Uranium In Groundwater In The Sedimentary Aquifer Of The Eastern Sector Of Valle De La Cruz, Córdoba, Argentina

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Abstract— **Uranium has a extensive distribution in nature, in granite rocks and in various mineral deposits. The presence in the environment is due to leaching and circulation from natural deposits but also from anthropogenic emissions. The objective of this work is to establish the origin and processes that may explain the Uranium dissolved in surface water and groundwater. Also, the Uranium natural background range was estimated and anomalies were detected using statistical methodologies. The uranium values in groundwater resulted generally low. The most likely natural source of uranium in the region would be the minerals that make up the rocks located in the Comechingones Mountains which are checked out to contain uranium and those belonging to the loessic deposits that are present throughout the basin. It was statistically estimated that the range of natural background values of total uranium in surface water and groundwater is between 0.47 and 17.3 µg/L, with a characteristic value (percentile 0.5) of 8.1 µg/L. Although in surface water, the total uranium values are within the natural background range, some groundwater samples show little high values anomalies, some of which were linked to agriculture and especially concentrated livestock, being uranium correlated to nitrates. The highest U concentrations are linked to more oxidizing sectors and higher pH. The lowest values are located in the wetland area, where the geochemical environment is characterized by a lower pH and a high organic matter content, which makes possible the U retention/precipitation as a consequence of possible formation of U- complexes with carbonates or organic matter or adsorption on iron and/or manganese oxides. Taking into account that the Argentine Food Code does not establish the Uranium limit value for human consumption, the international guideline was used (reference level of 30 µg/L), finding that 80% of the samples are below the mentioned limit.**

Index Terms— **Uranium , hydrogeology, groundwater, geochemistry.**

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I. INTRODUCTION AND OBJECTIVE

Uranium has a widespread distribution in nature, in granite rocks and in various mineral deposits. The presence in the environment is due to leaching and circulation from natural deposits but also from emissions from the nuclear industry, coal combustion and other fuels and the wide use of phosphate fertilizers (1). Like nitrates, Uranium has high mobility in soils and sediments in oxidant environments, also having a high capacity to form soluble anionic complexes in the aqueous medium. The highest adsorption occurs in the 5 to 8 pH range with partition coefficients (Kd) up to 1,000,000 ml/g (2). For pH below 5, the adsorption is generally produced by clays (smectite, montmorillonite) and for pH greater than 7.5-8 by iron and aluminum hydroxides, although in this case the adsorption diminishes due to the increase in dissolved carbonate concentration and the decrease of U-carbonate complexes formation. Uranium may also suffer adsorption processes on iron and manganese oxides (1). The organic matter (OM) is a highly effective complexing agent of Uranium in natural waters, whether the OM is insoluble or adhered to particles like hydrated iron oxides.

 Drinking water may contain Uranium, either naturally or from anthropogenic activities, implying a health threat because exposure, even at low doses, can increase the incidence of cancer in the long term. Mammals in general have a high sensitivity to U since it tends to accumulate in the body, preferably in kidneys, liver, spleen and bones (1) Other authors have reported nephrotoxic impact and also consequences for other body parts (3). No Detrimental health effects are expected if the water contains concentrations lower than the reference level of 30 ug/L established by WHO (4)

The study area (Fig. 1) is El Barreal stream basin, located in the eastern part of the Valley of la Cruz, Córdoba, Argentina. It is a typical rural area dominated by agriculture (soybean-corn-wheat) with intensive use of fertilizers (5) and pesticides (especially glyphosate and atrazine). In very few sectors groundwater is used for irrigation activities. Also, groundwater from the unconfined aquifer is used for all the extensive/intensive livestock endeavors and also for domestic and industrial activities. In the central sector of the basin an old tannery spills its effluents into a wetland which is drained by El Barreal stream. The only urbanized area is Elena town where 3,000 inhabitants live, which also use groundwater.

