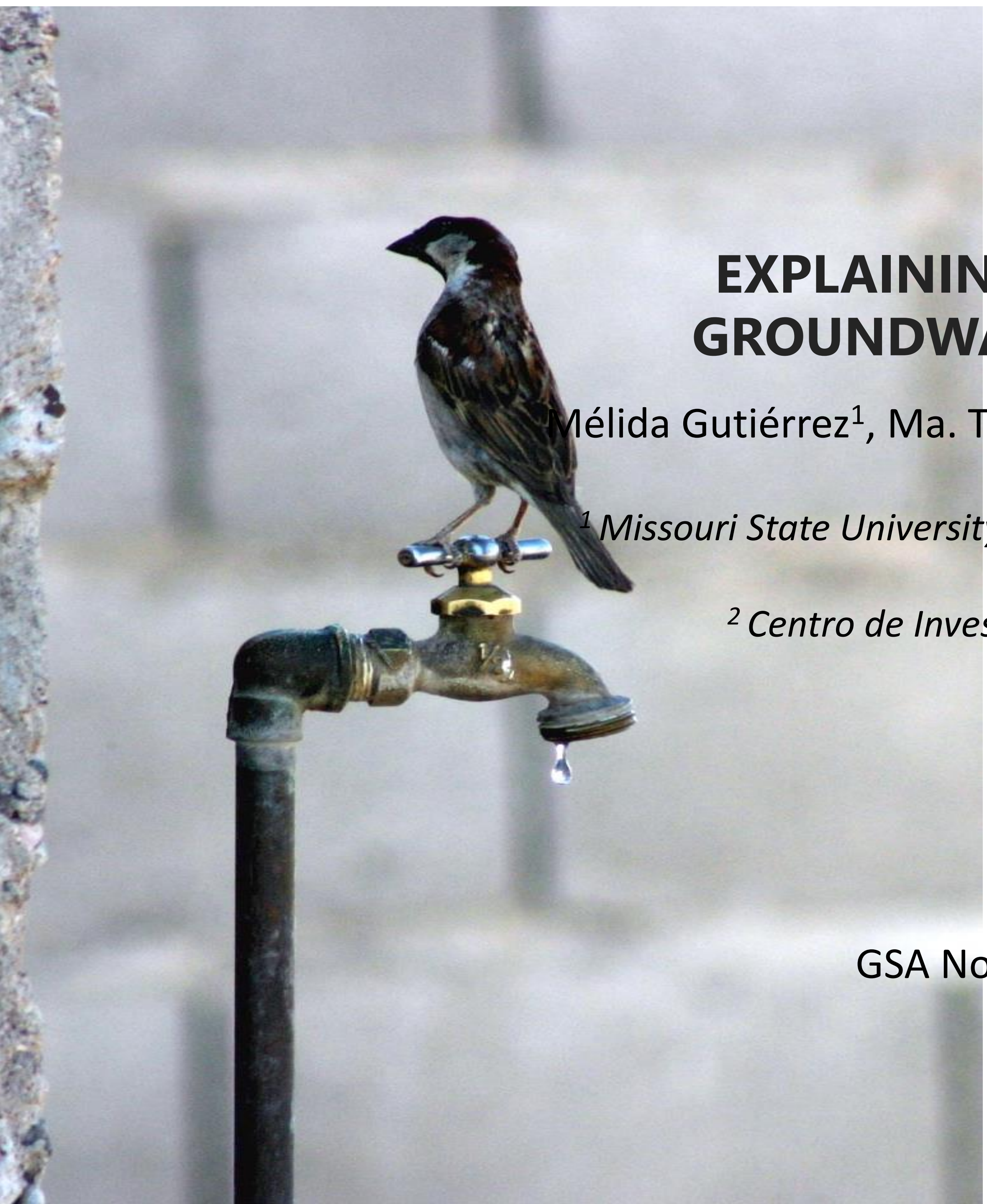

EXPLAINING THE PRESENCE OF FLUORIDE IN GROUNDWATER OF NORTH-CENTRAL MEXICO

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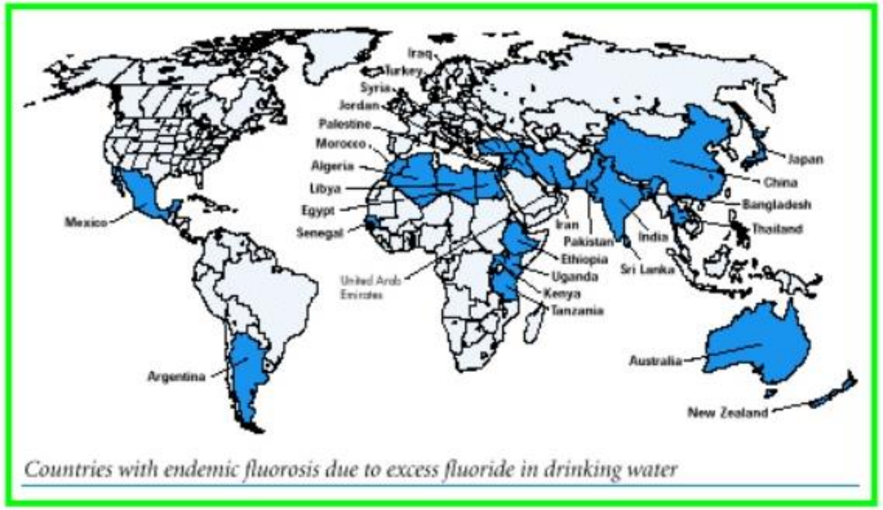
GSA North-Central South-Central Joint Meeting
Springfield MO , April 2024

Why fluoride? Health Concerns

UNICEF Map of Fluorosis



Countries with endemic fluorosis due to excess fluoride in drinking water

Guidelines for F in drinking water:
U.S. = WHO = Mexico = 1.5 mg/L F
But this limit also depends on the amount of water ingested

Chronic ingestion of >1.5 mg F^-/L results in teeth discoloration (a cosmetic effect, not a disease).

Concentrations above 4 mg F^-/L may produce skeletal fluorosis, which includes bone deformation, neurological (lowering of IQ), dermatological, endocrine, and/or reproductive complications.

A 2020 study reported that the highest content of groundwater F in Mexico occurs in its northern part, concurrently with arsenic. Concentrations of fluoride (F^-) are as high as 25 mg/L F^- (2012-2019 data) and have an average of 1.16 mg/L F^-.

Researchers agree that F and As have a common source and it is geogenic in nature.

Since then, there have been additional investigations to validate the origin of F, its range of concentrations, spatial distribution, how much is aridity an enrichment factor, and its relation to hydrological processes (closed *vs*. open basins, residence time).

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Co-occurrence, possible origin, and health-risk assessment of arsenic and fluoride in drinking water sources in Mexico: Geographical data visualization

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HIGHLIGHTS

- A groundwater arsenic-fluoride concentration map highlights enrichment zones.
- Volcanic glass is likely a primary source of arsenic-fluoride contaminated water.
- Evaporation in (semi)arid areas concentrates arsenic-fluoride in aquifers
- The states of Durango, San Luis Potosí, and Zacatecas have higher exposure risk

