# GEOGENIC SOURCES AND CHEMICAL CONTROLS ON FLUORIDE RELEASE TO GROUNDWATER IN THE INDEPENDENCE BASIN, MEXICO

by

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A THESIS

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# THESIS ABSTRACT

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Title: Geogenic Sources and Chemical Controls on Fluoride Release to Groundwater in the Independence Basin, Mexico

Groundwater in the Independence Basin of Central Mexico reaches over an order of magnitude greater than the World Health Organization limit of 1.5 mg $L^{-1}$, but sources and geochemical conditions responsible for releasing fluoride into solution are unknown. Objectives of this work determined aquifer rock types containing the greatest amounts of fluoride and investigate how changes in pH and specific conductance affect fluoride release into solution. Solid phase concentrations of fluoride in well drill cuttings displayed no apparent depth dependence, but were greatest within andesitic, alluvium, and conglomerate samples. Large amounts of fluoride were bound with metal oxides/oxyhydroxides in all samples. Batch experiments examining fluoride release from aquifer materials under evolving groundwater conditions revealed that fluoride was released into solution with elevated pH. Results here may be used to better predict fluoride contamination of aquifers. This thesis contains previously published/unpublished co-authored material.

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## OVERVIEW

The body of this thesis is original research prepared for submission to *Applied Geochemistry* with Dr. Matthew Polizzotto, Dr. Peter Knappett, Dr. Yanmei Li, and Dr. Isidro Loza as coauthors.

# CHAPTER II

## SUMMARY

High fluoride (F) concentrations in groundwater have been revealed as an environmental health concern. Groundwater in the Independence Basin of Central Mexico reaches maximum F concentrations of 15.5mg $L^{-1}$, over an order of magnitude greater than the World Health Organization limit of 1.5 mg $L^{-1}$, but sources and geochemical conditions responsible for releasing F into solution are still unknown. The objectives of this work were to determine aquifer rock types containing the greatest amounts of F and investigate how changes in Ph and specific conductance affect F release into solution. Solid phase concentrations of F in well drill cuttings displayed no apparent depth dependence, but were greatest within andesitic, alluvium, and conglomerate samples. Chemical extractions showed that large amounts of F were bound with metal oxides/oxyhydroxides in all samples. Batch experiments examining F release from aquifer materials under evolving groundwater conditions (i.e. increasing Ph and specific conductance) revealed that F was released into solution with elevated Ph but only slightly increased with specific conductance. Globally declining water levels impact F release and results from this study may be used to better predict F contamination of aquifers.

# CHAPTER III

# GEOGENIC SOURCES AND CHEMICAL CONTROLS ON FLUORIDE RELEASE TO GROUNDWATER IN THE INDEPENDENCE BASIN, MEXICO

Material in this chapter is being prepared for publication with Dr. Matthew Polizzotto, Dr. Peter Knappett, Dr. Yanmei Li, Dr. Isidro Loza.

## 1. Introduction

Concentrations of naturally occurring fluoride ($F^-$) exceeding 1.5 mg $L^{-1}$ in groundwaters causes health problems for over 200 million people around the world (Ayoob and Gupta, 2006). Dental caries result when $F^-$ concentrations are less than 0.5 mg $L^{-1}$ (Gomez and Quiroz Londoño, 2011) while dental and skeletal fluorosis result when $F^-$ concentrations are above 1.5 mg $L^{-1}$ and 4.0 mg $L^{-1}$ respectively (Fuge, 2019). Children suffering from malnutrition in developing countries are particularly vulnerable to fluorosis (Irigoyen-Camacho et al., 2016). Several case studies have documented aquifers containing geogenically sourced $F^-$ above the World Health Organization (WHO) limit of 1.5 mg $L^{-1}$ (Al-Amry, 2009; Alarcón-Herrera et al., 2012; Arveti et al., 2011; Chae et al., 2007; Gizaw, 1996; Li and Zhou, 2009), however there has been a growing body of literature documenting $F^-$ contamination throughout Latin America (Alarcón-Herrera et al., 2013; Armienta and Segoiva, 2008; Carrillo-Rivera et al., 2002; Gonzalez-Horta et al., 2015; Huizar-Alvarez et al., 2014; Jarquin-Yanez et al., 2015; Li et al., 2005; Malhknecht et al., 2003; Mahlknecht et al., 2004a; Mahlknecht et al., 2004b; Martinez-Prado et al., 2013;

Meza-Lozano et al., 2016; Morales et al., 2015; Navarro et al., 2017; Oretega-Guerrero, 2009; Reyes-Gomez et al., 2015; Valenzuela-Vasquez et al., 2006).

Groundwater extractions for agriculture in the Independence Basin (IB) in Central Mexico have intensified over the past two decades, creating more diverse recharge sources, and lowering water tables (Knappett et al., 2018; Mahlknecht et al., 2004a). Water is lost from the basin through increasing evaporation and transpiration (Knappett et al., 2018). Over-pumping has caused $F^-$ concentrations and groundwater pH in areas of the basin to increase in some areas due to deeper, more mineralized groundwater mixing with shallower water (Knappett et al., 2018). Current aquifer sources of F- are believed to include fluorite ($CaF_2$) in sedimentary deposits, rhyolites enriched in $F^-$, and apatite recently discovered in Quaternary or Miocene basalts (Shephard, 2018). Positive correlations between $F^-$, lithium, boron, and groundwater pH and temperature reveal hydrothermal fluids may also play a role in $F^-$ deposits (Knappett et al., 2018; Shephard, 2018). Fluoride release from these sources was discovered to increase under alkaline pH conditions (Shephard, 2018), although release under the evolving groundwater conditions of the IB including rising pH and specific conductance has yet to be discovered.

Previous studies state that $F^-$-rich groundwaters around the world often have neutral to alkaline pH and are typically Na-$HCO_3$ dominant with low concentrations of Ca (Edmunds and Smedley, 2013). Granites are frequently responsible for high $F^-$-groundwaters, although geothermal sources and other volcanic rocks may contribute (Edmunds and Smedley 2013). Fluoride is commonly found in these rocks because its charge and ionic radius allows it to substitute for hydroxyl ($OH^-$) groups in late forming minerals in igneous rocks (Edmunds and Smedley, 2013). In groundwater, $F^-$ is commonly found as a free $F^-$ ion, or complexed with $Ca^{2+}$, $Na^+$, and $Mg^{2+}$ or $H^+$ and $Al^{3+}$ in extremely acidic conditions (Edmunds and Smedley, 2013). Naturally high $F^-$ concentrations in groundwater occur from rock dissolution or from geothermal waters depositing fluorite ($CaF_2$) in hydrothermal veins (Edmunds and Smedley, 2013). Groundwater concentrations are typically dependent upon the solubility of fluorite, which is found to increase with temperature (Edmunds and Smedley, 2013). However, this may not be a factor if $F^-$ is from silicate minerals in lavas and ashes (Edmunds and Smedley, 2013).

Despite previous mineralogical studies, there is no knowledge on how changing groundwater geochemical conditions affect the release of various solid phases of $F^-$ in rock types throughout the IB and across Latin America, where $F^-$ contamination of groundwaters is particularly problematic. The purpose of this study is to elucidate subsurface processes releasing $F^-$ as groundwaters evolve in aquifers of the IB region. By exploiting well drill cuttings and numerous outcrop samples, this study specifically aims to 1) determine solid-phase $F^-$ hosts and environmentally available $F^-$ concentrations; and 2) elucidate subsurface processes releasing $F^-$ into the groundwater. Results from this study may be applied to $F^-$-contaminated aquifers experiencing rapidly falling water tables in order to understand how changing groundwater conditions can stimulate the release of $F^-$ to solution.