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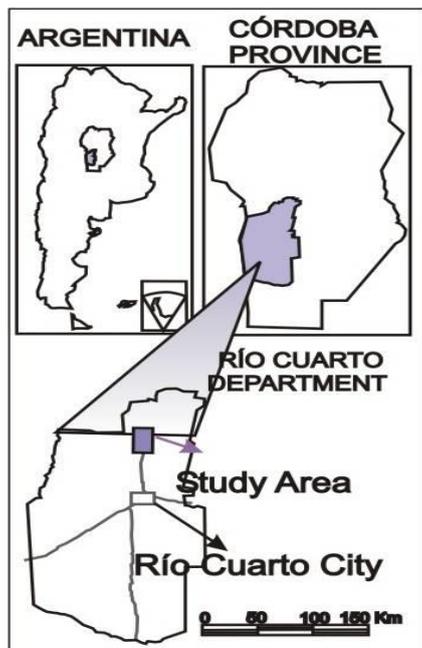

Fig 1. Location of the study area.

In this framework, the objective of this work is to determine the origin and processes that may explain the Uranium dissolved in surface water and groundwater, estimating the Uranium natural background values and detecting anomalies using statistical methodologies.

II. METHODOLOGY

The research was carried out at a scale 1:50,000 based on the analysis and compilation of satellite images (Google Earth, LANDSAT ETM +) and topographic charts from the National Geographic Institute (IGN). Background information (geological, geomorphological, climatic, etc.) of the study area was collected and analyzed (6). The precipitation data was analyzed and interpreted using a local 42 years series (1975-2017). Information about underground lithological profiles (approximately 200 m deep) taken from regional drillings was collected and interpreted. The sediment samples from boreholes were subjected to textural analysis (ASTM sieves, Udden-Wendworth scale), obtaining the histograms with percentages of the different granulometries. The obtained information was interpreted and used for the elaboration of the hydrogeological profiles.

The hydrogeological study was based on a survey of wells that extract water from the upper part (10-15 m) of the unconfined aquifer. Information related to lithology and wells was collected (screens longitude, diameter and depth, flow rates, water level drawdown and so on). In addition, the water table depths were measured with a Solinst piezometric probe. For the hydrodynamic analysis, the maps of spatial variation of hydraulic potentials and the water table depth were prepared and interpreted. Fourty three (43) water samples were collected from wells and ten (10) were taken from surface water bodies in different sites of the El Barreal stream, in the tannery effluent and finally, in the wetland where the effluent discharges.

The water temperature (T), the electrical conductivity (EC), the dissolved oxygen (DO) and pH were measured in situ with a Hanna multiparametric probe, which was calibrated using standardized solutions. For the groundwater sampling, the water renewal was guaranteed in each well, allowing a minimum of 3 well volumes to flow out. The samples were correctly conditioned (filtered at 0.45 μm and acidified with nitric acid until a pH <2 when necessary) packed in high density plastic bottles, refrigerated at 4ºC and transported to the laboratory for the analysis. The physico-chemical analysis, following Standard Methods (7) were carried out to the Geochemistry Laboratory of the Department of Geology of the National University of Río Cuarto (UNRC). The following ions and compounds were measured: carbonates (CO_3^{-2}) and bicarbonates (HCO_3^-), by titration with Orion-Thermo selective electrode; sulfates (SO_4^{-2}) by turbidimetry (with Macrotronic centrifuge); chlorides (Cl^-) by volumetric titration with silver nitrate, calcium (Ca^{2+}) and magnesium (Mg^{2+}) by titration with EDTA and sodium (Na^+) and potassium (K^+) by flame photometry (Metrolab 315 digital photometer). In all cases, the error of the chemical analysis was < 10%. In all the water samples and in two sediment samples (extracted from representative eolian and fluvial deposits in local drillings) (Figure 1), uranium values were determined by inductively coupled plasma mass spectrometry (ICP-MS) in an external laboratory (ActLabs - Canada). For the estimation on the natural background of dissolved Uranium in water, the statistical method of Walter (8) was used.

III. GENERAL CLIMATIC AND GEOLOGICAL CHARACTERISTICS

The regional climate is of mesothermal sub-humid-dry type with little to no water excess. The distribution of the precipitations exhibits a very marked seasonality, with a concentration of 75 % from November to March (spring-summer), with an average precipitation of 835 mm. The estimated recharge to the unconfined aquifer is approximately 40 mm/year and 50 mm/year for the slope of the Peñas and Comechingones mountains, respectively (9).

