

ABSTRACT

Chronic intake of fluoride (F⁻) in drinking water causes fluorosis. At low levels (<1.5 mg/L) it causes discoloration of teeth (dental fluorosis) and at higher concentrations (>4 mg/L) a more serious condition affecting the bones (skeletal fluorosis). The north-central part of Mexico has been identified as a region with high concentrations of geogenic F⁻, especially the states of Chihuahua, Durango and Zacatecas, with maximum concentrations of 16, 28, and 22 mg/L F⁻, respectively, according to 2017-2019 data reported by Mexico's Water Office CONAGUA. Chihuahua has a similar geologic setting as Durango and Zacatecas; however, groundwater quality is more sparsely reported and according to the fewer data available, the F⁻ levels are not as high as those of Durango and Coahuila. Geochemical processes possibly responsible for the amelioration are the presence of other ions (mainly Ca²⁺ and Na⁺), calcite saturation conditions, and residence time.

OBJECTIVES OF THE STUDY

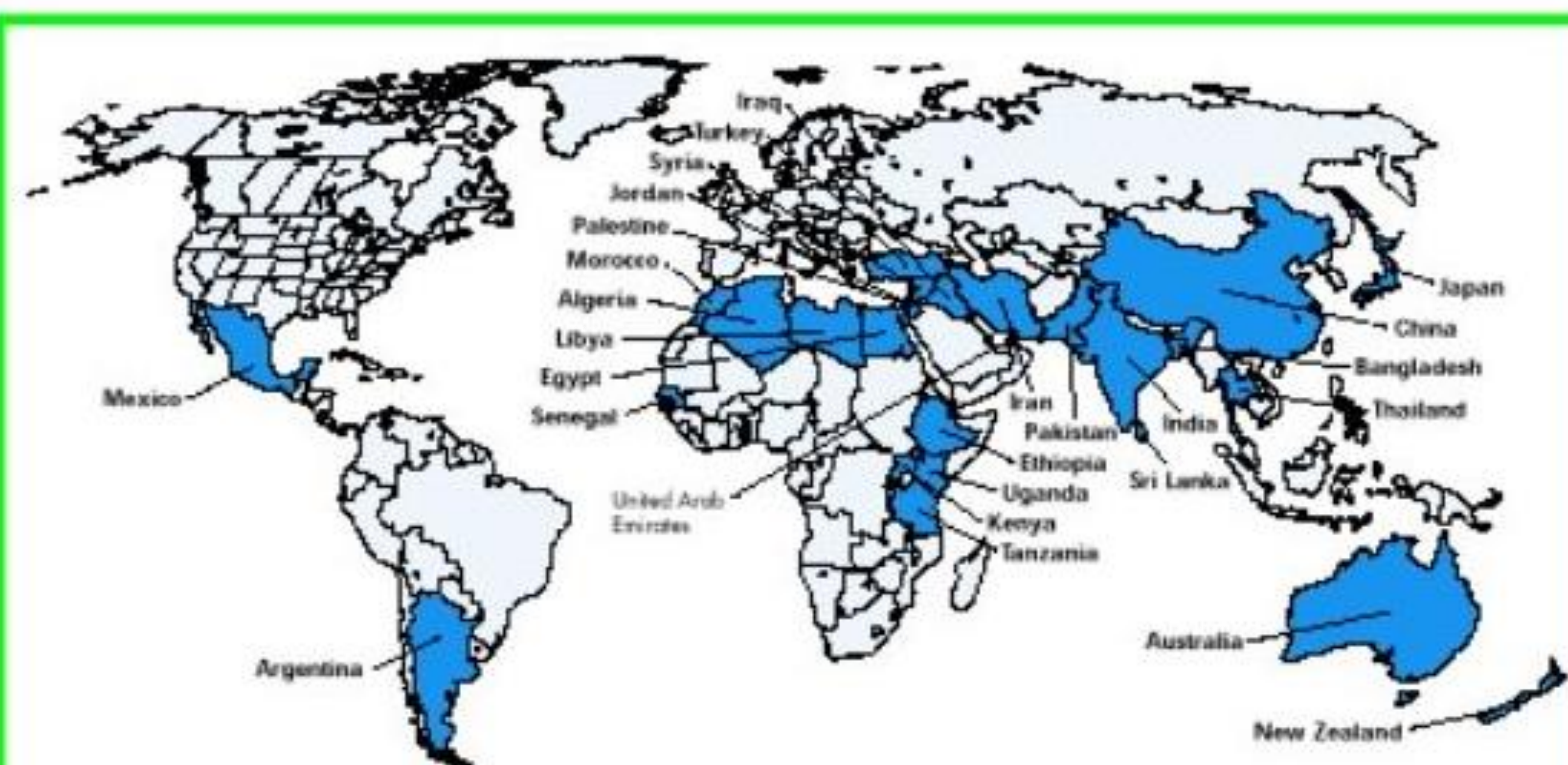
The objectives of this study were to list and rank the geological and geochemical constrains to the presence of fluoride in northern Mexico, especially for the state of Chihuahua. Results are based on recent studies reporting the controlling factors to F⁻ concentration in groundwater.

