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Hydrogeological features affecting spatial distribution of glyphosate and AMPA in groundwater and surface water in an agroecosystem. Córdoba, Argentina

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Abstract

The study area is located in the eastern slope of Las Peñas Mountain and its adjacent oriental fluvio-aeolian-plain. Agriculture is the main activity (soybean, maize, wheat, peanuts and alfalfa) with no-tillage farming and intensive use of agrochemicals (pesticides-fertilizers). Glyphosate (N-phosphono-methylglycine) is the most common used herbicide which suffers microbial biodegradation giving aminomethylphosphonic acid (AMPA), its main metabolite. The objective of this work is to evaluate hydrogeological features which influence the presence of glyphosate and AMPA in waters. In the study area, the main flow direction of surface and groundwater is NW-SE. The unsaturated zone thickness decreases in the same direction from 60 to 0 m, so groundwater surges in low areas in the eastern sector. From the total water samples collected, glyphosate was detected in 66% of surface water samples (0.2 to 167.4 μg/L), in 15.8% of the groundwater samples (1.3 to 2 μg/L) and in the harvested precipitation sample (0.2 μg/L). AMPA was found in 33% of surface water and 15.8% of groundwater. The herbicide detection was related to areas with the shallowest water table (< 4 m), low hydraulic conductivity in the aquifer (K= 1.5 m/d), low hydraulic gradient (i= 0.16%) and very low flow velocity (0.02 m/d). The most outstanding result is that the groundwater presents higher values in comparison with the surface water samples, which can be explained by the greater dilution capacity of streams. The detection of glyphosate and AMPA in the unconfined aquifer shows that the application for decades under the prevailing agricultural model exceeds the degradation potential of the soil and the unsaturated zone, causing groundwater contamination.

Keywords: Hydrogeological features, groundwater pollution; Glyphosate-AMPA; Córdoba (Argentina).

1 Introduction

The global increase in crop production has been achieved mainly through the intensive use of agricultural chemicals such as pesticides and fertilizers. The trend has been amplified by the expansion of agricultural land, the introduction of new crop varieties and a more intensive use of agrochemicals and agro technologies, while also transferring agricultural pollution to water (Mateo-Sagasta et al., 2017, Giuliano Albo et al., 2015, Giliuano Albo et al., 2019). The resultant water pollution presents demonstrated risks to aquatic ecosystems, human health and productive activities (UNEP, 2016).

Glyphosate (N-Phosphonomethyl glycine) is a post-emergent, non-selective, broad-spectrum herbicide used extensively and intensively to control most annual and perennial weeds in genetically modified glyphosate-resistant crops (RR crops), mainly in transgenic corn and soybean crops. Glyphosate has high solubility in water, a low octanol/water partition coefficient (Kow), and a high organic carbon partition coefficient (Koc) (Mayer et al., 2006). It is considered to have low mobility in soils because sorption is generally high (Okada et al. 2016; Gomez Ortiz et al. 2017; Maqueda et al. 2017).

Glyphosate undergoes microbial degradation in the soil, in aquatic sediments and water, a process which gives as a result its main metabolite, aminomethylphosphonic acid (AMPA) which is also water soluble and degrades more slowly than glyphosate (Grunewald *et al*.,2001). In 2015 the International Agency for Research on Cancer classified glyphosate as a probable human carcinogen, creating public concern about its presence in the environment (Guyton et al., 2015).

Argentina ranks third in the world in the use of herbicides (Pretty and Bharucha, 2015), with 240,000 tons of Glyphosate sprayed in 2013 alone (Avila-Vazquez and Difilippo, 2016). Currently glyphosate based herbicides represent 64% of total herbicides sales in Argentina and for transgenic soybean cultivation, they represent 76% of the total package of chemical used products (FAO, 2019).

The surface water in agricultural areas is more susceptible to agrochemical contamination through surface run-off, by direct overspray and spray drift. The study of Battaglin et al. (2014) has detected glyphosate in 52.2% of the total stream samples, in 70.9% of ditches and drains and in 33.7% of lakes, ponds and wetlands, with a maximum of 427μg/L in ditches and drains. Moreover, AMPA was detected in 71.6%, 80.7% and in 29.8% for each system respectively with a maximum of 0.43 μg/L. In Argentina, Aparicio et al. (2013); Lupi et al. (2015) and Primost et al. (2017) have detected glyphosate and AMPA in surface waters in a range between 0.5 and 7.6 μg/L.

