth lands are dominant over alkaline, except in humid regions (Matthess et al., 1982).

Igneous, metamorphic and crystalline rocks contain appreciable amounts of quartz minerals and aluminosilicates such as feldspars and micas. These minerals are formed at temperatures and pressures above that occur on the earth´s surface, they are thermodynamically unstable and tend to dissolve in water contact. Dissolution processes cause of dissolved constituents to adhere to water and rocks are mineralogically altered (Freeze and Cherry, 1979).

The chemical evolution of carbonate rocks, the dissolution of feldspars, micas and other types of silicates, are strongly influenced by the natural water chemical aggressiveness caused by the dissolution of CO_2. When CO_2 charges waters that are low in total dissolved solids, it finds high silicate minerals in cations, aluminum, silica; and residue releasing of aluminosilicate and cations with an increase in the Al / Si ratio. This residue is usually a clay mineral such as kaolinite, ilite or mortmorillonite. The cations released in the water are usually Na^+, K^+, Mg^{2+}, and Ca^{2+}. Another consequence of this process is the incongruous dissolution with pH and HCO_3^- concentration growth (Freeze and Cherry, 1979).

Based on the solubility of amorphous silica and the abundance of quartz in most hydrogeological systems, SiO_2 would be expected to occur in higher concentrations in groundwater, however, in natural waters, this is not the case. Quartz and amorphous silica generally do not exert an important influence on the silica level of the groundwater. The aluminosilicate minerals such as feldspars and micas are more important in that regard (Freeze and Cherry, 1979).

2.2.3.2 Groundwater in sedimentary rocks

The four most important sedimentary rocks are sandstones and other hard samitic rocks; clays, loam, and silty rocks; carbonates; gypsums, anhydrite, halite and potassium salts that give a characteristic impression to groundwater due to its soluble constituents. These differences can be fuzzy due to the appearance of important components such as carbonates, gypsum, anhydrite and other types of salts such as cemented material or lens intercalation (Matthess et al., 1982).

Groundwater in stratified sedimentary rocks

Many sedimentary rocks or unconsolidated deposits consist of a mixture of mineral assemblies derived from various sedimentary, igneous or metamorphic sources. Each individual stratum commonly comprises the mineralogical mixture of ensembles. Those ensembles may vary from layer to layer in layer sequences. This difference in variation can cause large differences in the geochemistry of groundwater from one layer to other from one region to other. One of the most important factors in groundwater chemical evolution is assembled layers mixture and their encounter order, this refers to the order in which water meets minerals or groups of minerals during its movement in the flow system (Freeze and Cherry, 1979).

Groundwater in sandstones and other samitic hard rocks

The sandstones have large contact surfaces and low relative permeability, with a long period of contact between the rock and the water. The groundwater dissolved solids in sandstones will depend on the rock material. Pure siliceous cementitious material is carried in groundwater with low concentrations of total dissolved solids. Groundwater in sandstones with soluble cementitious materials can show an appreciable amount of SO_4^{2-}, Cl^-, Na^+, Mg^{2+} and Ca^{2+}, even more so in carbonate rocks, particularly in hot and arid zones (Matthess et al., 1982).

Groundwater in unconsolidated geologic materials

When the unconsolidated layers contain silt or gypsum, a common feature in detrital rocks in general, the water shows a clear increase in the content of alkaline earth, hydrogen carbonates, and high sulfate contents. In another hand, sediments which have been derived from metamorphic or igneous rocks then contain much less soluble substances, hence groundwater shows a low content of total solids. Sulfate and chloride content are essentially low, while silica content is typically high, especially in the presence of volcanic material (Matthess et al., 1982).

Groundwater in limestones

The groundwater movement in carbonate rocks takes place mainly through joints and large fissures in the rock body. Thus the contact surface between water and rock is limited. The soluble salts in the carbonates, chlorates, and sulfates are released as the rock mass dissolves at the interface of the water channel. The weathering pores in rock can be leached more easily. The chemical quality of groundwater reflects the chemical composition of the limestones. Groundwater in limestone contains many alkaline earths and carbonate ions relative to alkalis, chlorine and sulfate (Matthess et al., 1982).

Groundwater in clays, loams, and silt rocks

The clays, marls and silts porosity decrease significantly as a consequence of mechanical pressures forces, which in turn depend on the depth of the overload. Water moves very slowly in these low-permeability rocks; thus it is in a long contact period. Due to the small size of its pores, there is a high contact surface between water and rock. By adsorption and cationic exchange of salts, chlorides and sulfates are particularly incorporated in these rocks. A fraction of these substances has been blocked during deposition with the spaces and cannot be easily leached outside due to the low velocity of the water (Matthess et al., 1982).

The groundwater deposits in clays-silts-marls are very rich in dissolved solids that are particularly attributable to the high content of SO_4^{2-} and Cl^-. The high SO_4^{2-} value is associated with high Ca^{2+} and Mg^{2+} content, and with high Cl^- and Na^+ content (Schoeller, 1965).

Groundwater in gypsum, anhydrous and salt rock layers

The high solubility of gypsum-anhydrite and salt rock layers allows the formation of karst phenomena that occurs in main courses of groundwater, while salt rocks in humid regions are rapidly dissolved. Groundwater with deposits of gypsum and anhydrite shows the content of SO_4^{2-} in combination with Ca^{2+} or Mg^{2+}, which are contained in the gypsum. These solutions are often saturated with respect to $CaSO_4$ so that only magnesium can enter the solution (Matthess et al., 1982).

2.2.3.3 Water-rock reactions in different temperatures

Water-rock reactions at low temperatures

In low temperature environments, the presence of silica minerals in the groundwater is derived from the breakdown of silica minerals, not from the dissolution of highly crystalline quartz. Amorphous silica species have high solubility. The solubility reaction of quartz is not reversible: crystalline quartz does not precipitate from cold solutions. Any silica taken in solutions by any reaction tends to remain in solutions (Kresic and Stevanovic, 2009).

Volcanic rocks such as basalts, andesites, and other roughly crystalline counterparts, such as gabros, contain minerals that have low concentrations of silica and high concentrations of magnesium and iron. These igneous minerals formed at high temperatures and are generally not stable in the presence of water. The igneous minerals that react with groundwater release alkaline ions such as Mg, Ca, and silica (Kresic and Stevanovic, 2009).

Water-rock reactions at high temperatures

In hot environmental, water easily takes Na^+, K^+ and SiO_2 from the rocks, but Ca^{2+}, Mg^{2+} are dissolved with more difficulty since their solubility is limited. Aqueous hydrothermal systems (water dominates over steam) are rich in SiO_2, Cl^-, B, Na^+, K^+, Rb^+, Cs^+ and As, than other cold groundwater sites. If there is deposited of SiO_2 on the surface or in shallow areas, it is a sign of a strong geothermal gradient, while if travertine (CO_3Ca) is deposited, it is a sign that the temperatures are very low in depth and limestone dissolution is possible by the added CO_2 (Custodio and Llamas, 1983).

2.3 Geochemical modeling

2.3.1 Conceptual models

To understand the geochemical processes is necessary to develop a conceptual model of the system, this model tries to simulate the chemical reactions in the system. This model must have sufficient site data to perform chemical process calculations, and the model must include the equilibrium constant for all reactions. The required data generally falls in two classes, water-rock composition site data and experimental data derived from equilibrium and velocity constants. The geochemical model collection data depends on study purpose, among these elements to be measured (Table 1) are major ions; pH (important in mineral solubility); Eh and dissolved oxygen (important in oxidation-reduction processes); trace elements (if the presence of clay minerals is suspected, ion exchange processes may occur); stable and radioactive isotopes (use in groundwater dating and discern in physical-chemical processes that affect the chemical composition) (Deustch, 1997). The geochemical models of aqueous systems are based on the assumption of chemical equilibrium among all species dissolved in the solution (Alley, 1993). The most common reactive minerals in groundwater are shown in Table 2.

Geochemical modeling consists in the application of physicochemical principles for geochemical systems interpretation. The objective of geochemical modeling is to create or to devise theoretical reaction models capable of explaining chemical reactions (physically and thermodynamically coherent) and water-rock interaction processes in the underground environment. For this, the greatest amount of information and data available (which are aqueous phase chemical analysis, hydrogeology of the system, mineralogy, gas composition, isotopic data, and so on.) is used to determine: a) the chemical reactions that have occurred; b) the extent to which have taken place; c) the conditions under which occurred (open vs. closed system, equilibrium vs. imbalance, constant temperature vs. variable) and how water quality and mineralogy will vary in response to natural processes and system disturbances (Fagundo and Gonzalez, 2005).

Table 1. Information required for geochemical models development (Deustch, 1997)

Data	Use
Major ions (Ca, Mg, Na, K, HCO_3, CO_3, Cl NO_3)	Complex calculation in solutions. Calculation of ionic strength and activity of the solute. Saturation index for minerals with these components
pH	Ionic speciation / complexation and mineral solubility
Eh	Ionic speciation / complexation and mineral solubility of sensitive redox elements
Dissolved gases (O_2, CO_2)	O_2; redox potential qualitative measure. CO_2: groundwater pH stability in contact with the atmosphere
Minor trace elements (Si, Fe, Mn, Al)	Balance in clay minerals and oxyhydroxides
Trace metals (Ba, V, Cr, Mo, Pb, Cu, Zn, Hg, Cd, B, and so on.)	
Semi trace metals (As, Se)	Mineralogical balance, competitive absorption
Non-trace metals (F, Br, I, P)	Complexation, mineralogical balance, competitive absorption
Organic components (fulvic/ humic acids, and so on.)	Complexation, mineralogical balance, competitive absorption
Stable isotopes ($^{18}O/^{16}O$, D/H, $^{34}S/^{34}S$)	Isotopic signature, mineral reactions
Non-stable isotopes (Tritio, C-14, Cl-36)	Dating

Table 2. Most common reactive minerals in groundwater (Deustch, 1997).

Solid phase constituents	System potential impact
Calcite	Mineral solubility control in solution concentration, partial measurement of neutralization capacity
Gypsum	Mineral solubility control in the concentration of a solution
Dolomite	Constituents solution source, a partial measure of neutralization capacity
Clay mineral identification, concentration and exchange capacity	Major cation exchange sites, control of mineral solubility at a solution concentration
Iron and manganese oxyhydroxides	Mineral solubility control in solution concentration, absorption substrates for minor trace elements
Pyrite	Mineral solubility control in solution concentration, absorption substrates for minor trace elements
Silicate minerals	Source of many dissolved components
Organic carbon	Medium absorption for organic and inorganic components, reducing agent, dissolved carbon source

These geochemical models have the ability to perform several calculations that are, according to Chapelle (1992), Deustch (1997), Drever (1997), Langmuir (1997):

- Speciation calculation: elaboration of the aqueous model and the oxide-reduction state.
- Mineral balance calculations.
- Mass balance.
- Electron balance.
- Isotopic balance.
- Mass transfer along a flow line.

2.3.2 Computational geochemical models

The development of a geochemical model can expand knowledge for natural and artificial systems and processes that occur in them. Modeling represents each of these complex systems in a schematic way that it is described by theoretical equations and it is solved using specialized software. As a result, additional information is received about the state of the system and its development. Sometimes this information can be verified if there are measurements, but sometimes these measurements are not available (Bundschuh and Zilberbrand, 2012).

The conceptual model is combined with computational codes capable of performing important calculations for those reactions that impact mass transfer between the system phases. The site combination of a conceptual model with a suitable computational code produces a site geochemical model that can be used to understand the existing conditions and it predict the system response when conditions change (Deustch, 1997).

2.3.3 Geochemical modeling methods

There are currently two types of models to describe hydrogeochemical reactions inverse and direct (Alley, 1993; Deustch, 1997; Martínez et al., 2000).

2.3.3.1 Inverse Models

Inverse or balance models are those that calculate the net reactions that have occurred in the physical environment between two points located on a flow line and in which the composition of the water is known. It is based on the known composition of an initial solution and final solution, as well as one or more sets of plausible reactions (conceptual geochemical model) that can take place in the system considered. The program uses the mass transferred net amount the different phases of the medium (liquid, solid and gas) for each of the specified reactions. In practice, this method provides more information about the operation of a system and it is required to have a good hydrogeological knowledge of the reactive medium to deduce the geochemical processes that operate in the hydrogeological system under study (Chapelle, 1992) and its scheme is (Deustch, 1997):

$$\text{INITIAL SOLUTION} \longrightarrow \text{REACTIONS FINAL SOLUTION}$$

This reaction explains the changes in water composition by the amount of reactants (in water moles per kilogram) that can dissolve within water and products that can precipitate from the solution such as water flow from site upward gradient (initial composition) to descending gradient of another site (final composition).

Because the inverse method is based only on mass balance calculations and that does not consider the system's thermodynamic limitations inherent. The model can predict that a mineral is precipitating when solution concentrations are not high enough to allow the mineral forms. Saturation index calculations are necessary for reactive phases to show that a particular model is realistic. Additional system data may allow the modeler to reduce the potential number of models that explain changes in water composition (Deustch, 1997; Parkhurst and Appelo, 2013).

Inverse models are most useful when reactive medium knowledge is greater and it is about quantifying processes that are plausible to explain the compositional changes observed on a flow line. Inverse modeling programs do not provide unique solutions and depend on most likely reactions choosing that may occur, on knowledge degree that is had of the actual conditions of the medium studied, that is the correct conceptual model formulation (Alley, 1993; Deustch, 1997).

Speciation Models

These models calculate the thermodynamic properties of aqueous solutions, including aqueous species molalities and activities and mineral saturation rates. The main purpose is to calculate mineral saturation indices, which are indicators of mineral saturation state with respect to water given composition (Alley, 1993).

Speciation-solubility models

The speciation-solubility models are about closed, static, batch or vessel type systems (Zhu and Anderson, 2002). These models evaluate the chemical species concentrations/activities (free and complexions) existing either in water samples or in a mutual (homogeneous) equilibrium solution with solids and/or gases of known composition under certain thermodynamic conditions. In addition, these models estimate solution saturation with respect to different gases and minerals conditions (Bundschuh and Zilberbrand, 2012).

When an ion exchange or surface complexation is considered, solubility speciation models can predict stable species composition in interchangeable ions and adsorbed surfaces. The results of equilibrium calculations can be used to evaluate kinetic velocities as a function of derivation for equilibrium (Zhu and Anderson, 2002).

Mass balance models

These models attempt to determine the nature and extent of chemical reactions, these reactions are occurring in groundwater systems to identify reacting minerals and to determine the amount of those minerals that they dissolve and precipitate The basic conceptual model for modeling the mass balance is when two waters (of which we have their chemical data) are in a single flow line since the first is part of the initial composition and the second is part of the final composition in the flow direction. Although a variation in this conceptual model is when two initial waters of different compositions to mix and produce geochemical reactions to produce the final water composition (Alley, 1993).

Mass balance models are limited to a special case of the general inverse problem that it assumes a steady state with respect to flow and chemical composition in the aquifer. If the analyzed water has been affected by transient chemical conditions or it is not within the same flow system, hence the mass balance modeling techniques can produce erroneous results. Therefore, care should be taken to apply this type or model of mass balance to systems with changing chemical compositions due to human activity. A common problem with groundwater samples is that they are collected from opening wells at a number of intervals at a single long interval: in this way the samples could be an agglomerate of several different water compositions. Interpreting the results of the mass balance for such groundwater mixtures often requires more data than is generally available (Alley, 1993).

2.3.3.2 Direct Models

Direct models are those that calculate the evolution of water composition during transport due to a set of known chemical reactions and initial water of known composition. They allow making predictions about the operation of a system and are specifically useful in the case of hypothetical situations or with a high level of uncertainty regarding the real characteristics of the environment and its scheme is (Deustch, 1997):

INITIAL SOLUTION + REACTIONS → FINAL SOLUTION + PRODUCTS

This reaction explains the amount of the reactants (in water moles per kilogram) dissolved in water and the amount of precipitating products, and the resulting solution is restricted either by reagents added mass or by mineral products solubility.

Direct models are very useful when we want to make predictions about how the mineralogy and water composition in the environment vary in response to natural processes and system disturbances, or when we want to know under which conditions a reaction has taken place (open or closed system, equilibrium or non-equilibrium, constant or variable temperature). However, in the case of investigating little known means, direct models are the more useful, when the uncertainty degree is greater about the real environment, that is, the simulated case is more hypothetical. In this way, it was possible to define with all detail that is desired the conceptual hydrogeochemical model (s) to verify.

Direct modeling has two types of models: reaction-path models and reactive-transport models. Reaction-path models predict water composition because it experiences reversible and irreversible chemical reactions. Direct models investigate geochemical reactions where analytical data is lacking. If the results of inverse modeling are used in these models and applied in reaction-path models, modeling will reproduce a final composition for used water. These types of models answer questions such as what is the calcite solubility if carbon dioxide partial pressure is 0 or 2 atmospheres? or what is the first phase that saturates as feldspars dissolve rainwater? or what is the water composition in a set of reversible and irreversible reactions? The reactive-transport models of minerals represent the chemical reactions meaning, but also include mechanisms for modeling advection and dispersion, which can be difficult to simulate in inverse models. Additionally, reactive-transport models can calculate groundwater and solids phases chemical compositions as functions of time and space (Deustch, 1997; Winter et al., 1998).

Reaction-path models

Reaction-path programs are based on a thermodynamic model that is very similar to speciation models. The speciation models have mass balance equations for each element (except hydrogen and oxygen) and mass action equations for each aqueous complex. The pH and redox conditions are especially explicit for speciation calculations (Alley, 1993).

The path-reaction model calculations require only an initial water composition and a set of reversible and irreversible reactions. Reversible reactions are those that occur near equilibrium in an equilibrium equation of the phase of mass action where it is included in the calculations. Irreversible reactions are those in not equilibrium and massive transfers in which must be specifically defined. There are several limitations to the application of these models in groundwater systems, the results of reaction-path modeling are a chemical reaction coordinates function, that is, the chemical composition of the groundwater is calculated based on the extent of the species' reactions. For groundwater studies, some of the most important information is the temporal and spatial variation in the composition of water within the flow system, and there is no direct way to convert the results of the reaction-path modeling within the coordinates of the space and of time (Alley, 1993).

Reactive-transport models

Reactive-transport models calculate the chemical composition changes in moving water caused by advection, diffusion and reactions with the solid phase. The coupling of both thermodynamic and transport calculations of these models is the most complex and requires a good knowledge of hydrogeology and geochemistry (Bundschuh and Zilberbrand, 2012). These models require an aqueous model and thermodynamic data for the solid phases, as reaction-path models and speciation models, which have uncertainties. In addition, reactive-transport models must calculate flow system flow field under study. Just as flow system hydraulic properties must be sufficiently known to calculate a realistic flow field for steady state or possible transient conditions. Others necessary points for reactive-transport modeling include a quantitative assessment of reactive minerals distribution and composition within flow system, initial composition of groundwater through the flow system, rates estimation of irreversible reactions through the flow system, and chemical charges history and/or groundwater extraction if transitory conditions are modeled. A greater amount of information can be assembled to apply this type of modeling in a specific investigation (Alley, 1993).

2.3.4 Combination of direct and inverse models

The mass balance results for inverse modeling determine the flow path net transfer mass, but these results are partially limited by thermodynamics in determining saturation rates at flow path initial and end points. Direct modeling can be used to demonstrate thermodynamic consistency in mass balance results, as long as a reaction route can be found where a product phase that forms an unsaturated solution never precipitates, and a reactive phase never dissolves in a supersaturated solution. Direct modeling can be used to test reaction test specific combinations to determine if reaction path results are thermodynamically valid. A mass balance model cannot be rejected if it is possible to demonstrate at least one valid thermodynamic reaction path for net mass transfer (Alley, 1993).

After the reaction models have been used in groundwater systems by inverse modeling use, these can be used in direct modeling to predict water quality at flow system points where there is no analytical data. Direct modeling assumes that inverse modeling derives velocity reactions for inverse modeling that can be applied in other parts of the system, and it does not produce other considered reactions in the direct and inverse model calibration (Alley, 1993).

2.3.5 Data required for hydrogeochemical modeling

Data for speciation-solubility models

Requires data are measurements in groundwater of main field parameters (temperature and sometimes pressure), redox potential and pH. It is necessary to have confidence measurements of those parameters that are especially important for deep pressure groundwater. The pressure decrease during sampling causes groundwater degassing and corresponding strong changes in Ca^{2+}, Mg^{2+}, Sr^{2+}, HCO_3^-, CO_3^{2-} concentrations and other ions (Bundschuh and Zilberbrand, 2012). Under these conditions, special methods of sampling and measurement should be applied at the site (Li et al., 1997; Meng et al., 1997; Ding and Seyfried, 2007).

Data for mass balance models

Requires water chemistry data and knowledge about the water movement in the study system, to know if there are flow paths mixtures. Additionally, a complete mineralogy analysis must be performed. And preliminary information is also required about possible hydrogeochemical processes in the order that realistic calculations of mass balance are performed (Bundschuh and Zilberbrand, 2012).

Data for reaction-path models

The reaction-path models need additional data on mineral and gas phases abundance. In these data, special care must be taken with solid solution presence and characterization. The kinetic reactions of the speed equations and their parameters must be previously obtained. When the gas phase is involved, it is important to know if the system is open or closed (Bundschuh and Zilberbrand, 2012).

Data for reactive-transport models

These models include a hydrogeological model, which requires hydrological boundaries definition and boundary conditions configuration, water sources and landfills definition, spatial propagation of each hydraulic conductivity and the specific storage/performance (for groundwater flow), or capillary conductivity and specific moisture capacity (for areas of unsaturated flow) (Bundschuh and Zilberbrand, 2012).

2.3.6 Modeling and result interpretation

An input file must be created with selected data to build the model, this file will concentrate all the relevant information about schematized configuration and the choice of the database. An analysis of errors caused by the use of PHREEQC (Parkhurst and Appelo, 1999) shows that modeling problems are originated from errors in the input file. As modeling practice is to run an input file using a chosen geochemical code, it is the modeler responsibility to build an input file correctly. In many cases, there are geochemical codes that do not provide troubleshooting to input files, except if they find syntax errors and sometimes errors consisting of the geometry of the hydrogeochemical configuration (Bundschuh and Zilberbrand, 2012).

It is possible to verify the plausibility analysis of the received results since they are important components of the modeling process. The speciation-solubility verification models can rarely be analyzed, and they can only see data regarding partial use of the development of precipitation or mineral dissolution. The results of the reverse modeling application can be verified by direct modeling of reaction-path and vice versa (Plummer, 1984).

Possible errors and loss of concepts in the development of a model

The main errors for the speciation-solubility and reaction-path models are (Deustch, 1997):

1. Erroneous data use of alkalinity characteristics and/or redox potential based on pH and pE values changes (measurements don´t correct in the field).
2. There do not include all relevant chemical components, minerals and gases.
3. To deny solid solutions presence.
4. To Lose concepts in defining the modeling characteristics of an open or closed system.
5. To ignore the kinetics.
6. To consider minerals or gases addition.

Geochemical modeling limitations

The geochemical model ability to accurately simulate natural systems is limited by some factors (Table 3). The system model is based on available information, in addition, the field and laboratory derived data must be accurate and complete. Equilibrium codes also require complete and accurate thermodynamic data for all aqueous species. Many used codes are limited to temperatures below 100 °C and to the ionic strength of less than 0.5. The EQ3 code (Worely, 1983) can be used to model high temperatures and pressures and PHRQPITZ can be used to model solutions with high ionic forces (Deustch, 1997).

Table 3. Geochemical modeling limitations (Deustch, 1997)

Limiting factor	Scope
Field and laboratory data	Field parameters (Temperature, pH, Eh, etc.). Laboratory analysis (accurate, complete). Characterization of the solid phase.
Thermodynamic data (aqueous species, solids, gases)	Database (accurate, complete). Activity coefficients calculation. Temperature constant calculation.
Balance constraint	Mineral, gas and redox state.
Solution and ionic strength	Ionic strength <0.5; ionic association theory. Ionic strength> 0.5 ion interaction theory.
Geochemical process range	Ionic complexation, mineral dissolution / precipitation, redox changes, equilibrium of the gas phase, absorption / desorption, solid solution.

2.3.7 PHREEQC software for hydrogeochemical modeling

PHREEQC is free and commercial development software that allows having the necessary capacity to perform speciation calculations and saturation indices; discontinuous and one-dimensional transport calculations with reversible and irreversible reactions, including aqueous, mineral, gas, solution solids, surface and ion exchange complexes, molar transfers in specific reagents, kinetically controlled reactions, solution mixtures, and pressure changes and temperature; as well as inverse modeling, which allows finding sets of molar transfers between gas and mineral moles, and determine the differences between two or more water types maintaining a specific degree of uncertainty in each model (Parkhurst and Appelo, 2013).

Its name is derived from the initials pH-REdox-EQuilibrium; originally it included functions based on calculations of chemical balances in aqueous solutions that began in 70's decade and that over time acquired different characteristics. In 1995 it was renovated and called PHREEQ C, referring to its programming in the C language (Parkhurst, 1995). This program integrates in its use different databases such as WATEQ4F.dat, MINTEQ.dat, PHREEQC.dat, LLNL.dat and PITZER.dat, which are automatically installed with the PHREEQC program and can be chosen for modeling (Merkel and Planer-Friedrich, 2008).

PHREEQC use

The geochemical model consists of several components (Merkel and Planer-Friedrich, 2008):

- Input files that describe the problem to be solved
- Geochemical database
- The analyzer that reads the input file deriving a series of equations
- The solver of a series of resulting nonlinear functions (Newton-Raphson)
- The output files that contain the results
- The option to present in graphical or table form the results

Where the Newton-Raphson method consists of simultaneously solving the conservation equations of mass. Due to simplicity and fairly rapid convergence, it is well adapted to a set of nonlinear equations of several unknowns (Albaréde, 1995).

PHREEQC is the core of the geochemical model that contains an analyzer and a solver. The analyzer extracts information species from input file and links which it based on the equations in the database non-linear reactions. These specific equations are replaced by moles and load balance equations. The equations aim is to find the equilibrium when all the relevant functions of the calculation of a specific equilibrium are equal to zero (Merkel and Planer-Friedrich, 2008).

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Chapter 3.

Study area description

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3.1 Location

The Basin of Mexico is a endorheic groundwater flow system (**Fig. 1**) recently defined as Anáhuac System by (Escolero, 2018). This basin is located in a volcanic-tectonic depression at high altitude, this is a closed basin placed in the eastern sector of the Trans-Mexican Volcanic Belt (TMVB) (Enciso-De la Vega, 1992). The relief of the TMVB consists of a series of stepped plains (Vazquez-Sanchez and Jaimes-Palomera, 1989). The TMVB is the result of the subduction of the oceanic plates of Cocos and Rivera under the North America plate (Pardo and Suárez, 1995).

The basin has an area of approximately 9600 km^2, is 100 km long and 80 km wide, and is NE-SW oriented with a horst-and-graben system in the northeastern portion (García-Palomo et al., 2018). This basin is limited by volcanic Sierra de las Cruces to the NNW-SSE (García-Palomo et al., 2008), the volcanic mountain range Sierra Nevada at N-S which includes Iztaccíhuatl, Popocatépetl, Telapón, and Tláloc stratovolcanoes, the Apan-Tezontepec volcanic field to the north (Vazquez-Sanchez and Jaimes-Palomera, 1989; Arce et al., 2013b) and the Sierra Chichinautzin to the south (Bloomfield, 1975).

The basin was cut-off in the southern part 1.2 million years (Ma) ago by the emergence of the Chichinautzin volcanic field during the early Pleistocene (Arce et al., 2013a). The surrounding mountains have altitudes of >5,000 meters above sea level (m. a. s. l.) and tip 121 toward the flat-lying center of the basin with an altitude of approximately 2,220 m a. s. l. In the lower parts of the valley floor, the Basin of Mexico consists mainly of clastic, volcanoclastic, and lacustrine deposits (Enciso-De la Vega, 1992). The Mexico basin is formed of seven large valleys such as Valley of Mexico to the southwest, Valley of Cuautitlán to the north, Valley of Pachuca to the north, Valley of Apan to the northeast, Valley of Tecocomulco to the northeast, Valley of Texcoco in the center of the basin and Valley of Chalco in the southeast (**Fig. 1**).

The climate in the basin is defined by INEGI (2019) and the Köppen modified classification (**Fig. 1)** (Garcia, 2004).

In the Mexico basin, a total of 406 water samples were collected for this research and are placed in **Figure 2**. Furthermore, unpublished data of CONAGUA for 2017 were used to define the water table configuration within the study area. The Kriging method (Franke, 1982¸ Cressie, 1993) was used to develop the spatial interpolation of water table elevation (**Fig. 2**). The water table shows that flow moves from the upper parts or watersheds toward the Valley of Texcoco, receiving water from a portion of Valley of Tecocomulco and Valley of Chalco. The Texcoco Valley has a large depression cone caused by intensive groundwater extraction. In valleys of Tecocomulco and Apan to the east of the basin, the groundwater moves north toward the Cuautitlán Valley where it is present a depression cone.