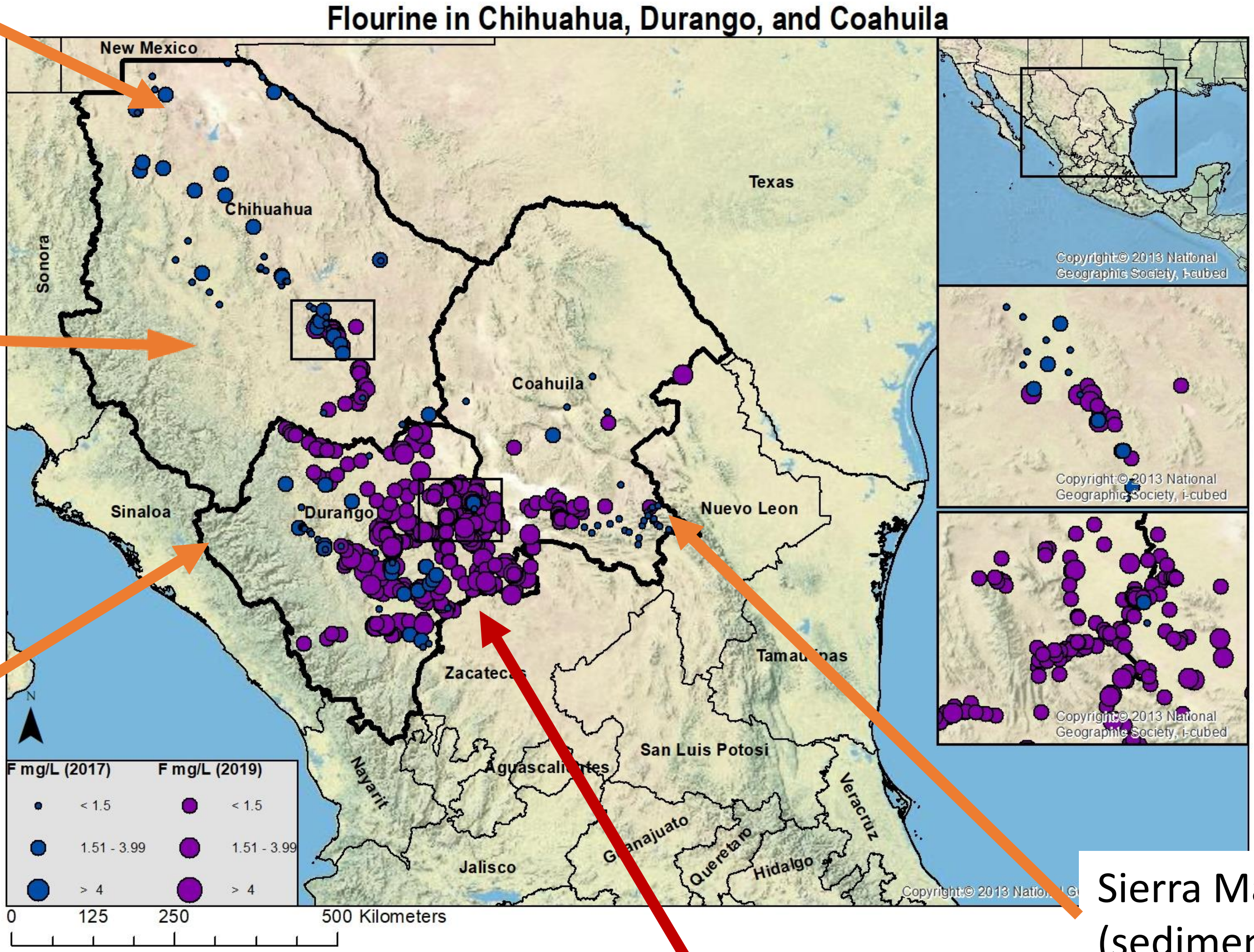
GRAPHICAL ABSTRACT

Some info about the physiography and geology of north-central Mexico

Endorheic basin (Closed basin)

Basin and Range

Sierra Madre Occidental (felsic volcanic rocks). Elev. 10,863 ft, length 932 mi. Has a canyon system deeper than the Grand Canyon.



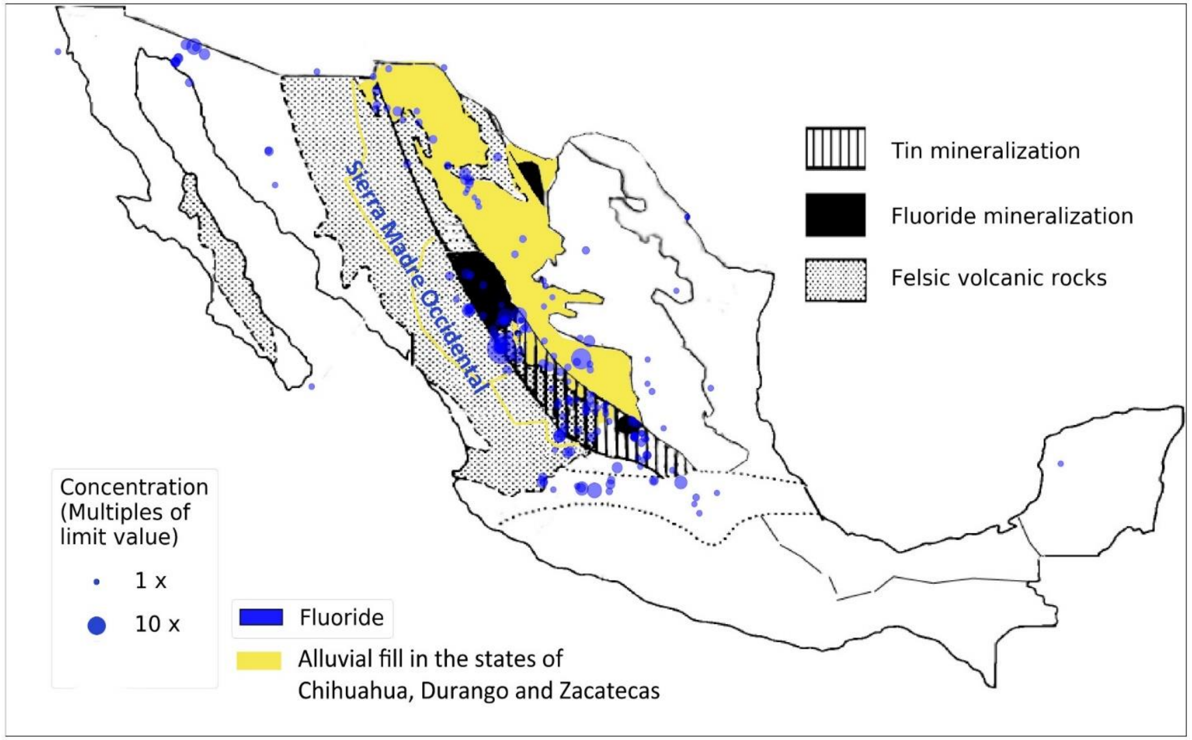
High Plateau in the center part, Flanked by the two mountain ranges