Groundwater pollution with herbicides is generally lower in groundwater than in surface water due to degradation in the unsaturated zone (Mueller and Senseman, 2015). Nevertheless, several studies have demonstrated the potential for leaching and vertical transport to groundwater (Lupi et al., 2015, Grondona et al., 2014, Aparicio et al., 2015, Okada et al., 2016, Pang et al., 2000, Labite et al., 2013). In this sense, the hypothesis that soil is an effective defense against contamination by pesticides often does not work (Costa et al., 2011). In Cataluña (Spain), Sanchis et al. (2012) analyze glyphosate in groundwater confirming that, despite the low mobility of this compound, the herbicide is capable of migrating towards the unconfined aquifer. In Argentina, Okada et al. (2018) have detected glyphosate and AMPA in 24% and 33% of the groundwater samples, with maximum concentration of 8.5 and 1.9 µg/L respectively. On a large scale, in Ireland, McManus et al. (2017) detected the highest frequency of occurrence of pesticides and their metabolites in groundwater present in high permeable sands and gravels as well as in shallow piezometers in poorly drained areas.

Alonso et al. (2018) have detected glyphosate and AMPA in more than 80% of rainwater samples, obtained from the Pampa region in Argentina, in concentrations from 1.24 to 67.3 µg/L and from 0.75 to 7.91 µg/L respectively. Glyphosate and AMPA were also detected in atmospheric dust, mainly in the finest particles of loess (8-18 µm), a situation which contributes to human exposure by inhalation (Bento et al., 2017; Aparicio et al., 2018; Mendez et al., 2017).

Córdoba Province is part of the country's highest soybean productivity area, being in the second place of annual production in the national campaign 2018/2019 according to BCR (2019), with a total estimate of 16.42 millions of tons produced. Groundwater is a vital water resource for human consumption, irrigation and cattle intake in the study area. Therefore, it is very important to evaluate the natural chemical composition and those changes derived from agricultural contamination sources to outline the quality degradation that may interfere with water uses and to explain environmental regional processes. The main general hypothesis is that, for similar land uses, the hydrogeological features condition the fate of herbicides which degrade the natural water quality. Therefore, the aim of this research is to determinate the main geological and hydrogeological features that contribute to the presence of glyphosate and AMPA in surface water and groundwater in an agricultural area producing soybean as leading crop.

2. Description of study area

2.1. Location, geology and climate

Located in the center of Córdoba province (Argentina), the research area covers 3,047 km^2 (Fig. 1). It comprises the piedmont of Las Peñas Mountains and an extended plain area with great geomorphological, stratigraphic and hydrodynamic peculiarities (Blarasin et al., 2014).

Fig. 1: Location of study area, water samples and hydrogeological profiles

Las Peñas Mountains, part of the Pampean Mountains, are made up of a typical bedrock of Precambrian - Lower Paleozoic age outcrops, formed by igneous-metamorphic complexes of granitoids, gneisses, schists, migmatites, amphibolites, quartzites, granulites and calcareous dolomite intercalations (Demichelis et al., 2004). The general configuration of the bedrock towards the oriental plain is a set of gradually descending blocks that act as the base of the sedimentary filling.

The Pampean Plain constitutes a great flat area that has received sediments since the Miocene, from the Andean Mountains uplift, and currently constitutes the pathway of these sediments towards the Atlantic shelf and continental slope (Chebli et al., 1999). The Pampean plain is a semi stable part of the cortical crust with a negative tendency. It is an area where thick continental and marine sedimentary sequences have accumulated from the Cambro-Ordovician period to the present.

In the study area, the piedmont sector is characterized by a smoothly undulating relief, with topographic gradients from 1.3% to 0.6%. The sedimentary materials correspond to Quaternary alluvial sequences of very fine sands with dispersed gravels and loess deposits covering the entire area. The active processes of water erosion (rills and gullies) as well as soil degradation by aeolian processes are significant. To the NE, the alluvial fan of the Ctalamochita River is recognized. It is one of the various great alluvial fans generated during Quaternary periods in this region, with a softy undulated relief and typical topographic gradients from 0.5% to 0.2%. It is formed mainly by coarse sediments like gravels and coarse, medium and fine sands, towards the oriental plain become more typical silty sand materials (Carignano et al. 2014). The soils in this area are in general Typic Ustorthents with sandy texture and 1% of organic matter (OM) content. To the SE, a typical aeolian plain is present with topographic gradients from 0.2% to 0.1%. This geomorphological environment is characterized by a poor drainage and discontinuous fluvial and aeolian paleo-features, where ephemeral or permanent small lwater bodies are installed. This drainage pattern, regionally called “spider like” drainage (Cantú and Degiovanni, 1984), is structurally controlled and presents a central depression and branches with different directions, filled with water. Processes such as flooding become more relevant in the flatter areas. Entic Haplustolls and Typic Natracualf soils predominate in this area, with silty texture (loess) and OM content from 1.7 to 1.9%.

The climate in this region is subhumid, characterized by a mean temperature of 16.5 °C and an average annual precipitation of 791.6 mm. Seventy one percent (71%) of the precipitation is concentrated during the spring-summer period, between September and February.