## 2. Description of field area and methodology

The Independence Basin is an inter-montane basin located in the state of Guanajuato, Mexico encompassing the northern portion of the Transmexican Volcanic Belt (TMVB). It has a surface area of 6,840 km$^2$ and is in a semi-arid region with a mean annual precipitation of 576 mm (Knappett et al., 2018). Annual recharge rates into the basin reach > 800 mm at higher elevations and <400 mm in lower elevations throughout the basin, mostly occurring near San Felipe and San José Iturbide, the northwestern and southeastern parts of the basin. Groundwater in recharge areas typically Ca-HCO$_3$ dominated and evolves to Na-HCO$_3$ dominated groundwater along flow paths (Mahlknecht et al., 2004a; Mahlknecht et al., 2004b). However, pumping of the aquifer with long well screens, combined with intensive irrigation practices is now playing a greater role in recharging the aquifers near the center of the basin (Knappett, 2017). Drainage of surface runoff from the basin occurs through the Rio Laja. This river begins northwest of San Felipe and exits the basin west of San Miguel de Allende (Mahlknecht et al., 2004b). Once it exits the basin it flows into the Lerma River and eventually discharges into the Pacific Ocean (Mahlknecht et al., 2004b).

Aquifers in the IB are dominated by volcanic rocks resulting from episodic volcanism during the formation of the Sierra Madre Occidental and TMVB volcanic arcs. Metamorphosed marine sediments (mudstone and sandstone) deposited in an island-arc marginal sea system during the Jurassic to Early Cretaceous makeup the lowest hydrostratigraphic unit (Pasqureet al., 1991; Mahlknecht et al., 2004b). These rocks are overlain by Tertiary mafic rocks as well as rhyolitic ash-flow tuffs and lava flows dating back to the Oligocene and early Miocene (Malhknecht et al., 2004b; Pasqure et al., 1991). Covering these rocks are more basaltic rocks (Upper Tertiary and Quaternary), with sandy to silty lacustrine and alluvium deposits which have filled in the valleys (Mahlknecht et al., 2004b; Mahlknecht et al., 2006). These sedimentary deposits are interstratified with Pliocene volcanic tuffs and conglomerates (Mahlknecht et al., 2004b; Mahlknecht et al., 2006). Mineralized faults occur in this area, some containing silver-rich ores, and some bordered by hydrothermal alteration (Mango et al., 2014).

Composition of groundwater in the basin is influenced by water interacting with these aquifer rocks, as evidenced by more mineralized waters found in lower topographic areas of the basin and less mineralized waters found in the recharge areas (Mahlknecht et al., 2004b). Specific conductance of groundwater across the basin typically ranges from 80 to 1,000 µS $cm^{-1}$ with higher values of 2000 µS $cm^{-1}$ near San Luis de la Paz likely resulting from water in deeper Cretaceous limestone units mixing with younger, shallower water (Mahlknecht et al., 2006). Groundwater pH is typically 6.0 to 6.5 in recharge zones and between 6.5 to 8.8 further downgradient (Mahlknecht et al., 2006). A more recent study has found the average pH of the basin waters to be 7.7 with a minimum of 4.6 and a maximum of 9.0 (Knappett et al., 2018). Groundwater temperatures in this area range from 14.7°C to 40.5°C with an average of 28.9°C (Knappett et al., 2018). By comparing the spatial distributions of groundwater pH and temperature between 1999 and 2016 this same study suggested that pH and temperature have slowly been increasing in certain areas of the basin (Knappett et al., 2018).

## 3. Methods and Materials

### *3.1 Materials*

The materials for measurements reported below consist of outcrop samples and drill cuttings from two wells (Figure 1) that were collected in August 2018. San Julian III (SJIII) provided samples taken every 2 taken from 0 to 56 meters depth. Each sample was of a felsic, pyroclastic rhyolite composition. Cuttings from La Puerta Ranch (LPR) were taken sporadically over a depth interval from 30 to 184 meters. La Puerta Ranch had volcanic tuff dominated samples from 30 to 165 m. The sample taken at 171 m contained mafic volcanic rocks. During drilling, the water table on this well was found at 72 m.

Both wells were drilled in the summer of 2018 and were still being drilled when cuttings were collected. San Julian III was drilled by SAPASMA, the potable water and sewage treatment system of San Miguel de Allende, Guanajuato, Mexico whereas La Puerta Ranch was drilled by a small drilling company for private irrigation use.

All drill cuttings from both wells were placed into HDPE 50 mL centrifuge tubes and put on a VWR Analog Rocking Platform Shaker. Cuttings were then washed with ultrapure (18.2 MΩ-cm) water from a Mill-Q system until the conductivity of the supernatant for each tube stabilized (about 5 washes at 30- minute intervals).

Outcrop samples, representing the rock types found in aquifers, were collected by hand in August 2018. Twenty-four different outcrops were visited to ensure all rock types previously reported to be in the basin were collected, with some outcrops having more than one sample collected at the site depending on the lithology present. At all outcrops surficial faces of rocks were hammered off to ensure samples were not altered by weathering. Outcrop samples are labeled based on their rock type (alluvium (Al), andesite (A), ash matrix (AM), basalt (B), conglomerate (C), ignimbrite (I), limestone (L), pink tuff (PT), rhyolite (R), rhyolitic tuff (RT), sandstone (S), slate (Sl), volcanic glass (VG), welded tuff (W), white tuff (WT)) and order in which they were collected (Andesite 1, Andesite 2…).

All acids and chemicals used in the following experiments were trace-metal-grade acids and ultrapure chemicals.

### *3.2 Strong Acid Digestions*

Drill cuttings from both wells were analyzed to determine environmentally available solid phase $F^-$ concentration depth profiles. Rocks collected from each outcrop were also digested to develop an idea of approximately how much $F^-$ is contained within the same rock units in the aquifer. Fluoride was analyzed following sample digestion by a modified version of EPA method 3050B to discover environmentally available $F^-$ in all samples. For digestion, 1 gram of sediment/rock was crushed to a particle size of ~350 microns with a mortar and pestle to expose the inner, non-weathered surfaces and then placed into a 50 mL Digitube digestion tube. Five mL of 1:1 ultrapure (18.2 MΩ-cm) water and 68 – 70% nitric acid ($HNO_3$) were added to each tube. The tubes were then vortexed and heated to 95°C for 15 minutes then removed and cooled for 10 minutes. Two and a half milliliters of 68 – 70% $HNO_3$ was added to each tube before they were vortexed and heated to 95°C for 30 minutes. After adding 2.5 mL more $HNO_3$, caps were removed and the tubes were heated to 95°C for 2 hours. Tubes were removed from the digestor block and 1.5 mL of ultrapure (18.2 MΩ-cm) water and 1 mL 30% hydrogen peroxide ($H_2O_2$) were added. Then tubes were then slowly brought to reflux. One mL hydrogen peroxide

($H_2O_2$) was continuously added until there was a total of 5 mL $H_2O_2$ in each tube, allowing time for effervescence to occur between each addition. Tubes were mixed on the vortex and heated to 95°C for two hours. After cooling, 2.5 mL of 12 M hydrochloric acid (HCl) was added to each tube before they were refluxed at 95°C while uncovered for 45 minutes. The tubes were cooled and filtered through Whatman #41 filter paper into 50 mL high density polyethylene (HDPE) centrifuge tubes. Ultrapure (18.2 MΩ-cm) water was input up to 50 mL to complete the volume.

