

Fluoride contamination in ground- and surface-water in La Aldea valley (Gran Canaria, Canary Islands, Spain): past and present.

Tatiana Cruz¹, Montserrat Espino-Mesa², Anetty Benavides¹, María del Carmen Cabrera¹, José Manuel Hernández-Moreno³

¹ Department of Physics, University of Las Palmas de Gran Canaria, Spain

² Area de Salud, Gran Canaria Island, Spain

³ Department of Soil Science and Geology, University of La Laguna, Spain

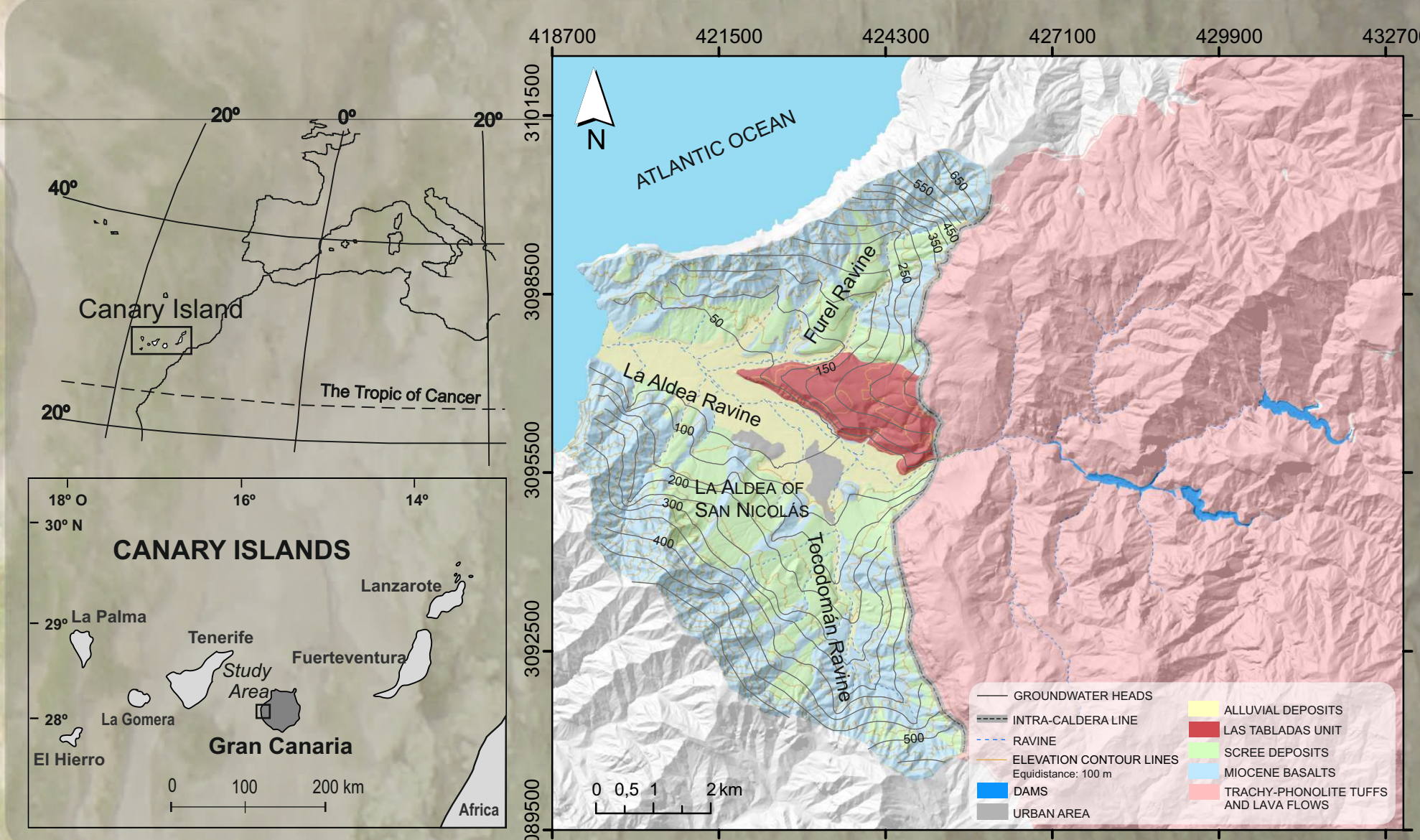
E-mail tcruz@becarios.ulpgc.es

INTRODUCTION

Dental fluorosis has had a high prevalence in some regions of the Canary Islands until the mid nineties when new water resources changed municipal water supplies. In these regions, large fluoride concentration in groundwater was associated with alkaline volcanism. One of these regions is La Aldea Valley, located on the coastal western side of the Gran Canaria Island. It is the lower part of a ravine where a sedimentary unit is located beneath a volcanic unit consisting of Miocene basalts. In this area, the major sources of drinking water were surface and groundwater. Earlier