2.2. Land use and agricultural management

The urban area occupies 0.04% of the total study region, with 14 settlements, towns or small cities, being Hernando city the most populated with 17,843 inhabitants according to the 2012 INDEC (National Institute of Statistics and Population) survey.

The land use is mainly defined by agriculture activities, with soybean,maize, wheat, sorghum and peanut cultivation in order of importance, with no tillage practice and a high use of agrochemicals. Horticulture is scarce and concentrated in peripheral areas of the small towns. Although extensive cattle breeding is practiced, the livestock activity is mainly concentrated in feed lots of cows and pigs. Dairy farms are also important, being the zone located within the “Villa María dairy basin” one of the most important of the country.

The most common glyphosate formulations reported by the regional farmers were glyphosate potassium salt (at 53 and 66.2% w/v) and glyphosate-monoammonium salt (36% w/v).The reported doses are 1.8 to 3.0 L/ha (liquid) or 1.5 to 1.8 kg/ha (solid). The agronomic calendar comprises mainly summer crops, like soybean and maize (both transgenic, RR crops). The seeding time takes place between October and December, with post-emergent glyphosate application during November, December and January in most of the surveyed farms. The harvest period covers the months of March, April and May, according to climate parameters such as rainfalls and temperatures as well as particular agronomical management in each farm. To replace conventional tillage methods for weed control, most farmers apply glyphosate from April to August during fallow time. This management framework suggests that there are a few months during which glyphosate is not applied. Therefore, in a regional scale, almost always, a field under pulverization can be found, either for application to crops or in fallow season. Figure 2 shows the rainfall values and temporal distribution along with the glyphosate application time.

Figure 2: Monthly average rainfall and application of glyphosate based herbicides.

3 Methods

The research was based on the compilation and analysis of topographic charts from the National Geographic Institute (IGN) at 1:50,000 scale and satellite images (Google Earth, Landsat ETM).

Background information (geological, geomorphological, climatic, etc.) of the study area was collected and analyzed (Degiovanni et al. 2005; Carignano et al. 2014, Blarasin et al. 2014).

The precipitation record was analyzed and interpreted using as representative, a local series from 1921 to 2017. The rainwater station belongs to the Agricultural Cooperative "La Vencedora" and is located in Hernando city (See figure 1: Town: Hernando). The series was selected taking into account the location of the station, the high direct correlation (r=0.99) with values belonging to other 5 surrounding precipitation stations and the length of the covered period.

The geological and geomorphological study was performed through the description of the relief and lithological outcropping profiles during field surveys. Also information from vertical electric sounding (VES) and from drilling samples from the Secretary of Water Resources of Cordoba province was considered.

The hydrogeological data were obtained through a survey of 74 wells which penetrate the upper 15-50 m of the unconfined sedimentary aquifer. The water table depth was measured using an electric piezometric probe (Solinst 101-P2). The surface water samples correspond to 3 streams, 2 ponds and 1 ditch. The sampling was carried out in November 2017 (spring season) during a 3 day field campaign.

For the hydrogeochemical characterization and Glyphosate + AMPA analysis, 19 samples were selected according to spatial representativeness and accessibility criterion. In each sampled site, water parameters were measured in situ: pH, electrical conductivity (EC) and temperature (T) using a multiparametric portable probe with GPS (Hanna HI 9829). The samples were collected with polypropylene bottles that had been rinsed three times with the pumped water before taking the sample. Upon arrival to the laboratory, water samples were conditioned and measured. The rain water is a sample harvested for one year in the south of Tancacha town, where the groundwater is not suitable for human consumption. Some local farmers collect the rainfall from the roof of houses and then store it in cisterns.

The water samples were analyzed using Standard Methods (APHA et al. 2005) in the laboratory of the National University of Rio Cuarto. Carbonates and bicarbonates were measured by titration with Orion-Thermo selective electrodes; sulfates by turbidimetry, chlorides by titration with silver nitrate; calcium and magnesium by titration with EDTA and sodium and potassium by flame photometry (Metrolab 315 digital photometer). Nitrates were determined by potentiometry with a selective ion electrode (Orion Model 9307), a reference electrode and an Orion 710-A potentiometer, using a suppression solution for interferences. Six reference standards were used (5, 10, 25, 50, 100 and 300 mg/L of nitrate) to calibrate the potentiometer. The mean percentage error of the chemical analysis did not exceed 8%.

In the case of samples extracted for the herbicide measurement, they were collected in 500 ml polypropylene containers and stored frozen (−20 °C) until further analysis. These samples were analyzed for glyphosate and AMPA by ultra-high performance chromatography coupled with a tandem mass spectrometer (UHPLC MS/MS) (Waters Inc., Milford, MA, USA) in EEA INTA Balcarce Laboratory (Argentina) with the methodology put forward by Aparicio et al. (2013).