Fluoride concentrations of digests were measured using an ion selective electrode (ISE) (Orion Fluoride Electrode 9609BNWP) that had a detection limit of 0.02 mg $L^{-1}$. Prior to measuring fluoride in solution, 5 mL of sample and 5 mL of total ionic strength adjustment buffer (TISAB IV) were mixed together to buffer the solution to a pH suitable for the probe (between 5.5 and 8). Matrix-matched calibration standards made up of a 1000 ppm fluoride stock solution, TISAB IV, and a control digestion solution were measured at the beginning and middle of each analysis for quality control checks. Standards were remade for analyses taking longer than two hours before they were measured again.

### *3.3 Sequential Extractions*

Sequential extractions enable us to determine where $F^-$ resides in each of the samples as follows: loosely and strongly adsorbed $F^-$, $F^-$ coprecipitated with metal oxides, and $F^-$ held in amorphous and crystalline iron oxides, carbonates, and sulfides (Keon et al., 2001). Drill cuttings for this method were chosen based on $F^-$ digestion results and outcrop samples were chosen to represent a variety of rock types found throughout the basin. Extractants for this method were those recommended by Keon et al., 2001 and Mehra and Jackson, 1958.

For each sample 0.4 g of crushed rock (~350-micron particle size) was placed into a 50 mL HDPE centrifuge tube along with 20 mL of each extractant. A 1 M solution of $MgCl_2$ (the first extractant) was created and added to each tube to target ionically bound $F^-$. This solution was buffered to a pH of 5 using a 0.1 N solution of sodium hydroxide (NaOH) before it was added to each tube. Tubes were placed onto a VWR Analog Rocking Platform Shaker for 2 hours. After shaking, the tubes were centrifuged for 25 minutes at 3200*g*. Extractant solutions were filtered through Whatman filter paper, Grade 41 circles diam 150mm. After one repetition all samples were washed with ultrapure (18.2 MΩ-cm) water from a Mill-Q system for 30 minutes then centrifuged for 25 minutes at 3200*g*. Ultrapure water was drained from the tubes before adding 20 mL of the next extractant (1 M $NaH_2PO_4$, herein mentioned as $PO_4$). Each tube and placed on the shaker for 16 hours and then 24 hours during repetition, targeting strongly adsorbed $F^-$. Prior to adding solution to each tube its pH was buffered to 5 using 0.1 N NaOH.

Each sample was centrifuged, filtered, and washed with water, then a 1 N solution of HCl was added to target $F^-$ coprecipitated with acid volatile sulfides (AVS), carbonates, manganese, aluminum, and very amorphous iron-oxides. Tubes were added to the shaker for 1 hour, centrifuged, and filtered before repeating the process. After samples were washed with ultrapure (18.2 MΩ-cm) water, a 0.2 M solution of ammonium oxalate with a pH of 3 (buffered with hydrochloric acid (HCl)) was added to each tube. Tubes were placed on the shaker for 2 hours while wrapped in aluminum foil, then centrifuged and filtered before the step was repeated.

After another water wash, the final extractant (sodium citrate-bicarbonate-dithionite (CBD)) was created and added to the tubes to target $F^-$ coprecipitated with crystalline iron oxyhydroxides.

Initial solutions of 0.3 M sodium citrate and 1 M sodium bicarbonate were created. Twenty mL of sodium citrate and 2.5 mL sodium bicarbonate were added prior to the tubes being heated to 80°C over a hot water bath. Once at the correct temperature, 0.5 g sodium dithionite was added. Tubes were then placed back in the hot water bath for 30 minutes at 80°C with intermittent shaking before they were centrifuged at 2000 rpm for 20 minutes. All samples were filtered; however, this extraction was not repeated.

The $MgCl_2$, $NaH_2PO_4$, and CBD solutions were preserved for analysis with 1 drop of concentrated $HNO_3$. Fluoride was measured using an ISE that had a detection limit of 0.02 mg $L^{-1}$. Samples were prepared the same way as described above, except standards were matrix-matched with a blank solution of each extraction prior to analysis.

### *3.4 pH Batch Study*

Two different batch studies were conducted to assess the possible natural geochemical conditions favoring the release of $F^-$ into solution. The first batch study addresses how groundwater solutions with varying pH affects the release of $F^-$. For this study, five outcrop samples (Alluvium 1, Andesite 3, Ignimbrite 1, Rhyolitic Tuff 1, and White Tuff 1) and five samples of drill cuttings (SJIII 44 – 46m, LPR 72 m, 123 m, 165 m, and 171

m) were subjected to 48-hour baths. Four different solutions with pH values of 5, 7, 9, and 11 were created and accompanied by background electrolytes chosen to mimic the major ion concentrations of groundwater in the IB. Solutions were buffered to a specified pH with 12 M HCl and 0.1 N NaOH if needed. One-gram of sediment was crushed with a mortar and pestle to an approximate particle size of 350 microns before being placed into a 50 mL HDPE centrifuge tube. Twenty mL of solution was then added to each tube before they were placed on the VWR Analog Rocking Platform Shaker for 48 hours. Solutions in each tube were pH-adjusted every 12 hours using either 12 M HCl or 0.1 N NaOH. After 48 hours the tubes were centrifuged for 20 minutes at 3200*g* before being filtered through Whatman #41 filter paper. Samples were acidified with concentrated nitric acid prior to being analyzed for $F^-$ using an ISE.

### *3.5 Specific Conductance Batch Study*

In the second batch experiment, one gram of the same five outcrop samples and five samples of drill cuttings (using LPR 105 m instead of LPR 123 m) were crushed with a mortar and pestle to an approximate particle size of 350 microns and placed in 50 mL HDPE centrifuge tubes with solutions of varying ionic strengths to determine how this affects $F^-$ release. The first solution, with a total specific conductance of 5,735 µS $cm^{-1}$, was diluted to 50%, 25%, 10% and 0% solutions having specific conductance's of 3,036 µS $cm^{-1}$, 1,575 µS $cm^{-1}$, 64 µS $cm^{-1}$, and 0.022 µS $cm^{-1}$ respectively. The specific conductance of the initial solution was roughly 2 times the values found in the IB, and subsequent dilutions were reflective of groundwater compositions typically observed.

Each solution was buffered to a pH of 7.70 ± 0.1, the approximate average pH of groundwater in the IB (Knappett et al., 2018), using 12 M HCl and/or 1.0 N NaOH with the amounts of acid or base added being calculated into the specific conductance of each solution. Twenty mL of each solution was added to each 50 mL HDPE centrifuge tube and placed onto the VWR Analog Rocking Platform Shaker for 48 hours, with solutions in all tubes being buffered every 12 hours. After 48 hours tubes were centrifuged for 20 minutes at 3200*g* before being filtered through Whatman #41 filter paper and acidified with concentrated $HNO_3$ for preservation. Fluoride was analyzed in each tube using an ISE.