The Valley of La Cruz is a tectonic depression between the Comechingones Mountains (predominantly formed by metagraywacke rocks) and Las Peñas Mountains (predominantly formed by meso siliceous and acidic igneous rocks), Fig. 2. The outcropping rocks in Las Peñas Mountains are schistose granites, orthoanfibolites, gneisses and gabbros (10). In the Comechingones Mountains the rocks are migmatites, amphibolites, granulites and granitic bodies, some of batholitic dimensions (11). The valley is filled with loesical sediments partially cemented with carbonates which are interlayered at different depths by sandy to gravel layers, corresponding to paleo-channels that came from the peripheral mountains. The strong structural control has generated different raised and tilted blocks shaped in the Upper-Holocene Pleistocene. The loess deposits of the Pampean region are characterized by a mineralogy formed by 50 to 80% of volcanic glass, quartz, plagioclase, potassium feldspar, biotite, amphiboles, pyroxenes, opaque, zircón, garnet, calcite (13).

In the general landscape the "Central Fluvial Strip Depression" (Fig. 3) may be highlighted, where an outcrop of groundwater occurs forming a wetland that gives origin to El Barreal stream, which flows from North to South.
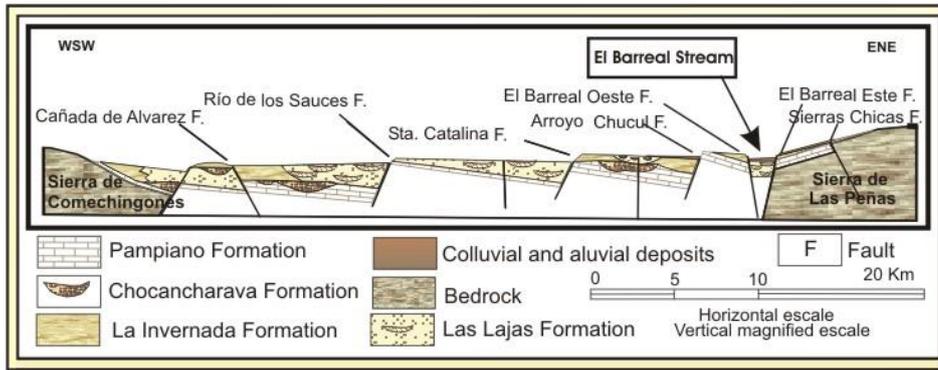
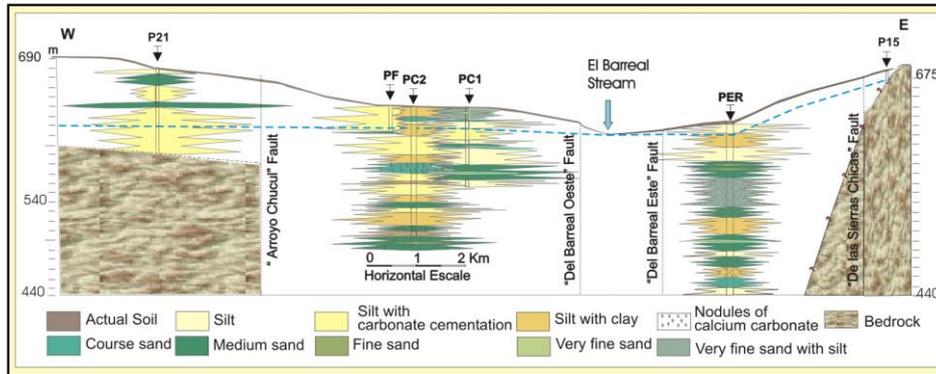Fig. 2. De La Cruz Valley Geological section. Modified from Degiovanni and Cantú (1997) (12).

Fig 3. Hydrogeological profile

IV. HYDROGEOLOGY

The unconfined aquifer has a variable thickness, from a few meters to almost 100 m, mainly because the sedimentary thickness is conditioned by the depth of the bedrock.

It exhibits a dominance of very fine sediments of eolian origin (with carbonate cementation) interlayered with thin strata of fluvial origin. The water table level is between 0 and 80 m and the groundwater flows centripetally towards the central depression of the basin feeding the stream (Fig. 4). The groundwater velocities are in the order of 0.50 m/d on the slope related to the Comechingones Mountains (right margin of El Barreal stream) and 0.75 m/d on the slope of Las Peñas Mountains (left margin). The groundwater electrical conductivity varies from 670 μS/cm to 9,300 μS/cm and the dominant geochemical types are sodium bicarbonate to sodium sulfate-bicarbonate, with pH from 7.4 to 8.9 (Fig. 5) (9).