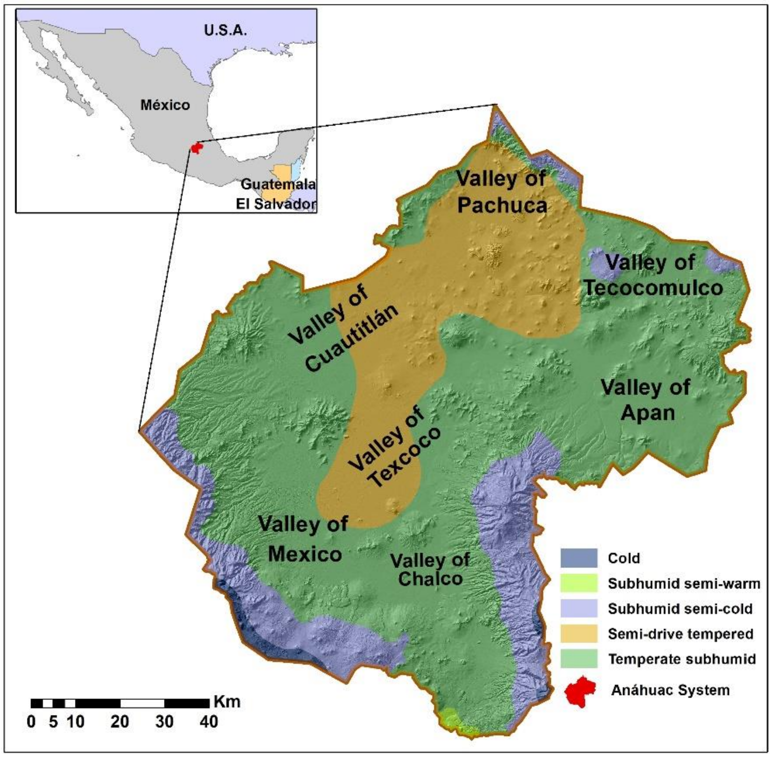

Figure 1. Climate classification in the Anáhuac System (Mexico Basin) from INEGI (2019)

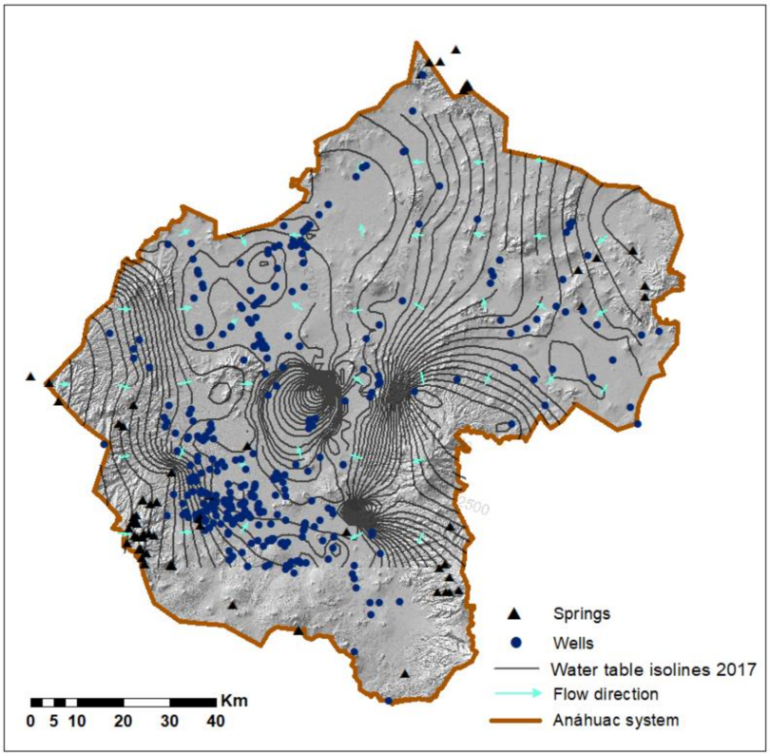

Figure 2. Water table map and samples site in Mexico Basin. Note: water table from Olea-Olea et al. (2019)

3.2 Geology and tectonic features

3.2.1 Geology

The geology of Mexico basin is depicted as complex because it was formed in an active sedimentary, volcanic, and tectonic environment, in the following paragraphs its units are presented (**Fig. 3**).

Morelos formation from Cretaceous, composed of marine limestones and dolomites, with flint nodules and a maximum thickness of 900 m (Fries, 1960). This formation is exposed to the N in the Morelos and Guerrero states where it is constituted by thick-bedded and massive rocks, covering the younger Mexcala Formation.

Mexcala formation from Cretaceous, dominated by argillaceous limestones of dark gray color with abundant planktonic foraminifera with a maximum thickness of 1500 m (Fries, 1960).

Balsas group from Eocene, defining a succession of continental deposits, composed of conglomerates, sandstones, siltstones, lacustrine limestones, pyroclastic deposits, and minor lava flows with a total thickness of 500 m (Fries, 1960) and intermediate composition to silicic rocks interbedded with conglomerates (Ortega-Gutiérrez, 1980).

Tilzapotla formation from volcanic Oligocene, which is a sequence of rhyolitic, rhyodacitic, dacitic lavas, and ignimbrites; this formation was reported in deep wells of the basin for instance Texcoco 1 well at 950 m depth, Mixhuca 1 well at a depth of 1281 m, and at Roma 1 well at a depth between 2207 and 2210 m (Perez-Cruz, 1988; Vazquez-Sanchez and Jaimes-Palomera, 1989).

Volcanic of late Oligocene - early Miocene is a variety of volcanic rocks and layered clastic deposits containing alluvial clasts. This unit is found in the deep wells since they are described as lava flow for example in wells of Copilco, Mixhuca and Roma. This unit has rocks that vary chemically from andesite to rhyodacite. Due to their lithological characteristics, age and stratigraphic relationships other rocks are considered for instance Tilzapotla Riolite (Vazquez-Sanchez and Jaimes-Palomera, 1989) with a maximum thickness of 400 m; Apán-Tezontepec volcanic field are the Petlalchique Sequence of the early Miocene; Andesite Chichicuautla as the caldera structure near the town of Singuilucan, Hidalgo and compound of porphyritic andesitic lava flows with plagioclase and hornblende phenocrysts; Ingnimbrite Matamoros is a massive late Miocene pumice flow deposit unit; Andesite El Picacho composed of intercalating lava with avalanche debris and ash and block flow (García-Palomo et al., 2002, 2018).

Pachuca group is a volcanic unit of Oligocene to Pliocene and this unit is placed between Pachuca and Real del Monte which is stratigraphically well defined by pyroclastics, clastic material, lava flows (of basalt to rhyolite composition with a wide abundance of andesite and dacite), volcanic gaps and stuffs, furthermore all units are separated by contacts erosive. The Pachuca, Real del Monte, Santa Gertrudis, and Vizcaína formations are thicker being composed of lava flows. The Cerezo and Tezuantla formations are the most superior and they are formed by volcanic breccia, lava and pyroclastic deposits (Vazquez-Sanchez and Jaimes-Palomera, 1989).

Tepoztlán Formation from volcanic Miocene, representing a sequence of volcanic debris of andesitic composition, including intercalations of lavas, pyroclastic deposits, and lahar with a maximum thickness of 800 m (Fries, 1960). This formation was reported in deep wells with lavas, pyroclastic and lahar deposits, with compositions varying from andesite to dacite, for example, Texcoco 1 well at depths between 920 and 814 m, Mixhuca 1 well at 1190 m of depth, Tulyehualco 1 well at 930 and 1740 m beneath the surface, Copilco 1 well at 1580 m of depth (Vazquez-Sanchez and Jaimes-Palomera, 1989); and San Lorenzo Tezonco at depths between 950 and 2008 m (Arce et al., 2013b, 2015).

Sierra de las Cruces volcanic sequence from Pliocene-Holocene, describing volcanic structures and domes with pyroclastic deposits, interspersed with lahar and debris (Arce et al., 2015). It is formed from N to S of the La Catedral, La Bufa, Iturbide, Chimalpa, Salazar, San Miguel, Ajusco, La Corona, and Zempoala volcanoes along with other smaller structures (García-Palomo et al., 2008). The chemical composition of this range varies from andesite to dacite (Arce et al., 2015). Rocks of Sierra de las Cruces was found in deep wells such as the San Lorenzo Tezonco and Mixhuca wells.

Sierra Nevada volcanic sequence, delineated by a set of stratovolcanoes, domes interspersed with pyroclastic deposits in heights, and by intercalations of pyroclastic and epiclastic deposits, as well as debris deposits by avalanches in the lowlands (Nixon, 1989; Siebe et al., 2017). This is oriented N-S and which is composed from north to south of Tláloc, Telapón, Iztaccíhuatl, and Popocatépetl stratovolcanoes. Tláloc and Telapón have a chemical composition varing from andesite to rhyolite, whereas Iztaccíhuatl and Popocatépetl span from andesite to dacite (Nixon, 1989; Siebe et al., 2017; Sosa-Ceballos et al., 2015).

Pliocene-Holocene Chichinautzin volcanic field, consisting of more than 220 monogenetic structures and a wide range of chemical composition, although most of the products are basaltic andesite, basalts, and dacites (Siebe et al., 2004; Arce et al., 2013a); Arce et al. (2019) group the structures of Cerro de la Estrella, Peñón del Marqués, Sierra Santa Catarina, Tlapacoya in the Chichinautzin Volcanic Field based on age, type of structures, and chemical composition.

Apan-Tezontepec volcanic field is compound by 40 basaltic-andesitic volcanic structures and the magmatism was largely controlled by NE-SW and NW-SE trending tectonic features according with Vazquez-Sanchez and Jaimes-Palomera (1989). Tecocomulco sub-basin had a half-graben structure bounded by NE-SW normal faults with 500-m of alluvial infilling (Alatriste-Vilchis, 1999; Campos-Enríquez et al., 2003).

Quaternary alluvial deposits represent the most recent deposits in the plains of Apan, Tizayuca, and the Tochiac Basin. Sedimentary volcanic filling has been identified of approximately 600 m (Alatriste-Vilchis, 1999). These deposits can have a thickness of 500 m with the material of the size of little consolidated gravel, sands, silts, and clays (Fries, 1960). These deposits have been found in deep wells for instance in Mixhuca 1 (167 to 520 m); Rome 1 (74 to 330 m); Tulyehualco 1 (300 to 550 m); in Texcoco 1 well were found sands, silts, clays and intercalations of fine-grained tuffs and lapilli (Vazquez-Sanchez and Jaimes-Palomera, 1989). In the center of the Cuenca de México these deposits are known as the Tarango formation (Fries, 1960; García-Palomo et al., 2018).

Pleistocene-Holocene lacustrine deposits interconnected with volcanic rocks (Perez-Cruz, 1988; Caballero and Guerrero, 1998; Brown et al., 2012; Arce et al., 2013b).

Lacustrine sediments have been studied in shallow driver wells between 30 to 300 m of deep (Caballero and Guerrero, 1998; Brown et al., 2012; Lozano-Garcia et al., 2017) and deep wells such as San Lorenzo Tezonco well from surface to 604 m interbedded with volcanic rocks (Arce et al., 2013b), Tulyehualco 1 well with lacustrine sediments at appearing at 700 m beneath the surface and are intercalated with volcanic layers (Perez-Cruz, 1988).

3.2.2 Tectonic features

The main tectonic features of Mexico basin are depicted in **Figure 3**.

The normal Mixhuca fault is oriented in NW-SE direction dipping to the W and produces the ‘Fossa Roma’ a depression of about 1500 m filled by volcanic deposits (Perez-Cruz, 1988). Arce et al. (2019) interpret the Mixhuca fault as part of a graben-like structure that might have controlled the Sierra de las Cruces formation and affected the Miocene volcanic rocks.

A normal and dextral faults system with NE-SW orientation has been described in Sierra de las Cruces while in the Apan region it occurs as series of blocks bounded by horst and grabens with Pliocene-Pleistocene (García-Palomo et al., 2018).

The E-W normal faults such as Xochimilco (Campos-Enríquez et al., 2015; García-Palomo et al., 2008), Santa Catarina graben (Arce et al., 2013b).

The normal Xicomulco fault is oriented E-W and coincides with some longer E-W alignment of volcanoes (Marquez et al., 1999).

Vazquez-Sanchez and Jaimes-Palomera (1989) infer normal faults buried in the Sierra de Chichinautzin and Santa Catarina areas where they analyze the movement direction with the surface geology and the W-E gravimetric low along the Chalco plain, or Chalco graben (Vazquez-Sanchez and Jaimes-Palomera, 1989;Urrutia-Fucugauchi and Chávez, 1991).

Faults such as Texcoco graben, Santa Catarina graben, horsts of these grabens (Arce et al., 2013b) and other faults that have not been named (Arce et al., 2019).

García-Palomo et al. (2002) identified five faults dubbed as Axaxalpa, Apan-Tlaloc, Texcoco, Tizayuca, and Tolcayuca. These faults border the Tolcayuca-Zapotlán, Cerro Gordo-Las Navajas, Rosario-Acoculco, and Chignahuapan horsts, respectively.

Apan-Tlaloc fault system is a linear fault system that locally develops convex scarps with salient and triangular facets (García-Palomo et al., 2018) and this system forms steps from 2000 to 1300 m to the NW caused by synthetic secondary faults (Alatriste-Vilchis, 1999).

Texcoco fault is locally concave toward the NW and is associated with fractures and faults. The fault transects pyroclastic rocks and domes of Tlaloc volcano, tilting them 27°–30° toward the SE producing the collapse of volcanic structures, and the displacement of stratigraphic units (García-Palomo et al., 2018) and this fault is segmented in two portions (Hernández, 2008).

Tizayuca fault is 50-km long and 10 km wide fault system and it has a NE trend and dips to the NW, with a vertical displacement of 2400 m (García-Palomo et al., 2018).

Tolcayuca fault system is at least 12 km in length and 4 km wide. The fault limits a series of horsts and grabens with different stratigraphy, structure, and elevation (García-Palomo et al., 2018).

Cerro Gordo-Las Navajas horst is bounded by the Tizayuca and Las Navajas fault. This horst has 50-km long, and 15-km wide and NNE-SSW trend, and is composed of andesites and basaltic rocks (García-Palomo et al., 2018).

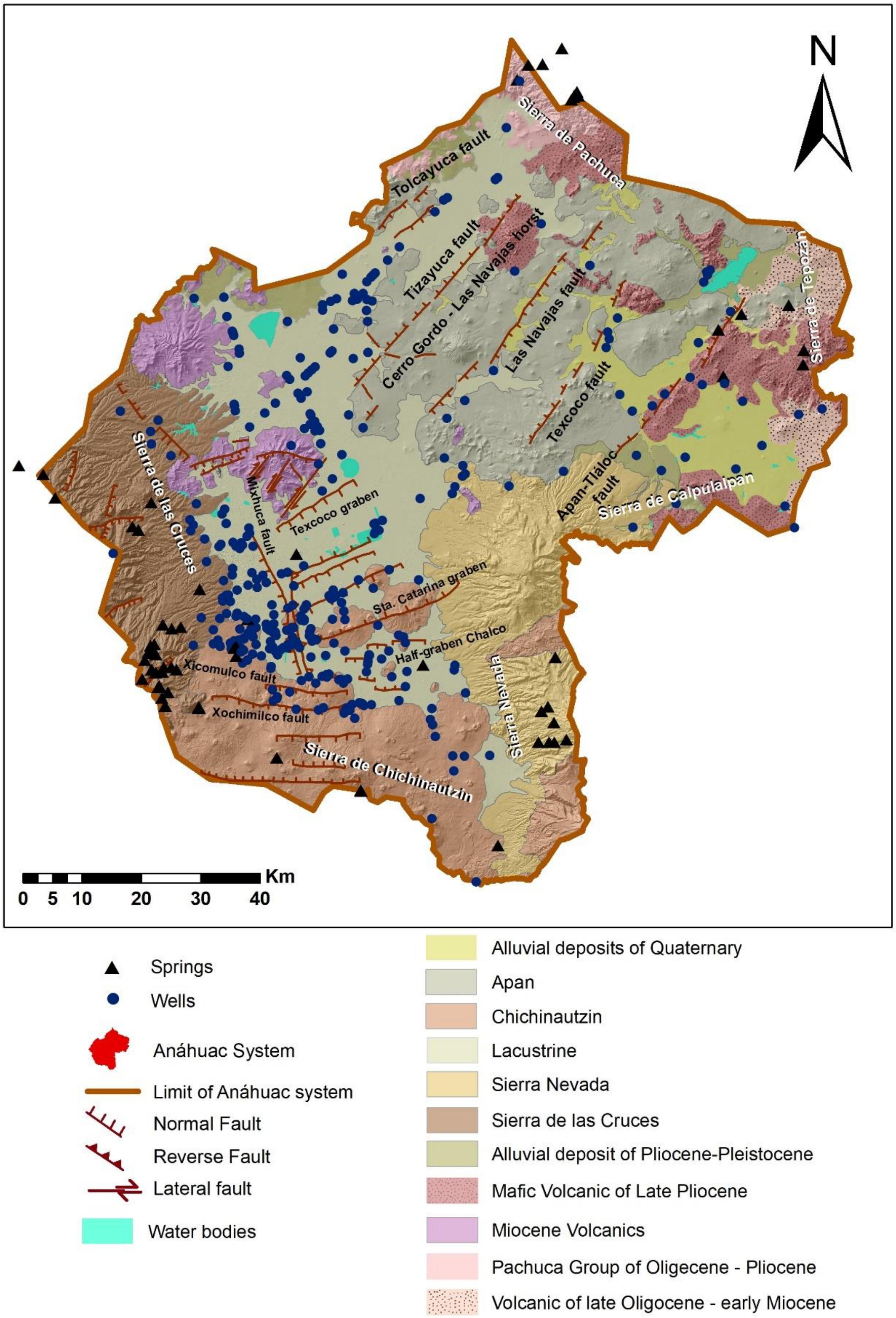

Figure 3. Geology and tectonic features map with samples sites. Note: geology from Arce et al. (2019) and García-Palomo et al. (2002)

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Chapter 4.

Methodology

Chapter 4. Methodology

4.1 Prior information collection

To plan the development of this research was necessary to review all the previous investigations to know the information available. We review technical reports from National Water Commission (CONAGUA) and Mexico City Water Utility (SACMEX); thesis and scientific papers from various sources. Wells data such as location; geology; wells design; physical, chemical, and isotopic values were compiled with approximately 3500 wells. Once these data were obtained, chemical, graphic, and spatial evaluation were developed to generate a general vision of the basin and the possible flow components. After that, sampling sites were chosen that were representative of the possible components identified that were distributed in the basin.

As well as unpublished data of the water table in the area were compiled for the year 2017 to establish the general water table configuration in the basin.

4.2 Field sampling and hydrochemical analysis

Based on the compiled information, 406 sites were selected for sampling (333 wells and 73 springs). Sampling was conducted from June to October 2018. Electrical conductivity and pH were measured with a multi-parametric probe (Oakton PC 300), temperature (T) was measured using a digital thermometer (Hanna HI98509 Checktemp), and alkalinity with a test kit (Lamotte 4491-DR-01). Polyethylene bottles were used to sample main anions, main cations and trace elements. At the collection site, samples were filtered through 0.45-μm Millipore cellulose nitrate filters. The samples collected for cation and trace element analyses were also acidified with HNO_3^- to pH~2 (Appelo and Postma, 2005). Other samples were taken from stable isotopes ($\delta^{18}O$, δ^2H) and radioactive isotopes ^3H and C-14, these samples have not been fully analyzed and are not included in the results of this investigation.

All samples were stored in a cooler at approximately 4 °C. Anions (HCO^{3-}, Cl^-, SO_4^{2-}, NO_3^-, PO_4^{3-}) and cations (Na^+, K^+, Ca^{2+}, Mg^{2+}) were analyzed by liquid chromatography in the Chromatography Laboratory, and trace elements (Al, As, B, Ba, Cd, Co, Cr, Cu, Fe, Li, Mn, Mo, Ni, Pb, Se, Si, Sr, V, Zn) were analyzed by inductive coupling plasma (ICP) with an optical emission spectrophotometer (OES) (ICP-OES) in the Atomic Spectroscopy Laboratory (Institute of Geology, National Autonomous University of Mexico). All samples were compiled whit an acceptable charge balance error of <10% (Freeze and Cherry, 1979; Appelo and Postma, 2005).

4.3 Graphic analysis

The water table was constructed using groundwater depth measurements and the topographic surveys of the wells that were made by CONAGUA which were used to calculate the water table elevation. Spatial interpolation of water table elevation was done using the ordinary Kriging method (Franke, 1982; Cressie, 1993). The general movement of groundwater was considered perpendicular to the isolines of water table elevation (Domenico and Schwartzm, 1990).

A set of diagrams was used to understand the relationships of groundwater with chemical composition and delineate the groundwater flow components.

Mifflin (1968) diagram represents the relation between $Na^+ + K^+$ vs $Cl^- + SO_4^{2-}$ in the geochemical evolution of groundwater moreover it was used together with the hydrogeochemical evolution sequence of Chebotarev (1955). This diagram and the hydrochemical evolution sequence can provide a first approximation to the delimitation of the components of a flow system.

Piper (1944) diagram was useful in showing chemical differences across the study area and helped to classify groundwater in chemical facies, which were helpful in defining groundwater flow paths. This diagram can be used to observe end-members in a data set and mixture relationships.

Gibbs (1970) diagram was used to understanding of the hydrogeochemical processes and their relation with the predominant process including rock weathering, evaporation and precipitation dominance. Its usage is more representative to interpret the flow components when graphing previously classified samples.

The ion exchange diagram graphed ions relations such as $Ca^{2+} + Mg^{2+} - HCO_3^- - SO_4^{2-}$ vs $Na^+ + K^+ - Cl^-$ to know the ion exchange between Na and Ca, this diagram is useful to identify the presence of this type of processes in the flow system components.

Normalized bivariate plots of Ca^{2+}/Na^+ vs. Mg^{2+}/Na^+ and Ca^{2+}/Na^+ vs. HCO_3^-/Na^+ were employed to analyze the underlying mechanisms for modification of ion concentrations in groundwater such as carbonate dissolution, silicate weathering, and evaporate dissolution (Gaillardet et al., 1999). Similarly, this diagram is applied once the components of the flow system are known to evaluate the processes that may be occurring between them and the geological environment.

Stability diagrams are a useful tool to evaluate equilibrium trends between silicate minerals and natural water, based on thermodynamic calculations. This diagram in addition to identify processes in silicate systems is useful in identifying behavior patterns in the components of the flow system. Stability diagrams assist in evaluating the water equilibrium condition in relation to the existing mineral phases in the flow system.

4.4 The statistical analysis

In this research, a combined method is proposed using hydrogeochemical diagrams together with data analysis by statistical methods, which together generate a powerful tool to delimit the components in a complex flow system with multilayer geology, active tectonic zones, groundwater intensive extraction, and wells with variable depths of extraction.

4.4.1 The cluster analysis

The cluster analysis was used to classify the water samples in groups, for this process is very important to select the parameters that represent the variability of the components in a flow system. Fourteen physico-chemical constituents, the cations Na^+, K^+ Ca^{2+}, and Mg^{2+}, anions HCO^{3-}, Cl^-, and SO_4^{2-}, trace elements Si, Sr, and Zn and pH, t, EC and hardness were used for the multivariate statistical analysis. These data were selected using a correlation matrix and the hydrogeochemical groundwater sequence (Chebotarev, 1955). An agglomerative hierarchical cluster analysis was done by means of Ward's method (Ward, 1963) using squared Euclidean distances as a measure of similarity. Ward's method enables analysis of variance approach to evaluate the distances between the clusters in order to minimize the sum of squares of any two clusters (Michalik, 2008). The resulting groups of the cluster analysis were interpreted correlating the geology, hydrogeochemical evolution sequence (Chebotarev, 1955), and parameters of other investigations (this information can be consulted in Olea-Olea et al. (2019)) to identify the flow system components.

This method was used in 303 groundwater samples and it was as vague considered in the delimitation of the components of the flow system for the Mexico basin, due to the local variations in the whole system and because it was not possible to clearly delimit one component from others.

4.4.2 The End-Member Mixing Analysis

The knowledge in the research advances as new data or analysis methods are available, for instance, in this work once the sampling of 406 groundwater sites was completed, the results of the cluster analysis were used to consider another statistical method that could explain the variability observed in the data as well as to identify the flow components. The EMMA was chosen because of the possibility to relate end-members with components and since it can represent the mixture that occurs among these end-members. Mixture relationships were considered because in the cluster analysis no independent members were observed as well as the complex geology of the basin, well design and variable water extraction rates were considered.

The EMMA is a method that can be applied using multivariate or univariate data (Christophersen and Hooper, 1992; Carrera et al., 2004). This method assumes that the groundwater extracted from the wells is a mixture of two or more sources or end-members and that the mixing ratios can be estimated from the hydrochemical composition of the water samples. Four end-members are considered as representatives of the data variability as well as the hydrogeochemical evolution of groundwater (according to the sequence of Chebotarev (1955). The EMMA analysis was developed in each of the seven valleys of the basin, taking the local variations such as geology, presence of faults and fractures, well depth, pumping rates and hydrogeochemical values, this methodology was used to delineate the flow system components in the Mexico basin. For each valley, different variables related to local variations in water hydrogeochemistry were considered. In chapter 7 of this document is described the EMMA analysis in the Valley of Mexico. Other EMMA analyses are not included in this document but will be discussed in the conclusions.

4.5 Conceptual model creation

Once the variables and sources of EMMA are identified, mixing percentages are obtained and are classified to obtain the group classifications, these groups are correlated with geological data of the area, faults and fractures occurrence, well depth and design, the groundwater hydrogeochemical composition, pumping rates and the groundwater hydrochemical evolution sequence (Chebotarev, 1955).

Conceptual model creation starts from identifying of flow components that are representative of each of the groups obtained. Once the flow components have been defined, they are related to their environment to obtain their particular characteristics.

In this work, three conceptual models are presented, the first describes the presence of shallow groundwater and deeper groundwater without taking the groundwater flow system concept (Canteiro et al., 2019). The second focuses on classifying the entire basin from the groundwater flow system perspective where it is observed that there are local variations (Olea-Olea et al., 2019) and the third focuses on considering local variations to understand how the groundwater water system works (Olea-Olea et al., 2020a, 2020b).

It can be concluded that the conceptual model creation is an evolutionary process since as an area is analyzed, new evidence is described to adjust or correct the first approximations.

4.6 Geochemical modeling

Once the components of the flow system were delimited which the second step is understanding of the behavior considering the physical and hydrogeochemical reactions that occur among them. The geochemical modeling is a power full tool to study these processes and to explain the variations among different components.

To develop the geochemical modeling, it is necessary to consider the representative wells of all of the components, rocks, and minerals in the subsoil, as well as the possible hydrogeochemical reactions or inferred processes that may be occurring. Geochemical modeling confirms or not these suppositions through modeling the mass transfer of the matter to understand the processes of water-rock interaction or the mixture relationships among flows, and so on.

4.7 Summary of the methodology

In the following lines and **Figure 1**, a summary is made of the steps to follow in this methodology that was used in a complex flow system and which cannot be analyzed under a single method or methods with a traditional vision.

1. Compiling historical data from groundwater sites in wells and springs such as chemical analysis, location, geology, tectonic structures, and so on.
2. Analyzing historical data using spatial and graphic tools focused on delineate groundwater flow components to plan a sampling campaign.
3. Sampling groundwater sites and to analyze in the laboratory to obtain the hydrogeochemical data, furthermore to elaborate diagrams and maps to understand their spatial variation.
4. Applying statistical analyses to generate groups that can be correlated to obtain groundwater flow system components.
5. Correlating groups obtained in the statistical analysis with all the available information, for instance, physicochemical parameters; hydrogeochemical concentrations; geological and structural features; available information from wells or springs i.e., construction design, depth, discharge flow, and so on, as well as literature data of the flow system topic.
6. Defining the flow components in the system to understand the flow system functioning as one.

5\. Modeling hydrogeochemical processes such as water-rock interaction, ion exchange, mixing and so on that may be occurring among the flow system components to know their natural processes, as well as to understand the entire flow system as a single unit that is interconnected by components.

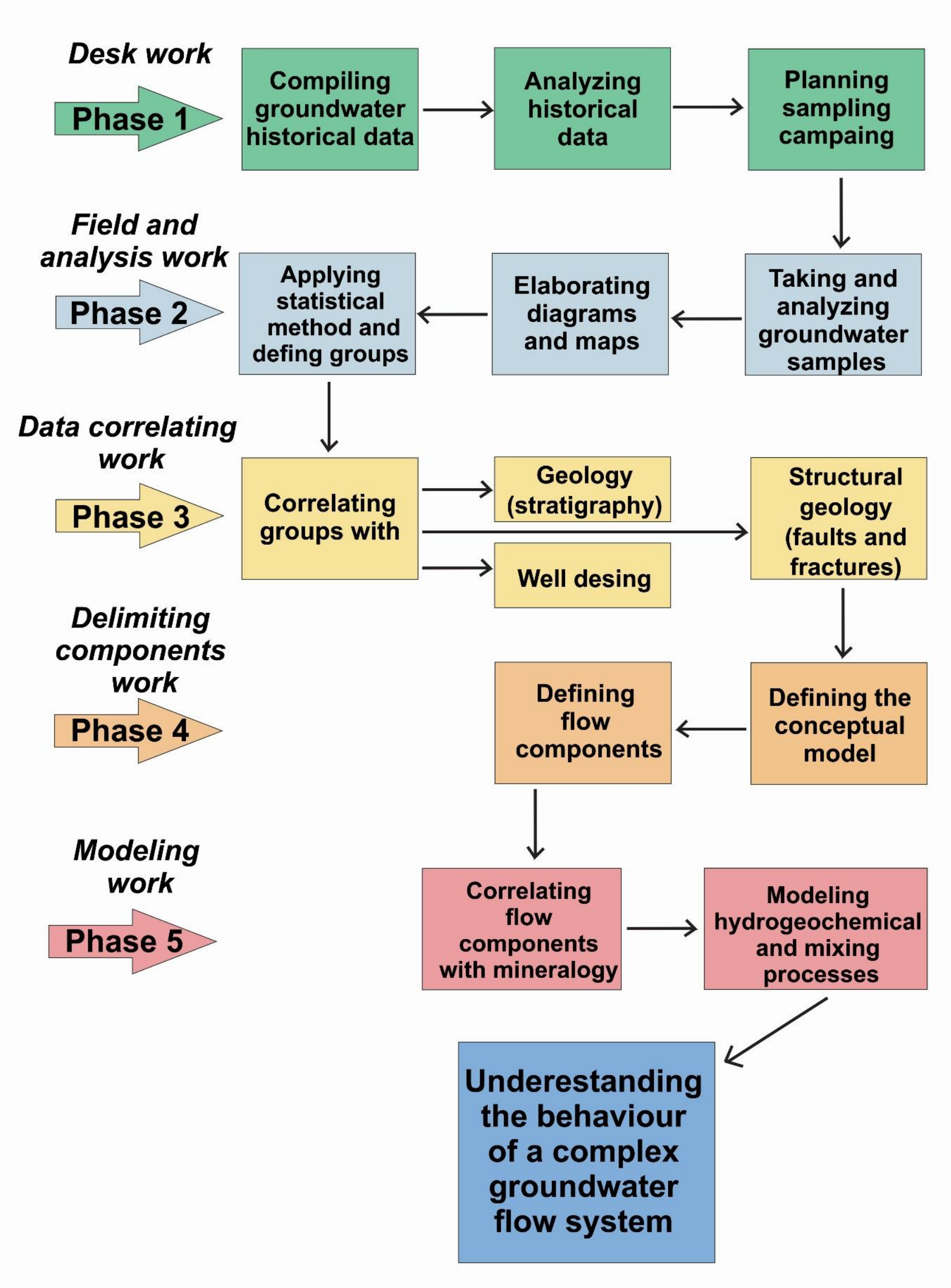

Figure 1. Methodology diagram used in the thesis work for delimiting groundwater flow components

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Chapter 5.

Relationships between urban aquifers and preserved areas south of Mexico City

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Relationships between urban aquifers and preserved areas south of Mexico City

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ABSTRACT

Mexico City is an example of intense socio-ecosystem interactions, particularly in water management. The groundwater under this city has complex structures and dynamics due to the coexistence of aquifers located at different depths. Through groundwater extraction, the main aquifer supports 71% of the water demand of the city. In this research, we describe the dynamics between aquifers and the surface, particularly in preserved spaces located south of the city. The results indicate the presence of a shallow aquifer that is relatively independent to the main one. The water of both aquifers has the same origin (rainwater) and the same water flow direction, but it has different recharge areas and residence times. Apparently, there is a strong interaction between the shallow aquifer and the surface, in which the small proportion of preserved green spaces (27 km^2), in relation to urbanized ones (53 km^2), may produce negative consequences on the quality and quantity of groundwater. The lack of knowledge about the dynamics of the shallow aquifer leads to its underappreciation for the water management of the city.