3.1 Statistical analysis

Finally, the whole analysis linking all the geochemical variables was made using descriptive statistical techniques (multivariate analysis) by means of specific software [SPSS Statistic v21]. Thus, a cluster analysis in R mode was carried out. Hierarchical methods provide a graphical representation of relatedness between the geochemical variables (dendrogram). The hierarchical cluster analysis was applied using the Ward linkage rule which linked iteratively nearby points through a similarity matrix to evaluate the distance between clusters. The squared Euclidian distance was selected as the similarity measurement. For the cluster algorithm, the data were previously log-normal transformed and all variables were standardized (z-scores) because of the different units of pH and EC in relation to the meq/L units used for the chemical concentrations. Taking into account the known relationship and dependence between pH and CO_3^2, the latter was not necessary to be considered for the multivariate analysis.

4 Results and discussion

4.1 Surface water

The entire area constitutes a non-typical hydrological system (Fertonani and Prendes, 1983). A part of three main water collectors that exceed the limits of the study area may be distinguished: Ctalamochita river, Cabral stream and Tegua river. The general flow direction of streams and rivers is NW–SE and all the water systems finally supply water to the Saladillo wetland area, located in the SE of the province of Cordoba (Blarasin et al., 2014).

The streams with headwaters in Las Peñas Mountains infiltrate into the piedmont area and show temporary or ephemeral regime. To the East, the courses act as gaining streams showing a permanent regime. The flow rates of these surface water systems vary between

0.39 m^3/s and 1.87 m^3/s with an average water velocity of 0.4 m/s. In the poorly drained area of the South-East sector, the water velocities are very low, the drainage pattern is anarchical and, depending on rainfall intensities, water stagnates and evaporates slowly in ponds in the most important topographical depressions. These water bodies occasionally dry out intra or inter-annually depending on the water table depth. The construction of artificial ditches to avoid flooding is common in cultivation areas. These systems have a very low water velocity, in the order of 0.09 m/s and drain groundwater and surface water that comes from farmed fields during the rainy season.

The EC in stream water changes from 650.0 µS/cm to1020.0 µS/cm in the flow direction, and all the samples were classified as freshwater of sodium bicarbonate geochemical type. The ponds (L3 and L4) have EC values from 2830.0 µS/cm to 2340.0 µS/cm and contain brackish water of sodium sulfate-chloride and sodium bicarbonate type, respectively. The sample from the ditch (Ca2) presents the highest salt content with an EC of 3780.0 µS/cm. It corresponds to brackish water of sodium sulfate-chloride geochemical type.

4.2 Groundwater

4.2.1 Hydrogeological and hydrodynamic characterization

The hydrogeological profiles (see location in Fig. 1), show the relationship between the topography, lithology and hydrological features. Topography is mainly controlled by a set of bedrock descending blocks, as a result of high angle reverse faults, according to the tectonic framework of the Pampean Mountains (Dalla Salda,1987).

A-A' profile (Fig. 3a) shows that the unconfined aquifer is formed by very fine sediments (very fine sands and silts) with scarce intercalations of coarser sandy materials. The aquifer base is the bedrock in the piedmont area and clay strata or cemented silty sediments (calcretes) that function as aquiclude or aquitard materials in the eastern area.

The spatial variation of the unsaturated zone is very noticeable, from 25 m at the piedmont to 3 m towards the East. Here the water table outcrops in topographical depressions, generating small and shallow ponds. In the eastern aeolian environment, the fine sand and silty sand fractions predominate. In the low land areas, an increase in the silt–clay percentage was observed. In this profile, some layers of sandy materials (around 230 m deep in the area of Dalmacio Vélez Sarsfield town) are found, which constitute confined aquifers. The unsaturated zone is composed of coarse sediments (gravels) in the piedmont and very fine sandy sediments and silty sands in the eastern plain.

B-B´ profile(Fig. 3b) shows that in the NW area the aquifer is constituted by alluvial sediments from the alluvial fan of the Ctalamochita river, that is, sands and gravels, although intercalations of thin strata formed by fine sandy and silt sediments can be observed. Towards the SE plain area, very fine sand and silt sediments (loess) prevail. The unsaturated zone thickness goes from 40 m near the apex of the alluvial fan to 2-3 m to the east. At depths of around 150-200 m, several strata formed by medium to coarse sand sediments exist, which correspond to paleo-channels that act as confined aquifer layers.

C-C' profile(Fig. 3c), which crosses the area in S-Ndirection, is a good example to show the bedrock depth and the overlaying sediments in the piedmont area. The unsaturated zone thickness goes from 25 meters in the south up to 60 meters in the central region, diminishing again near the Ctalamochita river, in the alluvial fan environment. The unconfined aquifer is made up by sands in the upper meters (southern sector) to very fine silty sands in the lower strata. In the central area very fine and clayish/silty sediments prevail while in the northern area, the sediments are typical fluvial coarse sands and gravels.