V. URANIUM IN GROUNDWATER

Based on the hydrogeological results, it was tried to establish the possible linkage of groundwater uranium concentrations from a natural origin with the mineralogy of regional sediments or rocks:

1) the loess deposits of the Pampean region 2) the outcropping rocks in the Las Peñas Mountains and 3) tthe outcropping rocks in Comechingones Mountains.

In this regard, Pinotti (14) determines U concentrations up to 3.4 ppm in the Cerro Aspero Batholith, to the west of the studied zone, and Nicolli et al. (15) up to 3.2 ppm of U in the volcanic glass found in the loessical deposits of Santa Fe province, similar to the loess of the studied area. In the present study, the geochemical analysis were carried out for the fraction < 125 μm in the sediments taken from the unconfined aquifer. U concentrations up to 10 ppm were
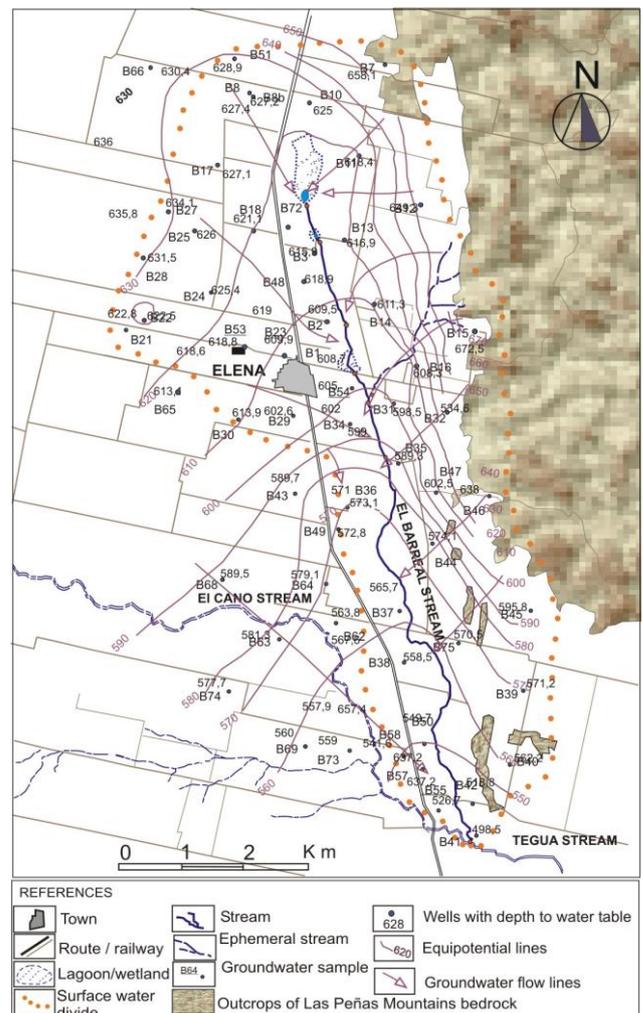

Fig 4. Equipotential map for the unconfined aquifer.

measured in materials of fluvial origin (sediments from the Sierra de Comechingones) and up to 2.4 ppm in local loess sediments. There are still no known geochemical studies showing the presence of U concentrations in minerals of Las Peñas Mountains.