1. Introduction

Cities are complex systems with constant interactions between their social and ecological variables, which generate the so-called socio-ecosystems (Fischer et al., 2015). In these interactions, green spaces are relevant because they increase landscape properties (Hough, 2004) that are critical providers of direct and indirect benefits to human well-being and health (Bennett et al., 2015). These areas must be properly managed to stimulate inclusive, sustainable and resilient cities (McPhearson et al., 2014). Thus, there are two approaches used to promote the preservation of these green spaces (Tallis and Lubchenco, 2014). The first is the instrumental approach, which focuses on the benefits, i.e., ecosystem services, that the green spaces provide to the urban population (Reid, 2006), and the second is the intrinsic value approach, which is used to preserve biodiversity (Acosta and Esperanza, 2011).

Mexico City is an example of intense interactions between ecological and social variables, especially regarding water. This city, with 22 million inhabitants, has a water demand of 77 m^3/s (Mazari-Hiriart et al., 2014). Part of this demand (71%) is supplied by groundwater extraction through wells from the main aquifer. The depth of this aquifer ranges from 70 to 500 m, and it is an heterogenous unit with granular materials and fractured volcanic rocks. Previous studies have divided this aquifer into two sub-units due to an increase of clays materials at 150 m of depth: the first sub-unit at 70–180 m and the second at 180–500 m (Morales-Casique et al., 2014). The main aquifer is overexploited to satisfy the water demands of human population. According to the National Commission of Water (CONAGUA in Spanish), this overexploitation is reflected in an annual extraction of 1103.98 Mm^3, which surpasses the amount of water that is infiltrated (CONAGUA, 2015). These numbers do not consider the water required by ecosystems dynamics, and therefore, values must be recalculated to have a more realistic understanding of the watershed hydrodynamics (Rohde et al., 2017). The overexploitation of the main aquifer has different consequences, such as the draining of shallow aquifers to the main one, which can generate land subsidence in different areas of the city— and consequently, more vulnerable citizens to earthquakes—and fissures in superficial water bodies (Kralisch et al., 2012; Legorreta, 2006).

The groundwater system has a complex structure due to the coexistence of aquifers that are located at different depths. These aquifers are nourished with water from diverse ecosystems that have multiple

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types of soil; therefore, numerous groundwater dynamics are generated (Tóth, 2015). This dynamics diversity starts from the regions in which they are recharged, and includes the distance and the speed at which the water travels. Each rocky area, lake, woodland, or urban region has different fluxes dynamics, which generate differences in the quality and quantity of water that is infiltrated into the groundwater system. Shallow aquifers are the most susceptible of being polluted by surface activities because of their proximity, and according to the characteristics of the surface, these aquifers are susceptible to different type pollutants. However, most of these aquifers are interconnected and, in consequence, pollution can spread throughout the water system, and all of them can be affected by the overexploitation of the main aquifer (Lee et al., 2015). The amount of sources of groundwater pollution in Mexico City (Soto et al., 2000) increases the urgency of understanding the water flow dynamics among the overexploited aquifers.

In Mexico City, the main sources of groundwater pollution are industries, solid waste disposal, the sewage system, gas stations, fuel tanks, the urban zone, and the abandoned water extraction wells (Soto et al., 2000). Within Mexico City, three municipalities are located above the shallow aquifer: Alvaro Obregon, Coyoacan, and Tlalpan. According to Soto et al. (2000), these municipalities have several sources of pollution that could affect the groundwater. Alvaro Obregon Municipality is mainly affected by pollution, and fuel tanks represent a major threat. Tlalpan Municipality is the least affected by pollution, and the main risk is generated by solid waste. Coyoacan Municipality has an intermediate level of risk, and urbanization is the major threat (Soto et al., 2000). Therefore, managing the sources of pollution on the surface above the shallow aquifer is crucial due to groundwater susceptibility of pollution.

In Mexico City, green spaces have become a cornerstone to provide water source to feed aquifers. The Pedregal is a good example of a preserved area in Mexico City. This area was formed by basaltic rock from the Xitle volcanic eruption that occurred approximately 1670 years ago, and this rocky formation has low presence of soil, which explains its name: Pedregal (rocky area). The Pedregal has an average annual temperature of 16.1 °C and an annual accumulated precipitation of 870.2 mm (Cano-Santana et al., 2009).

Due to the urban expansion that has occurred over the last century, the Pedregal has suffered a dramatic fragmentation and area reduction from 80 km^2 in 1954 to 40 km^2 in 1984. Currently, there are only two important green spaces within the original extension of the Pedregal: the Reserva Ecológica del Pedregal de San Ángel (REPSA) and the Tlalpan's forest. The Tlalpan's forest does not have the original characteristics of the Pedregal because it suffered human-related transformations in the creation of this urban park. Therefore, the provision of ecosystem services of the Tlalpan's forest has been influenced by humans (Calderón-Contreras and Quiroz-Rosas, 2017). The REPSA is a natural protected area where the pristine characteristics of the Pedregal have been preserved (Calderón-Contreras and Quiroz-Rosas, 2017). Currently, the REPSA is considered the last remaining area of the Pedregal, with only 2.37 km^2 based at the Universidad Nacional Autonoma de México (UNAM) (Alvarez Sanchez et al., 1994; Rojo Curiel, 1994) (Fig. 1). The fragmentation and reduced area of the Pedregal has a negative impact on the biodiversity and the ecosystem dynamics. However, the Pedregal still provides ecosystem services to the population of Mexico City (Nava-López et al., 2009).

The lack of green spaces can generate a reduction in the amount water infiltration because the soil in urbanized areas is practically impermeable, and the rainwater in this area is diverted to sewage systems. This often results in floods in the lowlands of the city (Zambrano et al., 2017). Despite having a large sewage system, the rainwater diversion process in Mexico City is inefficient (Candiani, 2014), particularly under extreme storms, which will be commoner with climate change (Zambrano et al., 2017). Because of the low presence of soil and the characteristics of the subsoil, the zone of the Pedregal has high hydraulic conductivity. Since this area promotes a fast water infiltration, the REPSA provides ecosystem services related to the regulation of water quality and quantity of the aquifer (Nava-López et al., 2009).

The human population living in the Pedregal ecosystem has always used water from the shallow aquifer, using the scattered springs that occur in the area. However, this water is underappreciated by managers, possibly because of the lack of knowledge on the dynamics of the aquifer. For example, throughout the entire city, it is common to redirect the water from springs to the sewage system once it appears while an infrastructure project is being built. The lack of knowledge about the characteristics of the aquifer may result in the detrimental use of water and the pollution of this scarce and valuable resource in the city.

Therefore, the objective of this research is to understand the relationship between the aquifers and to evaluate the influence of the surface area of the preserved Pedregal in the southern part of Mexico City.

2. Methods

Geological sections provide stratigraphy information, which helps to understand how groundwater moves between aquifers. To obtain information from the geological sections, the lithological columns from the water extraction wells that surround the REPSA were analyzed (data from SACMEX, which stands for Water System of Mexico City in Spanish). The lithologies were clustered according to the geological local map of Carrillo Trueba (1995). Twelve lithological columns from wells were used in Section I (direction: northeast to southwest), and eleven lithological columns from wells were used in Section II (direction: west to east) (Fig. 1).

Water sampling was made in June 24, 2016, at seven sites within the Pedregal (Fig. 1). Four of these sites were natural springs in private spaces (i.e., D, E, F and G), and three (i.e., A, B and C) were water extraction wells that were property of SACMEX. The water field parameters [electrical conductivity (EC), total dissolved solids (TDS), pH, temperature (T), redox potential (Eh)] were measured at all sites using multi-parameter equipment (Hanna Instruments 9812).

Water samples were collected to determine the main anions (HCO_3^-, Cl^-, SO_4^{2}-, NO_3^-, PO_4^{3-}), the main cations (Na^+, K^+, Ca^{2+}, Mg^{2+}) and the trace elements (Al, As, Ba, Cd, Cr, Cu, Fe, Mn, Na, Pb and Zn). At the collection site, samples were filtered through 0.45-µm Millipore cellulose nitrate filters. The samples collected for cation and trace element analyses were also acidified with HNO_3 to $pH \sim 2$ (Appelo and Postma, 2005). All samples were stored in a cooler at approximately 4 °C and transported to the Institute of Geology at UNAM. Anions and cations were analyzed by liquid chromatography in the Chromatography Laboratory, and trace elements were analyzed by inductive coupling plasma (ICP) with an optical emission spectrophotometer (OES) (ICP-OES) in the Atomic Spectroscopy Laboratory (Institute of Geology, UNAM). Cations and anions had a charge-balance error (CBE) from 0.7 to 5.3. Acceptable water analyses have CBE values less than ± 5% (U.S.G.S, 2007). Samples for stable isotopes (d18O and d2H (Wassenaar et al., 2009)) were collected and analyzed by laser spectroscopy in the Isotopic Laboratory of Davis University, California, United States of America. The results were expressed as the relative abundance with respect to the Vienna standard mean ocean water (VSMOW) and were compared to the local meteorological line. This line was determined based on rain water samples that were obtained from the *Sierra del Ajusco* at the top of the basin and complied with the equation: $d2H = 7.95\ d18O + 11.77$ $(r = 0.989)$ (Cortés and Farvolden, 1989). Additionally, the altitude above medium sea level where the recharge of the groundwater system occurred was calculated and complied with the equation $d18O = (-2.13z - 3.2)*1000$, which was based on isotopic data from Cortés and Durazo (2001).

The topographic elevation of the land was used to establish the altitude of the water table, because groundwater moves from high pressure to low pressure areas (Darcy, 1856; Domenico and Schwartz, 1990;

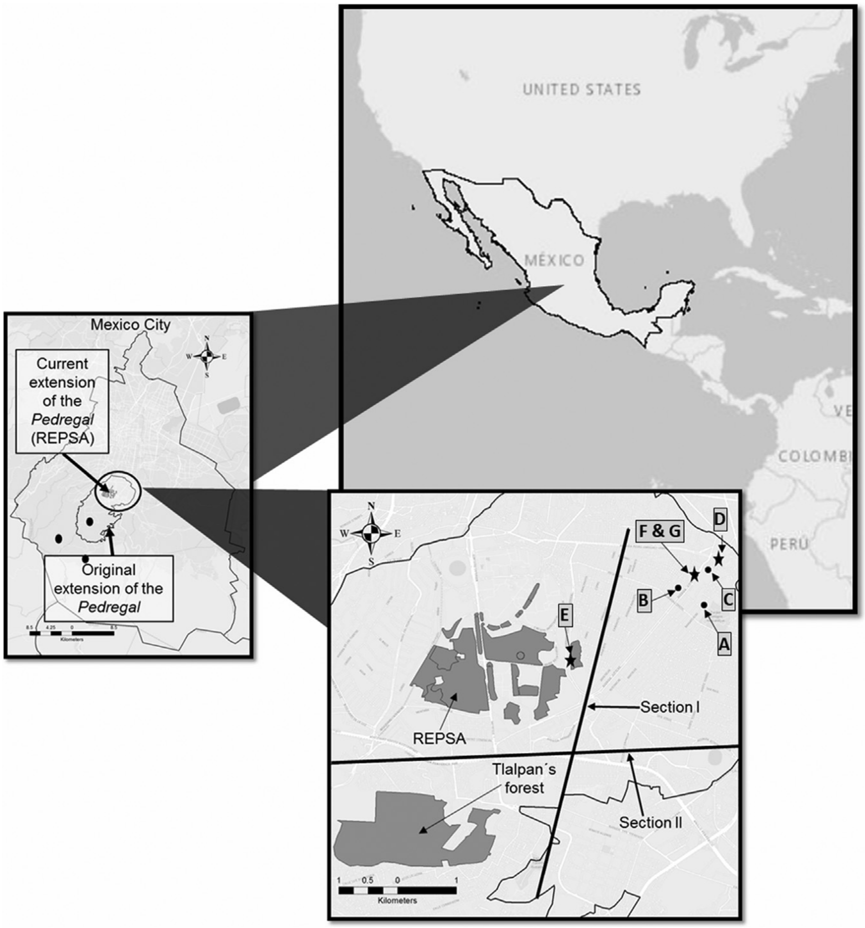

Fig. 1. The Pedregal location in Mexico City, including original and current extension. The zoom image shows the sampled sites. Water wells with dots and springs with stars. Lines are geological sections.

Tóth, 1963). The altitude of the water table was calculated with the equation: topography elevation (m.a.s.l.) – water table depth (m). The water table is where the surface water head is equal to the atmospheric pressure (Freeze and Cherry, 1979). The altitude of the water table in each well and the topographic elevation in springs were used separately to create isolines. The groundwater movement is perpendicular to these isolines. Therefore, flow network was created based on the direction of the groundwater movement and the isolines obtained from wells and springs (Domenico and Schwartz, 1990). In addition, the value of the flow was determined using the technique of Section Area and Speed at one of the sites (site E).

3. Results

Geological sections in the study area had three main layers. The first was composed of recent basalts, where the shallow aquifer was located; the second contained fluvio-lacustrine sediments and tuffs; and the third was based on andesites, where the main aquifer is located (Fig. 2). Based on these results it is possible to consider two aquifers: the shallow and the main one.

Not all the sampled springs have natural origin, springs E, F and G are outcrops of groundwater as a result of deep excavations. Spring E outcrops at 40 m depth, and springs F and G emerge at 8 m depth with respect to the original natural terrain. The average temperature of water in sampled springs was 19.4 °C, while the temperature of water from wells was 17.0 °C. pH values of the water samples fluctuated between 6.41 and 8.64 and the highest values were obtained at site D. The TDS values ranged from 154 mg/l to 347 mg/l; however, springs F and G were more similar to the water extraction wells than to the other springs, where the values were considerably lower (Table 1). Water from springs and wells has a similar chemical composition based on the concentration of major ions (Table 2). As can be seen in the Piper Diagram (Fig. 3) the samples are grouped in the central part due to this chemical similarity.

Stiff diagram (Fig. 4) shows that the water from wells A, B, C had the same behavior in the preferential cations: Na + K and Mg. Water from springs D, E, F and G was more enriched in Ca than water from wells. Anion values had a similar behavior: while springs had depleted values of Cl, wells were enriched. In addition, springs F and G, located in the excavated area site, have higher concentrations of Cl than other springs of the study area.

Isotopic results from water samples are distributed along a trend line, corresponding to the evaporation process (Fig. 5). Wells A, B and C are the closest to the local meteorological line, while springs D and E are located furthest away, suggesting that the latter two are more influenced by the evaporation process than springs A, B and C.

The direction of water flow was from southwest to northeast in both aquifers (shallow and main). The flow value (obtained only from site E) was 77.78 m^3/d in dry season and 10,160.64 m^3/d in rainy season. The results locate the REPSA and Tlalpan forest in the middle of the shallow aquifer. Therefore, their influence of these green spaces is towards the northeast region (Fig. 6a and b). Based on these results, a synthesis figure was generated to illustrate the position, the depth and the distance of both, shallow and main, aquifers (Fig. 4).

The water isotopic values of d2H ranged from −50.4‰ to −72.9‰, while the values of d18O ranged from −6.71‰ to −10.20‰. Fig. 4 shows the local meteoric line (LML - continuous line) determined by Cortés and Farvolden (1989). Here, isotopic data are

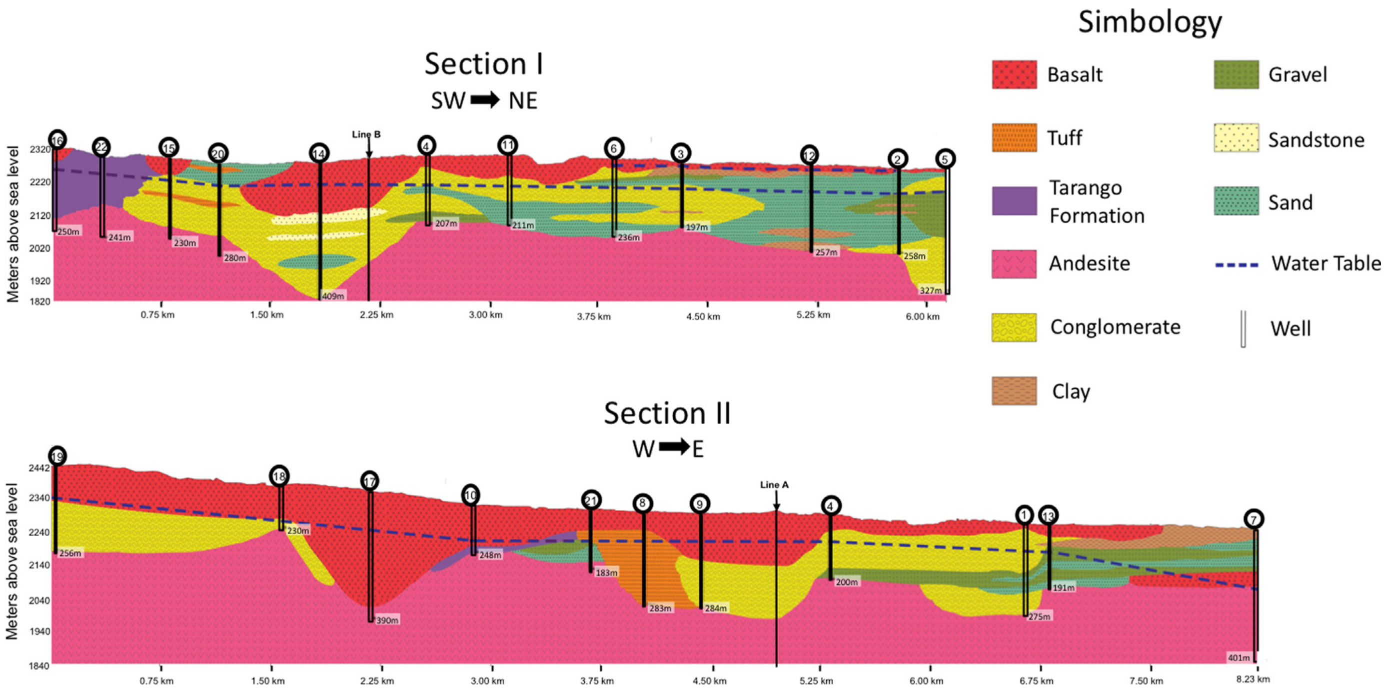

Fig. 2. Geologic sections. Section I goes from southwest to northeast and Section II goes from west to east. Circles shows the water extraction wells (Appendix 1). Intersection line shows the point in which both geologic sections cross.

Table 1
Physico-chemical parameters in study sites.

Site	Type of site	Coordinates			Temp. (°C)	pH	Eh (mV)	EC (µS/cm)	TDS (mg/l)
		x	y	z					
A	Well	484025.41	2136952.19	2260	17.03	7.16	−12.5	684	342
B	Well	483570.14	2137232.65	2267	17.83	6.64	−9.6	594	297
C	Well	484079.36	2137538.63	2253	16.16	6.41	−9.5	654	327
D	Spring	484253.67	2137713.53	2244	20.32	8.64	−13.5	308	154
E	Spring	481783.89	2135938.80	2274	17.96	7.66	−12.4	365	183
F	Spring	483865.91	2137455.71	2251	18.7	6.72	−3.6	660	330
G	Spring	483865.91	2137455.71	2251	20.53	6.68	−3.9	693	347

Table 2
Major ions data of wells and springs. LOD: Limit of detection.

Site	Type of site	HCO_3^- (mg/l)	Cl^- (mg/l)	NO_3^- (mg/l)	PO_4^{2-} (mg/l)	SO_4^{2-} (mg/l)	K^+ (mg/l)	Ca^{2+} (mg/l)	Mg^{2+} (mg/l)	Na^+ (mg/l)
A	Well	190.1	101.6	12	< LOD	25.7	7.53	12.37	25.29	77.17
B	Well	141.9	62.4	30	< LOD	40	6.63	10.13	19.48	60.32
C	Well	151.6	59.5	28.2	< LOD	46.7	7.4	11.81	21.32	58.61
D	Spring	99.4	20.5	7.9	< LOD	34.8	10.44	20.19	8.05	24.67
E	Spring	78.3	33.6	52	< LOD	47.9	6.54	22.08	12.86	33.37
F	Spring	126.5	72.8	82.8	9.2	81	12.46	27.87	19.1	73.61
G	Spring	154.4	78.7	81.2	10.3	98.5	14.41	33.74	20.26	81.83

aligned following the trend of an evaporation line (EL - dotted line). Springs D and E showed greater evaporation, while the other sampled sites remained close to the LML, which suggests that all sites have a common water source.

Water analyzed from wells A, B and C was infiltrated at an elevation of 3200 m above sea level (Fig. 7). Water from the springs F and G was infiltrated at an elevation of 2800 m above sea level (Fig. 7). The results for springs D and E were not considered due to the apparent high influence of evaporation.

There were low concentrations of most of the trace elements (Table 3), and some elements had concentrations lower than the level of determination (LOD). A possible exception is the concentration of Fe found in water of the well A, which can be interpreted as a consequence of basalt weathering at the site that resulted in clays that are rich in this element (Hem, 1992). With the exception of the mentioned variables, there were no other chemical differences between the samples, which suggested that all the groundwater was from the same water source.

4. Discussion

After analyzing the isotopic results from springs and wells (Appendix 2), two different components of the groundwater systems were identified: the shallow component and the main one. The main groundwater component was reported by Morales-Casique et al. (2015). However, the shallow component has never been reported before. Contrary to the main aquifer, this shallow component is unconfined.

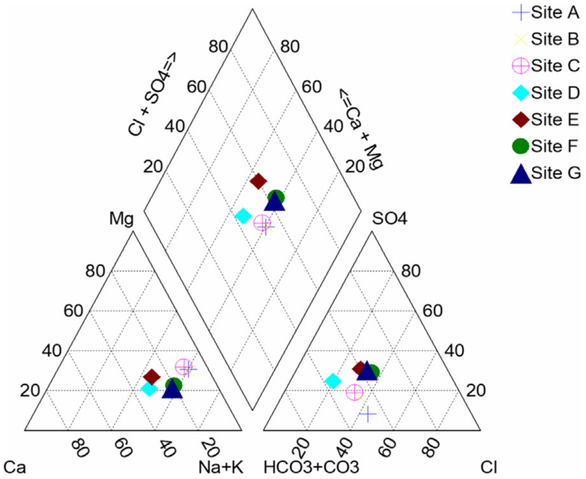

Fig. 3. Water classification diagram (Piper, 1944).

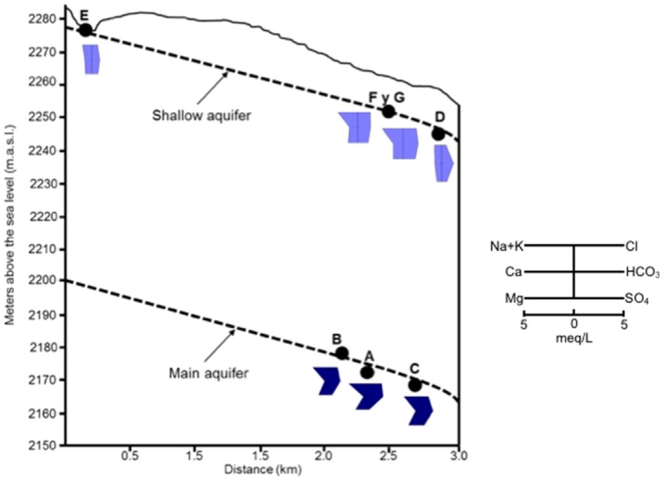

Fig. 4. On the left side the topographic profile and Stiff diagrams of each sampled and on the right side the general Stiff diagram (Stiff, 1951).

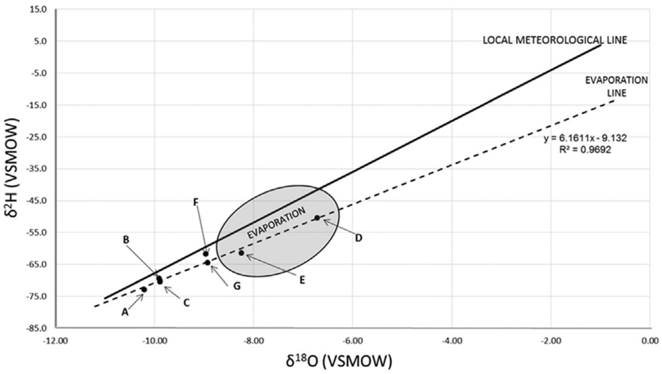

Fig. 5. Correlation between d2H and d18O and its relationship with the local meteorological line. The sample sites with dots.

A combination of conglomerate, tuff and clay layers separate these two components (geological sections, Fig. 2). This separation is due to the low hydraulic conductivity in these materials. The hydraulic conductivity assigned to clay is 0.000006 m/d (Based on data from Fetter, 2001), However, the aquifers can be hydraulically connected in zones where there is no presence of the layer with low conductivity or its thickness is small.

In addition, results suggest that the main aquifer is recharged at an altitude of 3200 m.a.s.l., which corresponds to the foothills of the *Sierra del Ajusco*, while the shallow aquifer is recharged at the elevation of 2800 m.a.s.l, which is in the high areas of the Xitle volcano. Although the soil and subsoil of the original extension of Pedregal provide a high infiltration zone, the majority of this region is occupied by urban area (63%). Therefore, the main recharge of the shallow aquifer occurs in the area close to Xitle volcanic cone. However, an important part of this infiltration may come also from the preserved green spaces.

The water tables of both aquifers in the geological sections provide an important tool for understanding aquifer dynamics and interactions. Through the geological section analysis, some characteristics of the shallow aquifer were identified, like the shallow aquifer thickness that has an average of approximately 10 m.

The isotopic and hydrochemical results suggest that both aquifers have the same origin, possibly from rainwater infiltration in the southern part of the valley, and that both receive the same mineral inputs. Additionally, places of the wells for water extraction (i.e., A, B and C) are close to the local meteorological line, suggesting they are principally originated from rainwater and they are not heavily affected by the evaporation process. Those places were springs are located are more distant from the local meteorological line, suggesting they may be more affected by the evaporation process (Craig, 1961). This high evaporation can explain the results from D and E, which are farther than the rest of the sampled springs. The level of evaporation suggests that the water from the extraction wells circulates in a deeper component than the water in springs that circulates near the surface. This is consistent with spring evaporation (E, F and G) that is shown in the Piper diagram.

The water chemical composition of both aquifers is similar, since water interacts with rocks from volcanic origin. Processes such as water-rock interaction could dominate behavior in wells and springs. Therefore, results suggest that wells are more influenced than springs by the water-rock interaction process. The ionic content is relatively low and similar in both aquifers. Because springs D and E (in the northeastern and southwestern regions respectively) have the lowest hydrochemical value, it is likely that water was recently infiltrated and had a short course through the subsoil (Chebotarev, 1955; Domenico, 1972; Freeze and Cherry, 1979).

The water flow of the shallow aquifer is contained in the basalt associated with the Xitle lava spills (Delgado et al., 1998; Siebe, 2000). The circulation of groundwater occurs through interconnected fractures, vacuoles and lava-flow tunnels. This generates highly variable groundwater flows most of them at high speeds compared to other groundwater dynamics. In the main aquifer the water circulation occurs in two types of rock with high hydraulic conductivity from the Quaternary age: dacite and andesite (Arce et al., 2015; Morales-Casique et al., 2015).

The same direction of groundwater flow (from southwest to northeast) indicates that the water in the strata of both aquifers moves gravitationally from the recharge zones in high topographic areas to the lower areas of the valley. These lower regions are located outside of the limit of the shallow aquifer, but it is probable that the isolating conglomerate and clay layers are highly reduced here, and both aquifers may be hydraulically connected. This assumption appears to be confirmed because the basalt strata from the Xitle ends in this region leaving only the basalt strata from the Ajusco, which was under the Xitle strata in higher areas. To support this, there is no record of springs or other type of water discharges from the shallow aquifer to the surface in the border area were Xitle strata ends. However, this potential hydraulic connection should be evaluated in future studies.

The extension of the shallow aquifer seems to correspond to the original extension of the Pedregal (80 km^2), and therefore enhances the potential influence of surface activates on the shallow aquifer. The land use in this area is divided into two categories, urban and green spaces, which respectively represent 73% and 27% of the original extension of the Pedregal (Lot and Cano-Santana, 2009). Additionally, green spaces

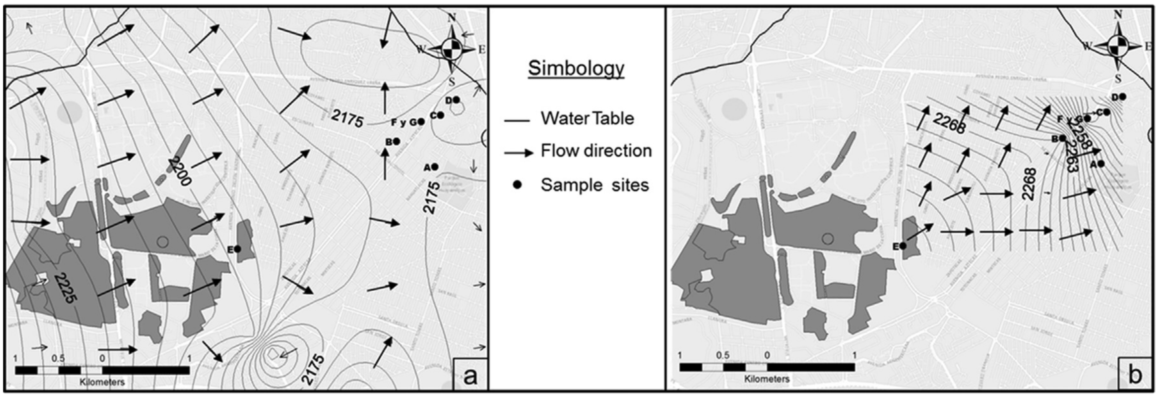

Fig. 6. Flow direction of both aquifers. "a" main aquifer, "b" shallow aquifer. The sample sites with dots.

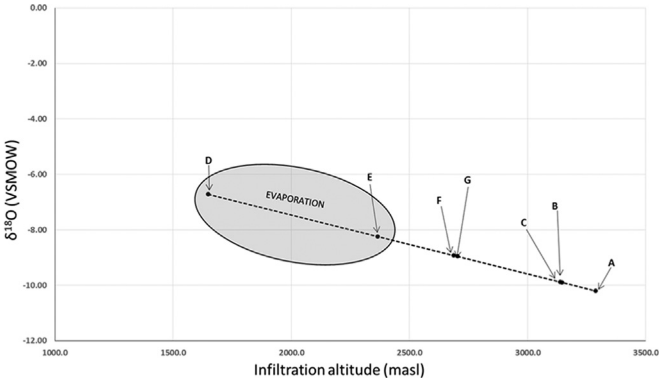

Fig. 7. Altitude above medium sea level of the estimated height of recharge of groundwater systems based in Cortés and Durazo (2001). The sample sites with dots.

above the shallow aquifer can be divided into two categories: green spaces that have suffered human modifications (e.g., parks), and green spaces with original characteristics (e.g., urban forests) (Calderón-Contreras and Quiroz-Rosas, 2017). The first type of green spaces, built with artificial materials and including exotic vegetation, represent 7% of the volcanic influence region and 47% of the green spaces. The second type of green spaces represent 8% of the volcanic influence region and 53% of the green spaces (based on Lot and Cano-Santana, 2009). There are also private gardens that have the same characteristics as the urban parks, but their size and distribution are unknown and thus they were excluded from the analysis.

