# TRACING NATURAL SOURCES OF FLUORIDE IN GROUNDWATER: CASE NORTHERN MEXICO


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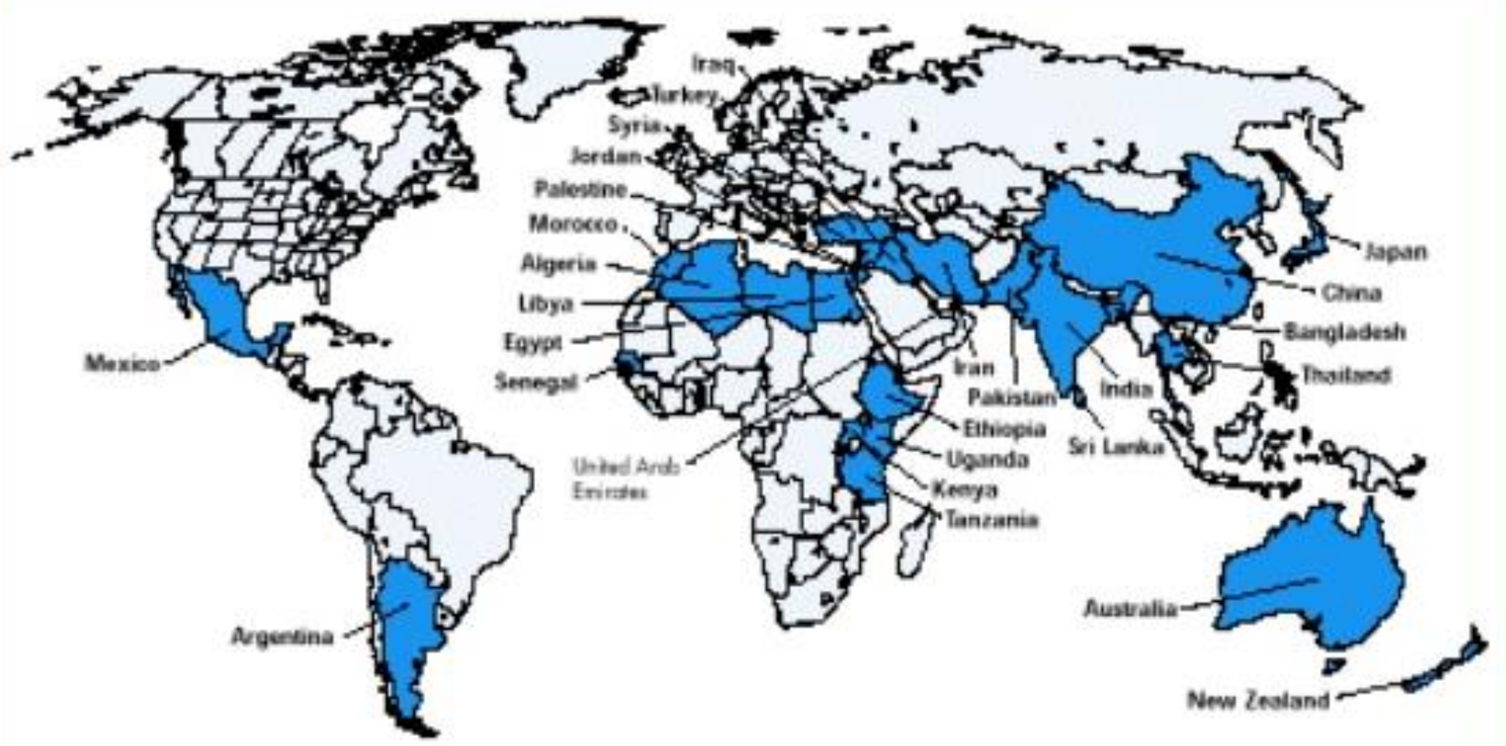
# UNICEF Map of Fluorosis