## 4. Results

### *4.1 Strong Acid Digestions*

Environmentally available $F^-$ concentrations varied with depth from SJIII and LPR drill cuttings, with overall higher concentrations in LPR (Figure 2 and 3). Fluoride data were more variable in LPR than in SJIII. Maximum concentrations occurred at 72 m (253 mg $kg^{-1}$) and 2 – 4 m (86 mg $kg^{-1}$) in LPR and SJIII, respectively. Minimum concentrations occurred at 150 m (42 mg $kg^{-1}$) and 20 – 22 m (25 mg $kg^{-1}$) in LPR and SJIII, respectively. Observed concentrations in borehole cuttings are similar to outcrop digestion data (Figure 4). Fluoride concentrations were greatest in Andesite 3, Alluvium 1, and Conglomerate 1 (228 mg $kg^{-1}$, 169 mg $kg^{-1}$ and 130 mg $kg^{-1}$) while Volcanic Glass 1, Rhyolite 3, and Ash Matrix 1 contained the least amounts of $F^-$ (9 mg $kg^{-1}$, 11 mg $kg^{-1}$, and 15 mg $kg^{-1}$). It should be noted, however, that other rhyolitic samples (Rhyolite 4) contained up to 116 mg kg$^{-1}$ of F$^-$. Sandstone, rhyolitic tuff, slate, and limestone samples on average contained 37 mg kg$^{-1}$, 51 mg kg$^{-1}$, 60 mg kg$^{-1}$, and 64 mg kg$^{-1}$ F$^-$, respectively.

### *4.2 Sequential Extractions*

Amounts of F$^-$ released in each extraction are shown in Figures 2 and 3. The HCl extraction (targeting F$^-$ coprecipitated with sulfides, carbonates, manganese (Mn), aluminum (Al), and very amorphous iron (Fe)-oxides) was responsible for releasing the most F$^-$ in all SJIII (average of 69.3 mg kg$^{-1}$ released) and LPR (average of 105.0 mg kg$^{-1}$ released) drill cuttings, with ammonium oxalate (targeting F$^-$ coprecipitated with amorphous iron-oxyhydroxides) and MgCl (targeting ionically bound F$^-$) releasing the second greatest amounts of F$^-$ in SJIII (30.4 mg kg$^{-1}$ and 23.5 mg kg$^{-1}$) and CBD (targeting F$^-$ coprecipitated with crystalline iron-oxides) and ammonium oxalate releasing the second greatest amounts in LPR (40.2 mg kg$^{-1}$ and 26.4 mg kg$^{-1}$). For SJIII, $PO_4$ (targeting strongly adsorbed F$^-$) and CBD released the least amounts of F$^-$ while MgCl and $PO_4$ released the least amount of F$^-$ in LPR. On average greater concentrations of F$^-$ were released from MgCl, $PO_4$, and ammonium oxalate extractions in SJIII than LPR.

Extraction data from outcrop samples is more variable than the drill cuttings, as shown in Figure 4. Magnesium chloride was responsible for releasing the greatest concentrations of F$^-$ in Rhyolitic Tuff 1, Ash Matrix 1, Rhyolite 4, Ignimbrite 1, and Pink Tuff 1 (22.9 mg kg$^{-1}$, 20.3 mg kg$^{-1}$, 18.0 mg kg$^{-1}$, 17.0 mg kg$^{-1}$, and 17.0 mg kg$^{-1}$ respectively). In contrast, for samples Slate 2 and Basalt 1, HCl released the most F$^-$ (125.1 mg kg$^{-1}$ and 113.4 mg kg$^{-1}$) while CBD released the most F$^-$ in Sandstone 1 and

Slate 1 (69.2 mg kg$^{-1}$ and 45.4 mg kg$^{-1}$). The $PO_4$ extraction released the most $F^-$ in Conglomerate 1 and Limestone 2 (80.0 mg kg$^{-1}$ and 89.2 mg kg$^{-1}$ respectively).

### *4.3 pH Batch Study*

Fluoride desorption at varying pH values from well and outcrop samples is shown in Figures 5 and 6. For LPR 123 m, 165 m, and 171 m $F^-$ release increased with pH. In the remaining drill cuttings (SJIII 44 – 46 m and LPR 72 m) $F^-$ concentrations decreased in tubes with pH ranging from pH 5 to 9, but then increased in tubes with pH 9 to 11. Similar trends can be found in the outcrop samples where $F^-$ increases with pH in Rhyolitic Tuff 1, Andesite 3, Alluvium 1, and Ignimbrite 1. White Tuff 1 shows the same general trend, however for this sample, the most $F^-$ was released at pH 7. In all samples except SJIII 44 – 46 m and White Tuff 1, the greatest quantity of $F^-$ was desorbed from sediments in the pH 11 solution. Across all pH treatments, samples LPR 72 and 165 m and Alluvium 1 released the greatest concentrations of $F^-$ into solution.

### *4.4 Specific Conductance Batch Study*

Fluoride release as a function of solution specific conductance is shown in Figures 7 and 8. Fluoride released from all drill cuttings increased when these samples were immersed in a solution with specific conductance greater than 1,600 µS cm$^{-1}$. San Julian III 44 – 46 m released 92.7% greater $F^-$ at 5,700 µS cm$^{-1}$ than at 1,600 µS cm$^{-1}$ and LPR samples released an average of 54.4% more. However, results from sediments immersed in solutions ranging from 0 to 1,600 µS $cm^{-1}$ are much more variable. In all samples, more $F^-$ was released at 650 µS $cm^{-1}$ than at 1,600 µS $cm^{-1}$ (averages of 15.9% more in SJIII and 32.3% more in LPR). Overall greater concentrations of $F^-$ were released in LPR cuttings than SJIII.

All outcrop samples, except Alluvium 1, responded similarly to variation in specific conductance as the drill cuttings (outcrop samples excluding Alluvium 1 averaged 45.1% more $F^-$ released from 1,600 µS $cm^{-1}$ to 5,800 µS $cm^{-1}$ and Alluvium 1 had 7.3% more $F^-$ released at 1,600 µS $cm^{-1}$ than 5,800 µS $cm^{-1}$). All samples, excluding Ignimbrite 1, released an average of 35.9% more $F^-$ at 650 µS $cm^{-1}$ than at 1,600 µS $cm^{-1}$ whereas Ignimbrite 1 released 0.6% less. Alluvium 1 released the greatest $F^-$ concentrations. From 1,600 µS $cm^{-1}$ to 5,800 µS $cm^{-1}$ all drill cuttings and outcrop samples, excluding Alluvium 1, appear to increase slightly and then level off suggesting the samples reached equilibrium with respect to the specific reactions controlling $F^-$ concentrations. For both drill cuttings and outcrop samples, pH differences drove greater variability in $F^-$ release than differences in specific conductance.

## 5. Discussion

### *5.1 Fluoride in Solid Phases of the Independence Basin*

Fluoride contained in well drill cuttings is mostly found within HCl extractions, indicating $F^-$ bound to acid volatile sulfides, carbonates, and metal oxides (Mn, Al, and Fe). Lesser amounts of $F^-$ are ionically bound and strongly adsorbed to these samples. La

Puerta Ranch contained overall greater concentrations of $F^-$ than SJIII samples, likely due to rock type or irrigation return flow recycling $F^-$ from groundwater below. Irrigation return flow undergoing evapotranspiration may have enhanced $F^-$ concentrations in soils and contributed to increased amounts of leachable $F^-$.