Figure 3. Hydrogeological profiles. a) A-A’. b) B-B’. c) C-C’. d) References

The aquifer or saturated zone shows an average thickness of around 80 m in the plain but is thinner in the piedmont because of the proximity of the bedrock (about 30-50 m). The unsaturated zone thickness is variable, fundamentally related to the topographic characteristics. Thus,the highest values are found in the NE area (>58 m) and the lowest (0–3 m) in the low topographical southern areas (Figure 4). The equipotential map also shows the NW-SE direction of the groundwater flow, in general according to surface water flow, both regulated by the topographic characteristics. Although the aquifer is recharged by precipitation in the entire area, the regional recharge sector is located in the piedmont and adjoining area,where the flow lines show a slight divergence. As can be seen in Fig. 4, the hydraulic gradients are variable: 1.5% in the piedmont because of the bedrock proximity and 0.1 % in the fluvio-aeolian plain, where the landform promotes a very low hydraulic gradient.

Figure 4: Equipotential map, unsaturated zone thickness and nitrate spatial distribution in the unconfined aquifer.

4.2.2 Hydrogeological units

Based on lithological and geomorphological features that control the hydrogeological characteristics, four Hydrogeological Units (UH) were defined (Fig. 6). Their main features, the hydraulic parameters and the groundwater velocities are shown in Table 1.

Table 1: Hydrogeological Units (UH), main features, hydraulic parameters and groundwater velocities.

Figure 5: Hydrogeological unit for the unconfined aquifer

4.2.3 Hydrogeochemistry

The groundwater from the unconfined aquifer exhibits variable EC from 709 μS/cm (freshwater) up to 7,900 μS/cm (salty water) (Fig. 6). The 47.3% of the samples are sodium bicarbonate, 26.3% sodium sulfate, 15.8% sodium bicarbonate-sulfate, 5,3% sodium sulfate-chloride and 5,3% sodium chloride water types.

Although the groundwater flow is towards the SE, the most saline groundwater is located in the piedmont where fine sediments predominate. These exert more interaction between water and sediments particles and then, generate more possibilities to incorporate solutes to groundwater. After that and due to mixing processes with rain water that recharges very coarse sediments in the alluvial fan of Ctalamochita River, groundwater becomes fresher. In this unit the major aquifer recharge values were found (in the order up to 25% of precipitation) measured with the chloride mass balance method (Healy, 2010). In the south and southeast area, the groundwater is brackish mainly due to fine sediments and low flow velocity, both factors that promote the increase of total dissolved salts by the greater water-mineral contact than in coarser sediments. This spatial distribution and the origin of chemical elements and compounds were corroborated with the numerical geochemical modeling (Parkhurst and Apello, 1999). The results demonstrate that solutes come mainly from dissolution processes of carbonate which may be found as nodules or calcrete layers in the sediments. Also gypsum or halite salts supplied by wind from hydro-halomorphic areas may be disolved. Another fundamental role is played by ion exchange processes, given the presence of exchangers like illites and smectites, which fundamentally provide cations to solution (especially Ca^{++} by Na^{+}). In addition, partial hydrolysis processes of silicate clasts or volcanic glass were identified (Becher Quinodoz et al. 2019). Finally the atmospheric input of the ions must be indicated, which was confirmed when the rainwater was analyzed (40-45 mg/L of dissolved salts).

The general distribution of the EC in the different hydrogeological environments, is locally modified by point source pollutants, which promotes an increase in the EC values by the incorporation of solutes derived from livestock activity, as in the case of Sample B16.

Figure 6: Spatial distribution of groundwater electrical conductivity in the unconfined aquifer and Stiff diagrams showing spatial changes in the geochemical type

In the studied area the nitrate values in groundwater were between 2.0 and 280.5 mg/L. and in surface water, between 1.0 and 5.0 mg/L. Taking into account some studies carried out in the region of Cordoba, which estimated that the natural baseline range (NBR) of NO_3^- in the unconfined aquifer is between 5.0 and 15.0 mg/L (Blarasin et al., 2008, Giuliano Albo and Blarasin, 2013) it can be established that 57.9% of the samples of the unconfined aquifer taken out in this study, exceed the NBR. The spatial distribution of the nitrate content in the unconfined aquifer is shown in Figure 4. It is noticeable the major impact was identified in the areas where there is a thin unsaturated zone (less than 10m).

4.3 Glyphosate and AMPA concentrations in surface water and groundwater

Glyphosate was detected in 66% of surface water samples, in a range from 0.2 to 167.4 µg/L. AMPA was found in 33% of the surface waters from 0.7 to 49.4 µg/L. The highest value corresponds to Ca2 with 167.4 µg/L and 49.4 µg/L of glyphosate and AMPA, respectively.