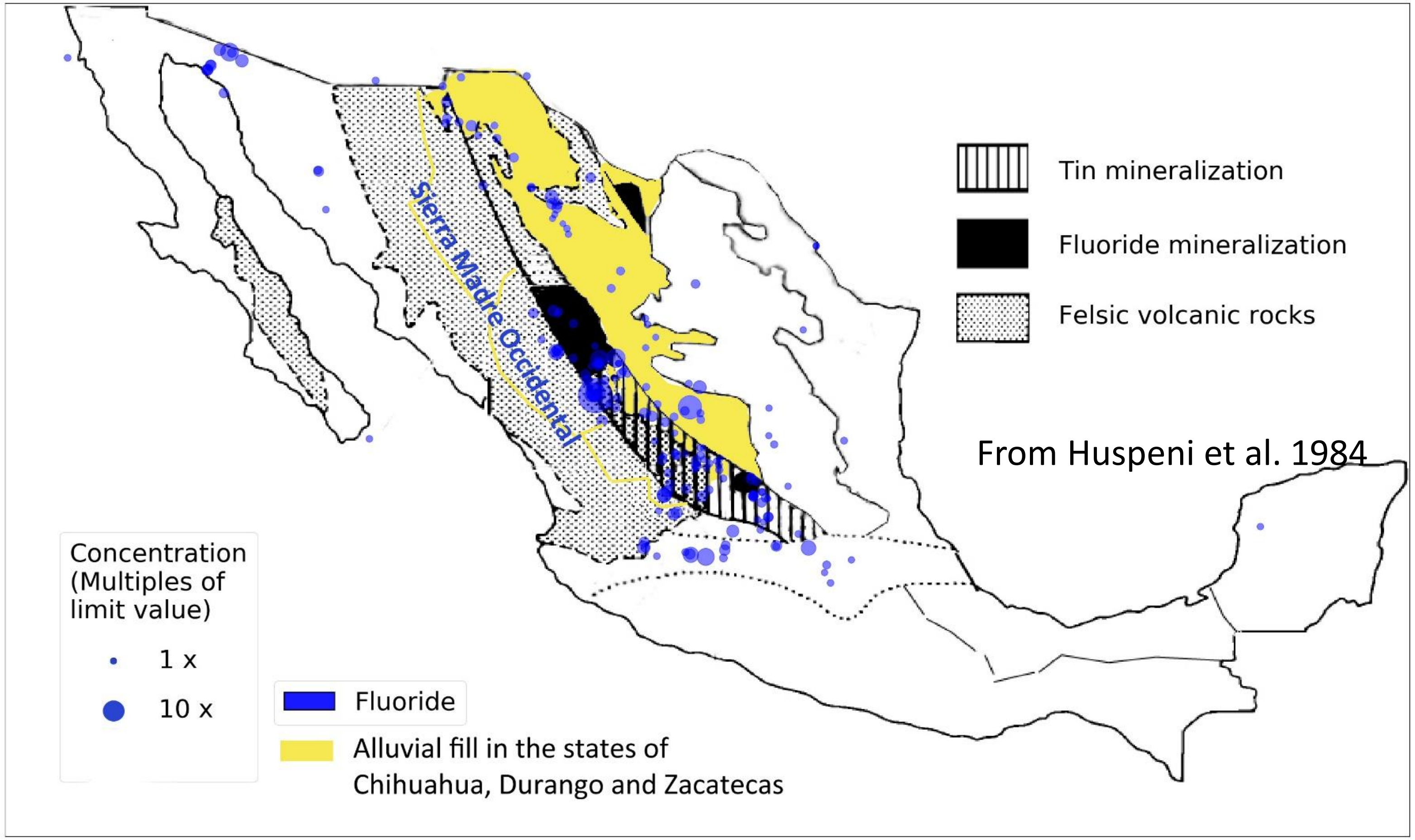

*Countries with endemic fluorosis due to excess fluoride in drinking water*

Chronic ingestion of water with >1.5 mg $F^-$/L results in teeth discoloration, which is a cosmetic effect, not a disease.