studies in La Aldea valley were carried out to assess the possible causes for high concentration of fluoride in surface and groundwater. Samples from several types of water and soils were analyzed and indicated elevated concentrations of fluoride up to 4 mg/L.

LOCATION MAP AND GEOLOGICAL UNITS



MATERIALS & METHODS

Water samples from dams, wells, supply, return flows and irrigation water were collected in the months of June and September 2010, up to a total of 30 samples.

Groundwater geochemistry information of the aquifer was gathered from previous works. The spatial and temporal distributions of major ions in groundwater and in the different sources of recharge have been studied to better understand the geochemical conceptual model and the different sources of salinity.

Total analysis of rocks, tephra and soils, including fluoride, were performed by alkaline fusion. Water soluble fluoride concentration in the later was also determined by a batch method (1/10 solid/water ratio, 24 hours). Fluoride concentration was analyzed by selective electrode.

Solution chemistry and mineral equilibrium were studied with the Aquachem computer program.

Mineralogy of hydrothermally altered greenish tuffs called "Azulejos" was studied by X-Ray Diffraction and Scanning Electronic Microscope.

HYDROGEOLOGICAL & HYDROCHEMICAL

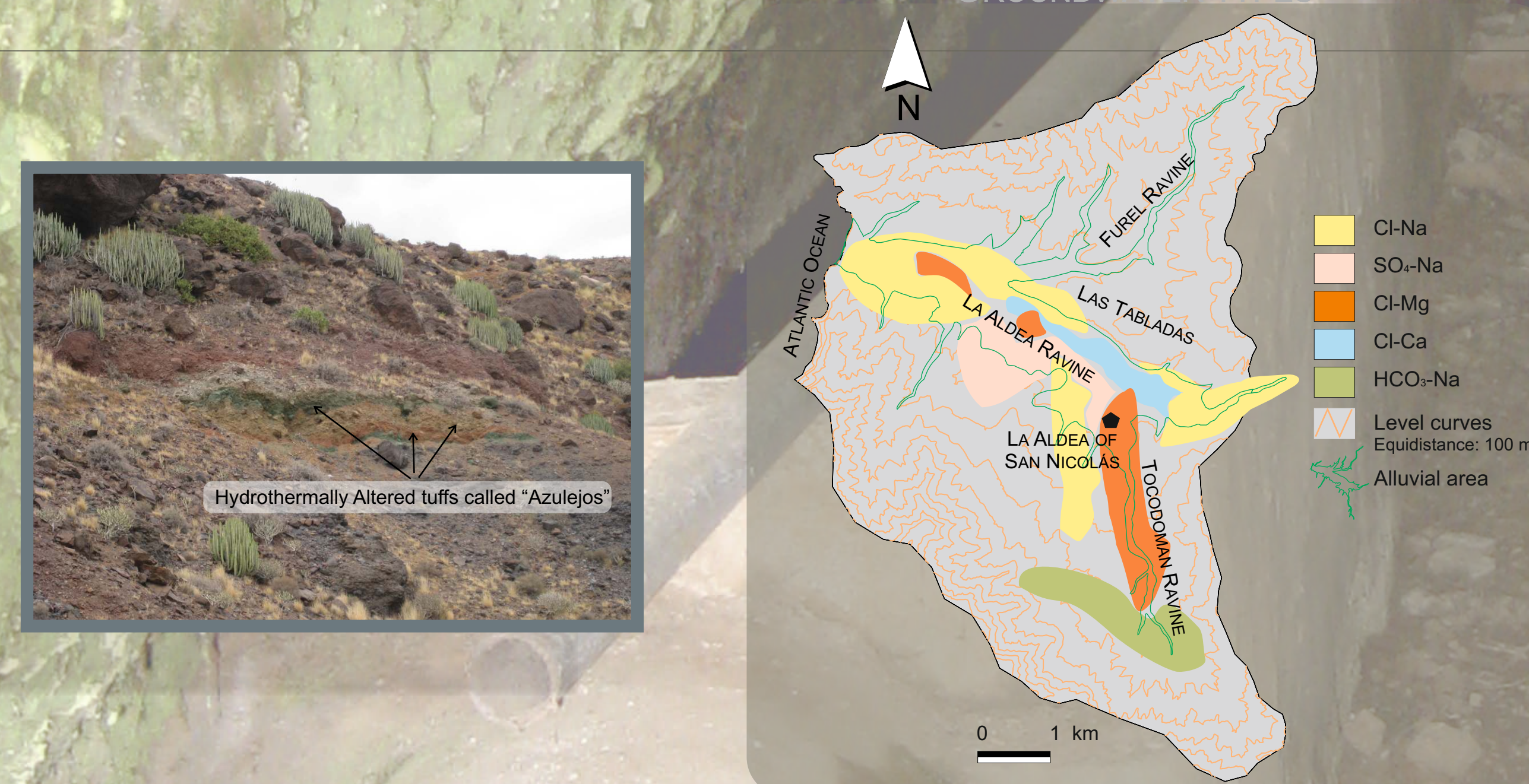
La Aldea aquifer is made up of sedimentary and volcanic materials. The sedimentary unit (consisting of detrital material with phonolites-trachytes, ignimbrites and basalts boulders) is located beneath a volcanic unit consisting of Miocene basalts. The eastern limit of the aquifer is constituted by a mechanic contact with a volcanic Miocene Tejada Caldera that was filled by rhyolite-trachyte and phonolitic tuffs. Hydrothermally altered tuffs crop up along the Tejada Caldera border locally named "Azulejos". There is a residual relief (Las Tabladas) in the study area with a complex geology, where interbedded landslide deposits of the aforementioned azulejos crop out.