A very good correlation was found between U and sodium bicarbonate waters (r = 0.86) and also with vanadium (R = 0.87, Fig. 7) another chemical element typical of groundwater from loess sediments (15).
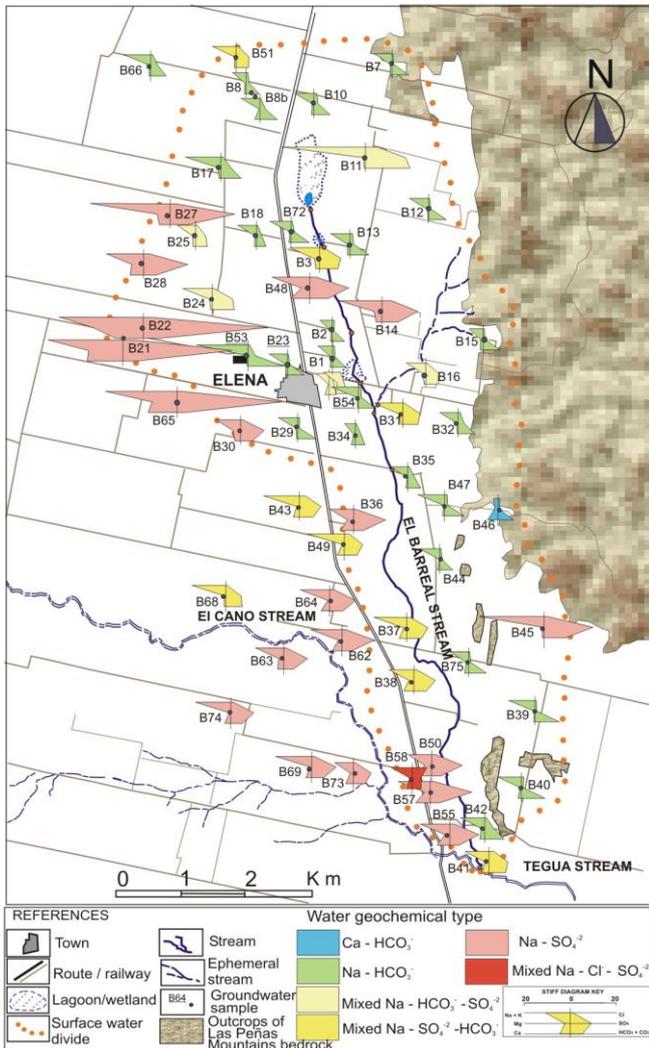

Fig 5. Groundwater geochemical types for the unconfined aquifer

Fig. 6. Relationships between Uranium values and a) stream margins, to interpret provenance b) land uses

The measured Uranium values are between 1.3 and 12.5 µg/L in surface water and between 8.8 and 97 µg/L in groundwater, ranges that match those determined by other authors in groundwater from loess and alluvial unconfined aquifers (16), (17), (18), (19).

In order to establish the existence of a possible predominance of U in the groundwater flow coming from the Las Peñas or Comechingones Mountains, box plots (Fig. 6 a) were made for the groundwater samples pertaining to both margins of the stream. Although the median value is similar, it was observed that the greatest dispersion and the highest concentrations are associated to the flow coming from the Las Peñas Mountains (left margin), although the Uranium values may be linked to the local aquifer sediments and not only to the mountains. In the box plots that link U values with land uses (Fig 6b) the higher median was found for that sites where agriculture and livestock were the dominant uses, although outliers were related to agriculture or livestock as unique activities.
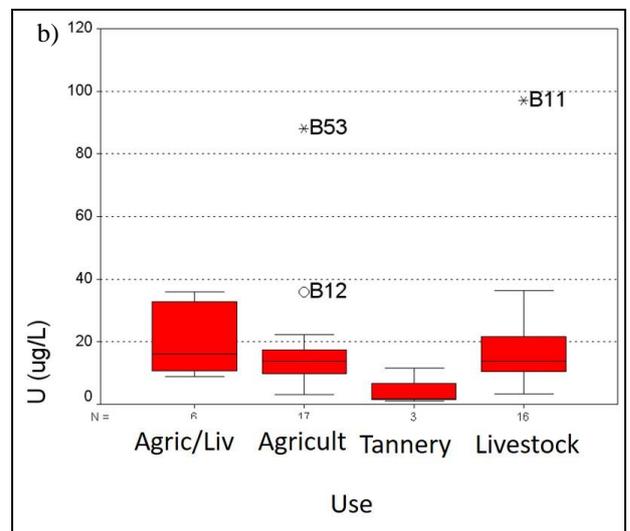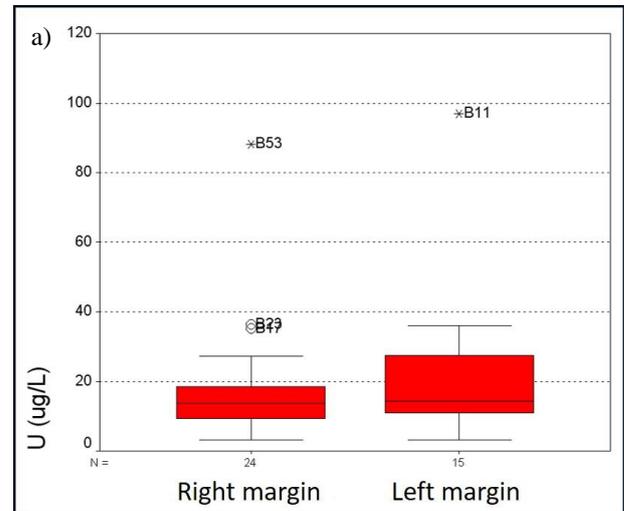
Taking into account the regional activities and being the Uranium a chemical element that, in addition to appearing naturally, may have an anthropic origin, the natural background values and possible anomalies were estimated.
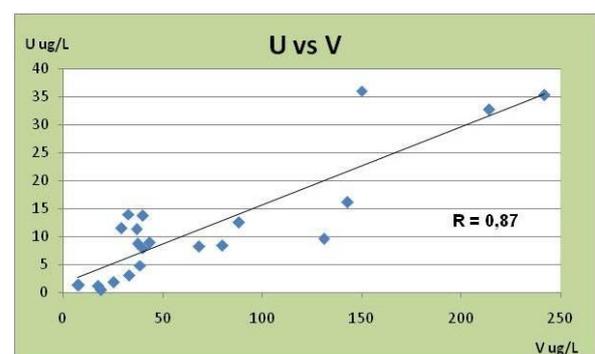