Nevertheless, because decision makers do not recognize the shallow aquifer, there has not been any planning or management strategy related to it (Kralisch et al., 2012). All the management strategies are focused on the main aquifer that it is overexploited and influenced by processes that occurred thousands of years ago, while the shallow aquifer is affected by recent events, such as urbanization south of the city. The absence of management implies short-term consequences for the city. These consequences are even more relevant since the shallow aquifer could be a complementary source of water supply if it is properly managed. In addition, due to the depth of the urban shallow aquifers and the types of rock and soil that are above them, these aquifers are highly sensitive to pollution from different kinds of sources on the surface, like industries, disposal of solid waste, sewage system, gas stations, fuel tanks, urban zone and abandoned water extraction wells (Soto et al., 2000). Therefore, the need of a proper planning and management strategy that includes land use, green spaces perseveration, is needed to prevent and reduce the pollution of both aquifers.

5. Conclusion

The results confirm the presence of a shallow component of the groundwater system in the south of Mexico City. The shallow aquifer is unconfined and hydraulically independent from the main aquifer, but it is possible they have a connection close to the border of the shallow aquifer. This aquifer could be considered as a complementary source of the water supply for the city. However, a deeper analyses of water quality and its relationship with the main aquifer is needed to understand its impact on water supply for the city. Green spaces located in zones above the shallow aquifer seem to be important for the recharge of the aquifer in urban zones, and land use management must consider this interaction.

Around the world, the importance of shallow aquifers are increasing for a sustainable hydric management. The time scale of their fluxes is short enough to react to human activities, and therefore, this allows to evaluate the effect of human actions on the water supply. On the contrary, deeper aquifers have large time scale geological processes, implying that the present activities would modify water management thousands of years in the future.

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Table 3
Trace elements of wells and springs. LOD: Limit of detection.

Site	Type of site	Al (mg/l)	As (mg/l)	Ba (mg/l)	Cd (mg/l)	Cr (mg/l)	Cu (mg/l)	Fe (mg/l)	Mn (mg/l)	Pb (mg/l)	Zn (mg/l)
A	Well	< LOD	< LOD	0.032	< LOD	< LOD	< LOD	10.060	0.002	< LOD	< LOD
B	Well	< LOD	< LOD	0.037	< LOD	< LOD	< LOD	NA	< LOD	< LOD	< LOD
C	Well	0.020	< LOD	0.045	< LOD	< LOD	0.009	2.120	0.003	< LOD	0.024
D	Spring	< LOD	< LOD	0.014	< LOD	< LOD	0.016	NA	< LOD	< LOD	0.012
E	Spring	< LOD	< LOD	0.024	< LOD	< LOD	0.010	NA	< LOD	< LOD	< LOD
F	Spring	0.032	< LOD	0.022	< LOD	< LOD	0.023	0.087	0.004	< LOD	0.030
G	Spring	0.026	< LOD	0.027	< LOD	< LOD	0.022	0.068	0.007	< LOD	0.008

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Appendix 1. List of the water extraction wells used to do the geological sections

Coyoacan Municipality				
ID	Well name	Coordinates		
		x	y	z
1	AUXILIAR XOTEPINGO 3 - A	483462.90	2134632.80	2258.20
2	LA CIENEGA	482675.41	2137817.85	2252.59
3	METRO C.U.	481711.74	2136494.21	2271.56
4	PEDREGAL DE CARRASCO	482103.09	2134828.63	2284.41
5	PEDREGAL DE SAN FRANCISCO	482721.19	2138261.74	2253.41
6	PEDREGAL DE SANTO DOMINGO	482113.00	2136070.00	2287.00
7	PERIFERICO 3	485033.09	2134582.44	2241.10
8	PERIFERICO DIRECTO # 18	489229.00	2136506.00	2254.00
9	PERIFERICO DIRECTO # 19	488842.00	2136963.00	2238.00
10	PERIFERICO DIRECTO # 21	479702.91	2134315.98	2326.00
11	PERIFERICO DIRECTO # 24	482104.73	2135355.80	2302.00
12	PERIFERICO DIRECTO # 25	482888.62	2137328.47	2264.00
13	SANTA URSULA COAPA	483913.91	2134494.33	2252.22
14	PERIFERICO DIRECTO N° 17	482120.00	2134094.31	2260.47
Tlalpan Municipality				
ID	Well name	Coordinates		
		x	y	z
15	BELIZARIO DOMINGUEZ	481310.51	2133122.66	2287.99
16	FUENTES BROTANTES No. 1	481285.01	2132363.97	2316.55
17	JARDINES DE LA MONTAÑA 1	479035.24	2133959.74	2376.00
18	JARDINES DE LA MONTAÑA 2	478453.00	2133987.00	2264.00
19	PADIERNA PICACHO	476859.00	2134206.00	2439.00
20	SAN FERNANDO TLALPAN	481499.32	2133539.36	2282.00
21	VILLA OLIMPICA No. 2	480485.47	2134005.18	2292.24
22	XOCHITL	480772.03	2132665.91	2320.03

Appendix 2. Isotopic results from springs and wells

Site	Type of site	d18O	d2H
A	Well	− 10.20	− 72.9
B	Well	− 9.90	− 69.5
C	Well	− 9.88	− 70.5
D	Spring	− 6.71	− 50.4
E	Spring	− 8.24	− 61.4
F	Spring	− 8.96	− 61.7
G	Spring	− 8.92	− 64.5

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Chapter 6.

Geochemical characterization of components of the groundwater flow system in the basin of Mexico

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Geochemical characterization of components of the groundwater flow system in the basin of Mexico

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Abstract. More than 21 million people live within the Basin of Mexico. Water is the main concern of this large population, where groundwater has been intensively exploited, leading to subsidence and fracturing of the ground. It is for this reason that it's very important to understand the behavior of groundwater flow system components. This knowledge can help to more effectively manage water use and conserve the recharge zones. The main purpose of this study is to identify and characterize the components of groundwater flow system. Cluster analysis was used to classify 303 groundwater samples into groups. The groups show that chemical concentrations increase along the trajectories of groundwater flow. We describe these groups and identify three components in the flow system; the upper zone, the intermediate zone and the inferior zone. Different water management policies are suggested for each system component, because they have different response times to the actions taken in their use and conservation.

1 Introduction

The Basin of Mexico is a closed catchment located in the Mexico Trans-volcanic Belt [1]. The basin has a drainage area of about 9600 km^2. The abrupt relief of the surrounding mountains, with altitudes of more than 5000 m a. s. l, inclines towards the flat-lying center of the basin to an altitude of approximately 2230 m a. s. l [2]. Thermal mineral springs occur along lineaments thought to be fractures in the rocks below the alluvial fill [3].

People have occupied this basin for some 15,000 years and Mexico City has developed within the basin, so that today a population of more than 21 million inhabitants reside within the basin [4]. Additionally, several million people live in other communities nearby. Groundwater extraction in the last 60 years has caused a decline in the groundwater level and land subsidence. In recent years, water quality, rather than quantity, has become a

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concern in some areas of the country. Mexico City depends heavily on shared groundwater: more than 72 % of the water supply is pumped from groundwater systems by neighboring states [5]. Lack of knowledge of the functioning of the flow system is one of the reasons for the intensive exploitation of the groundwater in the basin. Therefore, it is very important to understand groundwater behavior in the basin in order to design better strategies for water exploitation, water management and water conservation. We therefore study and evaluate the components of this system using the cluster analysis, a very powerful classification tool.

2 Methodology

This study used unpublished data from the National Water Commission of Mexico for the year 2017 to create the water table map of the basin. A total of 303 groundwater samples were collected during June to October 2018 from 43 springs and 260 wells, with in-situ measurement of the following field parameters: electrical conductivity (EC), temperature, pH and hardness. The samples were collected in polyethylene bottles and filtered in situ through 0.45 μm Millipore cellulose nitrate filter. Cations and trace elements samples were also acidified with HNO3 to pH ~ 2 [6]. All samples were stored at approximately 4 °C before analysis. Major chemical constituents were analyzed by liquid chromatography and trace elements by inductively coupled plasma optical emission spectrometry (ICP-OES).

Fifteen physico-chemical constituents, the cations Na^+, K^+ Ca^{2+}, and Mg^{2+}, anions HCO^{3-}, Cl^-, and SO_4^{2-}, trace elements Si, Sr, and Zn and pH, t, EC and hardness were used for the multivariate statistical analysis. Agglomerative hierarchical cluster analysis was done by means of Ward's method [7] using squared Euclidean distances as a measure of similarity. Ward's method enables an analysis of variance approach to evaluate the distances between the clusters in order to minimize the sum of squares of any two clusters [8]. The cluster package in RStudio was used for the multivariate statistical analysis.

3 Results and discussion

The entire basin is considered as a single unit where groundwater moves. Groundwater flows within the basin are in contact with basic volcanic rocks (basalt, andesite, tuffs, ash deposits), conglomerates with volcanic clasts, sands and gravels of volcanic and sedimentary origin. Wells have depth from 100 to 450 m, 3 wells reach depth greater than 900 m, and the deepest well extends to 2020 m.

Water map (Fig. 1) shows groundwater flow direction in the basin. Water moves mainly from the southeast and northeast towards the middle of the basin.

Based on the standardized physico-chemical data, cluster analysis was performed to classify water sampling points. Figure 2 shows cluster dendrogram classification of the basin. Groundwater is classified into four groups (1, 2, 3, 4) (Fig. 1). These groups show different characteristics. Chebotarev [9] concluded that groundwater tends to evolve chemically with time towards the composition of seawater, i.e. from $HCO^{3-} \rightarrow HCO^{3-} + SO_4^{2-} \rightarrow SO_4^{2-} + HCO^{3-} \rightarrow SO_4^{2-} + Cl^- \rightarrow Cl^- + SO_4^{2-} \rightarrow Cl^-$. The groups respond to this chemical evolution, group 1 being least evolved and group 4 most evolved. This evolution is controlled by water-rock interaction and residence times. We also use cluster classification and water table map to define recharge zones in the basin. For example; Group 1 waters lie in the southwest boundary region of the basin and are related to a less evolved chemical composition. Group 1 can be considered a recharge zone.

Group 2 waters are observed after Group 1 in the flow direction, which according to the Chebotarev evolution could be related to the increase of mineral composition as a consequence of longer subsurface residence time.

Groups 3 and 4 are progressively located along the direction of flow. They are divided into two zones. The first flows from the southwest area into the central part of basin and the second from northeast area to the central part of basin. In the first zone, the four water groups follow the groundwater flow direction, with Group 1 to 4 progressively evolving from less evolved waters to waters with higher dissolved contents along groundwater flow paths. The water evolves from its recharge zone as it interacts with the rocks until reaching the last stage of the Chebotarev sequence.

Within the second zone are mainly groups 3 and 4. Group 2 is present in a small proportion and group 1 is present only on 1 site in middle part of basin. The waters of group 3 and 4 must have evolved since recharge in the subsoil. One cause could be that water recharges in the NE zone and continues to evolve in the direction of flow to its location in the NW. Another possibility could be that water recharges in the NW and continues to evolve in the direction of flow to its N location. We do not consider inter-basin flow because there is no other basin topographically higher than the Basin of Mexico.

Temperature and EC are two variables very related in the study of groundwater flow systems (Fig. 3). Group 1 has low temperature and low EC, this may be due waters of recent infiltration (had little time to interact with rocks for mineral dissolution). Temperature responds to recharge temperature of the area, with colder waters that are characteristics of mountain climate. Groups 2, 3 and 4 have water temperature that increase with EC. Groups 3 and 4 have the highest temperature and highest EC. The elevated EC values reflect increasing mineral dissolution along groundwater flow paths. The Chebotarev chemical evolution could explain the increase in EC. Temperature increase could be related to input of geothermal waters into the deeper portions of the basin [10]. The Mixhuca fault [11] and Santa Catarina graben [12] (Fig. 1) favor the circulation of fluids that come from greater depths. For example; there is a thermal spring near Santa Catarina graben.

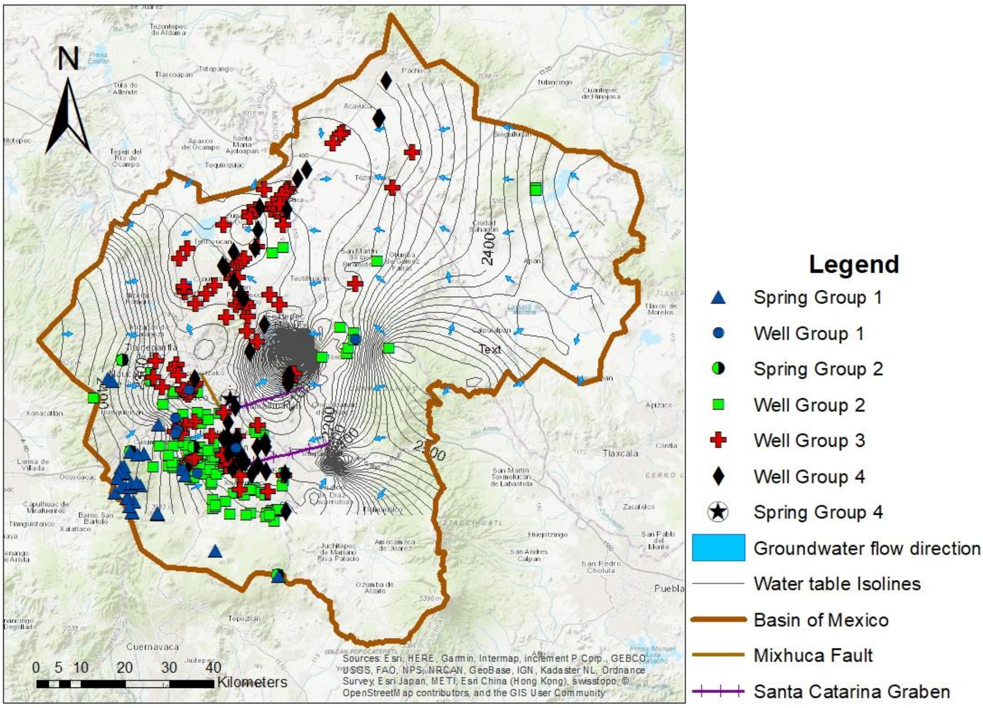

Fig. 1. Water table and sample location map showing geological structures [10, 11].

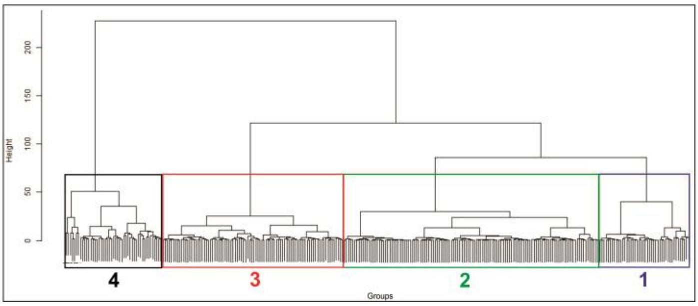

Fig. 2. Classification dendrogram for 303 groundwaters of the Basin of Mexico.

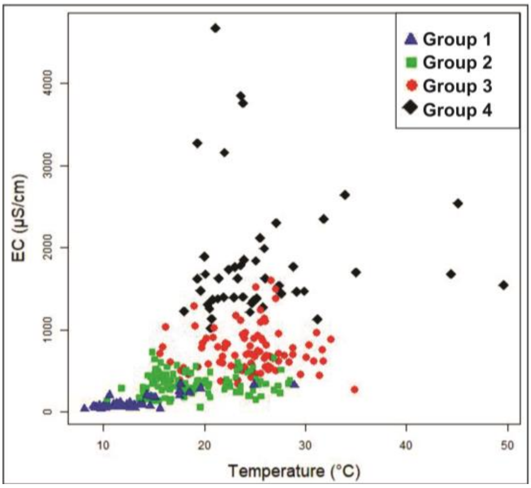

Fig. 3. Scatter plot of electrical conductivity (EC) versus temperature (T).

Makarenko [13] proposes to divide the components of the flow system into 3 zones; the upper zone, the intermediate zone and the lower zone. This classification is related to climatic conditions, travel speed and discharge zone. We relate; Makarenko (a); cluster analysis (b); water table map (c); scatter plot (d) and the Chebotarev chemical evolution (e). We propose that flow system components for the Basin of Mexico are:

1. Group 1 as the upper zone: active flow (a); least chemically evolved (b, c and e); strongly influenced by climatic conditions (a); cold water temperatures (d); recharge zone (c).
2. Group 2 as an intermediate zone: delayed flow (a); medium chemical evolution (b, c and e); little climatic influence (a).
3. Group 3 and 4 as lower zones: very slow flow (a); greater chemical evolution (b, c and e); no influence of the current climate (a); hot water temperatures (d); influenced by geothermal gradient (d).

5 Summary and Conclusions

Identifying the components of the flow system of the Basin of Mexico is essential to understand its functioning. The use of techniques such as cluster analysis, scatter diagrams and chemical evolution of Chebotarev gave us 3 components; superior, intermediate and inferior. The upper zone is related with recent infiltration. This zone is located in the southeast boundary area of the basin. The intermediate zone reflects the water´s geochemical progressive evolution. Groundwater evolves along the flow path from SW and

NE towards the middle of the basin. Water-rock interactions are the main process of chemical evolution. The inferior zone is related with high chemical evolution. Higher temperatures are related with geothermal gradient in the inferior zone. Groundwater evolves with residence time along the flow path.

Differences found in components of the flow system can be used to carry out water management strategies. The upper zone that has strongly been influenced by the climate must be managed by a policy that considers climate fluctuations in its extraction and conservation. This zone has active flow, so any change or action that is made on it can be reflected in a short time. However, the lower zone with no influence of the current climate and with very slow flow will not be affected in the short term by the actions taken for its management and conservation.

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Chapter 7.

Identification of the components of a complex groundwater flow system subjected to intensive exploitation

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Identification of the components of a complex groundwater flow system subjected to intensive exploitation

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ABSTRACT

The Mexico City region, like many other densely populated regions in the world, has problems in guaranteeing the supply of drinking water to its inhabitants. Its groundwater flow system is subject to intensive exploitation. To ensure proper water management, it is important to understand the behavior of groundwater flow system components under conditions of intensive exploitation. In this study, we analyzed 169 samples from drinking water supply wells, according to their chemistry. The principal components of the flow system were inferred using exploratory statistical analysis and analysis of the mixture of the end-members of the hydrochemical dataset. Four components were identified: (1) waters of recent infiltration and local circulation, (2) waters with evidence of intermediate chemical evolution, (3) waters that are chemically more evolved and of large flow trajectories, (4) waters that are chemically more evolved and of deep circulation. A relationship between the components, the structural geology, and the recharge zones was established. The mixing proportion of the four components in each water sample extracted from drinking water wells was identified. It was observed that the faults and the design of screened section of the well tubes influenced the mixtures captured by the wells. The impact generated by the intensive exploitation with respect to the distribution of the components within the flow system was evaluated.

1. Introduction

Groundwater is important for the socio-economic development of society. More than 2 billion people around the world depend on groundwater for their daily supply. Agriculture, irrigation, and industries depend to a large extend on groundwater (Kemper, 2004). Some aquifers in the world are intensively exploited for groundwater, which means that the natural functioning of groundwater and its relationships with other bodies of water has been significantly modified (Custodio, 2002). Thus, it is necessary to understand its behavior from the point of view of flow systems.

A groundwater flow system is a single system and is composed of components or flow paths. The concept of a groundwater flow system has evolved over time. Delesse et al. (1862) was the first to consider groundwater as a flow system using a map with piezometric levels. Posepny (1889) explained the difference between superficial and deep groundwater flow systems. Furthermore, Lichkov (1933) proposed a groundwater flow classification. Lange (1947) suggested a groundwater flow components distribution in different areas. Makarenko (1948) was the first to introduce a division of the groundwater flow system into three components or flow paths, depending on climate influence and base level discharge of groundwater flow. Norvatov and Popov (1961) resumed Makarenko's idea and divided the flow system into four components. However, Tóth (1963) revised these proposals and differentiated between the three flow system components, namely local, intermediate, and regional. He used mathematical models in a theoretical case and differentiated the flow system components using flow networks and hydraulic potential. Latter, Mifflin (1968) applied the

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Tóth theory to a practical case in Nevada, USA. He demonstrated that detailed information about the three-dimensional variations of hydraulic potential would be necessary to apply the approach with an adequate level of precision. Hence, he proposed to delimit groundwater flow system components using hydrogeochemistry, based on the water evolution concept of Chebotarev (1955), and combined it with groundwater temperature and residence times.

In geologically complex systems under modified natural conditions, understanding the behavior of these flow components is not straightforward. The Mexico City region, which represents such a complex system, has been settled for the last 15,000 years (Durazo and Farvolden, 1989). Currently, this region is one of the most populated in the world with more than 21 million inhabitants (United Nations, 2018). Groundwater extraction began in 1846, and in 1912 there were approximately 1400 production wells in operation. In 1928, 1946, there were approximately 2500 and 3000 wells, respectively, that were active (De la O Carreño, 1954). Gayol (1925) was the first to report land subsidence in the urban areas of Mexico City. Intensive groundwater exploitation during the past 60 years has caused a sharp decrease in the groundwater level (Martinez et al., 2015). Cardona and Hernandez (1995) reported a mixing process in groundwater extraction from the analysis of the change of flow directions due to intensive exploitation, stiff diagrams, and stable isotopic data. Recently, Escolero, 2018 defined the endorheic groundwater flow system of the Basin of Mexico as the Anáhuac System. The Anáhuac System covers the same surface area as the Basin of Mexico, with the Mexico City region being a part of it (Fig. 1).

The annual water availability in Mexico City is in the order of 74 m^3/inhabitant (CONAGUA, 2012, 2009), which is considered as one of the lowest in Mexico and in general. Water supply in Mexico City includes a complex administrative structure where institutions of different levels and states interact, as described by Escolero et al. (2016). In addition, the planning, design, and construction of wells is constrained due to cost issues and is based on obsolete decision schemes.

Due to intensive extraction of water in the Mexico City region, it is necessary to determine how the components of the groundwater flow systems behave and to what extent each of them contributes through drinking water wells. Thus, the objectives of this study are to: (1) Identify the components present in an endorheic system modified by intensive exploitation; (2) Find the mixture of the components in the pumping wells that supply drinking water to the city; (3) Identify the impact of intensive exploitation on the components of the flow system.

2. Study area

The Basin of Mexico, located in a volcanic-tectonic depression at high altitude, is a closed basin placed in the eastern sector of the Trans-Mexican Volcanic Belt (TMVB) (Enciso-De la Vega, 1992). The relief of the TMVB consists of a series of stepped plains (Vazquez-Sanchez and Jaimes-Palomera, 1989). The TMVB is the result of the subduction of the oceanic plates of Cocos and Rivera under the North America plate (Pardo and Suárez, 1995). The basin has an area of approximately 9600 km^2, is 100 km long and 80 km wide, and is NE-SW oriented. It was cut-off in the southern part 1.2 million years (Ma) ago by the emergence of the Chichinautzin volcanic field during the early Pleistocene (Arce et al., 2013a). The basin is surrounded by volcanic

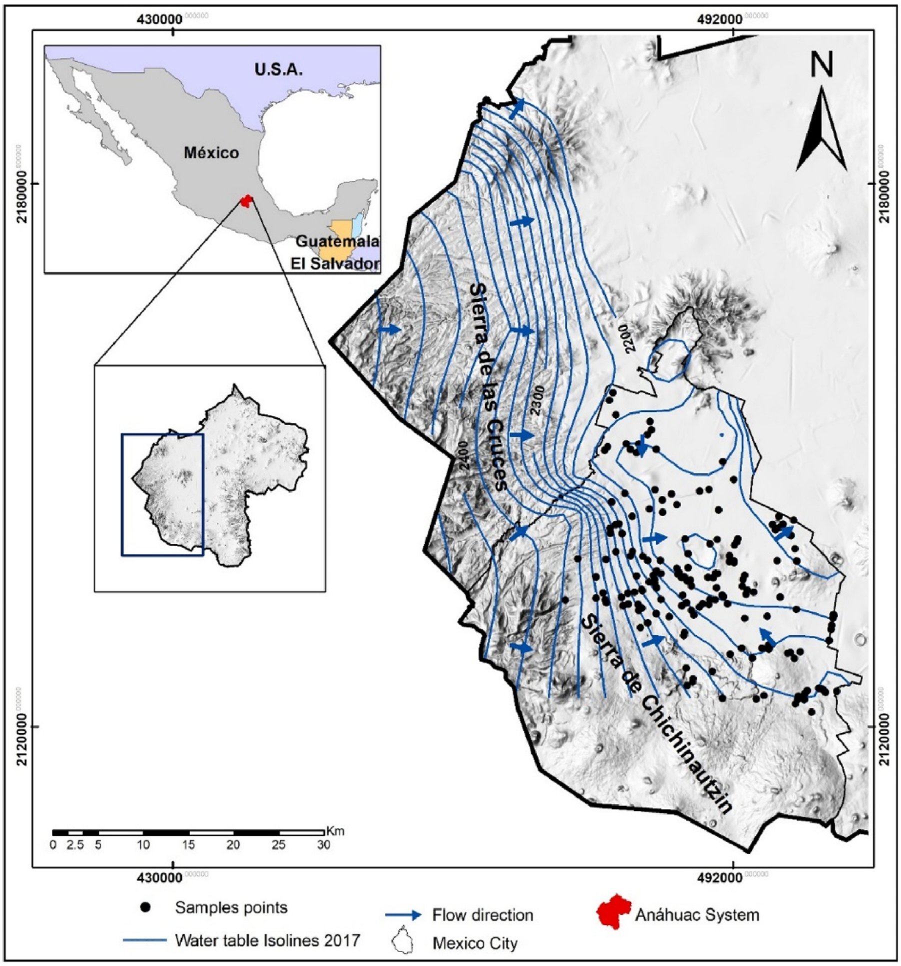

Fig. 1. Location of study area, elevation model, samples points, and groundwater table configuration.

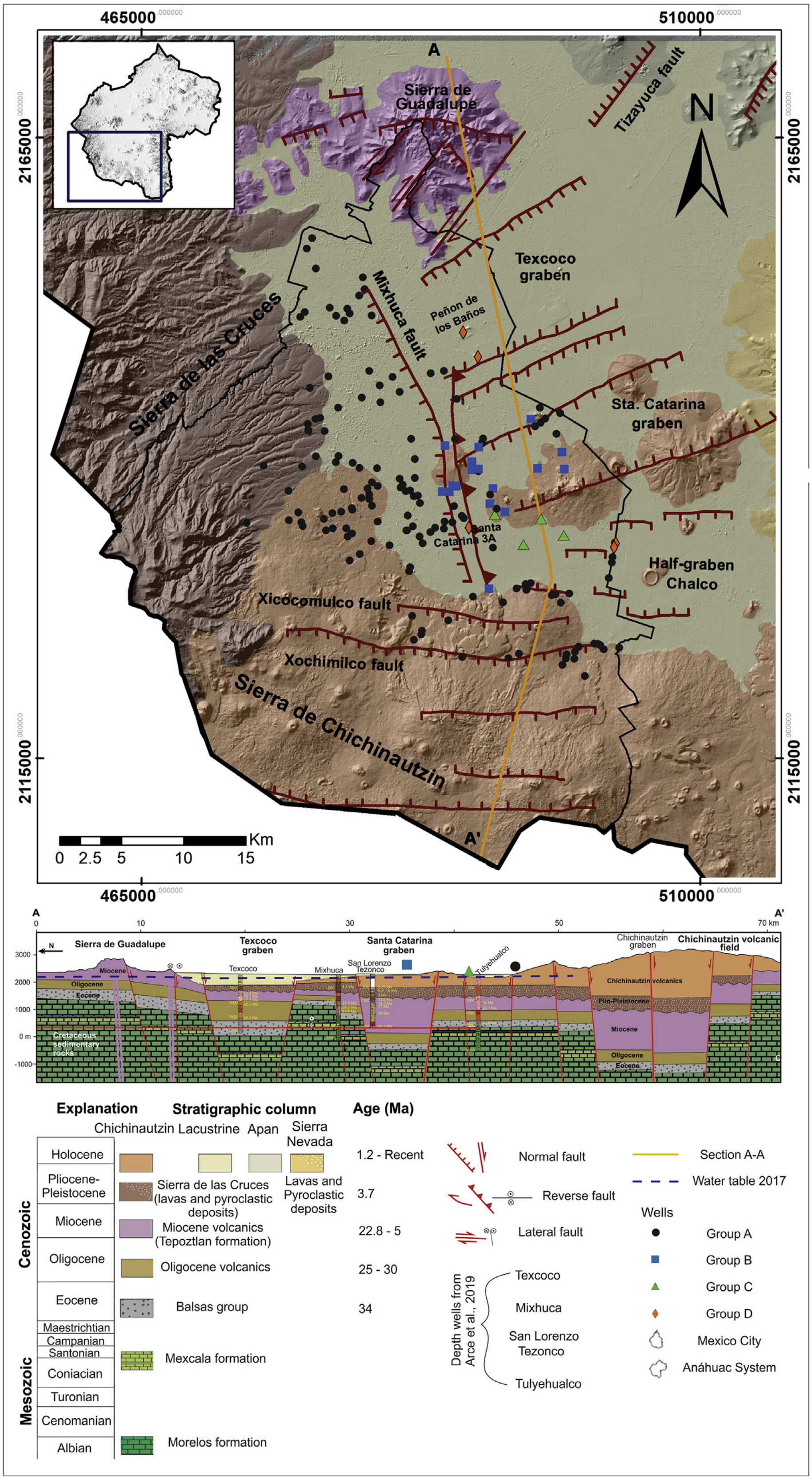

Fig. 2. Geologic map, vertical geological section, and end-member mixing analysis groups (modified from Arce et al., 2019).

mountains comprising of andesitic and dacitic compositions, namely Sierra de Guadalupe (~20–~13 Ma), Sierra de las Cruces (3.7–0.03 Ma), Sierra Nevada (1.4 Ma to Recent), and Sierra de Chichinautzin (1.2 Ma to Recent) (Arce et al., 2019). The relief of the mountains tends to reach altitudes of more than 5000 m above sea level (m asl). These fall towards the central plain of the basin located at an altitude of approximately 2220 m asl. In the lower parts of the valley-floor, the Basin of Mexico consists mainly of clastic, volcanoclastic, and lacustrine deposits (Enciso-De la Vega, 1992) (Fig. 2).