The aquifer is unconfined and the alluvial deposits and the basalt rocks can be considered to be a single aquifer with two sub-layers: the upper alluvial deposits layer and the lower basalt layer with a lower permeability than the alluvial deposits. The flow has a main east to west direction in the La Aldea ravine, so La Aldea Valley represents a discharge area from the aquifer to the sea.

Meteoric infiltration (20%) and irrigation return flows (60%) recharge mainly the aquifer. Natural outflow occurs into the sea; artificial outflow occurs through intensive extraction of groundwater from wells.

Water flows from the basalts to the alluvial deposits. In general, there is agreement between the direction of groundwater flow and the increased ion concentrations attributed mainly to the aridification of the recharge and airborne salinity. Exploited groundwater shows mixed hydrogeochemical characteristics. Most groundwater is of the sodium-chloride type, which has been attributed to the aridification of the recharge and airborne salinity like the water of the calcium-chloride type. When the influence of marine aerosol is low (at higher altitudes and farther from the sea) the water is of the sodium-bicarbonate type. The exploitation of basalts produces water of the magnesium-chloride type and the influence of the irrigation return flows produces water of the sodium-sulphate type. The electrical conductivity of groundwater ranges from 837 μ S/cm in sodium-bicarbonate type water to 11370 μ S/cm in sodium-chloride type water.

GROUNDWATER TYPES



RESULTS

The fluoride concentration in groundwater of this region varied between 0.3 and 3.3 mg/L with a mean of 1.6 mg/L. 48% of the samples have high concentration of fluoride, i.e., above 1.5 mg/L. The concentration of fluoride in groundwater increased as the carbonate and bicarbonate content of water increased, and it decreased with decreasing calcium and magnesium content.

Overall, high pH, high carbonate plus bicarbonate, and low calcium plus magnesium in groundwater lead to leaching of fluoride, producing an increase in the concentration of fluoride in groundwater.