Fig 7. U vs. V

Following the Walter (8) method and taking into consideration the lognormal probabilistic distribution that the values showed, the anomalous data were discarded, as the method suggests, considering that the anomalous values are those that could derive from pollution. Thus, a natural uranium range of 0.47 to 17.3 ug/L was obtained with a characteristic natural background value (0.5 percentile) of 8.1 µg/L (Fig. 8) similar to background values of 0.1 to 10 µg/L mentioned in the scientific literature (20). The values considered anomalies are all those above the mentioned natural range. From the total groundwater samples 70 % showed values lower than 17.3 µg / L, while in the stream all the U concentrations are also part of the natural background range.
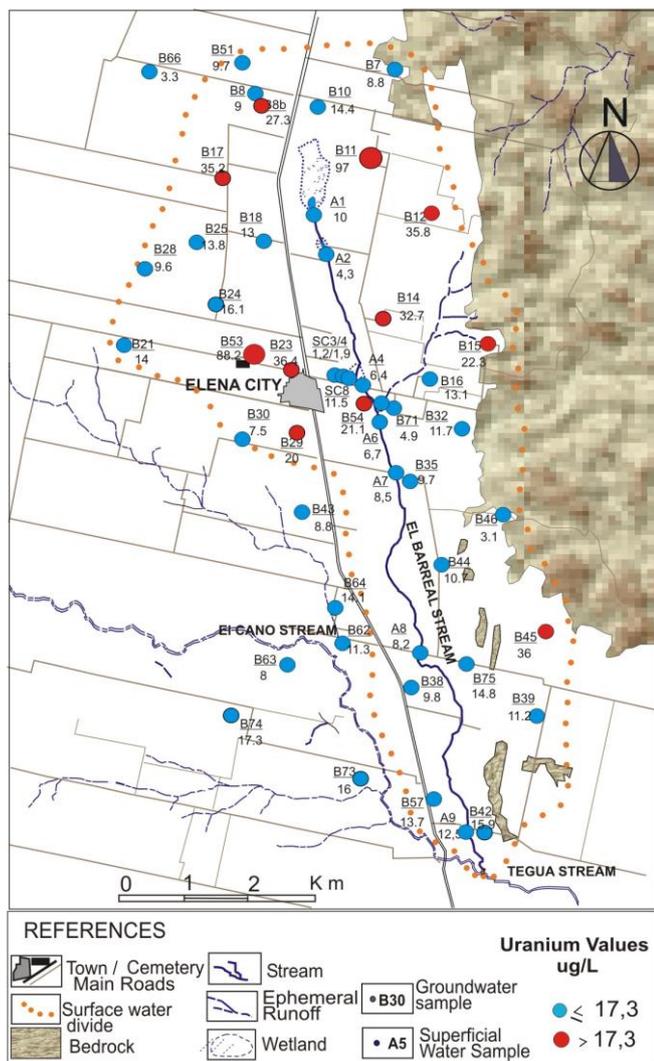

Fig. 8. Uranium values in groundwater and surface water taking into account the estimated threshold of the natural background value.