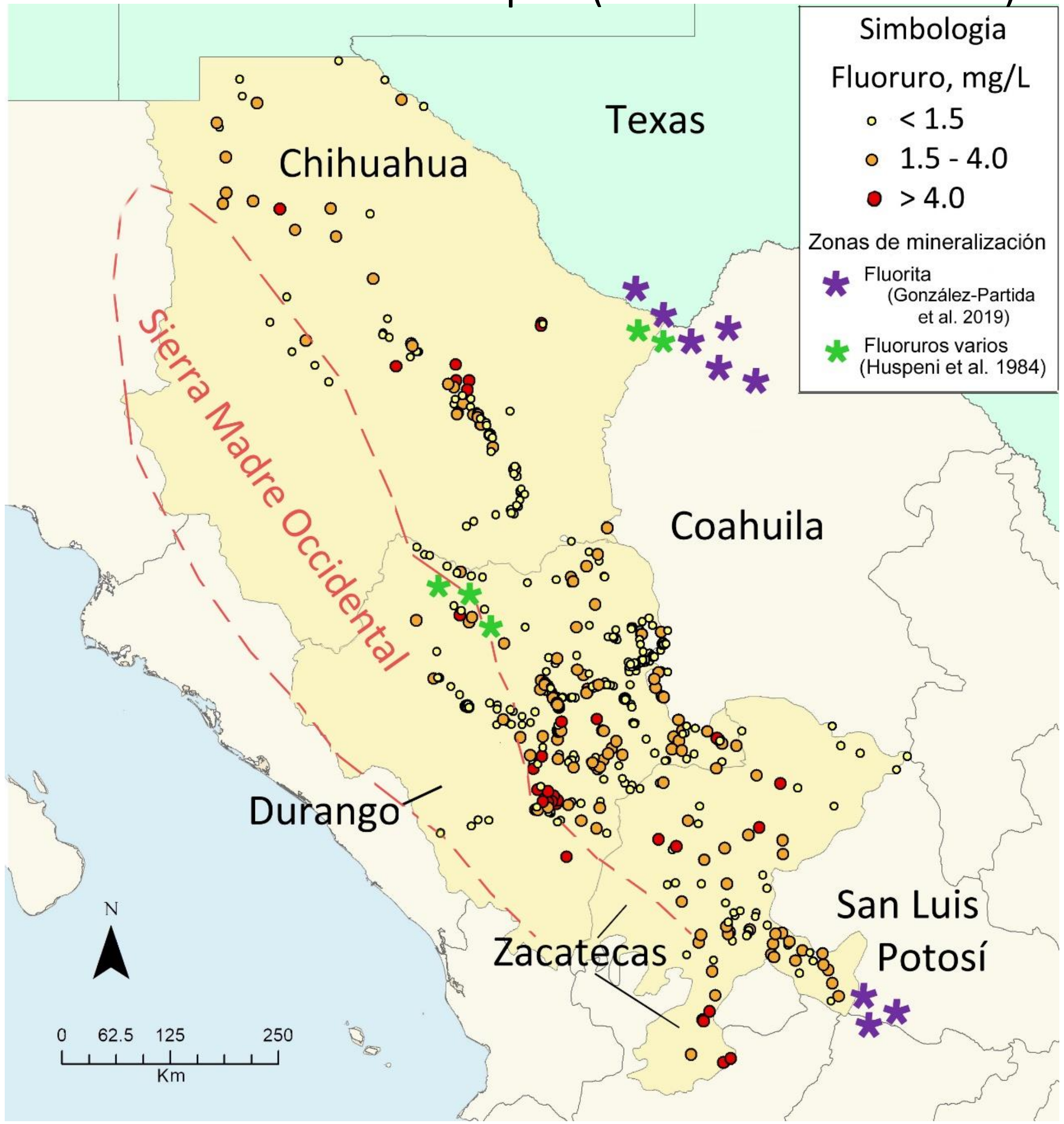
Concentrations above 4 mg $F^-$/L may produce skeletal fluorosis. This has have severe health consequences, including bone deformation, neurological (lowering of IQ), dermatological, endocrine, and reproductive complications.

# Source of Groundwater Fluoride

A 2020 study using 2017 well water data, identified Durango, Zacatecas and Chihuahua, states in north-central Mexico as the states with highest $F^-$ concentration.



Distribution of water samples (CONAGUA 2017-2019)




The source and the factors that cause F- enrichment are investigated here after a database containing 1,131 data were analyzed

- Disperse concentrations
- Independent relatively from fluoride mineralization areas
- Independent from possible anthropogenic sources (brick making, P-fertilizer industry)

# Fluorine in rocks (a possible source of $F^-$)

Fluorine content in rocks within the study area is not reported*. However, fluorine content for rocks and alluvial material of similar composition and age has been reported for Argentina (Nicolli et al. 2010) and central Colorado (Wallace, 2010).