Sierra Madre Oriental (sedimentary and metamorphic rocks)

Investigating the Source of Groundwater Fluoride and Arsenic

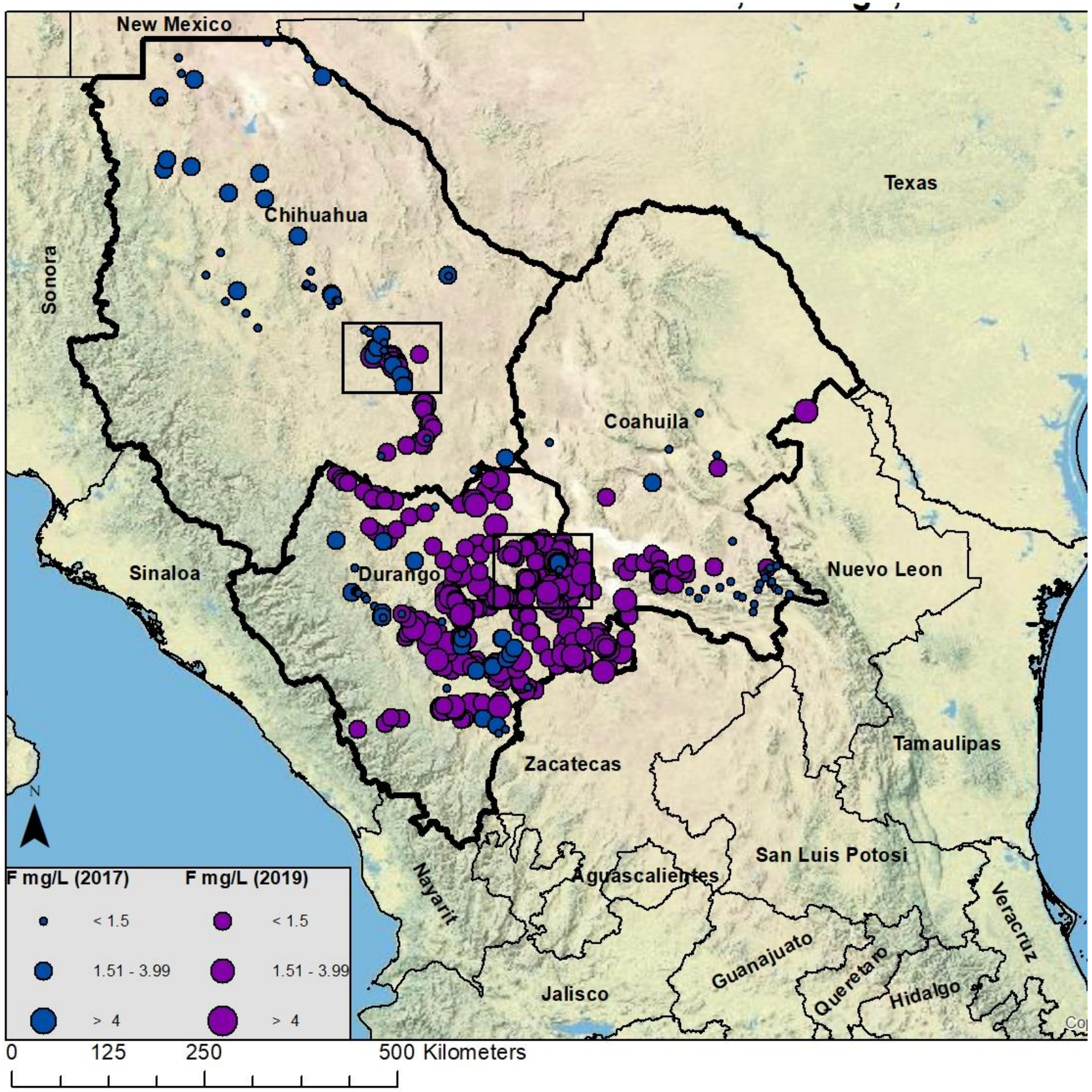
Fluoride concentrations were expected to concentrate around fluorite (CaF_2) deposits; however, the concentrations do not follow this pattern. Instead, the disperse distribution of As, F concentrations points to dissolution and adsorption/desorption of F from the alluvial fill.