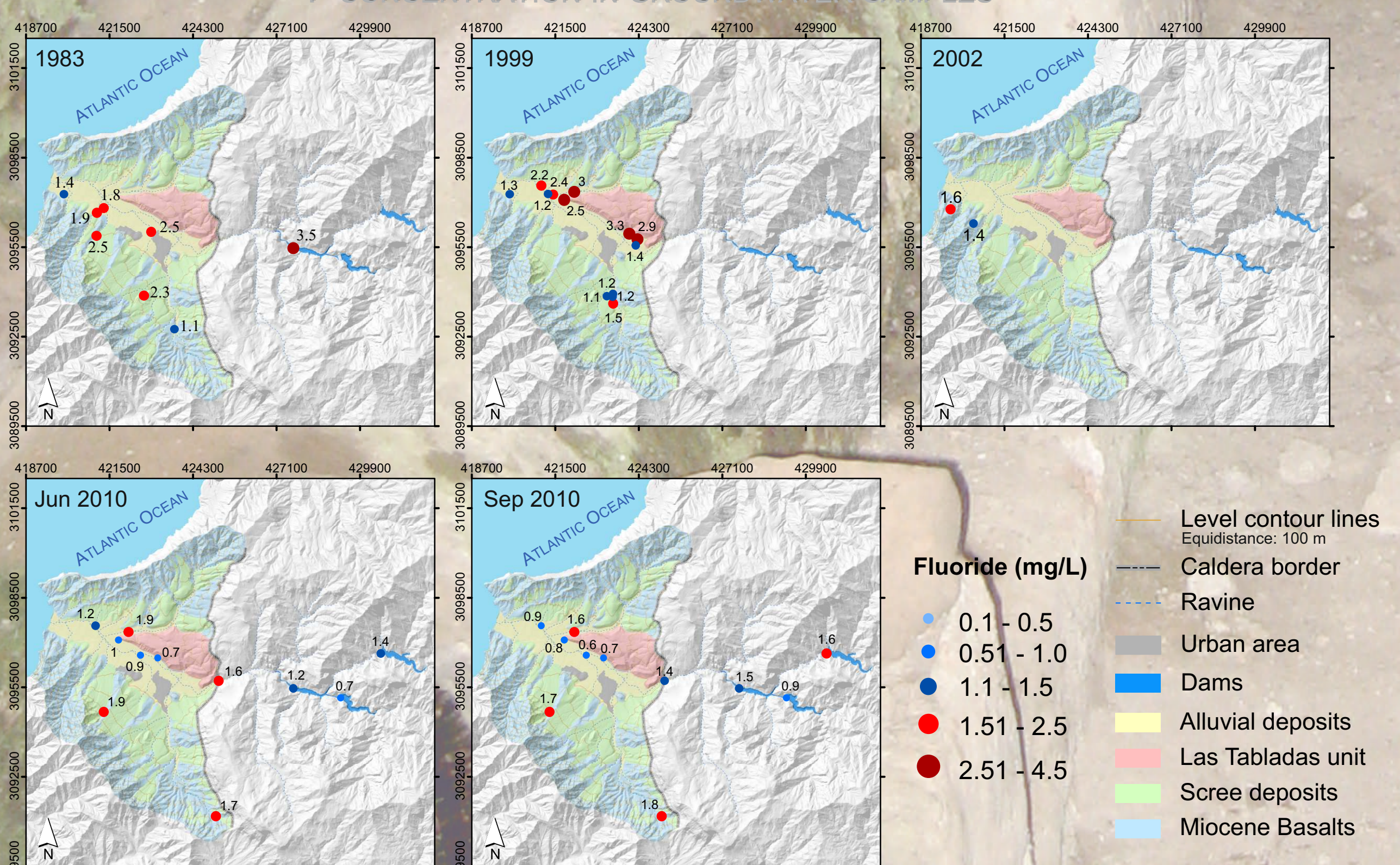
Currently, fluoride concentrations in dams are not as large as those obtained in 1983, however, values exceeding 1.5 mg/L have been observed. The intensity of evaporation cycles can probably have contributed to this result, thus in the years previous to 1983 the mean annual precipitation was lower than 100mm while in the 2010 preceding years precipitation was higher than 200 mm.

Total fluoride was largest in the hydrothermally altered greenish tuffs (1500-2900 mg/kg); in the consolidated rocks, the range was 400-750 mg/kg.