Assuming a porosity of 0.10 (typical of fractured rock aquifers (Klein and Johnson, 1983)) and solid phase particles with a density of 2.65 g $(cm^3)^{-1}$, only 0.066% of environmentally available $F^-$ would need to be released from andesitic rocks to create groundwater $F^-$ concentrations of 1.5 mg $L^{-1}$, the WHO standard. Biotite, hornblende, and apatite minerals in these rocks are likely primary sources of $F^-$ (Mahlknecht et al., 2004b; Ortega-Guerrero, 2009; Shephard, 2018; Vasak, 1992). However greatest concentrations of $F^-$ in basaltic-andesitic rocks were hosted within with acid volatile sulfides, metal oxides, and amorphous Fe-oxyhydroxides suggesting primary minerals containing $F^-$ have already weathered. This suggestion is supported by the fact that kaolinite is close to saturation in both recharge and discharge groundwaters throughout the basin (Mahlknecht et al., 2004b; Mahlknecht et al., 2006; Ortega-Guerrero, 2009).

Volcanic tuff samples did not contain as much environmentally available $F^-$ as other rock types. However, the reactivity of these samples makes them vulnerable to releasing $F^-$. Samples Rhyolitic Tuff 1 and Pink Tuff 1 contained environmentally available $F^-$ concentrations of 108 mg $kg^{-1}$ and 42 mg $kg^{-1}$ respectively, most of which is ionically bound and strongly adsorbed to a minerals surface. Fluoride precipitated on a volcanic tuffs surface is likely bound with sodium, magnesium, or calcium formed when halogen gases react with solidified silicate material below temperatures of 700°C as recently erupted ash cools (Óskarsson, 1980). Considerable amounts of $F^-$ in these samples are also bound with Mn/Al – oxides and amorphous and crystalline Fe-oxyhydroxides.

In all samples there is a large amount of $F^-$ coprecipitated with amorphous and crystalline metal oxides, which are possibly acting as a sink for $F^-$. These minerals ultimately result as secondary minerals from weathering or from hydrothermal alteration (Strawn, 2015). Hydrothermal alteration of aquifer rocks occurs in the State of Guanajuato (Mango et al., 2014) and could be a weathering mechanism contributing to formation of oxides as well as kaolinite (Edmunds and Smedley, 2013), as mentioned above. Minerals deposited from these fluids are potentially another source of $F^-$. Elements are often leached out of older, deeper rocks and brought closer to the surface when the fluid cools or evaporates, leaving behind precious ores as well as contaminants such as $F^-$, lead, and arsenic (Mango et al., 2013). Hydrothermal fluids are responsible for the large fluorspar deposit in Las Cuevas, a mine located northeast of San Luis de la Paz (Gonzalez-Partida et al., 2018), as well as for the deposition of silver-gold minerals throughout the basin along faults and within sedimentary and intrusive igneous rocks (Mango et al., 2013) such as those found in Mineral de Pozos. Accordingly, hydrothermal activity may be a significant driver of $F^-$ cycles in the IB.

### *5.2 Mechanisms of Fluoride Release*

pH is the main factor controlling $F^-$ release to groundwater in our experiments, with higher pH values generally leading to greater amounts of $F^-$ desorption. As groundwater evolves along its flow path and its pH rises, clay and metal oxide surfaces become more negatively charged and begin to desorb anionic molecules, such as $F^-$. As this occurs $OH^-$ groups in solution become more abundant and may exchange with sorbed $F^-$ anions as the system tends toward equilibrium. All samples incubated in solutions ranging from pH 9 to 11 showed an increase in $F^-$ released from well and outcrop samples, with some samples showing this trend across the complete pH range of 5 – 11 (Figures 5 and 6). This increase likely reflects the changing surface charge of oxide surfaces and exchanges of $OH^-$ for $F^-$.

Other samples (SJIII 44 – 46 m and LPR 72 m) also have high concentrations of $F^-$ released at pH 5 and 7 which could be due to dissolution of Al-Si layers releasing $F^-$ bound within their structure (Bia, 2015). Aluminum-silica layer dissolution via pH occurs in volcanic tuffs under extremely alkaline or acidic conditions and would occur either when fresh recharge has entered the basin or after groundwater has evolved and has a higher pH of ~9 (Bia et al., 2015). In alkaline conditions the aluminum-silica layer is broken down by $OH^-$ groups bonding with Al producing $Al(OH)_4^-$ and $SiO_2$ whereas $SiO_2$, free $Al^{3+}$, and $H_2O$ are formed in acidic conditions (Bia, 2015).

At the basin scale, increasing pH of groundwaters in the IB is caused by the dissolution of silicate minerals releasing $F^-$ into solution (Malmstrom and Banwart, 1997). These minerals have been consistently discovered in rocks throughout the basin (Mahlknecht et al., 2006: Malhknecth et al.2004a; Mahlknecht et al., 2004b; Ortega-Guerrero, 2009; Shephard, 2018). During weathering, $F^-$ is preferentially released from biotite, hornblende, and apatite because it is more stable within these minerals at higher temperatures such as those found during mineral formation (Edmunds and Smedley, 2013). Dissolution of these minerals contributes to rising pH in the basin (Equation 1 &

2) (Rajesh et al., 2012; Knappett et al., 2018), which may further enhance $F^-$ mobilization to groundwater via the following reactions:

1. $2K(Mg,Fe)AlSi_3O_{10}(OH,F)_2 + 7\,H_2O + 4\,CO_2 \rightarrow 2\,K^+ + 2\,Mg^{2+} + 2\,Fe(OH)_3 + 4\,HCO_3^-$ (Biotite) $4\,F^- + Al_2Si_2O_5(OH)_4 + 4\,SiO_2$

2. $2NaAlSi_3O_8 + 2H_2CO_3 + 9H_2O \rightarrow Al_2Si_2O_5(OH)_4 + 2Na^+ + 4H_4SiO_4 + 2HCO_3^-$
   (feldspar) (silicate weathering) (clay)

As groundwater evolves along its flow path, $F^-$ release may also be affected by increasing specific conductance in addition to pH. High concentrations of $F^-$ were released at 0 µS cm$^{-1}$ (18.2 MΩ water ) and ~1,600 µS cm$^{-1}$ because there were little to no ions in solution, therefore greater amounts of $F^-$ were desorbed into solution. Once all the water-soluble $F^-$ is desorbed, $F^-$ in the samples gets released through the process of anion competition.

All samples, excluding Alluvium 1, released more $F^-$ with specific conductance values greater than 1,600 µS cm$^{-1}$. This is due to an increase in competition for cation and anion sorption sites on the minerals surface. Ions that are weakly attracted to the surface via electrostatic attraction such as $Na^+$ can be exchanged for other ions ($Ca^{2+}$) that have a greater electrostatic charge or higher concentrations in solution (Strawn, 2015). Fluoride is often exchanged for $OH^-$ at Earth's surface because it forms a stronger inner-sphere bond with mineral surfaces. It could also be exchanged for $Cl^-$, a weakly bound outersphere anion, if there is high enough $Cl^-$ concentration in solution. These types of reactions take place after groundwater has been flowing down gradient for some time and has increased ions in solution from dissolution of minerals nearer to the recharge site or when older, more mineralized waters are mixed with shallower waters during groundwater extraction. However, little to no exchange occurs above specific conductance values of ~2,000 $\mu S\ cm^{-1}$ likely because $F^-$ has reached equilibrium in the system.