The highest content of F corresponded to:

granite: 1,000 – 2,000 mg $F^-$/L (Wallace 2010),

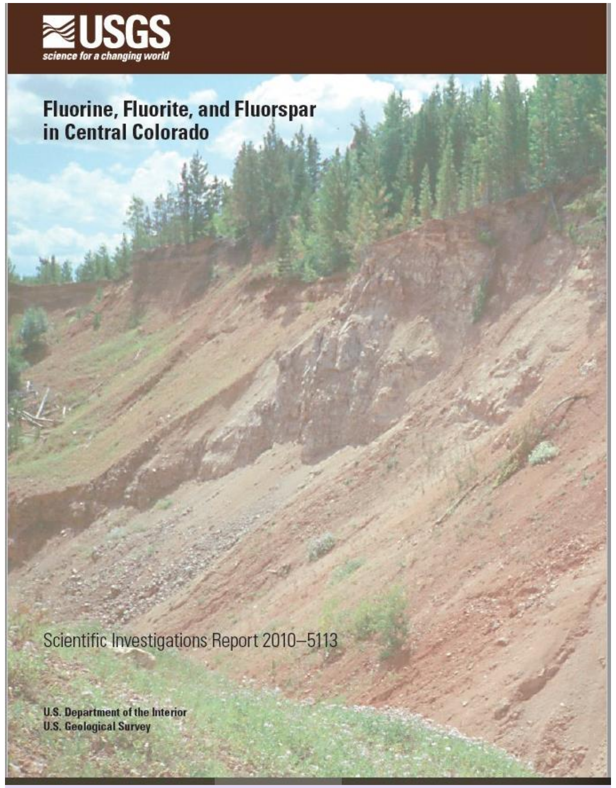
rhyolite: 930 mg $F^-$/L (Wallace 2010),

volcanic glass: 722 mg $F^-$/L (Nicolli et al. 2010)

volc. alluvium (loess): 750 mg $F^-$/L (Nicolli et al. 2010)

Limestone rich in detrital clay: 900 mg $F^-$/L (Wallace 2010)