GROUNDWATER DATA SOURCE

Data were obtained from Mexico's government water agency CONAGUA website <https://www.gob.mx/conagua/articulos/calidad-del-agua> for the years 2012-2019; a total of 1,968 samples collected from 225 wells.

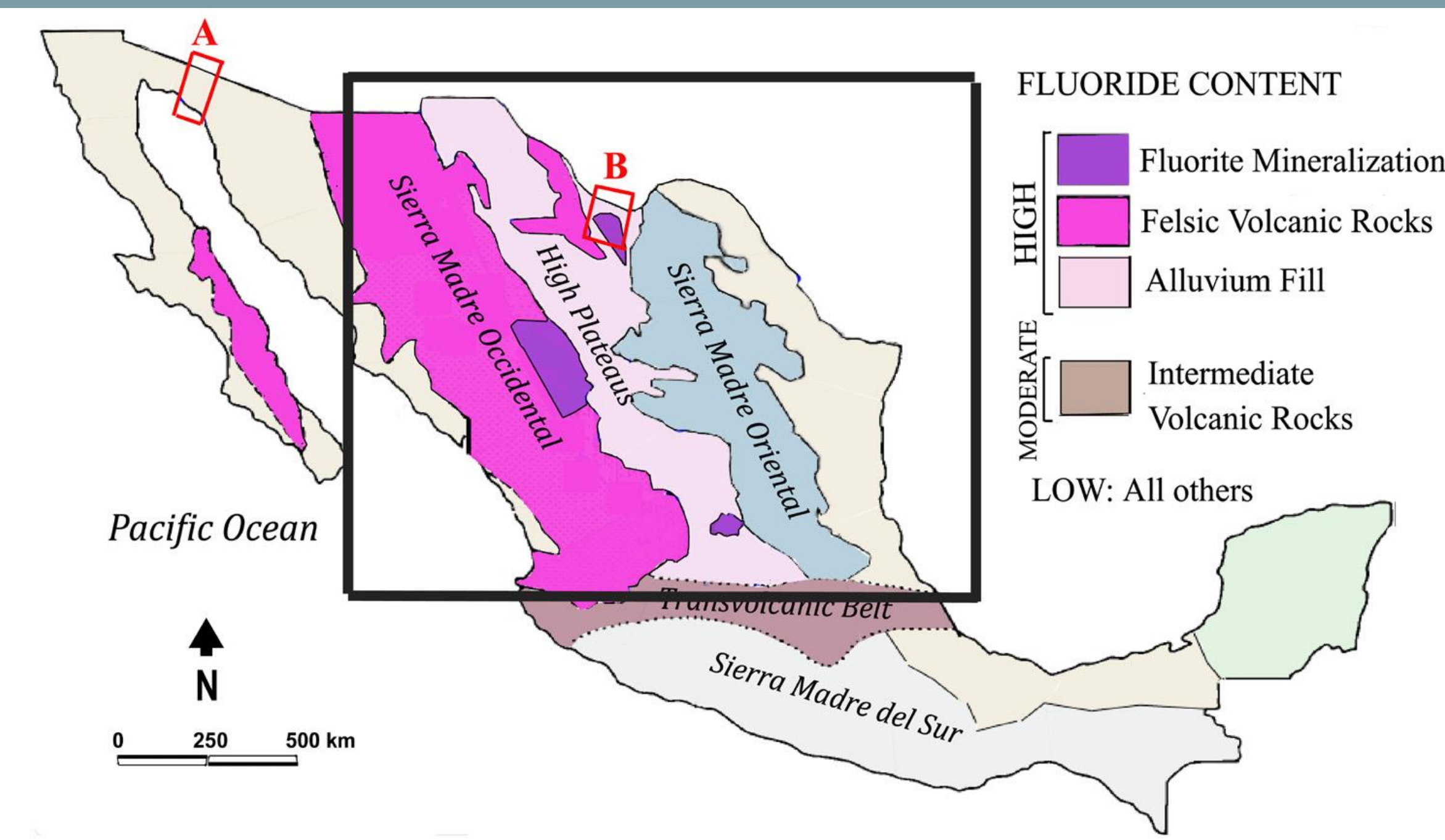
The aquifers are alluvial, unconfined, and with a depth that varies from 100 to 1,000 m. The aquifers' fill is comprised of rock fragments from the surrounding outcrops and abundant clays and iron oxides.