### *5.3 Implications for Well Water Management*

The IB is home to ~586,000 residents who rely on contaminated groundwater as their main source of drinking water. All drill cuttings and outcrop samples were found to contain naturally high amounts of environmentally available $F^-$, most of which was coprecipitated with amorphous and crystalline metal oxides/oxyhydroxides. Increasing pH values in the basin lead to greater concentrations of $F^-$ desorbing from these oxides due to their negative surface charge. Several studies have addressed the rapidly declining water levels (Knappett et al., 2018; Mahlknecht et al., 2006; Mahlknecht et al., 2004a; Mahlknecht et al., 2004b), but there is a need to examine $F^-$ concentrations and sources at known depths in the aquifer to determine if deeper groundwater truly contains greater amounts of $F^-$.

In an attempt to limit groundwater decline, regulations have been set to control the number of wells installed and the volume of water extracted. However, due to broken well meters and finite regulators, there are now more than 17,300 wells extracting unlimited amounts of water in the state of Guanajuato leading to an average water level decline of 0.8 – 1.2 m $yr^{-1}$ in the last decade (Hoogesteger, 2019; Mahlknecht, 2006) with more urban cities, such as San Miguel de Allende, experiencing water level declines of 3 – 4 m $yr^{-1}$ (Caminos de Agua, 2019). Groundwater extractions and increases in $F^-$ concentrations in this basin are likely to continue until the aquifer is dry unless there are more strict regulations set into place and increased inspections on all wells in the basin.

The Independence Basin is an exemplary location to relate laboratory results studying geochemical conditions controlling $F^-$ release to field analyses because of an increase in pH and mixing of deeper, more mineralized waters with shallower waters seen from the years 1999 to 2016 (Knappett, 2018). Results from this study reveal increasing pH values in the basin to be the main mechanism responsible for releasing $F^-$ into solution. Understanding the affects the rapidly declining water table has on mineral dissolution and pH is key to understanding the controls on $F^-$ release.

## 6. Conclusions

Fluoride release from characterized sources in response to changing groundwater chemistry has not previously been examined in the IB. Results from this study demonstrate that $F^-$ is abundantly derived from all rock types with oxides and clays acting as a sink for $F^-$, suggesting weathering from primary minerals has already occurred. Concentrations in solution are greatly affected by changes in pH and only slightly influenced by changes in specific conductance. If groundwater pH rises above its current maximum of 9, much greater amounts of $F^-$ are likely to be released into solution. Applying more strict regulations on the volume of water extracted from the IB per year could lead to a static or increased water level in an effort to reduce pH. However, more studies are needed to conclude what effect this would have on $F^-$ concentrations in groundwater.

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## APPENDIX

## FIGURES AND CAPTIONS

**Figure 1.** Study area displaying rock and sediment sampling locations within the Independence Basin. Well borehole locations are represented by blue circles with a black cross through them and outcrop samples are represented by circles filled with various colors based on rock type. Outcrop samples are abbreviated based on rock type and the order in which they were collected.

**Figure 2.** Environmentally available F contained in San Julian III drill cuttings is shown in black dots (linked by solid lines) plotted against sequential extraction results (stacked, horizontal bars where each color represents the amount of F extracted using a different extraction solution). Error bars on digestion data represents the standard deviation of the mean for duplicate measurements.

**Figure 3.** Environmentally available F contained in La Puerta Ranch drill cuttings is shown in black dots (linked by solid lines) plotted against sequential extraction results (stacked, horizontal bars where each color represents the amount of F extracted using a different extraction solution). Error bars on digestion data represents the standard deviation of the mean for duplicate measurements.

**Figure 4.** Environmentally available F contained in outcrop samples is shown in black dots plotted against sequential extraction results (horizontal bars with various colors, each

color representing a different extraction). Environmentally available F displays concentrations of each rock type averaged together (i.e. Andesite 1, 2, 3, 4, and 5 results averaged). Error bars on digestion data represents the standard deviation of the mean of all similar rock types averaged together.

**Figure 5.** Fluoride released from drill cuttings with varying pH. The San Julian III well sample is in black, and the La Puerta Ranch samples are in red, green, blue, and pink. Error bars represent the standard deviation around the mean value derived from triplicate measurements.

**Figure 6.** Fluoride released from outcrop samples with varying pH. Alluvium 1 is black, Andesite 3 is red, Ignimbrite 1 is blue, Rhyolitic Tuff 1 is green, and White Tuff 1 is pink. Error bars represent the standard deviation around the mean derived from triplicate measurements.

**Figure 7.** Fluoride released from drill cuttings with varying specific conductance values. San Julian III well sample is black and La Puerta Ranch samples are red, green, blue, and pink. Error bars represent the standard deviation of the mean for triplicate measurements.

**Figure 8.** Fluoride released from outcrop samples with varying specific conductance values. Alluvium 1 is black, Andesite 3 is red, Ignimbrite 1 is blue, Rhyolitic Tuff 1 is green, and White Tuff 1 is pink. Error bars represent the standard deviation around the mean derived from triplicate measurements.