Limestone crustal average is: 300 mg $F^-$/L



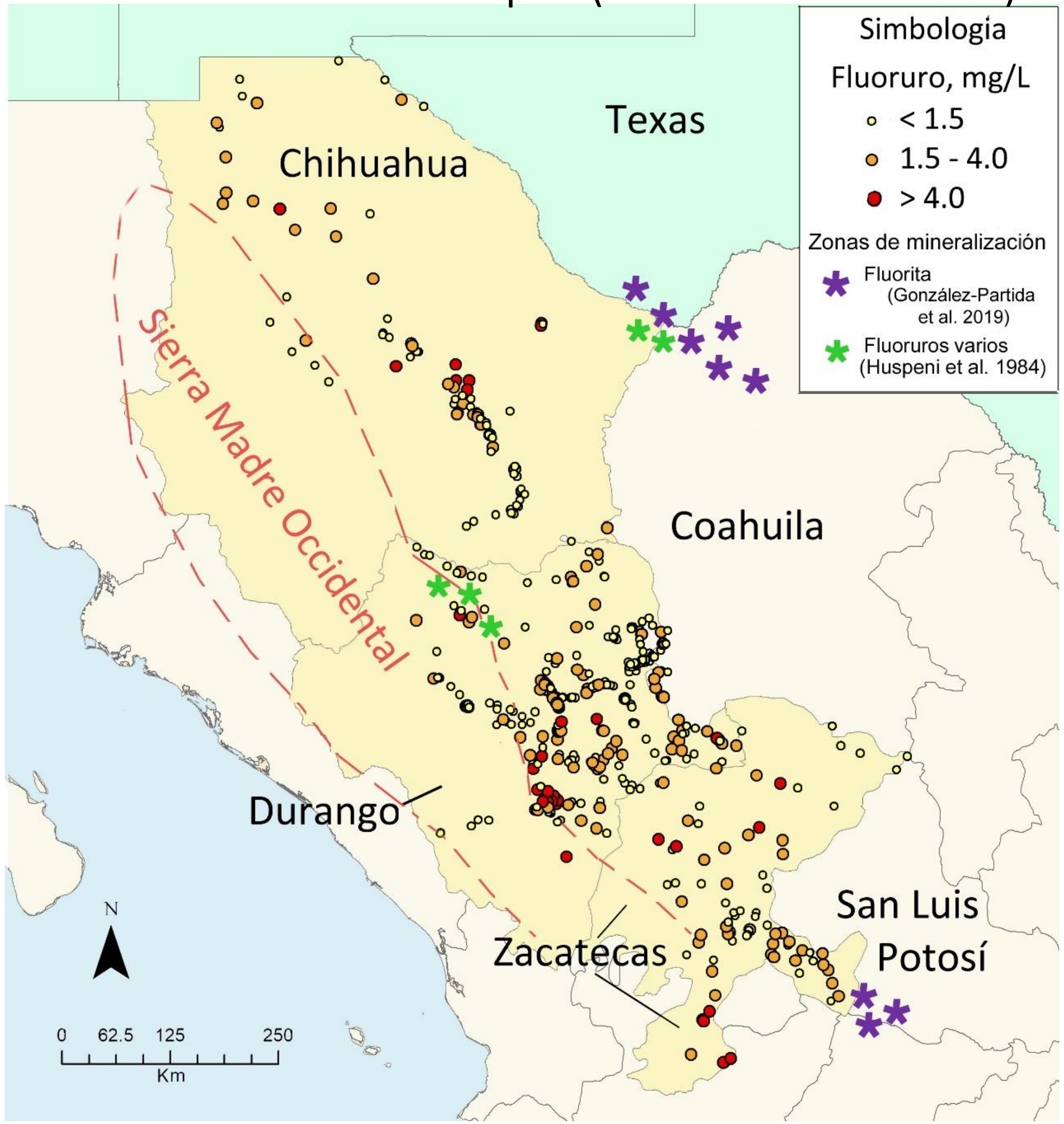

* Elaborate analytical determination. Lithium metaborate/tetraborate fusion of the sample followed by F ion-selective electrode (ISE)

# Alluvial fill

The alluvial fill resulted from erosion of the Sierra Madre Occidental. The Sierra Madre Occidental is a large rhyolitic province that was emplaced in several (five or more) different pulses or volcanic episodes (Ferrari et al. 2007) between 100 to 20 m.y.a., which relate to the subduction of the Farallon Plate and separation of Baja California from the Mexican mainland. Extensional forces soon after produced a basin and range deformation.

The composition of the alluvium within the study area has been reported (Reyes-Gomez et al. 2013) as being primarily rhyolite (quartz and volcanic glass), and minor amounts of limestone (clays, calcite), shale (clays, iron oxides), and basalt, in that order.

Distribution of water samples (CONAGUA 2017-2019)