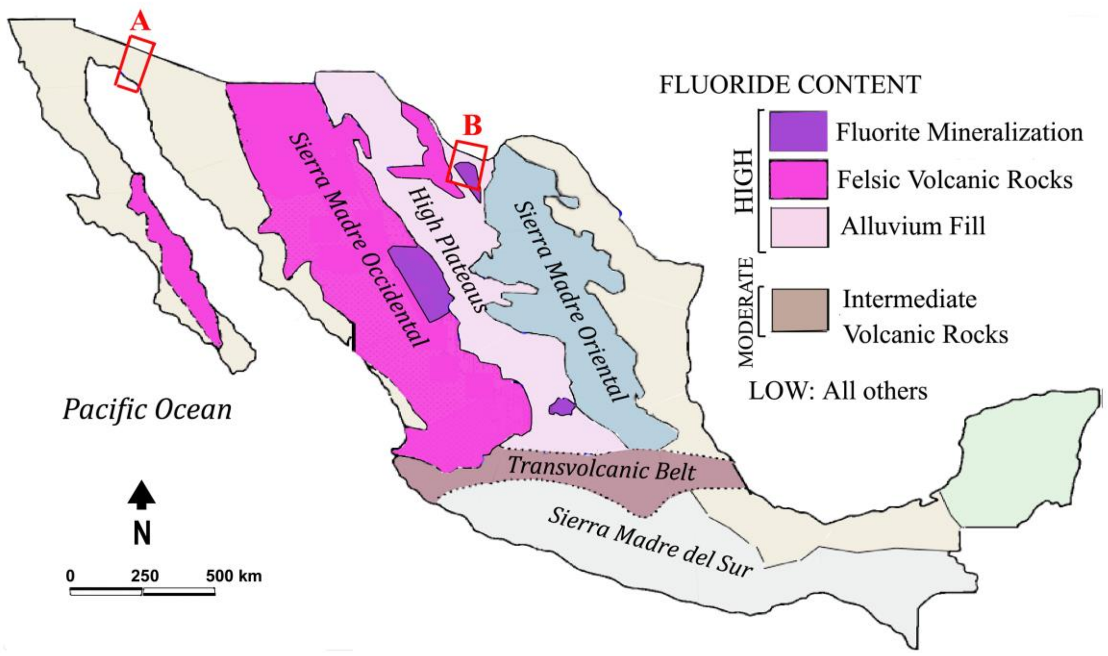
Comparing between the western and eastern parts of the high plateau, the concentrations increase near felsic volcanic rocks (tuff, ignimbrite, rhyolite) of the Sierra Madre Occidental, pointing to it as the likely source.