ENDEMIC FLUOSOSIS MAP (UNICEF 2019)



Countries with endemic fluorosis due to excess fluoride in drinking water

LITHOLOGICAL CONSTRAINS

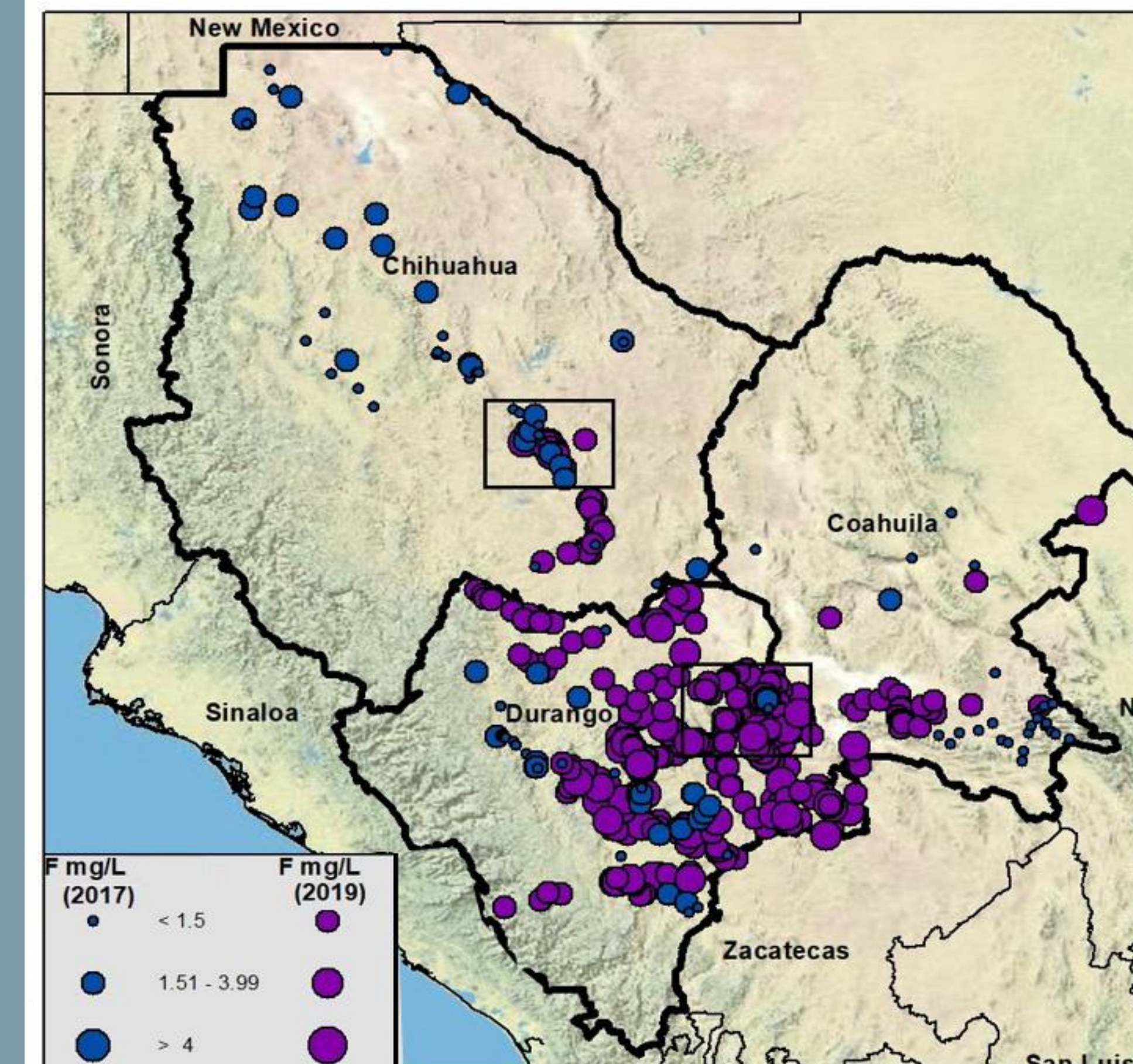


Spearman correlations: $\rho_{F-As} = 0.31$ ($p < 0.01$) confirm a moderate correlation between F⁻ and As. A positive ρ_{F-Ca} correlation is interpreted as dissolution of fluorite (CaF₂) and, if negative, co-precipitation of F⁻ with precipitating calcite (CaCO₃), the latter a more likely process operating in this (arid) area with a -0.30 ($p < 0.01$) correlation coefficient.

CONCLUSIONS

- F in groundwater has geogenic origin,
- shares a common origin with arsenic,
- Follows different geochemical paths for As and F,
- Has a disperse pattern and high variability of concentrations,
- High concentrations of F a risk to human health in places,
- Evaporation and residence time are relevant concentration factors,
- Not necessarily concentrated in endorheic basins, and
- Upward trends are not yet a concern.

CONCENTRATION SPATIAL DISTRIBUTION



F⁻ concentrations plot in a dispersed pattern; do not follow the known location of fluorite deposits (shown at left in purple)