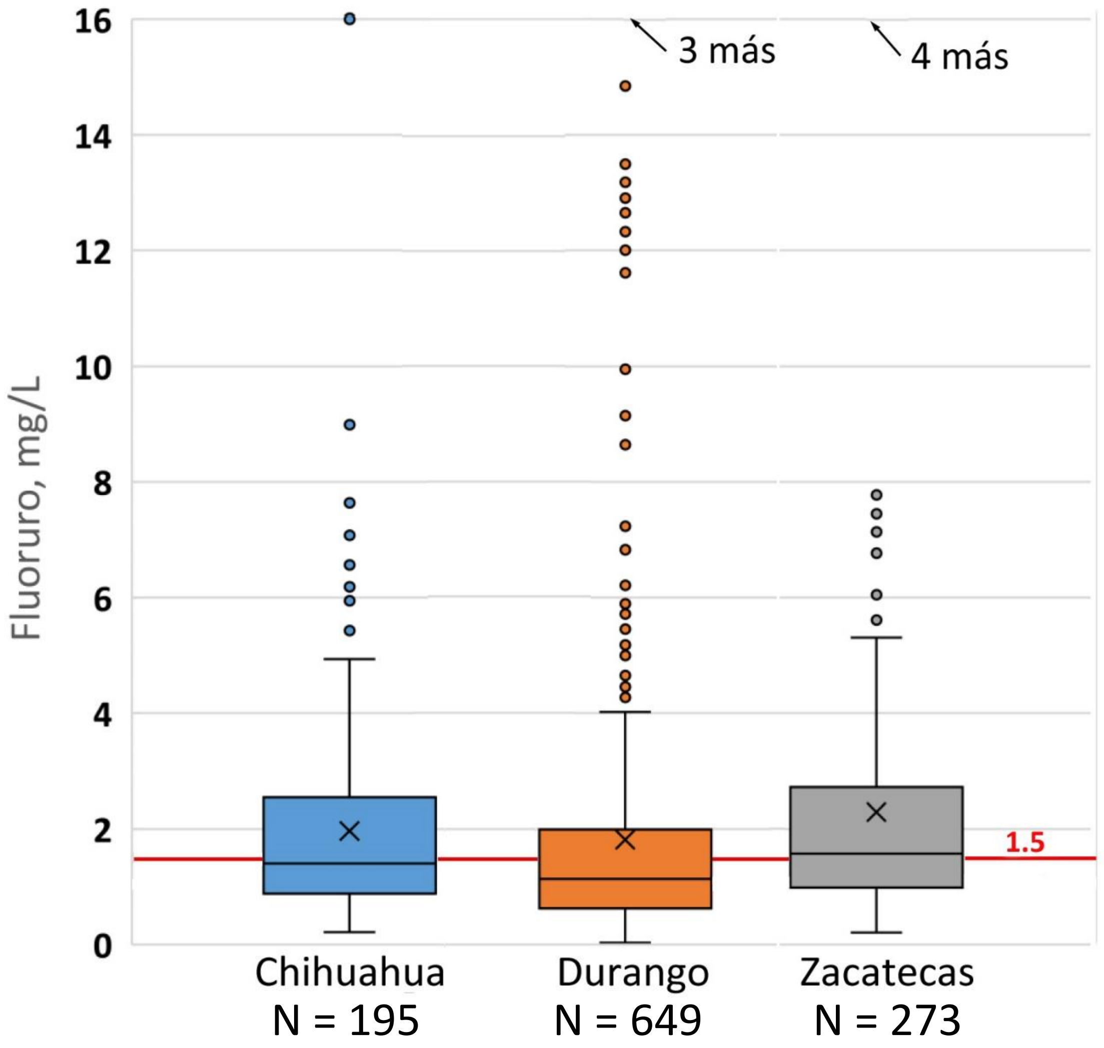

# Results

- Geogenic origin, most likely leached from alluvial fill material (rhyolite and ignimbrite fragments, some limestone)
- Aridity and alkaline pH (known causes of $F^-$ enrichment in groundwater)

# Possible relation with

- Total dissolved solids
- As
- Ca/Na
- Well depth

# Tuckey Diagram of F-concentrations



# Enrichment factors other than aridity and alkaline pH

Pearson correlation + significance of correlation coefficient

- Temperature
- TDS
- Ca/Na molar ratio
- Well depth

| | r (**F-Temp.**) | r (**F-TDS**) | r (**F-Ca/Na**) | r (**F-As**) |
|---|---|---|---|---|
| Chihuahua | **0.28** | 0.15 | **-0.30** | **0.40** |
| Durango | 0.06 | 0.01 | **-0.20** | **0.47** |
| Zacatecas | 0.17 | **0.44** | **-0.23** | **0.80** |

# Chemical Speciation

Two wells were selected as representative samples. Their chemical composition was entered to Visual Minteq to obtain its chemical speciation.

Speciation affects F solubility, toxicity and the effectiveness to water treatments such as reverse osmosis.

The chemical species under alkaline conditions and solutes present were mainly F-, MgF+, and $AlF_2$.

| | Well 1 | Well 2 |
|---|---|---|
| pH | 7.44 | 8.09 |
| As (mg/L) | 0.016 | 0.073 |
| $F^-$ (mg/L) | 3.91 | 7.78 |
| TDS (mg/L) | 311.8 | 325.7 |
| Species (%) | | |
| $F^-$ | 96.88 | 99.05 |
| $MgF^+$ | 2.05 | 0.26 |
| $CaF^+$ | 0.74 | 0.27 |
| NaF(aq) | 0.36 | 0.45 |
| $AlF_3$(aq) | $3.7 \times 10^{-5}$ | $1.8 \times 10^{-6}$ |

# CONCLUSIONS

- $F^-$ concentrations had a similar median (and average) among all three states, suggesting a common origin that is geogenic in nature,
- Origin is related to the chemical weathering of felsic igneous rocks of the surrounding sierras, which host fluoride mineralization zones,
- Aridity and alkalinity play a role in F content. Other factors of enrichment reported for other areas such as water temperature, TSD, and Ca/Na are not significant players in this area,

- Median and average values were above the limit the 1.5 mg F-/L guideline in ~ 45% of wells.
- The 4 mg F-/L (skeletal fluorosis) value was exceeded in ~12% of wells
- Co-occurrence with arsenic aggravates the health concerns and calls for a strategic plan for preventing water of high F-As to be used as drinking water source unless undergoing treatment.

# Thank you!

Common inhabitant of the study area