From Huspeni et al. 1984

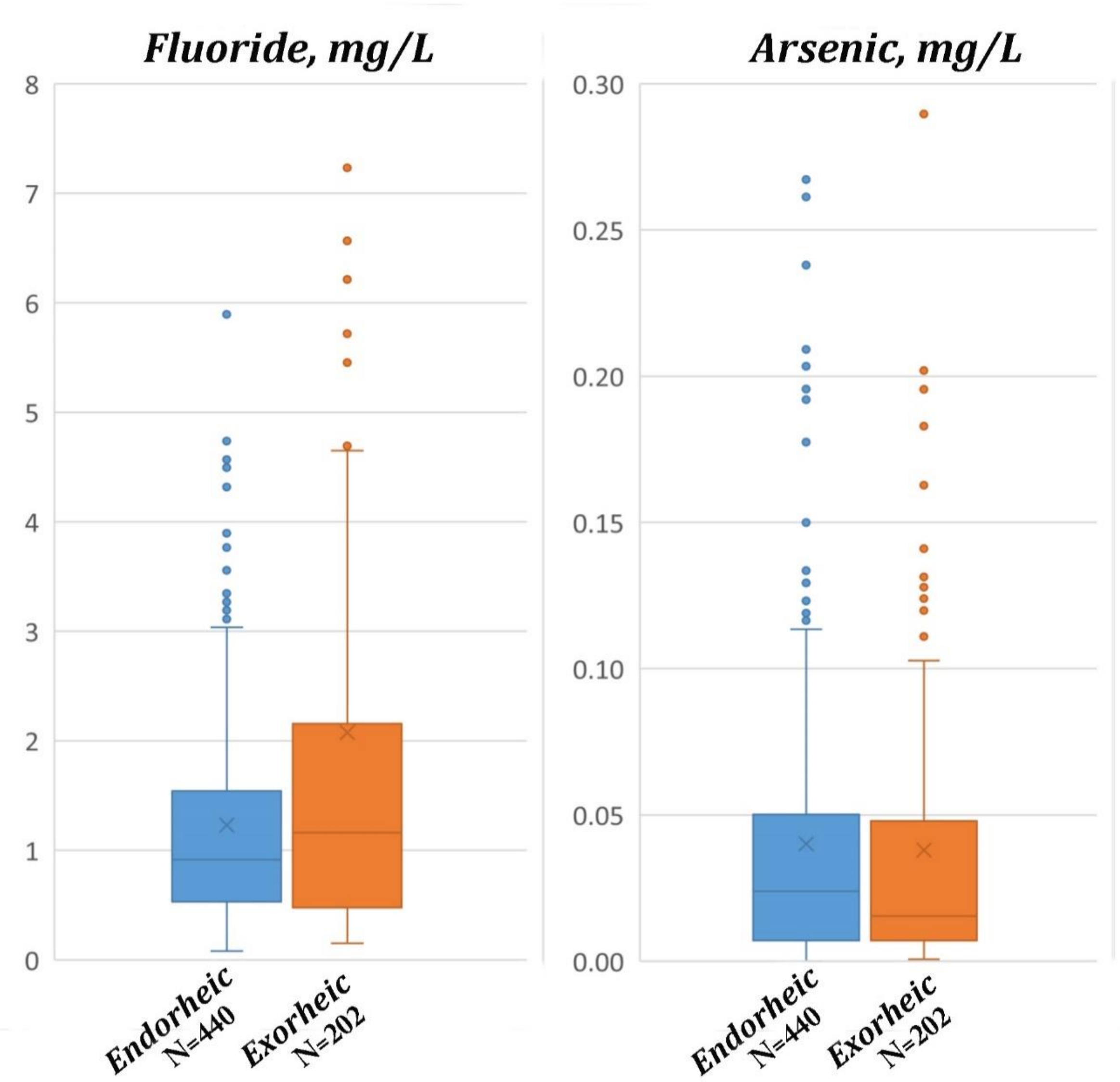
Results: F concentrations mapping and their uneven distribution





The uneven distribution (large and small concentrations next to each other following no pattern) points to the alluvium as the likely source of F (and As). These are unconfined alluvial aquifers filled with fragments that
eroded rom surrounding rocks and its secondary minerals.

Surface area covered by endorheic basins



Environ Monit Assess (2023) 195:212
https://doi.org/10.1007/s10661-022-10818-x

Arsenic and fluorine in groundwater in northern Mexico: spatial distribution and enrichment factors

M. Gutiérrez · M. T. Alarcón-Herrera ·
A. P. Gaytán-Alarcón

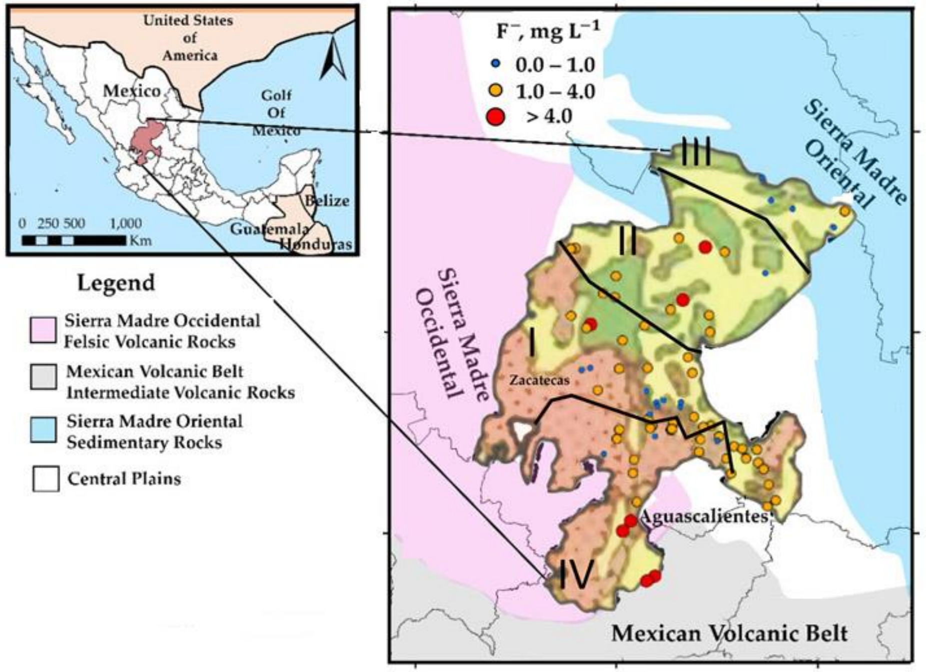


Table 1. Median and range of values (minimum–maximum) of target contaminants and their associated parameters for each section of the study area. Also included are the Spearman correlation coefficient (As-F^-) at $p < 0.01$ and the physiographic characteristics of the sections.