In relation to streams, only one sample (A6) presented glyphosate (0.2 µg/L). The ponds L3 and L4 showed glyphosate in a range of 0.5 to 0.7 µg/L and only L3 had AMPA (0.7 µg/L).These results showed that lentic ecosystems present a greater contamination degree than the lotic ecosystems. The Ca2 ditch has very low velocity (0.09 m/s) and limited dilution potential.

Similar results are reported by Battaglin et al. (2014) who pointed out that the highest concentrations of glyphosate and AMPA were found in ditches. The Glyphosate values found in this study are similar to those found in other studies carried out in our country, such as that of Sasal et al. (2017) in the province of Entre Rios, where the values are between 0.1 to 240.0 μg/L in surface water. In Córdoba and Buenos Aires, Alonso et al. (2014) detected glyphosate in a range of 1.5 - 16.0 μg/L in surface water samples taken from ponds and streams. These values are higher than those found in the present study (0.2 to 0.7 μg/L). The mentioned authors also carried out a groundwater sampling and did not detect glyphosate and AMPA in the unconfined aquifer.

In the present study, glyphosate was detected in 15.8% of the total groundwater samples, in a range from 1.3 to 2.0 μg/L. AMPA was detected in the same samples, with values from 1.5 to 3.1 μg/L (Table 2). Those sites where both molecules were detected in groundwater are related to areas where the water table is less than 4 meters deep. A numerical model using MACRO 5.0 (Larsbo and Jarvis, 2003) was used to corroborate in some sites the transport of glyphosate (Lutri et al., 2019). These glyphosate values are similar to those found by Okada et al. (2018), which range from 0.1 to 8.5 μg/L in groundwater of the Argentinian Pampean plain. In the case of AMPA, our values were slightly higher to those detected by the mentioned authors, who measured a maximum of 1.9 μg/L. The values found in groundwater in the present study resembled those determined by studies from Sanchis et al. (2012) and Battaglin et al. (2014), who determined maximum glyphosate concentrations of 2.5 μg/L in Catalonia, Spain and 2.0 μg/L in the United States, respectively. Furthermore, the latter found AMPA in groundwater in maximum concentrations of 4.9 μg/L.

Glyphosate was detected in rainwater (0.2 μg/L) which is related to the way the pesticide is sprayed and to the fact that the rainwater harvesting comes from the roofs of houses, which are not always correctly cleaned.

Regarding the suitability for human consumption, in Argentina there are two legal criteria, one is contained in Law 24,051 on Hazardous Wastes, which follows the Canadian Water Quality Guidelines of 280 μg/L (Health Canada, 2017) and the other coming from the National Secretary of Water Resources which refers to studies of the US-EPA with maximum allowed concentration of 700 μg/L (US. EPA, 2002) for glyphosate and AMPA. None of the groundwater samples in our study exceeded the limits established by both criteria. However, taking into account the most restrictive limit defined by the European Union (European Directive 98/83/EC) of 0.5 μg/L of the combined maximum residue level (MRL) of glyphosate and AMPA, all the groundwater samples exceeded this limit.

4.4 Statistical analysis of hydrogeochemical data

Figure 7 compares the results obtained from the analysis of glyphosate and AMPA in groundwater and its hydrogeological location. It shows that UH4 is the most affected unit, followed by UH3.

Taking into account the described characteristics of UH4, it can be defined as a more vulnerable unit due to agricultural pollution, since, from a spatial point of view, it is located in a regional discharge zone, where groundwater flows from western large areas. The shallow water table depth (4 meters or less) increases the aquifer vulnerability. Also, given the low values of hydraulic gradient and hydraulic conductivity, the groundwater velocity and associated potential for dilution are low.

The comparison of glyphosate and AMPA concentrations in both surface water and groundwater, shows that surface water presents a greater median value, due to the highest concentration detected in the ditch. This result highlights that pollutants from agricultural activities are more likely to reach surface water bodies due to their direct exposure to runoff from farmed lands. The glyphosate and AMPA values in groundwater are significant and may occur as a result of the very low dilution capacity of this hydrological system.

Figure 7: Box plot of concentration of a) glyphosate in the Hydrogeological Unit. b) AMPA in Hydrogeological Unit. c) Glyphosate and hydrological systems and d) AMPA and hydrological systems.

The multivariate statistical evaluation of groundwater data (figure 8) shows the conglomerates of the different chemical variables, where two main groups stand out. The first one (G1) clusters the major ions with EC, which define the mineralization processes and explain the natural chemical composition of groundwater, where the most saline waters are those of sodium sulfate geochemical type. The second group (G2) is clearly linked to the alteration of the natural background of water composition due to anthropogenic contamination processes. The first subgroup (G2A) links glyphosate and AMPA, corroborating the same origin, that is the agricultural pollution source. The second one (G2B) is represented by nitrates, bicarbonate and pH, which may be interpreted as an indicator of contamination processes like the incorporation of nitrates derived from fertilizers or from the incorporation of organic matter from livestock, whose degradation generates HCO_3^- ions and can diminish the pH.