Arce et al. (2019) defined nine stratigraphic units of the basin, based on Fries (1960): (1) Morelos formation from Cretaceous, composed of marine limestones and dolomites, with flint nodules; (2) Mexcala formation from Cretaceous, dominated by argillaceous limestones of dark gray color with abundant planktonic foraminifera; (3) Balsas group from Eocene, defining a succession of continental deposits, composed of conglomerates, sandstones, siltstones, lacustrine limestones, pyroclastic deposits, and minor lava flows; (4) Tilzapotla formation from volcanic Oligocene, which is a sequence of rhyolitic, rhyodacitic, dacitic lavas, and ignimbrites; (5) Tepoztlán Formation from volcanic Miocene, representing a sequence of volcanic debris of andesitic composition, including intercalations of lavas, pyroclastic deposits, and lahar; (6) Sierra de las Cruces volcanic sequence from Pliocene-Holocene, describing volcanic structures and domes with pyroclastic deposits, interdispersed with lahar and debris (Arce et al., 2015); (7) Sierra Nevada volcanic sequence, delineated by a set of stratovolcanoes, domes interspersed with pyroclastic deposits in heights, and by intercalations of pyroclastic and epiclastic deposits, as well as debris deposits by avalanches in the lowlands (Macías et al., 2012; Nixon, 1989; Siebe et al., 2017); (8) Pliocene-Holocene Chichinautzin volcanic field, consisting of more than 220 monogenetic structures and a wide range of chemical composition, although most of the products are basaltic andesite, basalts, and dacites (Arce et al., 2013a; Siebe et al., 2004); (9) Pleistocene-Holocene lacustrine deposits interconnected with volcanic rocks (Arce et al., 2013b; Brown et al., 2012; Caballero and Guerrero, 1998; Perez-Cruz, 1988).

The tectonic settings of the Anáhuac System are described by Arce et al. (2019). The main tectonic features in the study area are Texcoco graben, Santa Catarina graben, horsts of these grabens (Arce et al., 2013b), Mixhuca fault (Perez-Cruz, 1988), Chalco half graben (Urrutia-Fucugauchi and Chávez, 1991; Vazquez-Sanchez and Jaimes-Palomera, 1989) and other faults that have not been named (Arce et al., 2019) (Fig. 2).

3. Methods

3.1. Preparation, field campaign and laboratory analyses

Unpublished data from the National Water Commission (Comisión Nacional de Agua - CONAGUA) was obtained for the year 2017 to establish the general water table configuration in the basin. The groundwater depth measurements and the topographic surveys of the wells that were made by CONAGUA were used to calculate the water table elevation. Spatial interpolation of water table elevation was done using the ordinary Kriging method (Cressie, 1993; Franke, 1982). The general movement of groundwater was considered perpendicular to the isolines of water table elevation (Domenico and Schwartzm, 1990).

Based on the information obtained from CONAGUA and Mexico City Water Utility (Sistema de Agua de la Ciudad de México), 169 wells were selected according to their geographic distribution in the city area. Once the sampling permissions of these wells were obtained, available information on well construction and lithology was collected. The selected wells have a depth of 300 and 450 m below ground level, with some reaching 900, 1300, and 2036 m. Sampling was conducted from June to October 2018. Electrical conductivity and pH were measured with a multi-parametric probe (Oakton PC 300), temperature (T) was measured using a digital thermometer (Hanna HI98509 Checktemp), and alkalinity with a test kit (Lamotte 4491-DR-01). Water samples were collected in new, pre-rinsed polyethylene bottles to determine principal anions (HCO_3^-, Cl^-, SO_4^{2-}, NO_3^-, PO_4^{3-}) and cations (Na^+, K^+, Ca^{2+}, Mg^{2+}). Prior to sampling, water was filtered through Millipore cellulose nitrate filters (0.45 µm). In addition, samples collected for the cation analyses were acidified with HNO_3^- at pH ~2 (Appelo and Postma, 2005). All samples were stored in a refrigerator at approximately 4 °C. Anions and cations were analyzed by liquid chromatography in the Chromatography Laboratory (Institute of Geology, National Autonomous University of Mexico). All samples were complied with an acceptable charge balance error of $< 10\%$ (Appelo and Postma, 2005; Freeze and Cherry, 1979).

3.2. Interpretation techniques

A preliminary statistical description of water chemistry and a graphical evaluation of chemical differences were employed using well-known diagrams that helped to delineate groundwater flow components. The use of ($Na^+ + K^+$) vs ($Cl^- + SO_4^{2-}$) diagram (Mifflin, 1968) assisted in the identification of groundwater flow components. Similarly, the trilinear diagram (Piper, 1944) was useful in showing chemical differences across the study area and helped to classify groundwater into chemical facies, which was helpful in defining groundwater flow paths. The chemical composition of groundwater is controlled by many factors, including the composition of rainfall, geological structures, lithology, mineralogy of the strata, and temperature during the time water flows through the system. The interaction of all these factors eventually leads to several water facies (André et al., 2005). The final composition of the groundwater extracted in the wells is the result of numerous processes. However, in many systems, mixing processes also play a role, especially in systems with high flow rates in fractured media (Gu et al., 2017).

Similar to other regions of Mexico, the well tubes in the study area have large well screens that cross different lithological units. For example, if a well has a depth of 400 m, casing typically reaches from the surface to a depth of 50 m, and the rest of the well depth consists of a screened tube that serves as intake of the well. Thus, the extracted groundwater from such a production well represents a mixture of different components of the flow system that are captured along the depth of the well. These components can be differentiated according to their chemical composition, and are considered end-members (sources) in the final mixtures of the water extracted by the wells.

The end-member mixing analysis (EMMA) is a method that can be applied using multivariate or univariate data (Christophersen and Hooper, 1992; Carrera et al., 2004). This method assumes that the groundwater extracted in the wells is a mixture of two or more sources or end-members, and that the mixing ratios can be estimated from the hydrochemical composition of the water samples. A methodology was developed by Carrera et al. (2004) to calculate mixing ratios with uncertain end-members. In this study, four end-members, based on the hydrogeochemical evolution (according to the sequence of Chebotarev (1955)) were proposed. The chemical composition of water samples are understood as a mixture of the following end-members: (1) waters with little hydrogeochemical evolution (predominantly HCO_3^- type); (2) waters with intermediate hydrochemical evolution (rich in SO_4^{2-}); (3) more evolved cold waters, rich in Cl^-; (4) more evolved hot waters, also rich in Cl^-. The latter two end-members were selected, based on exploratory data analysis, where waters rich in Cl^- behaved differently. To select end-members, the temperature (T) vs. Cl^- (Fig. 5) and ($Na^+ + K^+$) vs. ($Cl^- + SO_4^{2-}$) (Fig. 7) scatter plot diagrams were employed in combination. End-member 1 was selected as the sample of least evolution with respect to the Mifflin diagram (Fig. 7), indicating low T and Cl^- values (Fig. 5). End-member 2 was selected for its intermediate values of T and Cl^- (Fig. 5). End-members 3 and 4 were selected as the two ends of the T vs. Cl^- scatter plot, indicating the highest content of Cl^- in the study area combined with lowest and highest T, respectively (Fig. 5).

EMMA method typically requires the use of conservative species (Christophersen and Hooper, 1992; Pelizardi et al., 2017). The use of non-conservative species is generally disputed for possible changes or reactions of these species in water. However, some species that are typically not considered conservative have been used in EMMA studies

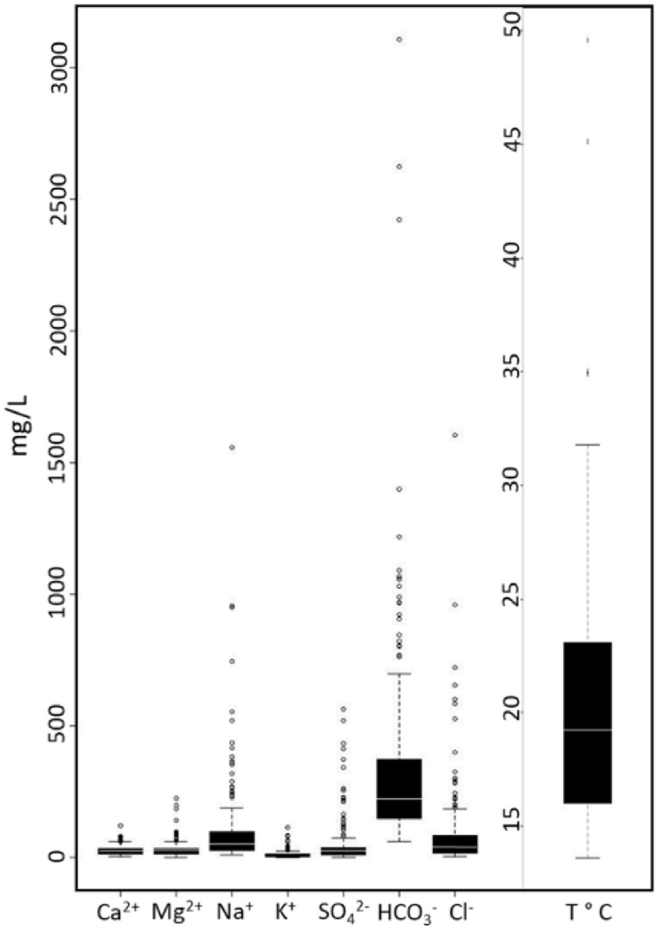

Fig. 3. Box plot of 169 wells, major ions and temperature.

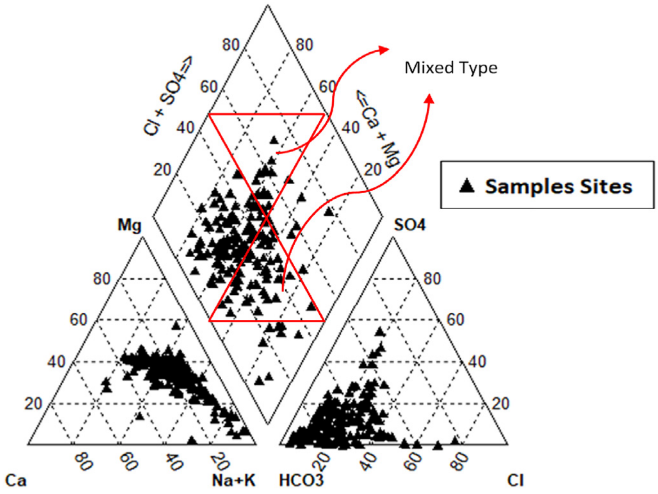

Fig. 4. Trilinear diagram of water chemistry.

successfully because they may aid in explaining mixing process variations. For example, Morales-Casique (2012) found a contrasting concentration among the end-members, when both SO_4^{2-} and Ca^{2+} were included with Cl^-. Tubau et al. (2014) proposed a methodology where the concentrations of the species had to vary widely among the sources; moreover, they also recommend the use of the hydrochemical conceptual model with the most useful species. They used Cl^- and non-conservative considered ions, including SO_4^{2-}, Na^+, HCO_3^-, Ca^{2+}, Mg^{2+}, and K^+. Kim et al. (2017) employed EMMA to identify geochemical processes and to develop a hydrogeochemical model. They used Cl^- and non-conservative considered ions, including Na^+, K^+, Ca^{2+}, Mg^{2+}, SO_4^{2-}, HCO_3^-, and identified Ca^{2+} for Na^+ exchange and sulfate reduction processes with the use of mixing analysis. They concluded that EMMA is a useful tool for evaluating complex hydrogeochemical processes. Tubau et al. (2014) also used mixing analysis to identify deviations from the mixing lines and to trace chemical and mixing processes. Other approaches that used non-conservative elements included that of Katsuyama et al. (2009) that utilized Na^+, Mg^{2+}, and SO_4^{2-}, and Burns et al. (2001) that considered Ca^{2+}, Mg^{2+}, K^+, Na^+, and SO_4^{2-}. Due to the chemical variations that may occur during mixing of the flow components, this study proposed the use of eight markers (Ca^{2+}, Mg^{2+}, Na^+, K^+, Cl^-, SO_4^{2-}, HCO_3^-, and T), four end-members, and a set of arbitrary initial mixing ratio. These elements are considered to be representative of the hydrochemical evolution and mixing processes in the study area.

As a result of the EMMA, the "true" concentrations of the end-members (groundwater flow system components or flow paths) and the "true" ratios or mixtures of the components in the water sampled in each well were obtained. From the predominance of each component in the mixing ratios of the water in the wells, four groups of wells were established (identified as A to D). The criterion used to establish each group is the apportionment of the end members in each sample/well. Those samples/wells that had dominant mixing proportions of end-member 1 were included in group A; those that had a major contribution from end-member 2 were considered in group B; samples/wells with high mixing ratios of end-member 3 were assigned to group C; and high mixing ratios of end-member 4 belonged to group D.

4. Results

4.1. Characterization of groundwater flow and chemistry

Groundwater flow directions in the water table configuration show that groundwater of the Anáhuac System originates mainly in the west of the basin, along the Las Cruces and Chichinautzin mountain ranges, and flows towards the lacustrine plain in the lowest part of the basin (Fig. 1).

Table 1 shows the descriptive statistical summary of concentrations of chemical elements and T of 169 groundwater samples. Among the cations, Ca^{2+} varies between 3.1 and 121 mg/L (average 26.5 mg/L), Mg^{2+} between 1.5 and 223.7 mg/L (average 32.1 mg/L), Na^+ between 10.7 and 1556 mg/L (average 110.8 mg/L), and K^+ between 1.2 and 113.9 mg/L (average 11.8 mg/L). Among the anions, HCO_3^- ranges from 61.3 to 3108.1 mg/L (average 354 mg/L), SO_4^{2-} between 0.4 and 562.8 mg/L (average 50.8 mg/L), and Cl^- between 2.9 and 1602.9 mg/L (average 95.5 mg/L). It can be observed for Na^+, SO_4^{2-} and Cl^- that the standard deviation is practically twice as large as the average, suggesting a large chemical variation. Similarly, T shows a wide range between 13.6 and 49.6 °C (average 20.0 °C), reflecting the wide spectrum of elevation among the wells and a possible influence from the earth's geothermal gradient.

The box plot of all 169 samples (Fig. 3) shows high variations for HCO_3^-, Cl^-, and Na^+ with numerous outliers, while K^+, Ca^{2+}, and Mg^{2+} show lowest variations. The T has a wide range of values with three outliers. This large variation could be related to the effect of a geothermal gradient as mentioned above.

The chemical composition and differences among groundwater samples are illustrated in the trilinear diagram (Fig. 4). It can be observed on the left (cation) triangle that the trend moves from sodium-type to mixed or no-dominant type, and on the right (anion) triangle, one trend moves from bicarbonate type to sulfate type and another from bicarbonate to chloride type. A large number of sample plots are in the central left part of the diamond (Ca–HCO_3 type) and reflect shallow, fresh groundwater in areas close to recharge formation. However, most samples are located in the mixed zones of the diamond (red triangles)

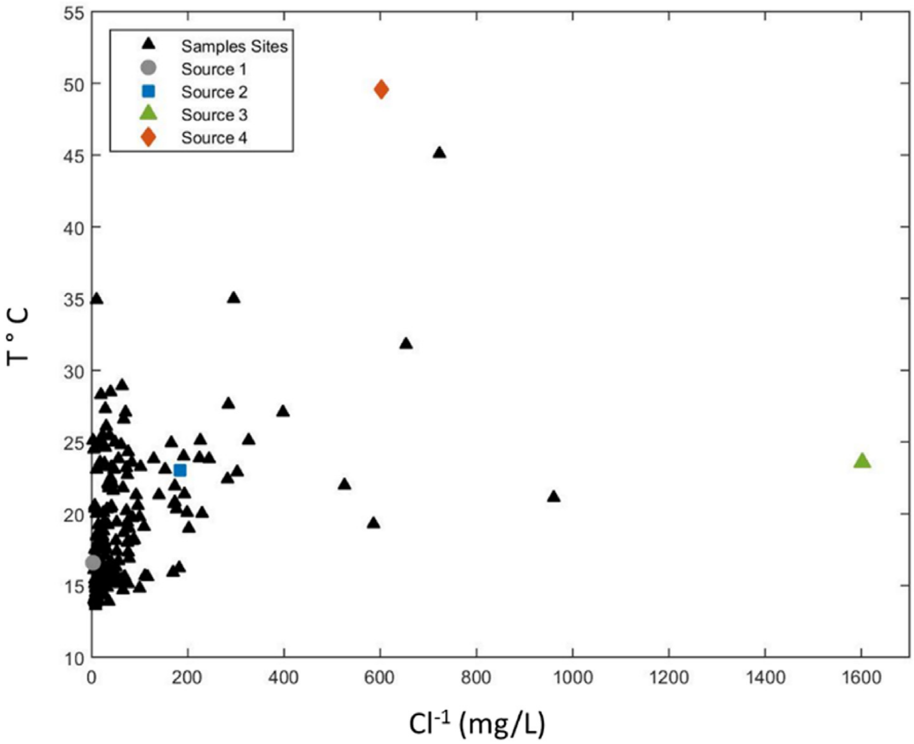

Fig. 5. Scatter plot and end-member (source) selection.

and represent several processes, including weathering of silicates, mixing processes, and ion exchange. Arce et al. (2015, 2013b) and Morales-Casique et al. (2019) reported the presence of basaltic glass and plagioclase in the rocks of the study area, which are a rich source of Na^+, besides other ions. As water enters the recharge zone, a gradual change occurs from the calcium-magnesium facies through the calcium-sodium facies and the sodium-calcium facies to the final sodium facies via groundwater flow circulation. Plots of a few samples are seen in the lower part of the diamond (Na–HCO_3 type), which match Ca^{2+} for Na^+ ion exchange on clay surfaces. Arce et al. (2013b) reported the presence of montmorillonite as an important clay mineral in the study area. On the other hand, the ratio of ($Ca^{2+}+Mg^{2+}$-HCO_3^--SO_4^{2-}) vs. ($Na^+ + K^+$-Cl^-) is indicative for the importance of ion exchange in groundwater chemical processes. If ion exchange plays a predominant role in the system, then the values are close to −1. In our case, the average ratio is −1.1 with significant correlation ($R^2 = 0.96$), indicating that ion exchange is important. Finally, a handful of samples can be observed at the central right side of the diamond, which indicate marine or deep ancient groundwaters.

To obtain the EMMA analysis, ion concentrations of four samples were used as initial sources (Table 2), as described in the methodology. These concentrations and the mixing ratios obtained by a linear correlation of the initial sources were used as a starting point for calculations with Mix software (Carrera et al., 2004). Thus, the final mixing ratios were obtained.

4.2. Mixing patterns

The mixing ratios of the four components were obtained for each well, using the EMMA method and were based on the initial ion concentrations of the sources (Table 2). Table 3 presents the statistical summary of the estimated mixing ratios. On average, components 1 (water with little evolution) and 4 (more evolved, hot water) contribute 38% and 32%, respectively. This is the highest contribution in the water samples. On the other hand, component 2 (water with intermediate evolution) shows 22% and component 3 (more evolved, cold water) shows the lowest contribution with only 8%, on average.

The boxplots in Fig. 6 illustrate the behavior of each group. Group A is representative of flow component 1 (Fig. 6a) and has the smallest range of concentrations in the majority of ions (Ca^{2+}, Na^+, HCO^{3-}, SO_4^{2-} and Cl^-) and T. Atypical low values in group A in major ions are associated with the process of mixing between less evolved and more evolved components. Group B is representative of component 2 (Fig. 6b) and has elevated values, as well as remarkable high SO_4^{2-} concentrations. Group C reflects component 3 (Fig. 6c) with increasing values of HCO_3^- and higher concentrations of Na^+ and Cl^-. Group D matches component 4 (Fig. 6d) and depicts the highest Cl-concentration and T.

The minimum and maximum ranges of the content of the selected markers in the different groups of wells are shown in Table 4. Group A presents the lowest T and salinity (Cl^-); group B is the highest in terms of SO_4^{2-} concentration; group C presents the highest concentrations in Na^+, K^+, and HCO_3^-; and group D presents the highest T, Mg^{2+}, and Cl^- contents.

Fig. 2 presents the spatial distribution of the four groups of sampled wells. Group A is mainly found in the “Rome pit” located west of the Mixhuca fault and towards the south along the tectonic structures of Xicocomulco fault and Xochimilco fault. Group B is found predominantly within the Santa Catarina graben, with some wells along the Mixhuca fault at the same height as the mentioned graben, with one exception located to the south outside this area. Group C is located inside the horst structure south of the Santa Catarina graben. Group D is a dispersed population represented by few samples distributed in the Texcoco graben, Mixhuca fault, and the Chalco half graben.

A ($Na^+ + K^+$) vs. ($Cl^- + SO_4^{2-}$) diagram (Mifflin, 1968) was generated for a better understanding of the geochemical evolution and for comparison with the groups obtained from EMMA (Fig. 7). According to this diagram, group A corresponds to lesser evolved waters, chemically equivalent to recently infiltrated water from recharge zone, group B is located in the middle part of the valley and represents intermediate flow in the transition zone, and groups C and D correspond to chemically more evolved waters, or regional flow, in the discharge

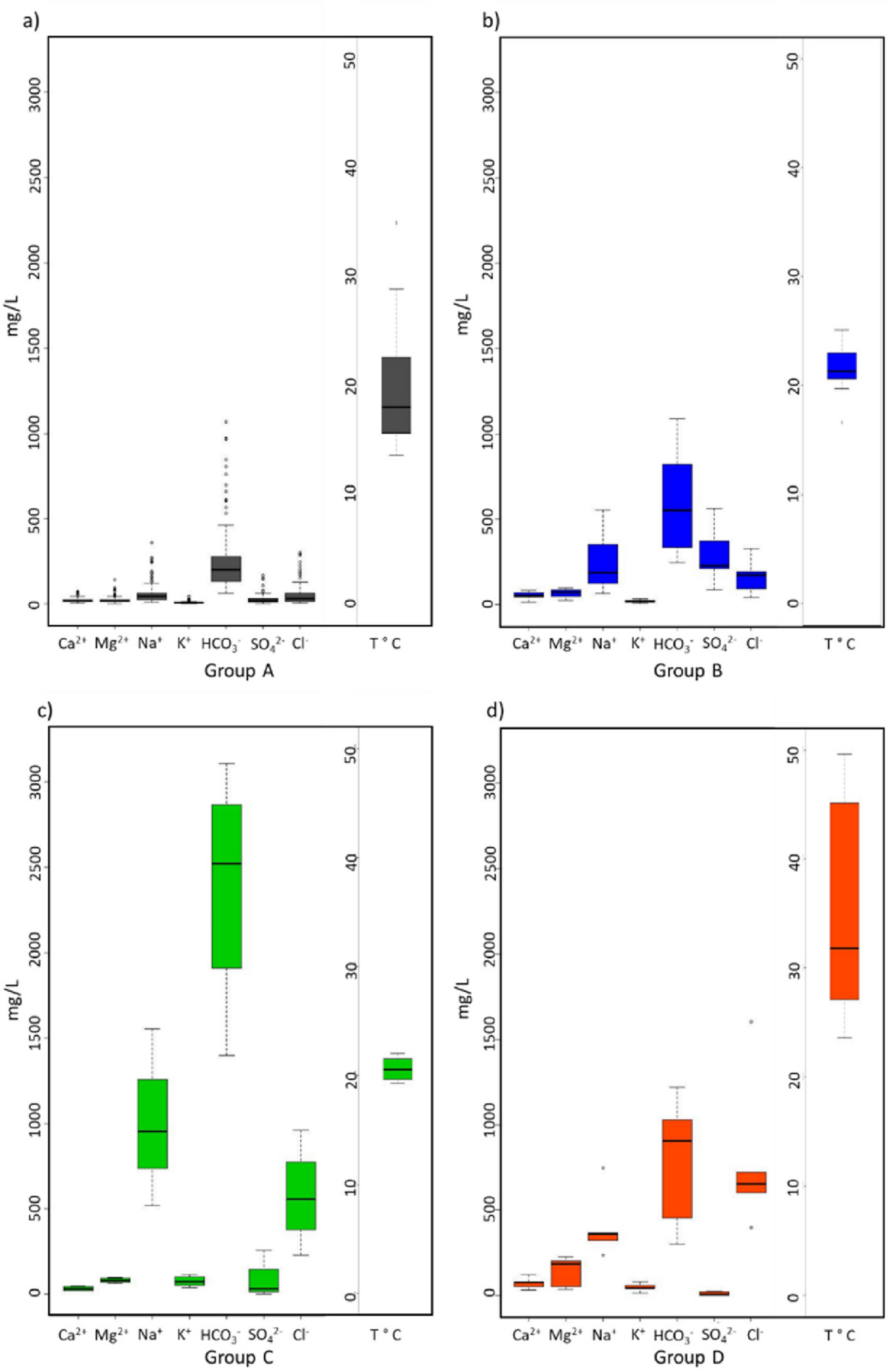

Fig. 6. Boxplots of major ions and temperature used in EMMA analysis; group A(a), group B(b), group C(c), and group D(d).

zone. The difference between group C and D is that group C has a higher alkali metal content than group D.

The geological section of the study (Fig. 2) show that the water table varies between 2220 and 2135 m asl. One well of group C intersects the section line, while the wells of groups A and B are very close to the section line.

5. Discussion

The groundwater flow configuration (Fig. 1) shows a preferential direction from east to west, following the topographic slope from the highest parts of the ranges to the valley floor. This flow appears to be relatively uniform and is only controlled by topography. From this, it can be inferred that the main recharge zones occur in the Sierra de las Cruces and in the Sierra de Chichinautzin as a result of rainwater infiltration. The high hydraulic gradients observed in mountainous areas can be associated with high velocities of groundwater circulation in fractured volcanic rocks.

Meanwhile, the distribution of the chemical composition of the water presented in the Piper Diagram (Fig. 3) shows a large dispersion. Thus, despite the fact that groundwater in this area has the same origin (infiltration of the rainfall), it acquires a diverse chemical composition during its circulation through the subsoil given the different trajectories and its contact with different strata of the subsoil (water-rock

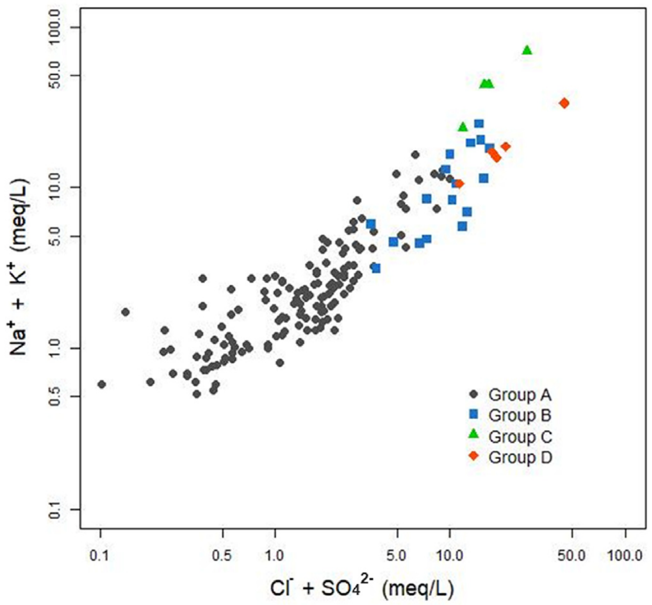

Fig. 7. ($Na^+ + K^+$) vs ($Cl^- + SO_4^{2-}$) diagram to elucidate the hydrochemical evolution.

Table 1
Descriptive statistical summary for the chemical analysis of groundwater samples, Note: Min, Max, Avg, and SD stands for minimum value, maximum value, average, and standard deviation.

	Ca^{2+}	Mg^{2+}	Na^+	K^+ (mg/L)	HCO_3^-	SO_4^{2-}	Cl^-	T (°C)
Min	3.1	1.5	10.7	1.2	61.3	0.4	2.9	13.6
Max	121.2	223.7	1555.9	113.9	3108.1	562.8	1602.9	49.6
Avg	26.5	32.1	110.8	11.8	354.0	50.8	95.5	20.0
SD	19.9	33.2	184.9	15.0	417.8	92.8	180.1	5.3

Table 2
Initial ion concentrations and temperature of the sources used in the EMMA analysis.

Source	Ca^{2+}	Mg^{2+}	Na^+	K^+	HCO_3^-	SO_4^{2-}	Cl^-	T (°C)
	(mg/L)							
1	11.58	8.91	11.45	3.93	114.15	0.85	2.94	16.60
2	51.74	84.68	381.96	31.30	804.41	562.79	184.41	23.00
3	80.14	223.67	746.21	42.94	1218.32	0.40	1602.89	23.60
4	52.19	33.40	359.20	40.23	301.64	24.42	601.57	49.60

Table 3
Descriptive statistical summary of the mixing proportions of the four components in the groundwater samples from the set of wells sampled. Note: Min, Max, Avg and SD stands for minimum value, maximum value, average, and standard deviation. The mixing proportions of the individual water samples are given in Table S1 of the Supplementary Material.

Components				
Mixing ratios	1	2	3	4
Min	0	0	0	0
Max	0.465	0.567	0.921	0.725
Avg	0.384	0.217	0.083	0.317
SD	0.088	0.065	0.125	0.092

interaction processes). In the trilinear diagram, it can be seen that a number of waters evolves from Mg–Ca–HCO_3 to Mg–Na–SO_4–HCO_3 type, while the others change from Mg–Ca–HCO_3 to the Na–Cl–HCO_3 type, which is an indication of the different trajectories of chemical evolution of the samples. This confirms different components within the same groundwater flow system.

Cardona and Hernandez (1995) proposed the mixing between two groups, which were to be determined from the application of stiff diagrams, flows directions and stable isotopic determinations. However, in this study (using the EMMA approach), we identified four components of the flow system, which confirms what Norvatov and Popov (1961) and Mifflin (1968) proposed, that is, the number of components in a groundwater flow system can be disaggregated by more than three components, depending on the criterion to be applied to differentiate the components. The mixing proportions of these four components in the sampled wells are directly related to the geographical location, depth and distribution of the screened sections of the wells. Thus, all wells capture at least two different components of the flow system (Table 3 and Table S1 of the Supplementary Material).

Samples of group A correspond to the wells that mainly capture component 1, which has the least evolved chemical composition with a dominance of the HCO_3^- anion. Most wells are located in the "Roma pit" (Fig. 2) in the vicinity of the recharge zone; therefore, they can be associated with recent infiltration waters with a minimum time of interaction with the geological environment (Chebotarev, 1955; Mifflin, 1968). This group can be related to a flow component in the upper zone, with very active circulation and high climate influence/variation, according to Makarenko (1948). We define it as a local component in the groundwater flow system.