**Figure 1.**

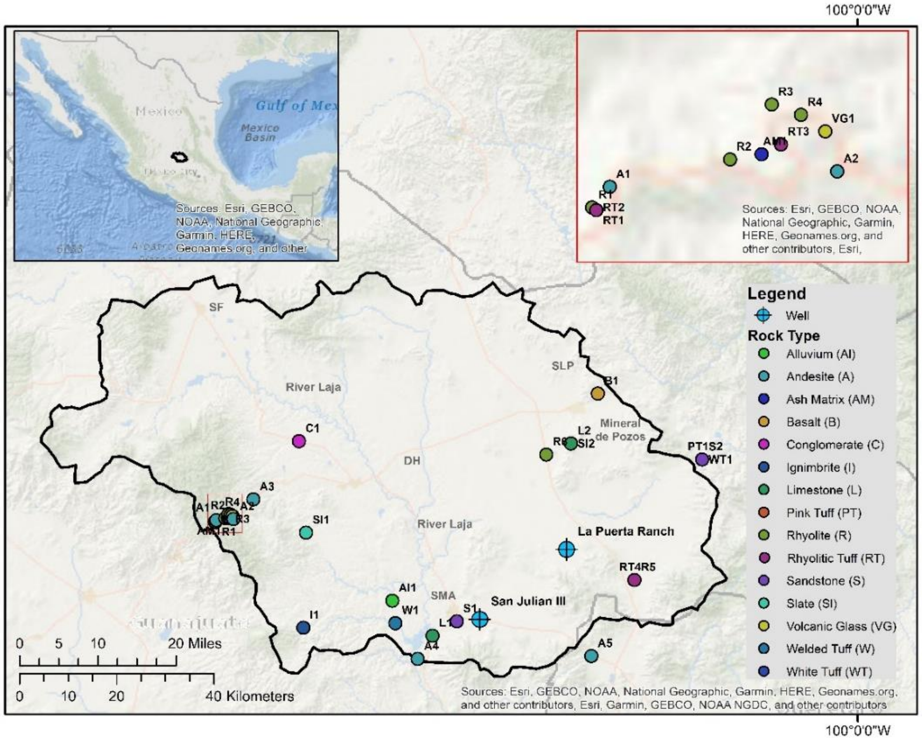


**Figure 2.**

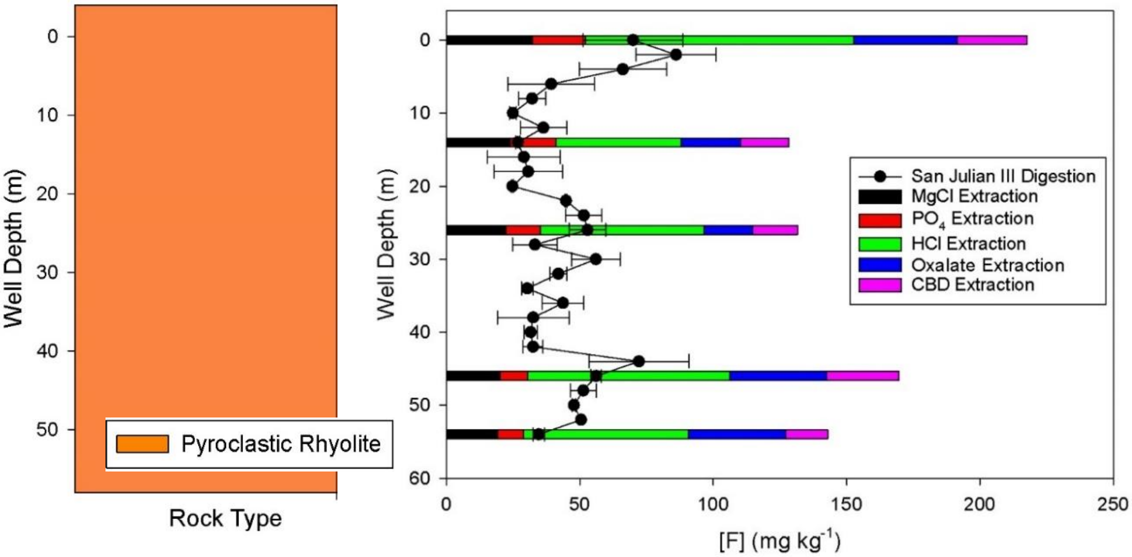
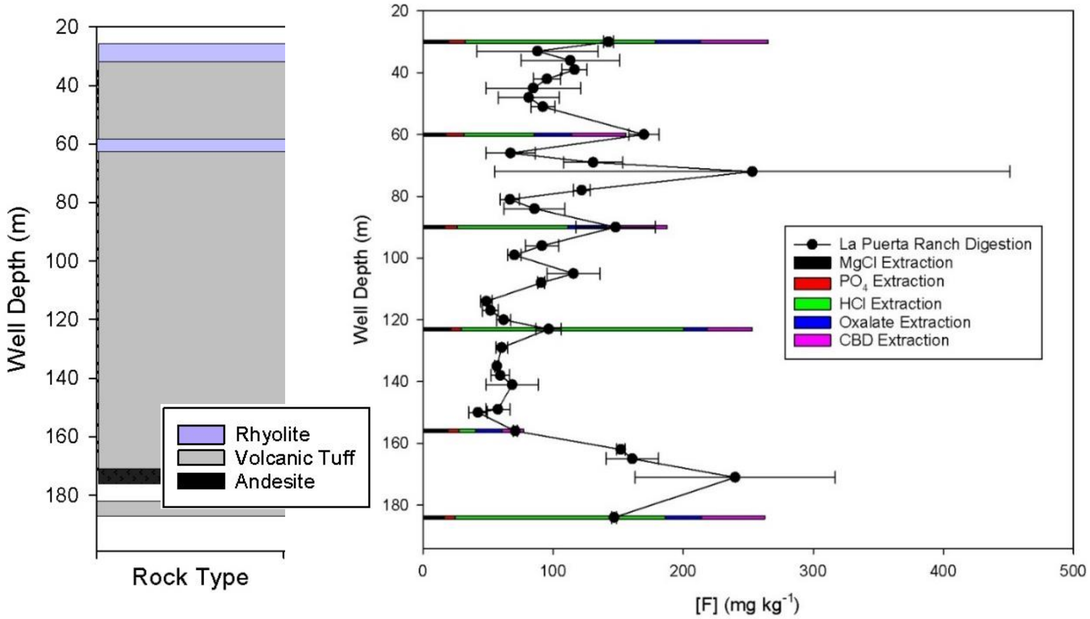


**Figure 3.**



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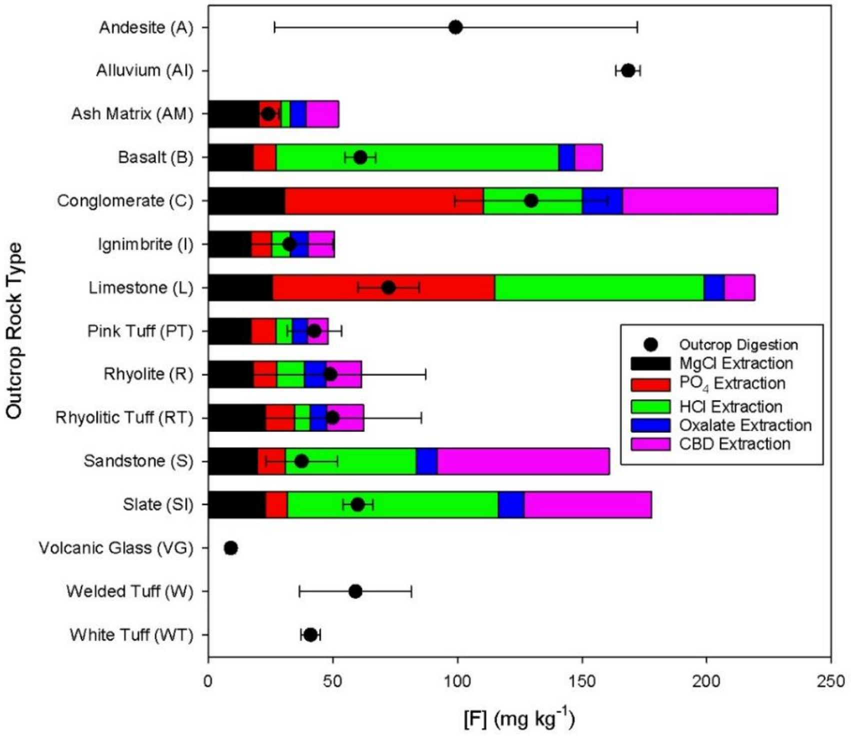

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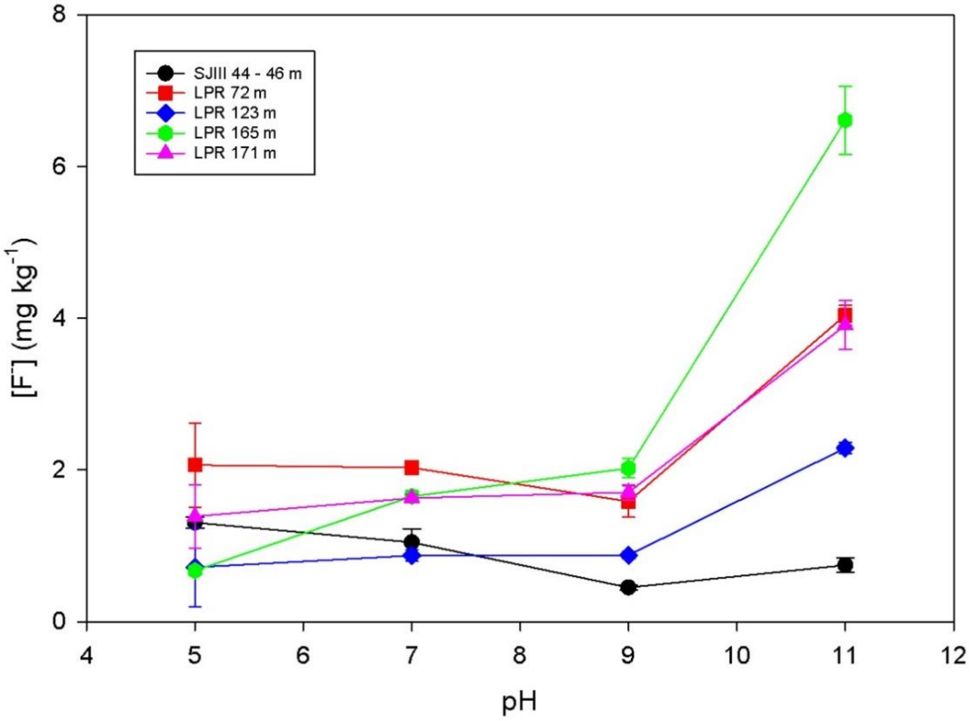