Figure 8: Dendrogram obtained by Average Linkage Clustering in R mode. (G: Group.)

5 Conclusions

The hydrogeological study made it possible to define an unconfined sedimentary aquifer as multilayered, heterogeneous and anisotropic with variable thickness. It is made up mainly by aeolian sediments of Quaternary age (very fine silty sands) with different cementation degree at different depths. Also, some layers are made up by medium to coarse psefitic sediments (sands and gravels) related to the alluvial fan of the Ctalamochita river. The base of the unconfined aquifer is constituted by an igneous- metamorphic bedrock in the piedmont zone, while in the rest of the area it is represented by aquitard/acuiclude materials (very fine sands and silts with carbonate cementation) or clay-silt sediments. The results obtained showed that the unsaturated zone, the groundwater flow direction, the hydraulic gradients and the groundwater velocity are fundamentally controlled by the landform and lithological characteristics which define the main hydrogeological units.

The hydrogeochemical analysis shows that the groundwater exhibits a marked spatial variation in salinity and geochemical composition, according to the defined hydrogeological units. Thus, the freshest waters of calcium-sodium bicarbonate geochemical type are related to the aquifer developed in the alluvial fan of the Ctalamochita river (UH3). In this unit, the coarse texture of sediments allows a higher flow velocity, with limited sediment-water interaction, which partially inhibits the weathering processes that contribute with ions and compounds to groundwater. Most salty and sodium sulphate-chloride waters are in the NW sector, related to the piedmont zone (UH1) where the aquifer is formed by very fine (silt-clay-sandy) sediments which increase the water-sediment interaction. In addition, the thick unsaturated zone delays the recharge process from rainwater and surface water and promotes the acquisition of solutes during the slow process of percolation towards the aquifer. In the UH2 unit, where greater sediment heterogeneity prevails, the water is sodium bicarbonate to sodium sulphate type. In the poorly drained unit (UH4), a zone of transit and partial discharge of groundwater, the fine aeolian sediments and the groundwater evolution from the occidental area, promote groundwater sodium sulphate type.

In relation to NO_3^- ion, a good indicator of human contamination, it can be observed that the greatest impacts are on the unconfined aquifer, with values up to 280 mg/L, above the natural-regional background values, and occur in sectors where the water table is shallow (less than 4 m), which enables the contaminant arrival at the aquifer. In these areas, the aquifer also has lower hydraulic conductivity and lower groundwater velocity, which partially diminishes the dilution processes by hydrodynamic dispersion. Conversely, where very coarse sediments prevail and although the water table is shallow and the land use is similar to the rest of the studied area, the NO_3^- values are lower (in the order of 2 mg/L). On the other hand, in areas with a thick unsaturated zone (like some piedmont sectors), the contaminant arrival at the unconfined aquifer is limited. The higher values of NO_3^- in groundwater can be assumed as derived from agriculture, especially fertilizers such as urea, which is the most used in the region, or from livestock activity, that generates significant organic matter waste, compounds whose degradation in the analyzed aerobic environment increase the bicarbonate ions in solution.

In surface water samples, the xenobiotics glyphosate and AMPA were detected in 66% of the samples in a range of 0.2-167.0 µg/L (glyphosate) and 0.7-49.4 µg/L (AMPA). The highest values in surface water were in the ditch, a site not only highly exposed to the pollutants arrival (especially in rainy seasons coinciding with the herbicide application) but also with very low water velocity that allows the compounds to persist in solution. In the streams the herbicide concentration is low, an aspect controlled by the flow rate values and higher water velocity, which allow dilution processes.

The unconfined aquifer is less exposed to contamination due to the protection given by the soil and the unsaturated zone. Although the glyphosate has physicochemical characteristics that explain its low mobility (such as its high Koc) and its possibility of retardation and degradation in the soil, it was found in the groundwater. The characteristics of the defined hydrogeological units influence the arrival of herbicides at the aquifer. Although glyphosate and its metabolite AMPA were measured only in 15.8% of the groundwater samples and the concentrations were low (glyphosate 1.3-2.0 µg/L and AMPA 15.8-3.1 µg/L) both molecules were detected in areas where the water table is less than 4 meters deep. This situation facilitates leaching processes through the vadose zone allowing the pollutants to reach the aquifer. Also these areas show low flow velocity which decreases hydrodynamic dispersion processes and the dilution of pollutant concentration.

The most outstanding result that emerges from the data is that the groundwater presents higher values in comparison with the stream water, which can be explained by greater dilution capacity of the latter. However, the highest value was detected in the ditch sample, that is, a site very exposed to the pollutants arrival and where the very low water velocity allows the xenobiotic to persist in solution.