Group B consists of wells that mainly capture component 2 and have higher concentrations of SO_4^{2-} (Fig. 6b). They are located in an intermediate zone between group A, and groups C and D (Fig. 2). According to Makarenko (1948) they can be associated with a component of less active groundwater circulation or delayed flow, which allows interaction with the geological environment to some extent. These wells are mainly located within the Santa Catarina graben. Consequently, it can be assumed that the chemical composition of these waters is related to this geological environment. These groundwaters recharge in the infiltration zone and move through flow paths, evolving to bicarbonate-sulfate waters or sulfate-bicarbonate waters. The geology in Santa Catarina graben provides conditions for reaching this sulfate range. For example, Arce et al. (2013b) reported the presence of pyrite in a depth section that extends between 1100 and 1500 m below surface in the San Lorenzo Tezonco well inside the graben (Fig. 2). Through the flow path, pyrite and other minerals dissolve, increasing SO_4^{2-} concentrations in groundwater. According to Chebotarev (1955) and Makarenko (1948), the sulfate predominance in water is indicative of a less active groundwater circulation, which has been defined as an intermediate component of the groundwater flow system.

The wells of group C extract water mainly from component 3, having the highest concentrations of alkali metals and HCO_3^-, second largest concentration of Cl^-, and a temperature range of 19–22 °C. This group of wells represents the most saline composition (Fig. 6c). It is related to the chemically most evolved water (Fig. 7), suggesting longer travel trajectories or high residence times to interact with the geological environment. This group of wells is located mainly within the horst area that is south of the Santa Catarina graben. This suggests that the chemical composition of water is dominated by the horst's own geology and faults in the same area. Component 3 is associated with a long flow path, but not very deep, because it not affected by the earth's geothermal gradient as component 4. This component infiltrates the recharge zone and follows a long and slow path that allows it to evolve from waters rich in bicarbonate to chlorinated waters. It can be deduced that the low temperatures, geographical location of wells in the structural highs (horst) and representative Cl^- values allowed longer travel trajectories until reaching its hydrogeochemical state. It is defined herein as cold regional component with a large trajectory in the groundwater flow system.

Waters from group D have the highest values of alkali earth metals,

Table 4
Statistical behavior of the content of the selected markers in the groups of sampled wells.

Group	Number of samples	Value	Ca^{2+}	Mg^{2+}	Na^{+}	K^{+}	HCO_3^{-}	SO_4^{2-}	Cl^{-}	T °C
			mg/L							
A	143	Min	3.0	1.5	10.7	1.2	6.3	0.8	2.9	13.6
		Max	72.4	142.5	359.7	45.3	1066.8	165.0	301.7	35.0
B	17	Min	13.4	22.5	67.1	8.0	246.5	87.4	41.8	16.6
		Max	81.7	96.9	553.2	33.9	1089.5	562.7	327.1	25.1
C	4	Min	21.3	63.2	519.8	37.8	1398.3	24.1	229.2	19.3
		Max	49.7	97.6	1555.9	113.8	3108.9	255.5	960.3	22.0
D	5	Min	29.7	33.4	234.2	13.3	301.6	3.9	398.3	23.6
		Max	121.2	223.6	746.2	81.1	1218.3	24.4	1602.9	49.6

Cl^{-}, and T, capturing water mainly from component 4. The high concentrations of Cl^{-} are characteristic of the most chemically evolved waters (Chebotarev, 1955; Mifflin, 1968), while high temperatures are an indication of flow at great depth due to the normal earth geothermal gradient (Albu et al., 1997; Mifflin, 1968). Edmunds et al. (2002) interpreted a thermal anomaly in the up-coning warmer water that comes from medium to greater depth beneath Mexico City. However, with the current available information from deep drilled wells in the Anáhuac System, it is possible to give precise information of flow affected by the normal earth geothermal gradient. For example, groundwater from Santa Catarina 3A well, a recently drilled well with a depth of 2036 m below ground level, has a T at surface of 49.3 °C. If we apply the effect of the normal earth geothermal gradient, its temperature in its depth is 83 °C. According to Makarenko (1948), the water from these wells can be correlated with water from the lower part of the flow system, with a very slow groundwater flow. However, the presence of faults and regional fractures may enable a faster rise than is typical for deep circulation. Faults function as preferential conduits that allow deep hot water that are affected by normal earth geothermal gradient to rise through that conduit quickly without losing the effect of temperature increase. For example, the Santa Catarina 3A well captures water in a faulty section between 1000 and 2036 m below ground level (Morales-Casique et al., 2019). Similarly, the Peñón de los Baños spring provides thermal groundwater with accelerated flow through a set of interconnected fractures. The Mixhuca fault and the faults that formed the Texcoco graben and the Chalco graben are the conduits of these deep flows. It has been defined as a hot and deep regional component in the groundwater flow system.

Based on the chemistry of sampled wells and end-member mixture calculations, the average proportion of the components in the well water can be estimated as follows: component 1 provides 38%, component 2 contributes 22%, component 3 adds 8%, and component 4 makes up 32%. These mixing relationships of individual wells are variable and mainly controlled by drilling depth, length of screened well section, and intensity of extraction, which has modified the natural conditions of the flow system. The understanding of the components of the flow system, their origin, their chemical composition, and the mixing rates can be used to improve the management of groundwater in the area. This knowledge can be used to review the construction design of the wells and their geographical location with respect to the different geological structures in the subsoil.

6. Conclusions

A majority of authors have concluded that groundwater flow systems are integrated by three components (local, intermedium and regional). However, the particular conditions of each site indicate that this is not an approach that should be applied without prior characterization. Each flow system has geological, geochemical, and extraction characteristics that allow the defining of its components. It is important to mention that once the components of the flow system are determined, they are not static and can be modified through intensive exploitation.

Based on the study of Mexico City region, it can be confirmed that a flow system can be integrated by more than three components, depending on the criteria used to differentiate the components. Based on the chemical composition, four components were identified in this study: one local, one intermediate, and two regional (one related to large trajectories and the other with high temperatures and a deep circulation).

Waters from the sampled wells in Mexico City correspond to mixtures of two or more components. This is, mainly due to the important well construction depth and the length of the screened tube of the bores. The intensity of groundwater extraction represents an additional factor that enhances the mixture of the different components and modifies the natural relations of the flow patterns of the systems during the last century.

The ionic relationships suggest that groundwater is dominated by two trends, one from sodium bicarbonate to mixed sulfate type waters, and another from sodium bicarbonate to mixed chlorite type waters. It was inferred that incongruent weathering of silicates (i.e. basaltic glass, plagioclase) and ion exchange processes on clay surfaces (i.e. montmorillonite) are the processes responsible for most of the geochemistry, besides mixing of different flow components.

Groundwater management must be started with a preliminary characterization of the flow system using water chemical, geological and topographical data as well as information on wells. Understanding the functioning of a flow system should be one of the key elements for successful implementation of groundwater management. The analysis of water extraction by components, in turn, may be useful to prevent the extraction of water that is chemically more evolved, has a low recovery rate, and is of poor quality. In the case of Mexico City region as a system with intensive groundwater exploitation, we propose to review of the design of well construction. For a sustainable water extraction in the area, it is important to take into account the spatial distribution of the geological structures before the design, drilling, and location of the new extraction wells.

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Appendix A. Supplementary data

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Chapter 8.

Water-rock interaction and mixing processes of complex urban groundwater flow system subject to intensive exploitation: The case of Mexico City

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Water-rock interaction and mixing processes of complex urban groundwater flow system subject to intensive exploitation: The case of Mexico City

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ABSTRACT

In complex aquifer systems subject to intensive exploitation it is important to investigate hydrogeochemical processes in the components to understand the hydrodynamics of groundwater. In this respect, understanding the hydrochemical mechanisms of water-rock interactions and mixing processes eventually leads to the development of appropriate strategies for a sustainable groundwater management. In this study, we analyze water-rock interactions processes of the so-called Anáhuac groundwater system underlying part of the Mexico Valley comprising Mexico City and its suburbs. This intensively exploited system has four flow components: 1) local flow, 2) intermediate flow, 3) cold regional flow, and 4) hot regional flow. This is studied using inverse geochemical models, which consider uncertainties of analytical data and constraints from thermodynamic stability diagrams, speciation-solubility models, and petrographic data. Three representative modeling sections were selected for the implementation of the mass-balance approach. The general conceptual model in two sections suggests that rainwater infiltrates the subsoil and begins to dissolve CO_2 in the unsaturated zone; by reaching the saturated zone it reacts with silicate minerals of the host rock producing the final chemical composition of waters. On the other hand, the third section shows mixing as the main groundwater process, as well as water-rock interactions. In general, the identified processes of water-rock interaction are dissolution of CO_2, dissolution of calcite, gypsum, and halite, Ca/Na ion-exchange, and weathering of silicate minerals such as biotite, muscovite, plagioclase, epidote and pyroxene, and precipitation of kaolinite, SiO_2 and $Fe(OH)_3$. Changes between local and intermediate flow components suggest dissolution of andesite rocks and precipitation of pyrite. Changes between local flow component and the cold regional component are explained by large flow trajectories. Transformations between local and hot regional components indicate mixing flows and a deep circulation influenced by the geothermal gradient. The combination of the methods used in this study can be applied in other similar geoenvironments of the world and assist local water authorities to adequately address and manage groundwater.

1. Introduction

In many parts of the world, groundwater is a local and regional resource of vital importance for the sustenance of human life (Gleeson et al., 2012). Because groundwater is an accessible and affordable resource, it is used excessively, which causes intensive extraction,

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modification and/or mixing of hydraulic gradients, increased extraction costs, and a reduced water resources security over time (Sarkera et al., 2009; Li et al., 2019; Olea-Olea et al., 2020). For understanding the groundwater hydrodynamics in an intensively exploited system, it is convenient to study groundwater chemical processes. This can be approached by geochemical groundwater modeling. The geochemical composition of waters provides information of water-rock interactions, flow paths and flow regimes, recharge and discharge, ion-exchange processes, oxidation-reduction reactions, sorption and exchange reactions, evaporation, dissolution, precipitation, residence times or trajectory times, organic matter transformations and mixing groundwater processes (e.g. Güler and Thyne, 2004; Mahlknecht et al., 2004; Zabala et al., 2015; Möller et al., 2016; Morán-Ramírez et al., 2016; Gastmans et al., 2016). Groundwater flow typically evolves from recharge to discharge zones, while the dissolved chemical compounds are transformed by a variety of hydrogeochemical processes that change with time and space. More evolved waters usually reflect high residence times in the system (Chebotarev, 1955; Matthes, 1982). Groundwater flow develops water–rock interactions that generally refers to the interaction between the aqueous solution and rocks, including chemical and physical reactions (Chen et al., 2010). The interactions degree among groundwater and minerals depends on several factors, including temperature, pH, transit time and geology (Freeze and Cherry, 1979; Hem., 1985; Appelo and Postma, 2005).

Mass-balance models developed in volcanic rocks found that the typical processes controlling groundwater chemistry were weathering of silicate minerals and the consequent release of minerals components to solution, ion-exchange processes, and mixing of flow components (Güler and Thyne, 2004; Mahlknecht et al., 2004; Zabala et al., 2015; Hernández-Antonio et al., 2015; Gastmans et al., 2016; Möller et al., 2016; Morán-Ramírez et al., 2016; Knappett et al., 2018).

Mexico City is a megacity located within the Anáhuac System (Escolero, 2018). This region, hosting >21 million inhabitants (United Nations, 2018), is an intensively exploited area with more than 72% of water supply pumped from four aquifer units shared with neighboring states (Martinez et al., 2015). The first wells were drilled by 1928 (De la O Carreño, 1954) and its number increased over the years causing intensive extraction of groundwater and land subsidence (Gayol, 1925; Carrillo, 1947). The first study that attempted to apply a geochemical approach for the Anáhuac System was performed by Cardona and Hernandez (1995). They defined five main groups of groundwater within the basin using physicochemical data, stable isotope data and hydrological features. They applied the mass-balance program (Parkhurst et al., 1982) to determine the main processes such as Ca/Na ion-exchange, and redox reactions. Due to the lack of data on temperature, pH, and SiO_2 concentrations, water-rock interactions for instance silicate weathering were not addressed. Edmunds et al. (2002) performed an evolution model to elucidate water-rock interactions, such as Ca/Na ion-exchange, as well as the weathering of the basalt which increases geochemical concentrations along the flow path. They used PHREEQC code (Parkhurst, 1995) for determining element speciation and mentioned a thermal anomaly that comes from medium to greater depth. Morales-Casique et al. (2014) published the first work that shows the chemical composition of thermal water from a 2008 m deep well in the Anáhuac System. In the Iztapalapa zone, located to east of Mexico city, low water quality was reported by Ramos Leal et al. (2010) and associated with anthropogenic activities. Finally, Olea-Olea et al. (2020) defined and analyzed the flow system components in the Anáhuac System. They found four components describing the flow system and identified mixing processes among them. However, the water-rock interactions for each of these components have not been studied yet. In this study, we consider that understanding the entire flow system is a prerequisite to identifying the water-rock interactions among the flow system components.

The main aims of this work are: (1) to provide a better understanding of the hydrogeochemical processes based on the flow system components established by Olea-Olea et al. (2020); (2) to determine the main water-rock interactions; (3) to quantify the mixing processes between thermal and non-thermal components; (4) to establish whether the low quality area defined in previous works could be related with natural processes such as water-rock interactions.

2. Study area

2.1. General settings

The basin of Mexico, also called Anáhuac System (Escolero, 2018), is the groundwater flow system of the Mexican Valley that includes Mexico City with its suburbs. It is an endorheic catchment located in the eastern portion of the Trans-Mexican Volcanic Belt (TMVB) (Fig. 1) as a result of arc-volcanism controlled in part by a coeval system of faults (Pardo and Suárez, 1995; Gómez-Tuena et al., 2007). The basin is NE-SW oriented with an area of 9600 km^2. The surrounding mountains have altitudes of >5000 metres above sea level (a. s. l.) and tip towards the flat-lying center of the basin with an altitude of approximately 2220 m a. s. l.

2.2. Geology

Based on the work of Fries (1960), Arce et al. (2019) defined nine stratigraphic units in the basin (Fig. 1): 1) The Morelos formation of Cretaceous age is composed by marine limestones and dolomites, with chert nodules, 2) Mexcala formation, from Cretaceous, dominated by dark-gray argillaceous limestones with abundant planktonic foraminifers, 3) Balsas group, from Eocene, is a succession of continental deposits, constituted by conglomerate, sandstone, siltstone, lacustrine limestone, and minor pyroclastic deposits and lava flows, 4) Volcanic Oligocene formation is a sequence of rhyolitic, rhyodacitic, dacitic lavas, and ignimbrites, 5) Volcanic Miocene formation is a sequence of volcanic debris of andesitic composition, 6) Pliocene-Holocene Sierra de las Cruces, volcanic sequence, is an 11 km long volcanic range with volcanic structures and domes with pyroclastic deposits, interbedded with lahar and debris (Arce et al., 2015), 7) Sierra Nevada, volcanic sequence, has interbedded domes with pyroclastic deposits in heights, while the lower-lands are constituted by an intercalation of pyroclastic and epiclastic deposits, as well as debris avalanche deposits, chemical composition varies from andesite to rhyolite (Nixon, 1989; Macías et al., 2012; Siebe et al., 2017), 8) Pliocene-Holocene Chichinautzín is a volcanic field constituted by more than 220 monogenetic structures; chemical composition is a wide range, although most of the products are of basaltic andesite, basalts and even dacites (Siebe et al., 2004; Arce et al., 2013a), 9) Pleistocene-Holocene Lacustrine deposits are interbedded with volcanic rocks (Perez-Cruz, 1988; Caballero and Guerrero, 1998; Brown et al., 2012; Arce et al., 2013b).

Arce and coworkers summarized the main tectonic features in the study area. These are Mixhuca fault (Perez-Cruz, 1988), Texcoco graben, Santa Catarina graben, horsts of separating these grabens (Arce et al., 2013b), Chalco half-graben (Vazquez-Sanchez and Jaimes-Palomera, 1989; Urrutia-Fucugauchi and Chávez, 1991) and other faults that have not been named (Arce et al., 2019).

2.3. Mineralogy

The mineralogical phases interacting with groundwater in the Mexico Valley are strongly influenced by the occurrence of secondary minerals that are originated by alteration of the rock forming minerals of volcanoclastic deposits, lava flow successions, lacustrine deposits and minerals forming secondary veins.

Information on the lithology and mineralogy is available from different sources which are described below. First, the drilling project of Lorenzo Tezonco water production well, with a depth of approximately 2000 m, provides valuable information. In the following, rocks and mineral phases relevant to this study are reported according to their

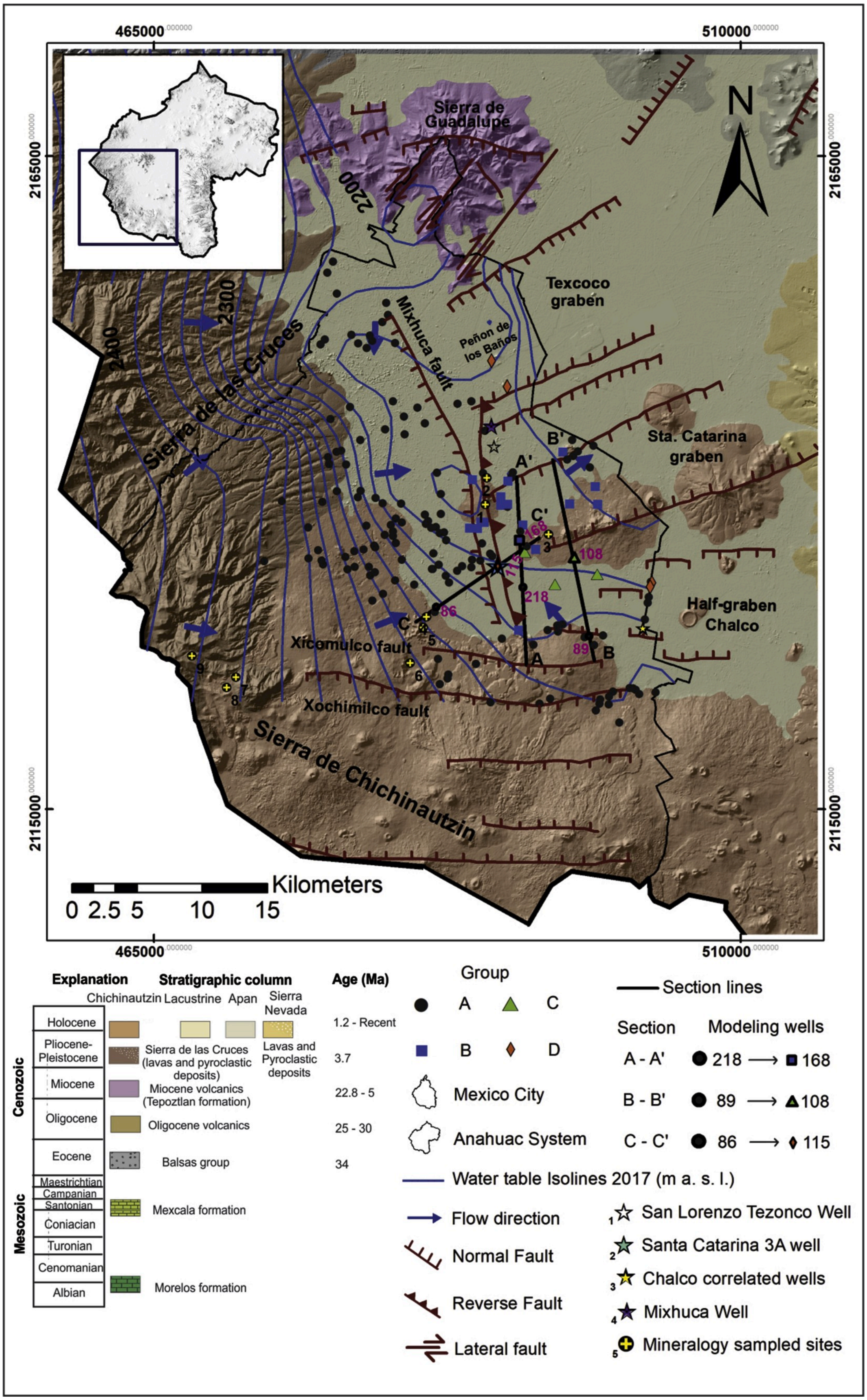

Fig. 1. Location and geology of the study area, group classification, modeling sections, and geologic structures. Modified from Olea-Olea et al. (2020).

depth range: andesite to dacite lava is identified at 120–180 m depth beneath ground level, with the occurrence of olivine, plagioclase, and pyroxene; dacitic lava and pyroclastic flow deposits at 580–700 m depth, with amphibole, plagioclase, and pyroxene minerals; ignimbrite at 760–875 m depth, with plagioclase and quartz; lava flows and pyroclastic flows andesitic composition at 875–998 m depth, with glass matrix, plagioclase, and pyroxene; andesite at 1164–1255 m and 1510–1800 m depth with epidote, Fe oxides, montmorillonite, plagioclase, pyrite, pyroxene, and glass matrix; dacite lava flow at 1470–1510 m beneath ground level, with glass matrix, plagioclase, pyroxene, and quartz; basaltic andesite lava at 1800–1930 m depth, with olivine, plagioclase, and pyroxene; andesite lava at 1930–2008 m beneath the surface, with glass matrix, plagioclase, and pyroxene (Arce et al., 2013b).

Second, the recent Santa Catarina 3A water production well project with directional drilling at approximately 2040 m depth provides unique information on rocks and minerals. Some of the geological features are highlighted as follows: dacite lava occurs at 547 m depth with biotite and plagioclase minerals; andesitic lava is recorded at 550–600 m, 620–800 m, 1040–1050 m, 1640–1760 m beneath ground level, with amphibole, Fe oxides, plagioclase, and pyroxene as main minerals; epidote an hydrothermal alteration mineral is observed between 1040 and 1050 m depth, as a result of secondary mineralization; ash fall deposits with dacite composition is situated at 820–860 m depth, with plagioclase and pyroxene minerals; lahar deposits are located at a depth of 619 m, 988–1000 m, and 1080 m, with chalcedony as secondary mineralization (Morales-Casique et al., 2019).

Third, the information of four wells drilled in Chalco lake was taken to define the geologic composition from surface to 122 m depth. Clastic sediments interbedded with volcanic materials for instance as tephra dominate along this section. The primary minerals are plagioclase, amphibole, glass, and minor amounts of pyroxene, olivine, kaolinite, smectite; and authigenic minerals such as pyrite, calcite, and struvite (Ortega-Guerrero and Newton, 1998; Pi et al., 2010; Ortega-Guerrero et al., 2015, 2017, 2018, 2020).

Fourth, information of the Mixhuca well, a well drilled to 2400 m beneath the surface, was taken to extract additional information. Pyroclastic flow of andesite-dacite blocks and ashes dominate between 470 and 479 m depth, with amphibole, plagioclase and pyroxene minerals; a pyroclastic flow of basaltic blocks and ashes is recorded at 799–808 m beneath the surface, with olivine and plagioclase minerals; ignimbrite is identified at 1431–1435 m depth beneath ground level, with the occurrence of calcite, chalcedony, glass matrix, plagioclase, and pyroxene; and carbonate rock such as limestone and calcareous breccia is found between 1581 and 2400 m beneath the surface (Jimenez Dominguez, 2020).

Fifth, local investigations on the mineral composition of important structures throughout the study area give additional information. The volcanic range Sierra de las Cruces in San Miguel Volcano and Xochitepec localities demonstrates that andesite and dacite lava, rhyolitic lava, and breccias are dominating rocks, and amphibole, biotite, Fe oxides, glass matrix, plagioclase, pyroxene, and quartz the prevailing minerals. The Santa Catarina graben in Yuhualixqui shows an andesitic-basaltic rock composition with minerals like olivine, plagioclase, pyroxene, quartz, and glass matrix. Cerro de la Estrella consists of andesites with Fe oxides, plagioclase, pyroxene, and quartz (Arce et al., 2015).

2.4. *Groundwater flow system components definition by a previous study*

The conceptual model of Anáhuac System, proposed by Olea-Olea et al. (2020), consists of four groundwater flow system components. These components were determined using an end-members mixing analysis (EMMA) (Christophersen and Hooper, 1992; Carrera et al., 2004). Each of these components is analogous to one of the four representative groups classified by physicochemical parameters (Fig. 1). Group A is representative of component 1 with less chemically evolved waters and active flow circulation; this is in the vicinity of the recharge zone and it is named local component. Group B is illustrative of component 2; which is associated with waters of intermediate chemical evolution and delayed circulation; it is located inside the Santa Catarina graben and called intermediate component. Group C is indicative of component 3; this is a chemically more evolved flow with longer travel trajectories and it is located inside the horst zone and close of faults connected to graben structures; this group is called cold regional component. Group D is characteristic for component 4, which is related to a very slow circulation, chemically more evolved waters and of a deep circulation flow affected by the geothermal gradient with the contribution of deep fluids associated with the presence of faults and regional fractures as the Mixhuca fault and the faults that formed the Texcoco graben and half-graben Chalco; this group is named hot regional component. Table 1 shows the minimum and maximum values of selected physicochemical parameters of each group to visualize the variations among groups.

The conceptual model defined by Olea-Olea et al. (2020) described that flow system components present mixing processes, where groundwater that is extracted from wells does not come from a single component, but from a mixture of at least two components. Deep flow components can be mixing with shallow flow components, which has been evidenced also in other studies of volcanic environments where groundwater is captured from different depths (e.g. Hernández-Antonio et al., 2015; Knappett et al., 2018). The reason is that subsurface geology of volcanic deposits with different eruptive events may contain discontinuities that bypass water flow. This flow is driven by changes in the hydraulic gradients that are associated with the intensive groundwater extractions (Florez-peñaloza, 2019) and the constructive designs of wells. Faults and fractures function as preferential conduits throughout which water can mixing between one component and other. Olea-Olea et al. (2020) concluded that groundwater that is extracted in the system in the average is a mixture of 38% from the local component, 22% of the intermediate component, 8% from the cold regional component and 32% of the hot regional component.

3. Methods

3.1. *Field campaign and laboratory analyses*

A total of 169 water wells were selected for water sampling according to their geographic distribution and based on the information obtained from the National Water Commission (Comisión Nacional del Agua – CONAGUA) and Water and Sanitation Agency of Mexico City (Sistema de Aguas de la Ciudad de México). Available information on well construction and lithology was collected prior to sampling. The selected wells had depths ranging from 170 to 2036 m, and well screens that cross different lithological units at variable depths.

Sampling was conducted from June to October 2018. Total Dissolved Solids (TDS) and pH were field-measured using a multi-parametric probe (Oakton PC 300) and temperature (T) was field-measured with Hanna digital thermometer. Pre-rinsed polyethylene bottles were used to sample water for main ions and trace elements. At the collection site, samples were filtered through 0.45-μm Millipore cellulose nitrate filters. The samples collected for cation and trace element analyses were acidified with HNO_3^- to pH~2 (Appelo and Postma, 2005). All samples were stored in a cooler at approximately 4 °C. Anions (HCO_3^-, Cl^-, SO_4^{2-}, NO_3^-, PO_4^{3-}) and cations (Na^+, K^+, Ca^{2+}, Mg^{2+}) were analyzed by liquid chromatography in the Chromatography Laboratory at the Institute of Geology, National Autonomous University of Mexico. Other elements (Al^{3+}, Fe^{3+}, SiO_2) were measured by inductive coupling plasma (ICP) with an optical emission spectrophotometer (OES) (ICP-OES) in the Atomic Spectroscopy Laboratory at the Institute of Geology, National Autonomous University of Mexico. Samples with a charge balance error of >10% were discarded (Freeze and Cherry, 1979; Appelo and Postma, 2005).

Table 1
Ranges of physicochemical parameters of groundwater flow components according to Olea-Olea et al. (2020).

Group	Component	Value	Ca^{2+}	Mg^{2+}	Na^+	K^+	HCO_3^-	SO_4^{2-}	Cl^-	T
			mg/L							°C
A	Local	Min	3.0	1.5	10.7	1.2	6.3	0.8	2.9	13.6
		Max	72.4	142.5	359.7	45.3	1066.8	165.0	301.7	35.0
B	Intermediate	Min	13.4	22.5	67.1	8.0	246.5	87.4	41.8	16.6
		Max	81.7	96.9	553.2	33.9	1089.5	562.7	327.1	25.1
C	Cold Regional	Min	21.3	63.2	519.8	37.8	1398.3	24.1	229.2	19.3
		Max	49.7	97.6	1555.9	113.8	3108.9	255.5	960.3	22.0
D	Hot	Min	29.7	33.4	234.2	13.3	301.6	3.9	398.3	23.6
	Regional	Max	121.2	223.6	746.2	81.1	1218.3	24.4	1602.9	49.6

3.2. Graphical data analysis

Unpublished data of CONAGUA for 2017 was used to define the water table configuration within the study area. The Kriging method (Franke, 1982; Cressie, 1993) was used to develop the spatial interpolation of water table elevation.

For a better understanding of the hydrogeochemical processes, Gibbs (1970) plot diagrams were constructed to identify the natural mechanisms controlling groundwater chemistry, including rock weathering, evaporation and precipitation dominance.

Normalized bivariate plots of Ca^{2+}/Na^+ vs. Mg^{2+}/Na^+ and Ca^{2+}/Na^+ vs. HCO_3^-/Na^+ were employed to analyze the underlying mechanisms for modification of ion concentrations in groundwater such as carbonate dissolution, silicate weathering, and evaporate dissolution (Gaillardet et al., 1999).

Stability diagrams are a useful tool to evaluate equilibrium trends between silicate minerals and natural water, based on thermodynamic calculations. These diagrams were developed for different silicate mineral phases at 25 °C and 1 atm, using the activities of dissolved species at thermodynamic equilibrium in a given set of conditions (T, pH, redox potential, total content of each metal in solution) determined with PHREEQC code (Parkhurst and Appelo, 1999). The dynamic equilibrium between solutions and coexisting solid phases is shown in the stability diagrams and they are used to interpret the geochemical behavior of natural water in terms of water-rock interactions (Garrels and Charles, 1965). Stability diagrams assist in evaluating the water equilibrium condition in relation to the existing mineral phases in the flow system.

3.3. Geochemical modeling

Geochemical models present plausible alternatives of hydrogeochemical processes along a flow path. These alternatives are simplified versions of the reality. A speciation-solubility code, PHREEQC (Parkhurst and Appelo, 1999), version 3.0 in combination with database phreeqc.dat, minteq.dat, and complementary hydrogeochemical phases (Table 2) was selected to evaluate the equilibrium state of groundwater in relation to selected mineral phases.

Inverse modeling was used to identify hydrogeochemical processes that explain the hydrochemical evolution of groundwater (Plummer, 1992; Plummer et al., 1983, 1994). This mass-balance approach uses two water samples from wells which represent initial and final chemical water compositions along a flow path to calculate the moles of minerals and gases that could enter or leave the solution to account for the differences in composition (Parkhurst et al., 1980).

When defining the possible mineral phases, it is very important for the inverse model approach that this is based on the mineral compositions of the geological environment, the chemical components of the groundwater and the condition of their occurrence (Güler and Thyne, 2004). In this study, the inverse and mixing geochemical modeling were constrained with the stability diagrams, speciation-solubility models and petrographic data from other studies that were compiled to reconstruct the mineralogy composition of rocks.