	Section I	Section II	Section III
No. data	383 (38 wells)	130 (14 wells)	48 (5 wells)
pH	7.85 (6.70–8.60)	7.90 (7.10–8.94)	7.40 (6.60–8.90)
As, mg L^{-1}	0.011 (0.0007–0.095)	0.019 (0.0007–0.505)	0.019 (0.001–0.121)
F^- mg L^{-1}	1.22 (0.10–4.90)	2.38 (0.23–29.60)	0.54 (0.22–1.24)
ρ (As-F)	0.245	0.363	none

Table 2. Trends (2012-2021) obtained for F^- according to the Mann-Kendall significant at $p < 0.05$. Only wells with 10 or more consecutive data.

Trend	**Section I**	**Section II**	**Section III**
	Cities, hilly	**Semiarid, rangeland**	**Arid livestock**
	No. wells	**No. wells**	**No. wells**
F^-			
Upward	**1**	**0**	**1**
Downward	**0**	**0**	**0**
No trend	**32**	**4**	**2**
Total No. wells	**33**	**4**	**3**

Minerals **2023**, *13*(9),1145; https://doi.org/10.3390/min13091145

minerals MDPI

Article

Upward Trends and Lithological and Climatic Controls of Groundwater Arsenic, Fluoride, and Nitrate in Central Mexico

Heriberto Morales-deAvila [1], Mélida Gutiérrez [2,*], C. Patricia Colmenero-Chacón [2], Hugo E. Júnez-Ferreira [1] and M. Vicenta Esteller-Alberich [3]

Aridity as an enrichment factor

Evaporative concentration has been reported as an important F^- enrichment factor at global (*Podgorski and Berg, 2022*); U.S.A. (*Mc Mahon et al., 2020*) and Mexico (*Alarcón-Herrera et al. 2020*) scales.

The effect of evaporative concentration in *northern Mexico* has also been reported as being an important factor for Durango (*Gutiérrez et al. 2023*), Zacatecas (*Morales deAvila et al, 2023*) and Chihuahua (*Gutiérrez et al. 2022*). Various methods have been utilized to arrive to this conclusion, including machine learning, statistical comparisons between precipitation and F^- concentration, relation F^- and TDS, and Gibbs Diagram.

Citations:

Alarcón-Herrera *et al*. 2020. Co-occurrence, possible origin As and F in Mexico*. Sci. Total Environ*.

Gutiérrez *et al*. 2022. Factores de concentracion de As y F en norte-centro de Mexico. *Tecnociencia Chihuahua*

Gutiérrez *et al*. 2023. As and F in groundwater from northern Mexico. *Environ. Monit. Assessm*.

McMahon *et al*. 2020. Fluoride occurrence in United States groundwater. *Sci Total Environ*.

Morales deAvila *et al*., 2023. Controls of groundwater As and F in north central Mexico. *Minerals.*

Podgorsky and Berg, 2022. Global analysis and prediction of fluoride in groundwater, *Nature.*

Relation to well depth

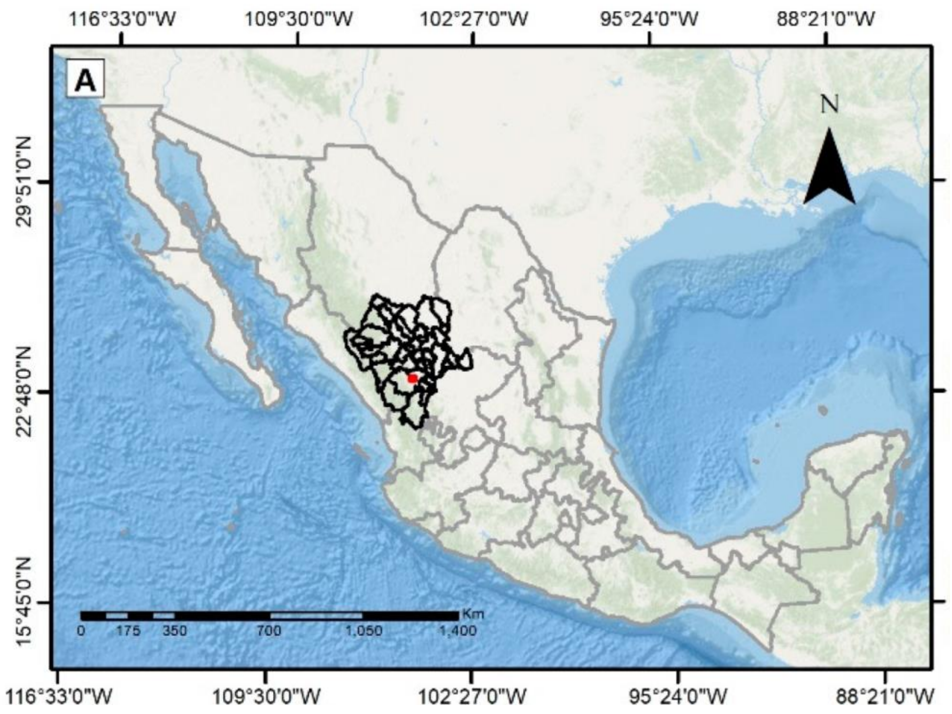
Some authors have hypothesized that the highest concentrations of As and F occur in the deeper parts of the aquifers of northern Mexico. However, rather than depth of the aquifer, the residence time seems to be the controlling factor (*Espino-Valdes et al., 2023*), in agreement with other studies elsewhere (*e.g., McMahon et al., 2020*).