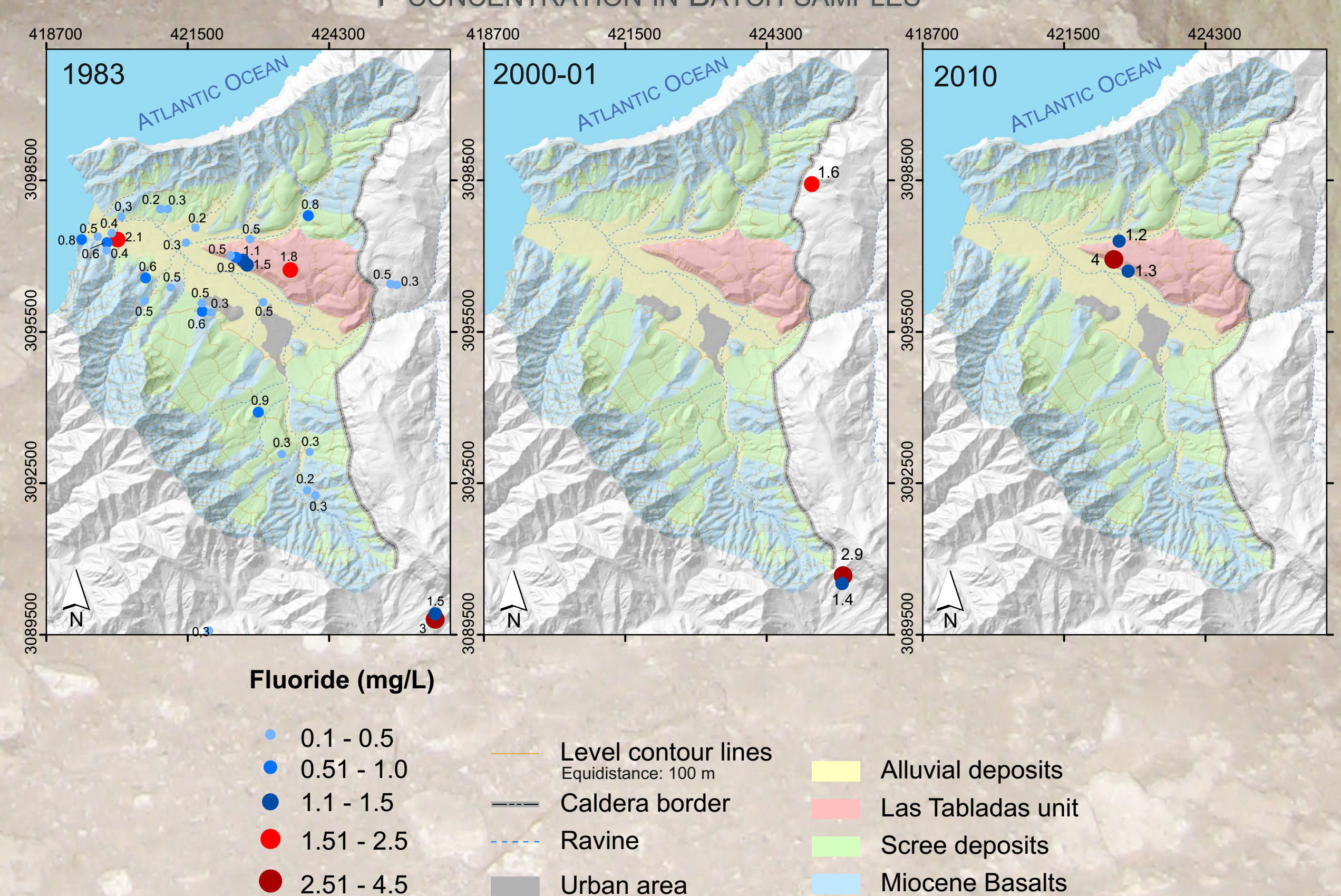
The highest concentrations of water-soluble fluoride were also found in the hydrothermally altered greenish tuffs (up to 4 mg/L). The greenish tuffs showed high surface area minerals such as mica (illite), smectite, and zeolites (analcime, clinoptilolite).

In 1983, municipal water for human consumption had concentrations in excess of 4 mg/L; nowadays, concentrations are lower than 0.1 mg/L. Currently, irrigation and return waters do not show high fluoride concentration because irrigation water is now a mixture of dam water and desalinated groundwater

F CONCENTRATION IN GROUNDWATER SAMPLES



F CONCENTRATION IN BATCH SAMPLES



CONCLUSIONS

In this region, the large fluoride concentration in groundwater seems to be mainly associated with alkaline volcanism. The hydrothermally altered tuffs present very high fluoride content. F-enriched gases could have been responsible of these large concentrations in the microcrystalline minerals.

Weathering of rocks, leaching of fluoride bearing minerals and evaporation of water are the major reasons which could have contributed to the elevated concentration of fluoride in groundwater, apart from anthropogenic activities, including irrigation.

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In 1983, water-rock interaction was probably the main reason for the high concentration of ions in groundwater increased by cyclic reuse of irrigation water. Nowadays, water reuse for irrigation does not occur due to the desalination of groundwater and this has reduced the concentration of fluoride in groundwater.

Acknowledgements

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