Three sections of geochemical models were selected (Fig. 1) to elucidate the different processes of water-rock interactions that occur along the flow paths. For the sections we used wells which lie along a selected flow path, with information on analytical data, wells depth, and available information on geology. Wells chemical compositions used in geochemical modeling are representative of mixing process among flow components (Olea-Olea et al., 2020). The selected three representative modeling sections were used to identify and describe quantitatively: 1) water-rock interaction processes that may explain water evolving from a local component to an intermediate component with a high content of sulfates (section A - A′); 2) water-rock interaction processes that lead water from the local component to the cold regional component rich in chlorides, bicarbonates, sodium and potassium (section B - B′); and 3) mixing and water-rock interaction processes between a non-thermal flow (local component) and deep thermal flow as a result of preferential flow until it evolves to the hot regional component which is rich in chloride, calcium, magnesium and high temperature (section C - C’).

Table 2
Set of possible mineral phases and their solution reactions considered in inverse and mixing models and bibliographic references.

Phase	Reaction	Ref.
$CO_2(g)$	$CO_2(g) = CO_2(a)$	a
Calcite	$CaCO_3 = Ca^{2+} + CO_3^{2-}$	a
Gypsum	$CaSO_4.2H_2O = Ca^{2+} + SO_4^{2-} + 2H_2O$	a
Halite	$NaCl = Na^+ + Cl^-$	a
$SiO_2(a)$	$SiO_2 + 2H_2O = H_4SiO_4$	a
CaX2	$Ca^{2+} + 2X^- = CaX2$	a
NaX	$Na^+ + X^- = NaX$	a
Kaolinite	$Al_2Si_2O_5(OH)_4 + 6H^+ = H_2O + 2H_4SiO_4 + 2Al^{3+}$	a
Biotite	$KMg_3AlSi_3O_{10}(OH)_2 + 6H^+ + 4H_2O = K^+ + 3Mg^{2+} + Al(OH)_4^- + 3H_4SiO_4$	a
Muscovite	$KAl_3Si_3O_{10}(OH)_2 + 10H^+ = K^+ + 3Al^{3+} + 3H_4SiO_4$	a
Plagioclase	$Na_{0.62}Ca_{0.38}Al_{1.38}Si_{2.62}O_8 + 5.52\ H^+ + 2.48H_2O = \backslash\ 0.62Na^+ + 0.38Ca^{2+} + 1.38Al^{3+} + 2.62H_4SiO_4$	a
Pyroxene	$CaFeSi_2O_6 + 4H^+ + 2H_2O = Ca^{2+} + Fe^{2+} + 2H_4SiO_4$	b
Olivine	$Mg_{1.86}Fe_{0.14}SiO_4 + 4H^+ = 1.86Mg^{2+} + 0.14Fe^{2+} + H_4SiO_4$	c
Glass	$Si_{1.0}Al_{0.35}O_2(OH)_{1.05} + 1.05H^+ + 0.95H_2O = 0.35Al^{3+} + H_4SiO_4$	d
$Fe(OH)_3$	$Fe(OH)_3 + H_2O = Fe(OH)_4^- + H^+$	e
Pyrite	$FeS_{1.72}+3.08O_2+0.72H_2O = Fe^{2+} + 1.72SO_4^{2-} + 1.44H^+$	f
Epidote	$Ca_2FeAl_2Si_3O_{12}(OH)+11H_2O + H_+ = 2Ca^{2+} + Fe(OH)^{4-} + 2Al(OH)^{4-} + 3H_4SiO_4$	g
Amphibole	$Ca_2Mg_5Si_8O_{22}(OH)_2 + 14CO_2 + 22H_2O = 2Ca^{2+} + 5Mg^{2+} + 14HCO_3^- + 8H_4SiO_4$	h

[a] Parkhurst and Appelo (1999).
[b] Université d’Ottawa (n.d.).
[c] Hövelmann et al. (2012).
[d] Galeczka et al. (2014).
[e] Merkel and Planer-Friedrich (2008).
[f] Battistel et al. (2019).
[g] Gysi and Stefánsson (2012).
[h] Walraevens et al. (2018).

In order to propose the minerals involved in geochemical modeling sections, the predominant minerals of basic to intermediate composition of clastic sediments and volcanic rocks reported by Ortega-Guerrero and Newton (1998); Pi et al. (2010); Arce et al. (2013b, 2015);

Morales-Casique et al. (2019); and Ortega-Guerrero et al. (2015, 2017, 2018, 2020) were used. The relationship between chemical groundwater composition and mineral in the hydrothermal alteration (Morales-Casique et al., 2019) was reflected accordingly, as well as the results from stability diagrams for silicates.

The following parameters were used in the modeling process: T, dissolved oxygen, pH, Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, Cl^{-}, SO_4^{2-}, HCO_3^{-}, Fe^{3+}, SiO_2, and Al^{3+}. For Al^{3+} values which were below the detection limit, an arbitrary value reflecting half of the detection limit was used. The phases used were CO_2 (gas), calcite, gypsum, biotite, muscovite, halite, SiO_2 (a), Ca/Na ion-exchange, pyrite, kaolinite, plagioclase, pyroxene, olivine, glass, $Fe(OH)_3$, epidote, and amphibole. These phases are believed to be reactive according to lithological and mineralogical information (Ortega-Guerrero and Newton, 1998; Pi et al., 2010; Arce et al., 2013b, 2015; Morales-Casique et al., 2019; and Ortega-Guerrero et al., 2015, 2017, 2018, 2020). Kaolinite and muscovite were selected from mineral stability diagrams in the silicate system. Halite is used as an active mineral phase in our study in the same way it was reported in other volcanic environments originating from volcanic gas condensation (Cartwright et al., 2004). Calcite was related while weathering of silicate minerals that dissolves Ca. Gypsum was selected as plausible source of SO_4^{2-} due to an equivalent occurrence of Ca^{2+}. The mineralogy studies used in the modeling process are indicated in Fig. 1: San Lorenzo Tezonco well (1) defined by Arce et al. (2015); Santa Catarina 3 A well (2) depicted by Morales-Casique et al. (2019); Chalco correlated wells (3) defined by Ortega-Guerrero and Newton (1998); Pi et al. (2010); Ortega-Guerrero et al. (2015, 2017, 2018, 2020); mineralogy sampled sites (5) depicted by Arce et al. (2013b).

The number of inverse models obtained was reduced to the minimum phase models that satisfy the restrictions within the specified uncertainty limits. The initial uncertainty limits of analytical data were set to 0.05. The minimum models imply that no model with any proper subset of phases and solutions could be found, by minimizing the number of calculations produced by the models that contain the most essential geochemical reactions (Parkhurst and Appelo, 1999).

According to mineralogy data in the study area we use different reactive phases described in Table 2. Montmorillonite and chalcedony could be considered as reactive phases, however, for simplicity reasons we consider that they are already being represented in chemical composition by kaolinite, plagioclase, and SiO_2. The physicochemical data used in geochemical modeling for each section are shown in Table 3.

3.3.1. *Section A – A'*

Section A – A' (Fig. 2) is located among Xicomulco fault and Santa Catarina graben, and represents a groundwater local component from group A (well 218, initial composition) that flows throughout the rocks to the intermediate component defined in Olea-Olea et al. (2020) from group B (well 168, final composition). Well 218 has depth of 249 m and the well tube has a screen from 100 to 249 m beneath ground level; well 168 has a depth of 299 m and two screens sections at 90–102 m and 144–299 m beneath the surface. These wells are separated from each other by 4 km approximately**.** The phases used in section A –A' were CO_2 (g), calcite, gypsum, biotite, halite, SiO_2 (a), Ca/Na ion-exchange, pyrite, kaolinite, plagioclase, pyroxene, olivine with an accepted uncertainty of 0.05.

The conceptual model for this section proposes that rainwater infiltrates the subsoil in the unsaturated zone and begins to dissolve CO_2, which originates mainly from the edaphic zone probably by organism respiration and organic matter decomposition (Freeze and Cherry, 1979). Upon reaching saturated zone, water reacts with silicate minerals of the host rock such as clastic sediments interbedded with tephra (Ortega-Guerrero and Newton, 1998; Pi et al., 2010; Ortega-Guerrero et al., 2015, 2017, 2018, 2020); basaltic andesitic to dacitic lava, andesite (Arce et al., 2013b) and andesitic basalts (Arce et al., 2015) producing the final chemical composition. Indeed the wells used in this section are approximately 300 m depth, nevertheless these wells capture deeper flows product of mixing in flow components (Olea-Olea et al., 2020) where groundwater could react with deep minerals. The high content of sulfates in the intermediate component could be related to sulfides measured in the field (well 168 presented a value of 10 ppm) and their relation with deeper flows and pyrite in shallow levels (Pi et al., 2010; Ortega-Guerrero et al., 2017). It was assumed that pyrite reduction could release sulfates. Domínguez et al. (2015) reported sulfate reduction and H_2S gas presence in Iztapalapa zone close to this section.

3.3.2. *Section B – B'*

This section (Fig. 2) is located among Xicomulco fault, Chalco half-graben and Santa Catarina graben and represents a groundwater local component from group A (well 89, initial composition) that flows throughout the rocks to a cold regional or more chemically evolved component with longer flow paths defined in Olea-Olea et al. (2020) from group C (well 108, final composition). Well 89 is 170 m deep and screened from 68 to 170 m beneath ground level; well 108 has a depth of 351 m and is screened at 60–76 m, 88–118 m, 150–160 m and 250–351 m beneath surface. These wells are separated from each other by 7 km approximately. The phases used in section B – B' were CO_2 (g), calcite, gypsum, muscovite, biotite, halite, SiO_2 (a), Ca/Na ion-exchange, kaolinite, plagioclase, pyroxene, glass, $Fe(OH)_3$ and olivine, with an accepted uncertainty of 0.10.

The conceptual model for this section proposes that rainwater

Table 3
Parameter values for the wells water groups used in inverse and mixing modeling calculations.

	Model section							
		A - A′		B - B′		C - C′		
	Well	218	168	89	108	86	115	Deep thermal well
	Group	A	B	A	C	A	D	
m	Deep	249.0	299.0	170.3	351.0	221.0	2036.0	–
°C	T	19.8	20.1	16.0	22.0	20.1	49.6	83.0
ppm	TDS	432.0	842.0	138.0	1560.0	190.0	770.0	–
ppm	DO	0.8	1.2	4.5	3.0	5.1	4.1	4.0
Standard units	pH	7.3	8.0	8.4	8.2	7.7	7.9	7.0
	Ca^{2+}	48.2	58.6	16.1	37.3	19.7	52.2	57.7
	Mg^{2+}	46.2	75.4	19.0	97.6	21.3	33.4	194.1
	Na^{+}	120.6	353.2	51.8	956.4	29.1	359.2	313.1
	K^{+}	9.7	24.9	4.3	64.3	4.8	40.2	39.1
mg/L	Cl^{-}	99.6	198.0	30.4	525.5	25.1	601.6	1732.0
	SO_4^{2-}	0.4	211.5	16.7	37.1	31.5	24.4	24.0
	HCO_3^{-}	612.1	1089.5	229.8	2421.3	168.6	301.6	302.0
	Fe^{3+}	0.9	0.1	0.01	0.03	0.01	0.2	0.3
	SiO_2	73.5	57.8	55.4	57.2	75.9	143.4	143.0
	Al^{3+}	0.001	0.0015	0.02	0.0015	0.02	0.002	0.002

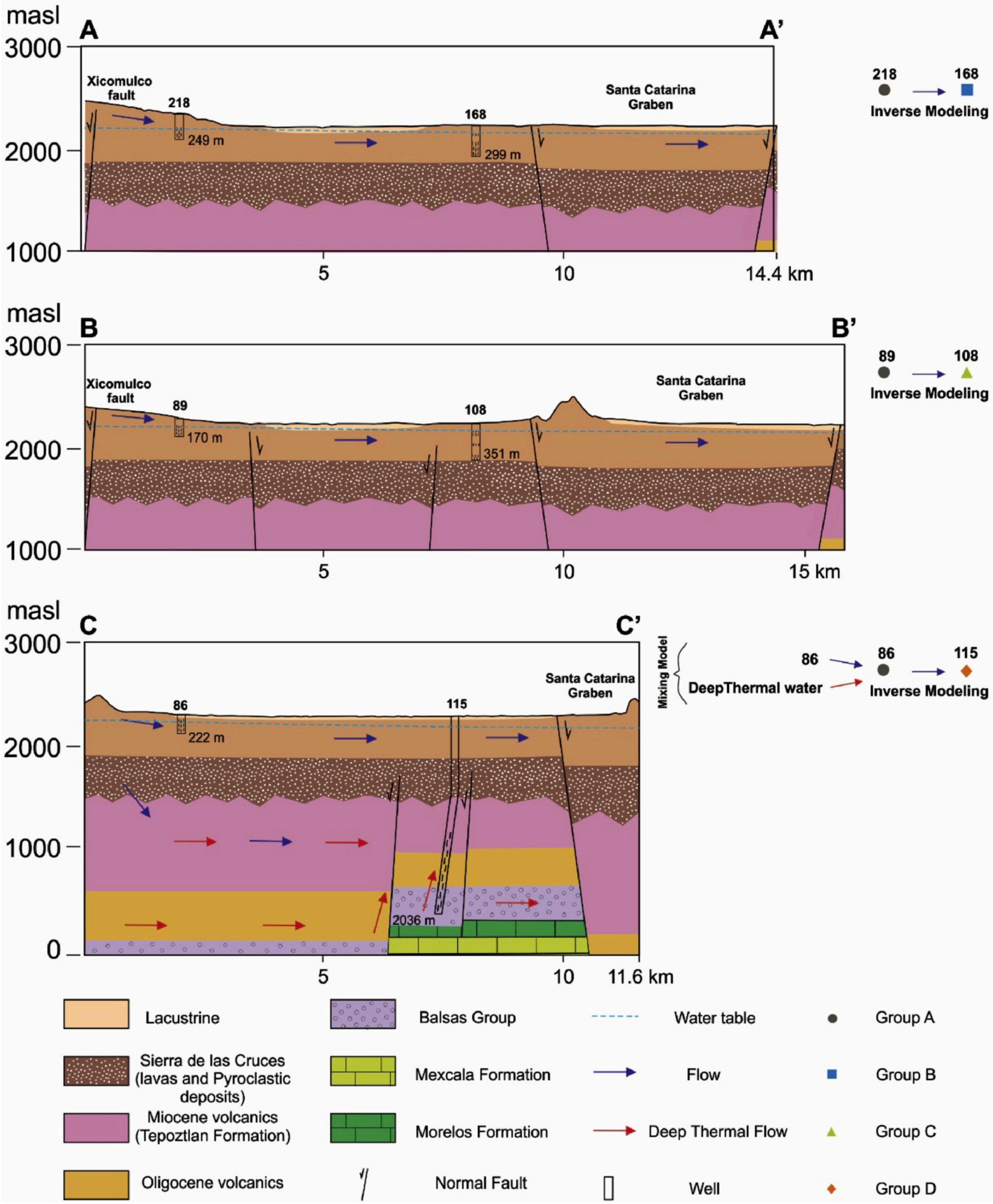

Fig. 2. Geological sections for geochemical modeling and used modeling approach. Geology is taken from Arce et al. (2019).

infiltrates the subsoil in the unsaturated zone and begins to dissolve CO_2, and upon reaching saturated zone it reacts with silicate minerals of the host rock, i.e. andesite basaltic and andesite (Arce et al., 2015) through long flow paths which produce the final chemical composition. Muscovite was used as active phase because this is a stable phase in the silicate stability diagrams. Long flow paths allow more time for water interaction with more resistant minerals to weathering such as muscovite. The groundwater flow circulates predominantly in andesitic rocks, which have a higher proportion of Na^+ and Cl^- than other types of basic igneous rocks (Garrels, 1967), and long flow paths allow water to interact with andesitic rocks and increase its Cl^- content.

3.3.3. Section C – C'

This section (Fig. 2) is located close to the recharge area in Sierra de las Cruces and among Mixhuca fault and Santa Catarina. It represents a groundwater local component from group A (well 86) or non-thermal flow that flows throughout the host rocks and mixes with deep thermal groundwater defined by Olea-Olea et al. (2020). The flow that results from the mix (initial composition) interacts with the hot regional component defined in Olea-Olea et al. (2020) from group D (well 115, final composition). Well 86 has a depth of 222 m its well tube is screened from 66 to 222 m beneath the surface; well 115 is 2036 m deep and is screened from 1168 to 2036 m beneath ground level. These wells are separated from each other by approximately 6 km. The mineral phases used in section C – C' were CO_2 (g), biotite, halite, SiO_2 (a), Ca/Na ion-exchange, kaolinite, plagioclase, pyroxene, epidote, and amphibole, with an accepted uncertainty of 0.19.

The conceptual model in this section supposes that rainwater infiltrates the subsoil in the unsaturated zone and begins to dissolve CO_2; then it flows though basaltic andesite rocks (Arce et al., 2015) and mixes with the deep thermal fluid component which is ascending from deep. The deep flow circulates in a medium with no atmospheric CO_2, which consists of andesitic and dacitic lavas, ignimbrite, lahar and ash deposits (Morales-Casique et al., 2019). It is affected by a geothermal gradient and rises to a lesser depth by preferential flow paths such as faults or fractures keeping its high temperature. As it rises and meets shallower flows, as the flow rises mixes with cold water from the local component (well 86), this mixture produces a new composition (initial composition).

The modeling approach used in this section was to treat mixing and water-rock interactions separately. First, a mixing model was applied, and then water-rock interactions between the mixing flow and the hot regional component or final composition (well 115) was modeled in an inverse geochemical model. The selected reactive phases are analogous to reported mineralogy by Arce et al. (2015) and Morales-Casique et al. (2019), where epidote is considered as reactive phase due deep thermal water flow contribution. Groundwater circulates at great depths and is affected by earth geothermal gradient allowing it to interact with the minerals present to achieve the composition of the hot regional component that is rich in chlorides, magnesium, and calcium.

As mentioned above, a mixing calculation was applied in section C - C' due to the presence of hot water related to deep flows that arise throughout the faults and fracture ducts in the area (Morales-Casique et al., 2019; Olea-Olea et al., 2020). Cardona and Hernandez (1995) identified a mixing process between two defined groups, but they did not quantify the mixing proportion. In this study, it is assumed that groundwater extracted in the wells is a mixture of two end members: non-thermal groundwater and deep thermal groundwater. Chloride ion was used to estimate mixing ratios because it generally does not participate in chemical reactions even at high concentrations and temperatures. Assuming conservative Cl^- behavior, mixing of cold water with thermal water is estimated using the equation (Han et al., 2010):

$$R = \frac{Cl_T^- - Cl_{MIX}^-}{Cl_T^- - Cl_C^-} x100(\%) \tag{1}$$

Where R is the mixing ratio, expressed as the percentage of non-thermal groundwater (%); Cl_{MIX}^- is the chloride concentration in the mixed groundwater; Cl_C^- is the chloride concentration in non-thermal groundwater; Cl_T^- = chloride concentration in the deep thermal water.

We selected as non-thermal water the well 186 (group A, local component) with 25.1 mg/L of Cl^-, as mixing groundwater the well 115 (group D, final composition) with 601.6 mg/L of Cl^-, and as deep thermal water the EMMA source estimated in group D by Olea-Olea et al. (2020) with 1732 mg/L of Cl^-. The results show that the water mixture (initial composition) contains 66% of non-thermal water and 34% of deep thermal water.

4. Results

4.1. Diagrams and groundwater chemistry

In the Gibbs diagram, Groups A and B are distributed in the rock dominance area; Groups C and D are situated in the upper limit of rock dominance area and in the lower limit of evaporation dominance area (Fig. 3 a, b).

In Fig. 4 a, b, most groundwater samples fall in the area of silicate member area, indicating in the graph that the majority of ions are originated from silicate mineral weathering.

Most of the water samples in the stability diagrams (Fig. 5 a, b, c, d) fall in the kaolinite stability field. In Fig. 5a two samples are placed in albite stability field. In Fig. 5b many samples stay in the muscovite stability field, while three samples are found in microcline stability field, and other samples in kaolinite stability field. Samples in stability diagram of Fe are in the Fe $(OH)_3$ stability field (Fig. 5e).

The diagram in Fig. 6 shows the ratio of (Ca^{2+} + Mg^{2+} - HCO_3^- - SO_4^{2-}) vs. (Na^+ + K^+ - Cl^-), where a ratio that approaches 1 is indicative of the ion exchange process. A similar result was previously identified by Olea-Olea et al. (2020).

4.2. Geochemical modeling

In section A – A', physicochemical parameters (T, TDS and pH) and major ions (Ca^{2+}, Mg^{2+}, Na^+, K^+, Cl^-, SO_4^{2-} and HCO_3^-) slightly increase along with the flow path. The highest change is observed with SO_4^{2-} (Table 3). Table 4 shows the results of mass-balance transfer along the modeled flow path. This section has two models that may explain hydrogeochemical possible processes that occur between the two defined compositions. Model 1 shows dissolution of CO_2, calcite, gypsum, biotite, halite; precipitation of SiO_2, pyrite, kaolinite, and pyroxene; and Ca^{2+} for Na^+ ion exchange. Model 2 presents dissolution of CO_2, gypsum, biotite, halite; precipitation of SiO_2, pyrite, kaolinite, plagioclase, and pyroxene; and Ca^{2+} for Na^+ ion exchange.

In section B – B', physicochemical parameters (T and TDS) and major ions (Ca^{2+}, Mg^{2+}, Na^+, K^+, Cl^-, SO_4^{2-} and HCO_3^-) and Fe^{3+} slightly increase along the flow path where Na^+, K^+, HCO_3^- have the highest concentrations (Table 3). The mass-balance model shows two minimal models that can explain hydrogeochemical possible processes that occur between these wells or in the long flow path (Table 4). Model 1 shows dissolution of CO_2, calcite, gypsum, muscovite, biotite, halite, pyroxene; precipitation of SiO_2, kaolinite and Fe $(OH)_3$; and Ca^{2+} for Na^+ ion exchange. Model 2 presents dissolution of CO_2, gypsum, muscovite, halite, plagioclase and olivine; precipitation of SiO_2, kaolinite and Fe $(OH)_3$; and Ca^{2+} for Na^+ ion exchange.

In section C – C', physicochemical parameters (T, TDS and pH), major ions (Ca^{2+}, Mg^{2+}, Na^+, K^+, Cl^-, and HCO_3^-) and trace elements (Fe^{3+} and SiO_2) slightly increase along the flow path (Table 3); two flows are mixing and along the mixing flow occur water-rock interaction processes, where Mg^{2+}, Ca^{2+}, and Cl^- show the highest concentrations. Two possible models (Table 4) shows the reacting mineral phases and can explain the hydrogeochemical possible processes that happened between these wells. Model 1 presents dissolution of biotite, plagioclase, pyroxene; precipitation of SiO_2, Kaolinite, epidote, and amphibole; and Ca^{2+} for Na^+ ion exchange. Model 2 shows dissolution of biotite, halite, plagioclase, pyroxene; precipitation of SiO_2, kaolinite, epidote, and amphibole.

5. Discussion

5.1. General groundwater processes

The combined use of diagrams helps to understand the processes of water-rock interactions. The dominant process in all groups is rock dominance, except for Groups C and D which marks an evaporation

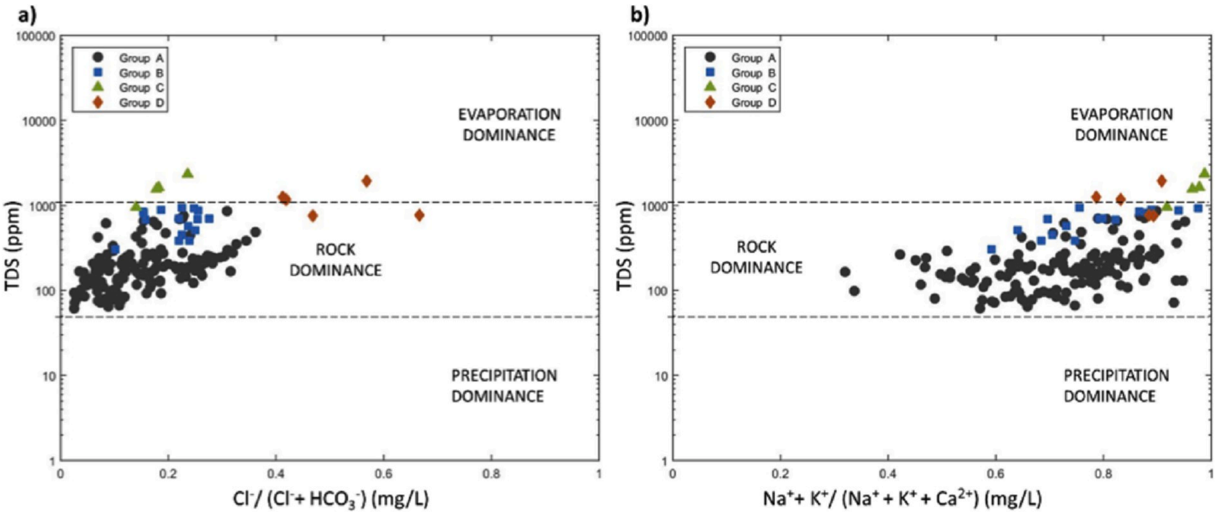

Fig. 3. Gibbs diagrams showing the controlling mechanism a) anions and b) cations (Gibbs, 1970). Note: Group A, B, C and D are described in the introduction section.

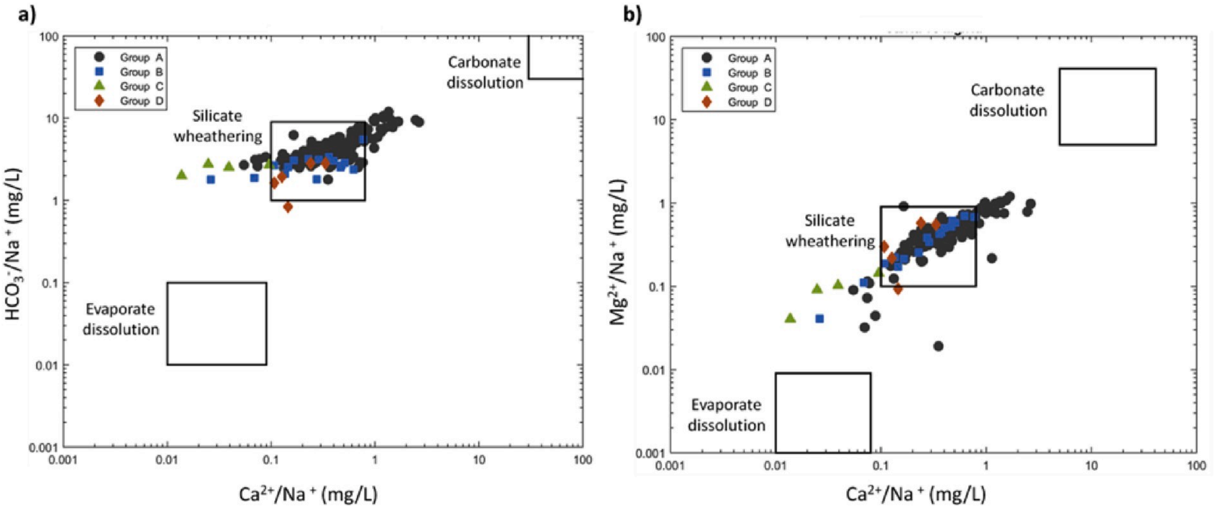

Fig. 4. Bivariate plots of a) Na^+/HCO_3^- versus Na^+/Ca^{2+}, b) Na^+/Mg^{2+} versus Na^+/Ca^{2+}.

trend according to Fig. 3. However, given the water table depth (Olea-Olea et al., 2020), evaporation is negligible because deep waters are not affected by evaporation processes (Marandi and Shand, 2018). Groups C and D are in this area because their concentrations of Cl^-, Na^+ and K^+ increase in the most evolved components, as do the TDS. Water-rock interactions potentially span most of the plot area in the Gibbs diagram.

According to study zone geology, most of groundwater samples reflect the processes that occur in silica-rich volcanic rocks, with having silicate weathering as the dominating process (Fig. 4). However, samples of group A show an increase in HCO_3^- (Fig. 4a) and Mg^{2+} (Fig. 4b) ratios which place them in carbonate dissolution influence. Sources of HCO_3^- and Mg^{2+} would probably include silicate weathering and they could be related to mixing process among flow components (Olea-Olea et al., 2020), causing its displacement to carbonate dissolution that can be explained by the relationship that they have with the other ions such as Ca^{2+} and Na^+. Other samples are located in the evaporate dissolution zone and could be associated with Na^+ gradual increase in the four groups, being higher in the cold regional component (group C). These may be also associated with mixing among components and Ca/Na ion exchange (Fig. 6).

The majority of samples tend to be thermodynamically stable in the kaolinite field (Fig. 5), which means that infiltrating water enriched with soil CO_2 reacts with silicate minerals from the host rocks and eventually converts into kaolinite and silica (Morán-Ramírez et al., 2016). According to Fig. 5b, groundwater is in equilibrium with kaolinite and muscovite, which is consistent with typical minerals in a zone with volcanic rocks. The forward chemical reaction that dominates the transformation of micas to kaolinite - e.g. (Muscovite) $2KAl_3Si_3O_{10}(OH)_2 + 2H^+ + 3H_2O \leftrightarrow$ (Kaolinite) $3Al_2Si_2O_5(OH)_4 + 2K^+$ (Walraevens et al., 2018) - implies an increase in the pH of water as the protons decrease. Some samples are in the limit of both mentioned mineral phases and have neutral to alkaline pH values (6.8–8.4), which is congruent with the consumption of protons during the weathering of mica.