A 2023 study in an intensively used (agricultural) alluvial aquifer in central Chihuahua presented the highest concentrations at the discharge points of the aquifer (*Espino-Valdes et al., 2023*), concluding that concentrations increase with residence time and not depth.

Citation:

Espino-Valdes et al., 2022. Relation of F concentration with well depth. *Environments.*

Other recent reports on the subject: Health risks



Sustainability 2023, 15,14630. https://doi.org/10.3390/ su151914630

sustainability

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Article

Probabilistic Risk Assessment of Exposure to Fluoride in Drinking Water in Victoria de Durango, Mexico

Emily García-Montiel [1], Francisco Zepeda-Mondragón [2], Miriam M. Morones-Esquivel [1,*], Hugo Ramírez-Aldaba [1], Pablito M. López-Serrano [3], Jaime Briseño-Reyes [1] and Eusebio Montiel-Antuna [1]

”Of the 70 wells and 2 tanks that were sampled, 90% of them were found to exceed the levels allowed by the regulations. In more than 70% of the wells, the adult population had a non-cancer hazard quotient (HQ) > 1.

Overall, the HQ for ingestion exceeded 1.8 at the 95th percentile, indicating a significant risk of fluoride-related health problems for the population”.

Potential Treatments.
In practice:
reverse osmosis

Other methods have been suggested but only reverse osmosis has been utilized

Polymers 2022,14,5219. https://doi.org/ 10.3390/polym14235219
polymers MDPI
Review

Lignocellulosic Biomass as Sorbent for Fluoride Removal in Drinking Water

Adriana Robledo-Peralta [1], Luis A. Torres-Castañón [1], René I. Rodríguez-Beltrán [2,*] and Liliana Reynoso-Cuevas [3,*]

Table 1. Fluoride removal-reduction technologies in drinking water.

Technology	Description	Advantage	Disadvantage
Coagulation-precipitation			
Chemical precipitation Electrocoagulation	When chemicals were added, the suspended charged particles were then neutralized and agglomerated to settle down.	Good efficiency. Easy to use. Continuous or batch operation (for small flows). Simple design. Low cost.	Lack of ability to reduce fluoride below WHO limits. It requires the removal of bulky and wet sludge. Secondary treatment is needed. It is necessary that a high conductivity of the water be treated. Species dissolution and by-product formation.
Membrane-based processes			
Reverse osmosis Ultrafiltration Nanofiltration Electrofiltration Dialysis	Water is forced through a semi-permeable membrane to separate contaminants.	Production of high-purity water. High efficiencies. Automatic control. Selectivity.	Relatively expensive to install and operate. Susceptible to membrane fouling and degradation. Operates at high pressures. Significant energy demands.
Ion Exchange and adsorption			
Ion Exchange resins Chelating resins • Adsorbents: activated carbons • Metal oxides • Nanomaterials	Process in which the ions in aqueous media are transferred to the adsorbent matrix by several mechanisms.	It allows the adsorbent material regeneration. High removal capacity. Anion selective removal.	Highly pH-dependent. Vulnerable to interference.

In conclusion, the presence of F^- in groundwater in northern Mexico has:

- Geogenic origin and shares a common origin with arsenic,
- Disperse pattern, high spatial variability of concentrations,
- Different geochemical paths for As and F,
- Evaporation and residence time are relevant factors,
- F^- not necessarily concentrated in endorheic basins,
- Upward trends are not yet a concern,
- Concentrations present a serious risk to human health in places,

Thank you,

any questions?

Centro de Investigación en
Materiales Avanzados, S.C.