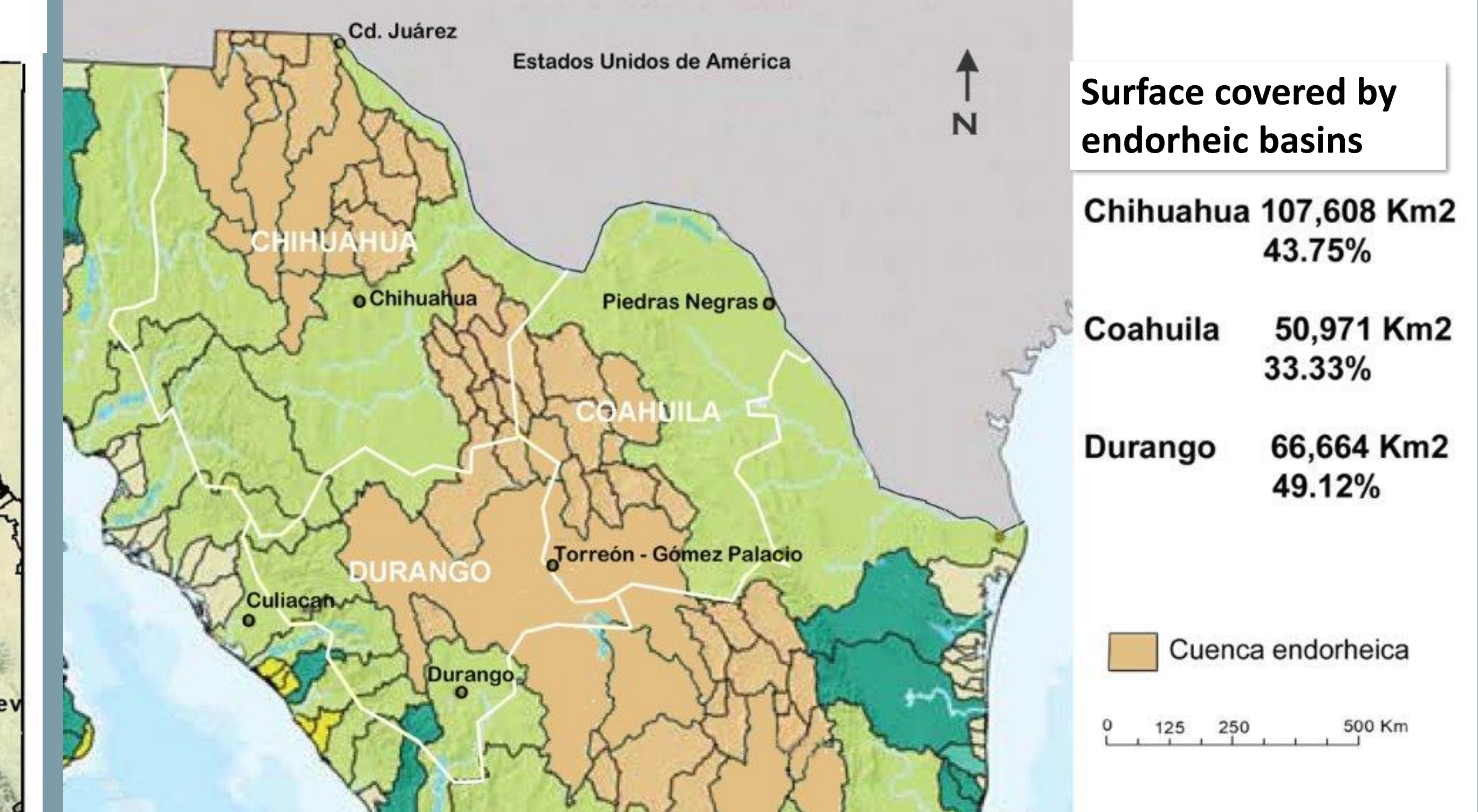
STATISTICAL ANALYSES

$N_{\text{Chihuahua}} = 480$ samples in 2012-2021; 54 sampling sites per year
 Max F⁻ concentration = 16 mg/L
 Min F⁻ concentration = 0.1 mg/L
 Average F⁻ concentration = 1.94 mg/L