5.2. *Mass transfer model of section A – A'*

The similarities in two models present nine representative transfer reactions, that are: Ca/Na ion-exchange; precipitation of SiO_2, pyrite, kaolinite, pyroxene; as well as CO_2, gypsum, biotite, and halite dissolution. Ion exchange is the major process where clay minerals like kaolinite may facilitate Ca/Na exchange. Local and intermediate components are the most influenced by ion exchange (Fig. 6). The

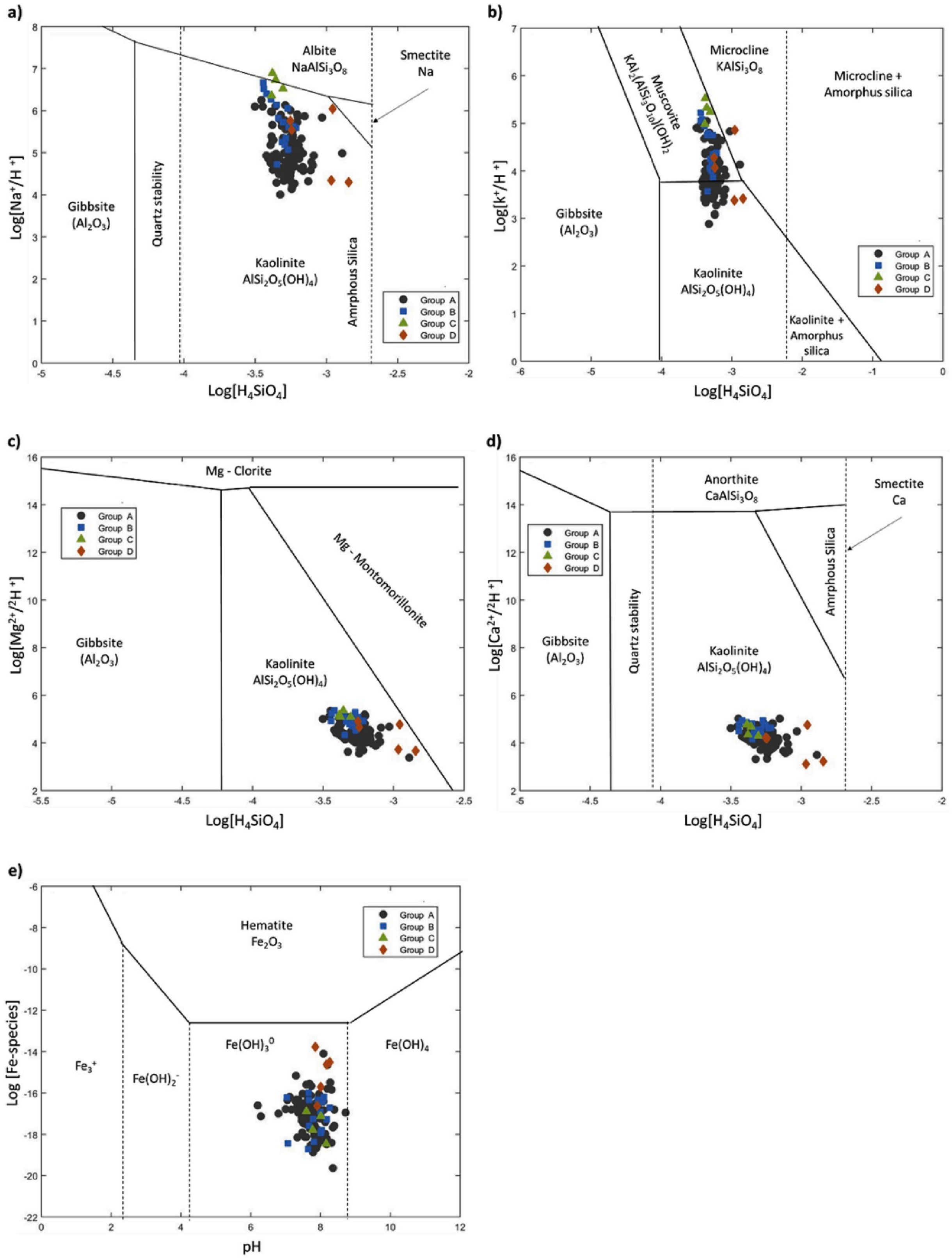

Fig. 5. Stability diagrams of a) Na_2O - SiO_2 - Al_2O_3 - H_2O; b) K_2O - SiO_2 - Al_2O_3 - H_2O; c) Mg_2O - SiO_2 - Al_2O_3 - H_2O; d) Ca_2O - SiO_2 - Al_2O_3 - H_2O; e) Fe-species vs pH using sample points in systems for different silicate mineral phases at 25 °C and 1 atm.

precipitation of SiO_2 could be associated with the presence of amorphous silica and chalcedony. Chalcedony was reported by Jimenez Dominguez (2020) in Mixhuca well in a depth section between 1431 and 1439 m beneath ground level in a welded ignimbrite. It is possible that chalcedony occurs also in other depths because the geology is not homogeneous. Pyrite precipitation could be connected with sulfate dissolution from andesitic rocks (Garrels, 1967) and sulfate compounds that originated in deeper flow components that are mixing with the

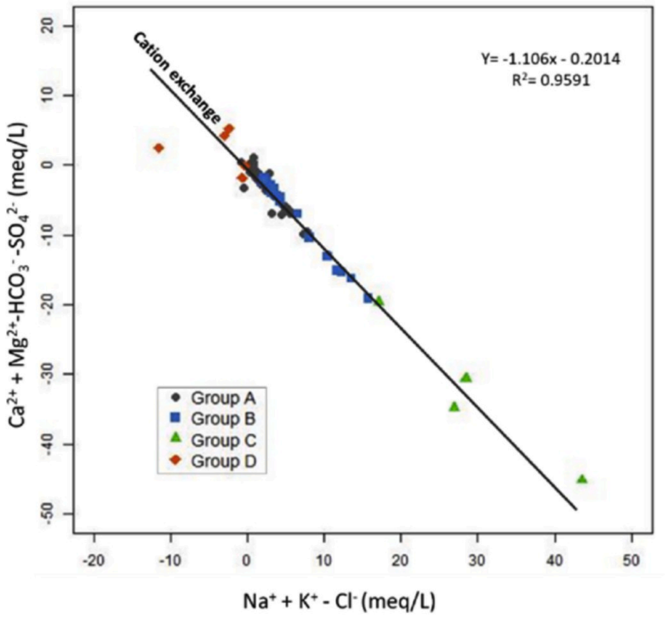

Fig. 6. Ratio of ion-exchange proposed as a reactive phase in the three modeling sections.

intermediate component. High sulfate contents can generate pyrite precipitation a rich sulfate mineral, for instance, authigenic pyrite reported in Chalco lake near to modeling zone (Pi et al., 2010; Ortega--Guerrero et al., 2017). Kaolinite precipitation could be associated with primary silicate weathering that results in the formation of clay minerals (Appelo and Postma, 2005). The precipitation of kaolinite and pyroxene is closely related to the water-rock interactions of the silicate minerals. CO_2 precipitation is related which its contribution as a reactive phase that is available throughout the flow path. Biotite dissolution can be a source of Mg^{2+} and K^+ (Gómez and Turrero, 1994), which increase from local to intermediate components (Table 1). Halite in the two models is associated with their volcanic origin (Cartwright et al., 2004), i.e. the rocks in the subsoil contain halite which is dissolved.

The differences in reactive phases are calcite dissolution in model 1, while absent in model 2, the lack of this phase could be connected to CO_2 amounts in both models. Calcite dissolution depends directly on CO_2 original concentration contained in water and on the amount of CO_2 supplied by exchange with some other gas phase (Freeze and Cherry, 1979). Model 1 has fewer moles of CO_2 that model 2, calcite in model 1 is associated with the smaller mass transfer of CO_2. Plagioclase is present in model 2 while absent in model 1, this lack could be associated with calcite presence in Model 1, which plagioclase and calcite are Ca rich minerals. Kaolinite precipitation has fewer moles per kilogram transferred in model 1 than in model 2; this variation could be associated with the different contributions in silicate weathering that are part of models phases.

Water-rock interaction processes increase the SO_4^{2-} concentration in solution, where pyrite precipitation could be related to sulfate releasing from andesitic rocks and mixing flows. While, plagioclase is described as an important mineral in areas close to modeling section and is depicted in model 2. Considering the water chemical evolution of the intermediate component that is rich in sulfate, the mineralogy described in areas close to the geochemical modeling section A – A', together with the conceptual model, it can be assumed that model 2 would be the more plausible model representing water-rock interaction processes that generate the intermediate component (Fig. 2).

5.3. *Mass transfers model for section B – B'*

The two models present eight similar mass transfers: Ca/Na ionic exchange (Fig. 6); dissolution of CO_2, gypsum, halite and muscovite, and precipitation of kaolinite, silica and Fe $(OH)_3$. The mole transfers of Ca/Na ion exchange are associated with kaolinite precipitation. CO_2 was assumed to be available throughout the flow path and is present in water-rock reactions. Kaolinite precipitation is linked to primary silicate weathering that results in the formation of clay minerals (Appelo and Postma, 2005). Incongruent dissolution of feldspars leads to precipitation of kaolinite and silicate (Gastmans et al., 2016). $Fe(OH)_3$ precipitation may be associated with the incongruent dissolution of silicate minerals like pyroxene (Model 1) and silicate minerals that contain Fe (Model 2), these may form Fe-oxides as an insoluble weathering product (Appelo and Postma, 2005). The dominance of chlorinated waters in the cold regional flow component or final composition (Table 1) causes a decrease in the mass transfer of the gypsum dissolution according to the natural groundwater chemical evolution sequence (Chebotarev, 1955). The mass transfer in the halite dissolution is greater due to increased Na^+ and Cl^- concentrations in the cold regional flow component, given the long flow paths in andesitic rocks (Garrels, 1967) which allow the

Table 4
Summary of mass transfers for selected inverse geochemical models. Phases and thermodynamic data are from PHREEQC and accompanying databases (Parkhurst and Appelo, 1999) and Table 2.

Phase	Section A (218–168)		Section B (89–108)		Section C (86–115)		Chemical formula
	Model 1	Model 2	Model 1	Model 2	Model 1	Model 2	
CO2(g)	4.74E-03	6.97E-03	2.16E-02	3.56E-02	–	–	
Calcite	2.23E-03	–	1.40E-02	–	–	–	CaCO3
Gypsum	2.10E-03	2.10E-03	2.14E-04	2.14E-04	–	–	CaSO4:2H2O
Muscovite	–	–	4.59E-04	1.54E-03	–	–	KAl3Si3O10(OH)2
Biotite	4.33E-04	4.33E-04	1.08E-03	–	6.08E-04	6.50E-04	KMg3AlSi3O10(OH)2
Halite	2.65E-03	2.64E-03	1.40E-02	1.40E-02	–	4.70E-03	NaCl
SiO2(a)	−1.10E-03	−5.11E-03	−2.51E-03	−2.71E-02	−3.68E-03	−2.54E-03	
CaX2	−4.00E-03	−3.00E-03	−1.38E-02	−7.47E-03	−6.09E-04	–	
NaX	8.01E-03	6.01E-03	2.76E-02	1.49E-02	1.22E-03	–	
Pyrite	−2.95E-06	−2.95E-06	–	–	–	–	FeS1.72
Kaolinite	−2.16E-04	−2.44E-03	−1.23E-03	−1.65E-02	−5.48E-03	−4.93E-03	Al2Si2O5(OH)4
Plagioclase	–	3.23E-03	–	2.05E-02	7.96E-03	7.14E-03	Na0.62Ca0.38Al1.38Si2.62O8
Pyroxene	−1.09E-05	−1.09E-05	1.89E-04	–	3.23E-04	3.23E-04	CaFeSi2O6
Fe(OH)3	–	–	−1.89E-04	−2.44E-04	–	–	
Olivine	–	–	–	1.75E-03	–	–	Mg1.86Fe0.14SiO4
Epidote	–	–	–	–	−3.20E-04	−3.20E-04	Ca2FeAl2Si3O12(OH)
Amphibole	–	–	–	–	−8.75E-04	−9.01E-04	Ca2Mg5Si8O22(OH)2

Note: Values in moles per kilogram H_2O (positive values indicate dissolution and negative values indicate precipitation). Dashes indicates that the phase is not present in the model.

release of Na^+ and Cl^- in groundwater. Muscovite dissolution is akin to the Goldich series (Goldich, 1938), where this is the penultimate mineral in weathering series (more weatherability). Its presence could be related to long flow paths that allowed more time to water-rock interaction and its dissolution.

The different reactions in geochemical models results reveal the following: muscovite dissolution exhibits lower mole transfers in model 1 compared to model 2; this variation could be because model 1 considers biotite dissolution, while model 2 does not. The absence of biotite phase in model 2 could send the potassium to muscovite and contributing an increase of muscovite mole transfer in model 2. SiO_2 precipitation transfers fewer moles per kilogram in model 1 compared to model 2; this variation could be complementary to silicate minerals presents in model 1, for example biotite and pyroxene. These minerals are not present in model 2; the absence of these phases could allow that more SiO_2 is available to precipitate in model 2. Kaolinite precipitation exhibits fewer moles per kilogram transferred in model 1 than in model 2; this variation could be connected with the different contributions in silicate weathering that are part of models phases. In model 1, calcite may be tied together with CO_2 presence to explain Ca^{2+} dissolution from andesite rocks (Freeze and Cherry, 1979). This mineral is not in reactive phases of model 2 because plagioclase with Ca^{2+} takes its place. In model 1, biotite dissolution can be a source of Mg^{2+} and K^+ (Gómez and Turrero, 1994). The cold regional flow component has the highest K^+ concentration with respect to the others (Table 1). Biotite does not participate in reactive phases of model 2 because it increases the mass transfer in muscovite, a mineral containing K^+. In model 1, plagioclase dissolution contributes Na^+ and Ca^{2+} to groundwater (Gómez and Turrero, 1994; Gastmans et al., 2016), releasing these compounds in the cold regional component, this component has the highest concentration of Na^+ and is associated at the same time with Ca/Na ion exchange. Plagioclase dissolution is not present in model 2, because of plagioclase dissolution apparently leads to the secondary formation of kaolinite. The mole transfers of kaolinite in model 2 are greater than in model 1. Pyroxene dissolution in model 1 and olivine dissolution in model 2 are tied together with the presence of silica minerals reported in the study area (Arce et al., 2015).

In general, the water-rock interaction processes increase the ion concentrations in solution. For example, the dissolution of pyroxene in the presence of atmospheric CO_2 may release Na^+ and HCO_3^- to solution (Gastmans et al., 2016); the dissolution of halite in andesite rocks may deliver Na^+ and Cl^- to water (Garrels, 1967); and the dissolution of biotite and muscovite may free K^+ to solution (Gómez and Turrero, 1994). The cold regional flow component has a long flow path that allows more interaction time of water with minerals, which could eventually makes viable the dissolution of resistant minerals for instance muscovite (Goldich, 1938). Considering the minerals reported in literature, stability diagrams, and inverse model calculations, we assume that model 1 would be the more feasible model to represent water-rock interaction processes in section B – B' that generates the cold regional flow component (Fig. 2).

5.4. Mass transfer model for section C – C'

The two models show seven similar processes, that are: dissolution of biotite, plagioclase and pyroxene, and precipitation of SiO_2, kaolinite, epidote, and amphibole. Both models do not consider CO_2 as a reactive phase, which may be related to the mixing process between non-thermal and deep thermal waters. In deep thermal water, the presence of atmospheric CO_2 is negligible and igneous rocks in depth do not represent a source of CO_2. There is a dissolution trend of plagioclase, biotite, and pyroxene in parallel to precipitation of SiO_2, kaolinite, amphibole, and epidote in both models. Biotite dissolution is a Mg^{2+} source (Gómez and Turrero, 1994), the hot regional flow component has the highest concentration of this element. Silicate weathering and incongruous plagioclase dissolution results in kaolinite and silicate precipitation (Appelo and Postma, 2005; Gastmans et al., 2016). Pyroxene dissolution could be complementary to silicate precipitation. The weathering pyroxene reaction is: $Ca\,(Mg)Si_2O_6 + 4H^+ + 2H_2O \rightarrow Ca^{2+} + Mg^{2+} + 2H_4SiO_4^0$. The high contents of Mg^{2+} and Ca^{2+} in the hot regional flow component (Table 1) are associated with weathering of silicate and ferromagnesian minerals for example plagioclase, biotite and pyroxenes. Amphibole is a mineral described in andesite lavas and ignimbrites (Morales-Casique et al., 2019); its precipitation could be linked to the dissolution plagioclase and pyroxene. Epidote is a typical hydrothermal alteration mineral in mafic rocks such as in this area (Browne, 1978; Henley and Ellis, 1983; Reyes, 1990). Its precipitation could be related with the light green color in the channel samples described in the study area at 1040–1050 m beneath the surface by Morales-Casique et al. (2019).

One of the main differences in the two models is that ion-exchange reaction is found only in model 1. Morán-Ramírez et al. (2016) demonstrated that ion-exchange reactions are relevant in cold and mixing groundwater, but not in hydrothermal water. This could be the reason why ion-exchange is only found to be reactive in one model. Therefore, we consider that ion-exchange is not a relevant process to achieve the hot regional composition. Halite dissolution in model 2 can be associated with the presence of volcanic halite of these rocks (Cartwright et al., 2004); this can be the source of Cl^- concentration in the hot regional component in addition to natural chemical evolution of water (Chebotarev, 1955) that circulates at great depths and longer periods of time.

Water-rock interactions occur between the mixing water (initial composition) and the hot regional flow component (well 115, final composition). The dominant process to achieve the chemical water composition is the weathering of silicate minerals in a deep circulation along with large times to interact with geological environment. The temperature of well 115 (49.6 °C) suggests the influence of this deep circulation. We consider that Ca^{2+} and Mg^{2+} increase in solution is due to dissolution of primary minerals for instance biotite, pyroxenes, and plagioclase, and Cl^- increase may come from circulation in rocks of intermediate composition such as andesite with more Cl^- content (Garrels, 1967) and the presence of volcanic halite.

Considering the conceptual flow model, the mineralogy of the area and the plausible rock-water interactions, it is proposed that model 2 represents the most feasible model that generates the chemical composition of the hot regional flow component in section C – C'. Carbonate rocks such as limestones (Fig. 2) are not reactive phases in this section; a possible evidence of its presence would be to have reactive phases of calcite or higher transference rates in Ca^{2+} rich minerals, or input of CO_2 that may come from carbonate rocks. Therefore, it is considered that the mixed flow and the hot regional flow component would not have a circulation throughout carbonate rocks.

5.5. Relationship between modeling sections

The proposed geochemical models explain the most significant chemical changes among the four flow components and their relationship with natural conditions which can be highlighted with three essential processes:

1) The weathering of andesite rocks, mixing flows and pyrite precipitation in section A – A′ control the chemical reactions. Weathering of andesite rocks and mixing process depicted in the deep component to the intermediate component may largely explain the high sulfate contents, while pyrite precipitation is influenced by high sulfate amounts in groundwater. Sulfates in water have been associated with low quality waters (Ramos Leal et al., 2010). From our geochemical models, it is evident that the sulfate-rich waters in this area are not of anthropogenic origin, but rather the result of a natural evolution process from bicarbonate to sulfate waters.

2) The presence of ions such as Na^+, K^+, HCO_3^- and Cl^- in long flow paths of section B – B′ can be explained by the dissolution of silicate minerals in andesitic rocks. Groundwater circulates in the horst area and does not reach great depths like in other areas. The dominance and high concentrations of these ions is the result of a longer circulation time and interaction with the geological environment. Therefore, regional flow presence is not necessarily conditioned to circulation at great depths.
3) The rise of thermal flows throughout failures and fractures that mix with cold flows and generate a new composition that evolves in the flow path direction to the hot regional flow component of section C – C′ reveals some processes in relation to thermalism and mixing in the Anáhuac System. The high concentrations of Cl^-, Ca^{2+} and Mg^{2+} comes from the dissolution of silicate minerals in conditions of deep circulation with a longer contact time with the medium and affected by the geothermal gradient of the earth.

The geochemical modeling results depend strongly on the selection of mineral phases, constraints, and conceptual models. Intensive groundwater exploitation in the area often generates mixing of different waters within the production wells. Changes in the particular extraction conditions can also change the rock-water interactions, because initial and final composition used in geochemical modeling respond to mixing relations defined by Olea-Olea et al. (2020).

Mass-balance models do not provide a unique solution, there might be other models and solutions connected to different assumptions and constraints used in the inverse modeling process. Even if this modeling approach included uncertainty in analytical data, thermodynamic calculations and petrographic evidence, it is important to consider that the obtained models are a possibility of many of the processes that could be occurring among water-rock interactions. Models can be constraint further as new, independent data is incorporated. For example, stable isotopes (^2H, ^{18}O, ^{13}C) may be included in geochemical models. In addition, radioactive isotopes (^3H,^{14}C) used for estimating groundwater residence times in the flow components may provide additional information.

6. Conclusions

Water-rock interaction and mixing processes of flow system were investigated by using thermodynamic geochemical modeling. The approach considered uncertainties of analytical data and constraints derived from thermodynamic stability and petrographic information. In general, the groundwater composition underlying Mexico City and its suburbs is directly related to the following, connected processes: dissolution of atmospheric CO_2; weathering of rock-forming minerals such as plagioclase, pyroxene, and biotite; dissolution of halite and gypsum; Ca for Na ion exchange on clay surfaces, and the secondary formation/precipitation of kaolinite and SiO_2.

The three main processes identified along three selected sections were: 1) dissolution of andesite and precipitation of pyrite from local to intermediate flow components, 2) weathering of acid silicates and ferromagnesian minerals for instance plagioclase, biotite and muscovite in a horst area, from local to cold regional flow components, 3) mixing of thermal and non-thermal flows, weathering of silicate and ferromagnesian minerals from local to hot regional flow components.

The processes that explain the chemical composition of each modeling section are 1) section A – A, dissolution of andesite rocks, mixing flows with sulfate compounds originated to deeper that release SO_4^{2-} to intermediate component; and the consequent pyrite precipitation; 2) section B – B, water-rock interaction in low flow paths inside a horst area with longer circulation time and interaction with the geological environment to achieve Na^+, K^+, HCO_3^- and Cl^- high concentrations in the cold regional component; 3) section C – C, mixing of thermal and non-thermal flows that produce a mixing relation that chemically evolves in conditions of greater depth and influenced by the geothermal gradient of the earth until it reaches the composition of the hot regional component with high values of Mg^{2+}, Ca^{2+} and Cl^-.

The geochemical modeling using groundwater flow system components is helpful to explain and differentiate between natural and anthropogenic processes. Likewise, the mixing of the groundwater flow components is difficult to identify and to quantify in systems with a multilayer geology and complex geological structures subject to intensive exploitation. Thus, the use of geochemical modeling has proved to be a powerful tool.

The methodology used in this work is a classic geochemical modeling methodology that incorporates the approach to analyze water-rock interaction and mixing processes from the groundwater flow system component definition. We consider this as a systemic approach to identify and understand hydrogeochemical processes using geochemical modeling since groundwater must be studied from a single system that is interrelated by means of components. This approach will help a better understanding of hydrogeochemical processes in groundwater.

It is fundamental to gain knowledge about the processes that occur among the different components of a complex flow systems. This allows to conceptualize the underlying groundwater flow processes and resulting chemical composition of groundwater. Besides, quantifying the mixing proportion of different flows provides valuable information about the water that is extracted from the system. These data can be used to design extraction strategies that favor the use of one or more components. The management of groundwater can be developed from alternative points of view such as the processes of water-rock interaction of the components and relate them to the use of water.

With the methodology used in this work is possible to identify hydrogeochemical processes that affect the inorganic chemical water quality, i.e. the presence of heavy metals. These processes can explain and contribute to the solution of the problems related to the use and distribution of groundwater in the flow systems. On the based on the foregoing, decisions regarding water policy, planning, and management can be made favoring sustainable principles.

This study is intended to help local water authorities adequately to address and manage groundwater and reveals the importance of hydrogeochemical processes in the components in a complex groundwater system subject to intensive exploitation. The methodology can be adapted to other systems with similar complex characteristics.

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Chapter 9.

Discussion and Conclusions

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In the hypothesis of this investigation, three flow components were expected to be found i.e. local, intermediate, and regional to be demonstrated through the hydrogeochemical behavior, nonetheless, this hypothesis is partially fulfilled because five flow components (which are small local, local, intermediate, cold regional and hot regional components) were found, this reflects that reality defeats the theory and the studied flow system is more complex than it was supposed. The positive scientific implications suggest that hydrochemical behavior is very relevant to delimited flow components, the negative scientific implications suggest that is important to consider more characteristics in the study of a complex flow system for instance flow paths, geology, tectonic features, and mixing processes.

The general and specific aims of this research were fulfilled, including the proposed new methodology. This methodology proposes to use a statistical method of End-Member Mixing Analysis (EMMA) (Christophersen and Hooper, 1992) to determine groups that will be correlated with data of geology (stratigraphy), tectonic features (faults and fractures), mineralogy, and well design. The methodology supposes that the complex flow system could present mixing processes as a result of intensive groundwater extraction combined with the mentioned characteristics. This methodology could work in sites with a complex flow system, with multilayer geology, presence of faults and fractures, intensive groundwater extraction, water extracted from different depths a cause of well design, and mixing processes presence. However, the proposed methodology may not be applicable to all flow systems, especially for those where the geology is uniform or does not present relevant tectonic structures or other parameters that change the normal flow paths. At the same time, it could be not applied in a flow system that lacks data used for the present analysis. In conclusion, this methodology can be adjusted to study other complex flow systems in the world where any of the following aspects are relevant: geology, tectonic structures, groundwater extraction rates, well design, and mixture presence.

The components of the flow system in the basin were studied from the perspective of a single flow system with interconnected components and local variations. By analyzing the dataset that was sampled several local variations were identified in every valley. For instance, the Valley of Mexico is composed of four components local, intermediate, cold regional, and hot regional and these are mixing one and other due to complex multilayer geology, well design, and intensive extraction. The mixing ratios are 38% of the local flow component, 22% of the intermediate component, 8% of the cold regional flow component, and 32% of the hot regional flow component (Olea-Olea et al., 2020). Other local variation found in the unpublished data analysis is the presence of springs in the mountain range zone of the valley to the west and which are part of a small local flow component. A small local component is related with low chemical concentrations, cold temperate like the present in mountainous recharge areas, short groundwater flow path, and short residence time.

In the Valley of Cuautitlán, unpublished data analysis of this work found also four components similar to the Valley of Mexico; local, intermediate, cold regional and hot components, where these present a mixture among them due to geology and high pumping rates, nonetheless, the mixing ratios are different to Valley of Mexico, this has approximately 71% of the local component, 22% of the intermediate component, 3% for the cold component, and 3% for the hot regional component. Mixing ratios variations could be associated with a not densely occupied area by wells as Valley of Mexico, in addition, faults are not inside the direct extraction area.

In the Valley of Pachuca, unpublished data analysis of this investigation suggests that springs located in the mountains range zones represent the small local flow component, the local flow component is placed in the lower parts, the intermediate flow component is close to the faults, the hot regional component is located between Tolcayuca and Tizayuca faults with an identified thermal well.

In the Valley of Tecocomulco, unpublished data analysis of this research infers that local and intermediate components are placed on Texcoco fault trace with an identified hot well near the Tecocomulco lake.

In the Valley of Apan, unpublished data analysis of this work displays that small local component is placed in the mountains range zones, local and intermediate components are located on the Apan-Tlaloc faults traces and in the basin limits to the north of the valley.

In the Valley of Chalco, unpublished data analysis of this thesis shows that the majority of wells are part of the local flow component, two wells are in the intermediate component, and two wells are in the regional component. Additionally, in the mountain range zone outside east of the valley small local component is presented.

The local variations that occur in the Mexico Basin flow system are a clear example of the importance to study these without losing the perspective of a unique flow system. In this system, it is important to consider the groundwater flow direction and if this is related to flow components, for example, at the beginning of water table map it tends to present the small local component and later the local and intermediate components, nevertheless, this chemical evolution sequence does not continue since the Mexico Basin is a complex system where flows can circulate to other depths and it is affected by mixing processes. These flows rise to wells through faults and fractures presence and/or high pumping rates in some parts of the basin. Therefore, five flow components were identified, small local, local, intermediate, cold regional, and hot regional, which are present in different areas of the basin due to local variations, which together form the flow system. In conclusion, after Mifflin's work (1968) where it is outlined that there could be more than three flow components as traditionally defined by Tóth, this work is the first to demonstrate the presence of more components in a flow system.

From another perspective considering the works presented in this thesis, it is possible to argue that groundwater study from the flow system perspective is an evolutionary process. In the first paper presented (chapter 5), two groundwater flows were identified without considering the flow system components. In the second article (chapter 6), the flow system of the Mexico basin was analyzed without considering the presence of local variations that could change the components that occur in one area or other. In the third investigation (chapter 7), the Valley of Mexico was analyzed to know its local variations and understand the functioning of the flow components. In the four work (chapter 8), the hydrogeochemical and physical processes that make a difference between one component and other were studied. The papers presented in this thesis show how this knowledge evolved to develop an adequate methodology that could be applied to complex flow systems such as the Mexico Basin considering the local variations e.g., mixing flows. In addition to the research presented and the flow system components described in the valleys, it can display the importance of studying the flow system as a single interconnected unit, since although the flow components in each valley were evaluated, it can be observed through the water table map and the presence of the same components for instance in the Valley of Mexico and Cuatitlan, that the system is interconnected.

With the groundwater flow description, it is possible to verify that reality defeats the theory since in the flow system four flow components were identified using wells in the Valley of Mexico, but when the springs are considered there can be five flow components, where the springs represent the small local component in the Valleys of Mexico, Pachuca, Apan and east of Chalco. The Mexico Basin is a complex system with multilayer systems and complex geological structures that may or may not be subject to intensive extraction resulting in mixing processes. It is important to consider that the mixture that occurs among the components is not exclusive to the pumping rates, this is a set of factors combined among flows that circulate in deep components and rise due to the presence of faults and fractures in the area, the wells depth, and well screen depth. The components of a flow system are not static over time, and depend on the exploitation way that is done due to mixture components could be generated. Similarly, components may change over time based on weather and long-term variations, e.g. Haitjema and Mitchell-Bruker (2005) have demonstrated where the recharge-controlled water tables tend to form regional components and those topography-controlled form local components, it can be concluded that if the recharge varies in the long-term, the components will also change.

The geochemical modeling used in this work becomes a valuable tool to identify interaction processes with rocks or estimate mixture relationships among wells of different components. Thanks to geochemical modeling, the study of this complex system can be simplified. The overall outcomes are that a flow system can be delimited by means of different approaches that include the analysis of the physical environment, chemical processes and their relationship with the present water extraction conditions, where applying the EMMA statistical method generates a new study methodology that is useful in complex systems. To conclude this methodology is easy to study a complex flow system and it can be adapted for other systems with similar characteristics.

In this research samples for analysis isotopes of δ^{18}O, δ^{2}H, ^{3}H, and C-14 were taken, although the samples were sent to different laboratories to analysis δ^{18}O and δ^{2}H in the TEC (Instituto Tecnológico y de Estudios Superiores de Monterrey), ^{3}H in IMTA (Instituto Mexicano de Tecnología del Agua), and C-14 in the University of Groningen, the results could not be integrated on the analyses of this work because they are still in processing by these laboratories. Nevertheless, this research needs to use stable isotopes δ^{18}O and δ^{2}H to establish relationships among flow components and the groundwater isotopic signature, in order to establish recharge heights and their correlation with the rainwater that recharged in the present or other geological time from the past. Furthermore, this work needs radioactive isotopes of tritium (^{3}H) and C-14 to estimate the groundwater residence time. In conclusion, it is necessary the use of stable isotopes of δ^{18}O and δ^{2}H and radioactive isotopes of tritium (^{3}H) and C-14 to adjust the delimitation of the flow components and geochemical models reactions that developed moreover to estimate the recharges of the current and past climates, as well as their relationship with geological events.

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