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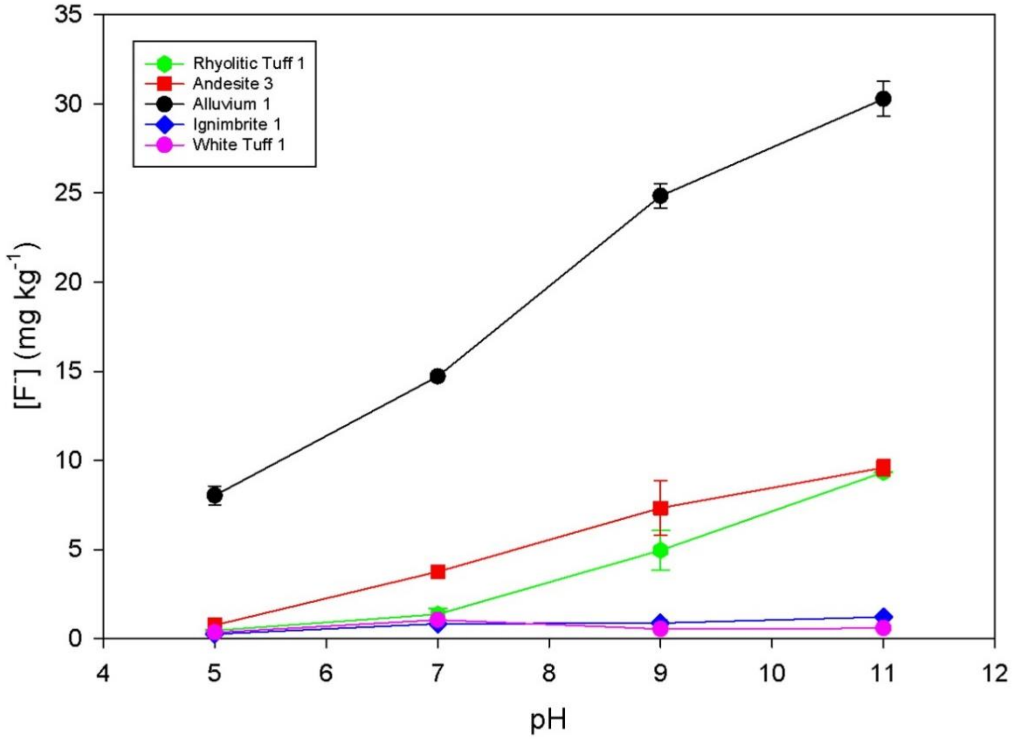

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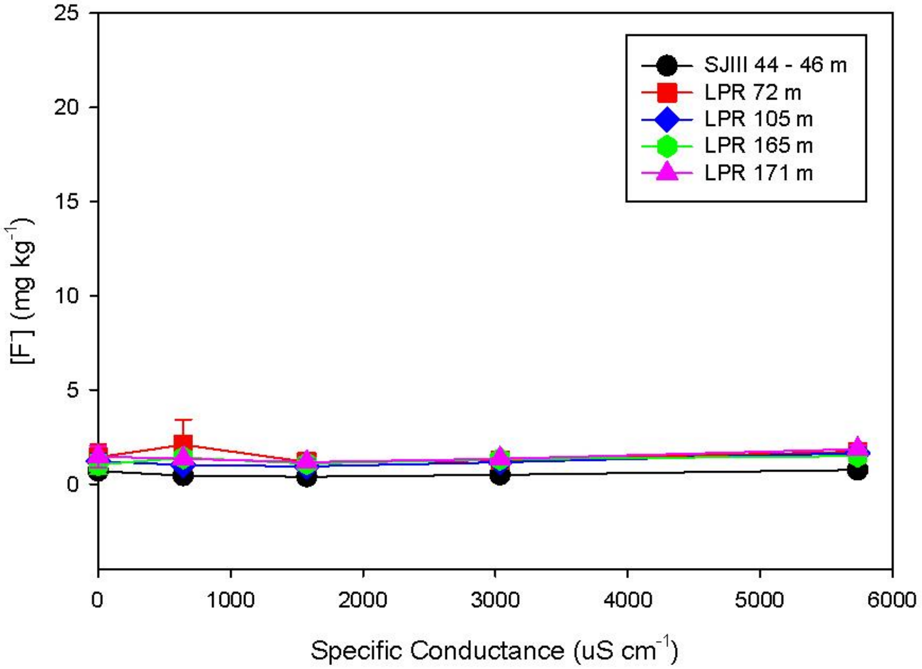

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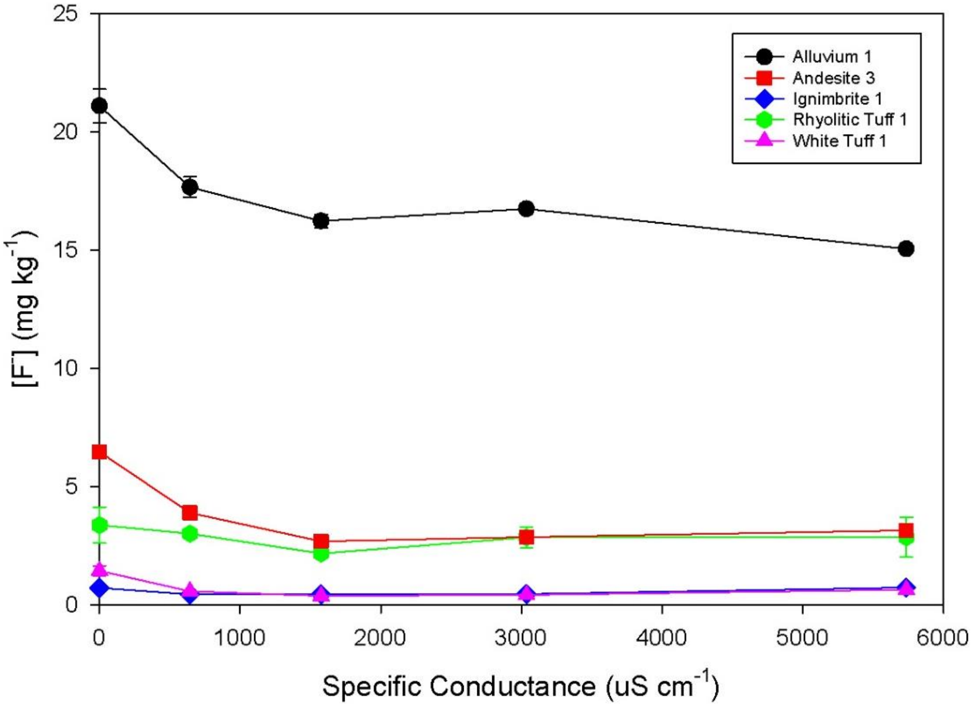

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