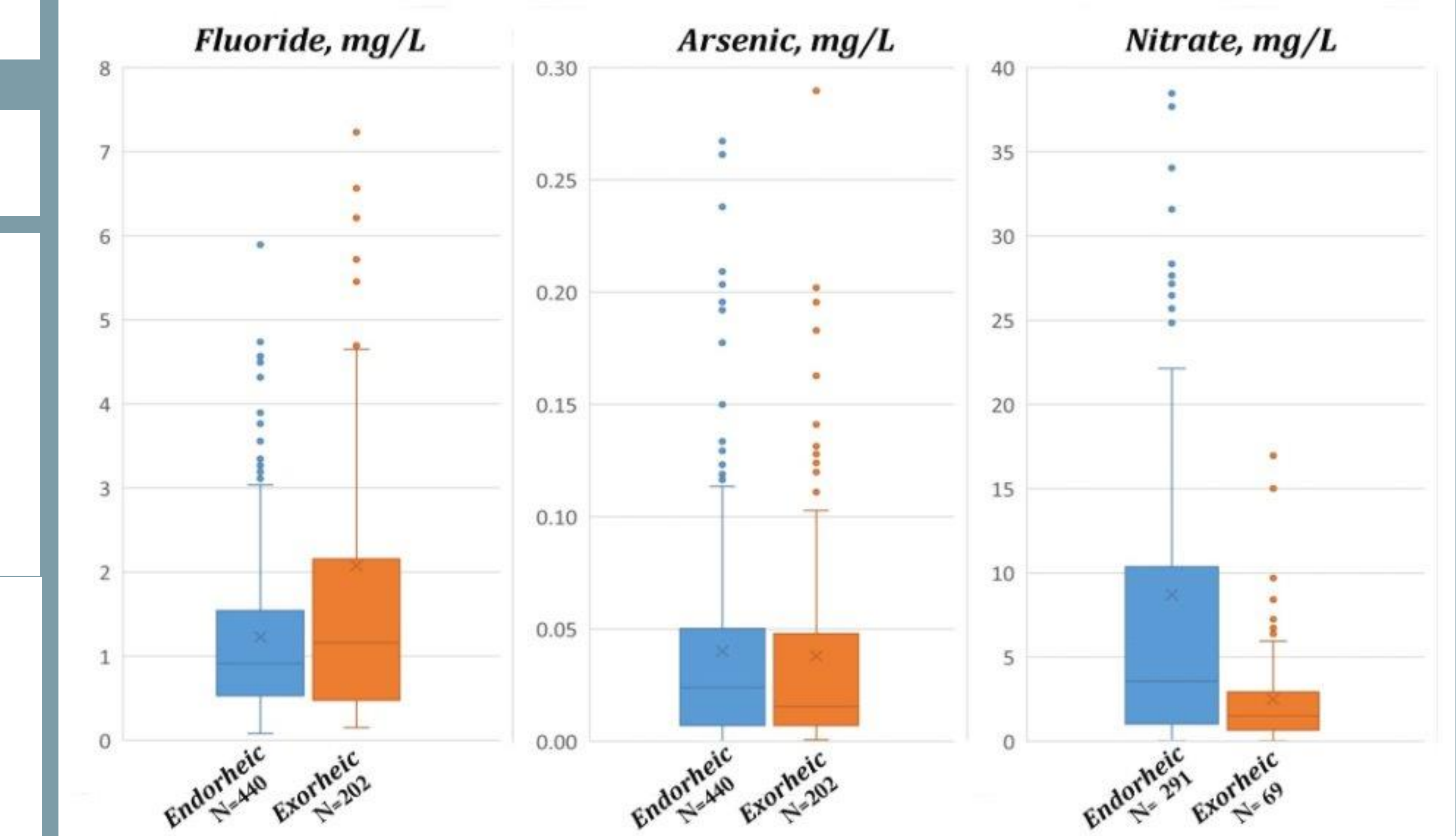
DATA SCARCITY CONSTRAINS

As seen in the concentration distribution map above, the official CONAGUA sampling points are less in some states (Chihuahua, Coahuila) whereas other states have many more data reported (e.g., Durango). This means that in Chihuahua, water quality of large regions are not represented while monitoring focuses in only a few sites, e.g., the cluster of data points in the southern part of the state correspond to an irrigation area.

OPEN vs. CLOSED BASINS



Above: Endorheic (orange) basins in northern Mexico occupy about half of the total surface area in each state. Below: Boxplot diagrams of F⁻, As (a co-occurring geogenic contaminant) and NO₃-N (anthropogenic contaminant) in each of endorheic and exorheic basins of northern Mexico.



SELECTED REFERENCES

Note studies are recent (2020+)

Northern Mexico

- Alarcón-Herrera et al. 2020. Co-occurrence, possible origin As, F in Mexico. *Sci. Tot. Environ.*
- Espino-Valdes et al. 2022. Relation of F concentration with well depth. *Environments*
- Gutiérrez et al. 2023. As, F in groundwater from northern Mexico. *Environ. Monit. Assessm.*
- Gutiérrez et al. 2022. Factores de concentración de As y F en norte de Mexico. *Tecnociencia*
- Morales et al. 2023. Controls of groundwater As and F in north central Mexico. *Minerals*

Other (USA and Global)

- McMahon et al. 2020. Groundwater fluoride in the U.S. *Sci. Tot. Environ.*
- Podgorsky and Berg, 2022. Global analysis and prediction of fluoride in groundwater, *Nature*