In those samples taken from wells located in farms, where agriculture with fertilizers is being carried out, a high correlation (r = 0.9) was found between U and NO3-, being the latter a typical pollution indicator. According to (21), in major aquifers of the United States the Uranium values in groundwater were moderately to strongly correlated with high nitrate levels, suggesting a link between nitrate and uranium contamination. After oxidation by nitrate, U

solubility by oxidative dissolution of reduced U (IV) minerals may be altered, allowing uranium to form chemical complexes with carbonate and calcium ions in groundwater, which allows it to move through the soil column and into the groundwater. Also, Nolan and Weber, (21) states that the nitrate reduction coupled to the oxidation of organic matter (for example from animal wastes) can generate alkalinity, mobilizing U (VI).

Also, the international literature indicates that P fertilizers may contain considerable amounts of U which range from less than 10 to more than 360 mg kg-1, depending on the origin of the phosphate rock from which they were produced (22), (23). Kratz y Schnug, (24) found mean concentrations between 6 and 149 mg/kg U in P containing mineral fertilizers, while mean concentrations in mineral fertilizers without P were below 1.3 mg/kg U. In Smid (25) to test the hypothesized fertiliser-derived U leaching to groundwater, samples from different depths were taken in an area intensively used for cropping production in Lower Saxony. The correlation between fertiliser-derived nitrate (NO3-) and U especially in shallow (< 15 m) groundwater samples indicates the anthropogenic origin of U. However, the aouthor indicates that there is not yet a clear picture of quantities and processes of U leaching from fertilised soils into groundwater.

In the studied area the highest U concentrations correspond to groundwater samples obtained from wells located in the Elena cemetery (88 µg/L) and in a farm with a feed lot of pigs and cowns (97 µg/L), both corresponding to aerobic environments (5 mg/L of dissolved oxygen) and basic pH (8.1 and 8.6). The remaining anomalies, although they are minor (17 to 36 µg/L), also correspond to livestock sites and could be due to the bioaccumulation in slurries that can percolate and reach the aquifer. In wells located in the wetland, with pH <8, where high organic matter contents and carbonate precipitates, the lowest U groundwater values were determined (1.2 -1.9 µg/L). However, in another well with pH> 8 the concentration increases (11.5 µg/L), denoting the importance of the pH in the U disolution.

VI. CONCLUSIONS

Taking into consideration the measured Uranium values, it could be established that the presence of U in groundwater and surface water does not represent a significant threat to the people. Thus, this type of studies is relevant to assess the current water resource state, acquiring significance from the environmental point of view as natural background values to be considered and monitored in future investigations.

The uranium content found in groundwater is generally low, similar to that measured by other authors in similar sedimentary aquifers. There is no evidence of a noticeable predominance in the typical concentrations (median value) that can be associated with the water flow coming from the Comechingones Mountains or from the Las Peñas Mountains that border the studied valley. However, the most likely natural source of uranium in the region would be the minerals that make up the rocks located in the Comechingones Mountains which are checked out to contain uranium and those belonging to the loessic deposits that are present throughout the basin.

It was statistically estimated that the range of natural

background values of total uranium in surface water and groundwater in the studied basin is between 0.47 and 17.3 µg / L, with a characteristic value (percentile 0.5) of 8.1 µg / L. The most of the water samples analyzed (70%) are within the estimated range.

Although in surface water, the total uranium values are within the natural background range, some groundwater samples show little high values anomalies, some of which were linked to agriculture and especially concentrated livestock, being uranium correlated to nitrates. The highest U concentrations are linked to more oxidizing sectors and higher pH. The lowest concentrations are located in the wetland area, where the geochemical environment is characterized by a lower pH and a high organic matter content, which makes possible the U retention/precipitation as a consequence of possible formation of U- complexes with carbonates or organic matter or adsorption on iron and/or manganese oxides.

Taking into account that the Argentine Food Code does not establish the Uranium limit value for human consumption, the international guideline was used (reference level of 30 µg/L), finding that 80% of the samples are below the mentioned limit.

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