The detection of this herbicide and its metabolite in the unconfined aquifer shows that the application for decades within the framework of the prevailing agricultural model interferes with the natural balance and exceeds the degradation potential of the soil system, causing groundwater contamination.

Future studies will be focused on the herbicide modeling in the unsaturated zone as well as the possible variation of the concentrations in groundwater in relation to the climatic seasonality, in order to better define the factors that influence its behavior.

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Table 1: Hydrogeological Units (UH), main features, hydraulic parameters and groundwater velocities.

Hydrogeological Unit	Sediments and relief	K (m/d)	Hydraulic gradient (%)	Groundwater velocity (m/d)
UH1. Eastern slope sector of Los Cóndores Mountains	Silty-sand sediments differentially cemented with carbonates. (re transported aeolian sediments with alluvial intercalations. Undulated relief.	0.5	1.5	0.15
UH2. Eastern slope sector of Las Peñas piedmont	Silty sands sediments (re transported aeolian sediments) with buried paleochannels, Undulated relief	2	1	0.20
UH3. Paleo alluvial fan of the Ctalamuchita River.	Fluvial sands and gravels. Moderately to smoothly undulated plain	40	0.2	0.32
UH4. Poorly aeolian drained area with spider-type drainage (southeast sector)	Silty sands mainly of aeolian origin. Smoothly undulated plain.	1.5	0.16	0.024

Table 2: Results of the chemical analysis of Surface water and groundwater in the study area.

Sample ID	UH	Site	Land use	Glyphosate (µg/L)	AMPA (µg/L)	NO_3 (mg/L)	pH	$CO_3^{=}$	HCO_3^-	$SO_4^{=}$	Cl^-	Na^+	K^+	Ca^{2+}	Mg^{2+}	USZ[m]	EC	Geochemical type
A2	3	Stream	A	<LD	<LD	1.0	8.8	0.0	352.5	18.1	22.9	122.4	7.9	34.4	8.3	-	661.00	SB
A6	3	Stream	A	**0.20**	<LD	1.5	8.1	0.0	450.0	81.8	48.6	173.9	14.4	44.0	14.2	-	1,020.00	SB
A7B	2	Stream	A	<LD	<LD	5.0	8.9	33.9	307.5	147.4	22.9	123.4	8.5	53.6	13.7	-	656.00	SB
Ca2	4	Ditch	A	**167.4**	**49.4**	2.2	8.6	36.4	765	1,355.0	371.4	1,011.1	70.9	62.4	40.0	-	3,780.00	SSC
L3	4	Pond	A	**0.5**	**0.7**	2.0	8.3	0.0	652.5	658.6	377.1	626.9	34.9	96.8	50.7	-	2,830.00	SSC
L4	4	Pond	A	**0.7**	<LD	1.5	8.4	12.1	1,127.5	253.6	142.9	574.3	54.5	30.4	16.6	-	2,340.00	SB
B3	3	UA	A	**1.2**	**1.7**	2.0	7.6	0.0	637.5	62.1	31.4	206.3	10.0	56.0	20.5	4.0	1,125.0	SB
B16	3	UA	FL	<LD	<LD	280.0	7.7	0.0	690.0	498.5	171.4	428.7	13.5	32.8	32.7	2.0	2,453.0	SBC
B22	3	UA	A	<LD	<LD	35.0	7.5	0.0	660.0	27.9	42.9	263.9	8.8	57.6	13.7	6.2	1,281.0	SB
B26	3	UA	A	<LD	<LD	25.0	7.7	0.0	300.0	83.4	28.6	116.3	7.2	64.0	9.8	25.0	756.0	SB
B33	4	UA	DF	<LD	<LD	2.2	7.8	0.0	597.5	789.5	357.1	1011.1	26.8	42.4	37.6	3.0	3,450.0	SS
B35	4	UA	A	**2.0**	**1.5**	2.0	7.9	0.0	382.5	675.3	242.9	455.0	20.5	40.0	34.2	3.4	2,360.0	SS
B36	4	UA	A	<LD	<LD	150.0	7.7	0.0	535.0	789.4	251.4	518.7	25.8	57.6	74.6	3.3	2,630.0	SSC
B37	4	UA	A	**1.4**	**3.1**	120.0	7.8	0.0	387.5	618.2	371.4	651.2	26.4	72.0	40.0	3.0	2,670.0	SBC
B39	4	UA	A	<LD	<LD	10.0	7.9	0.0	550.0	329.8	157.1	424.7	29.6	41.6	24.9	2.2	1,940.0	SB
B42	2	UA	A	<LD	<LD	100.0	7.9	0.0	300.0	123.4	45.7	171.9	8.4	40.0	9.8	4.5	709.0	SB

B43	2	UA	A	<LD	<LD	120.0	7.8	0.0	745.0	229.7	137.1	485.3	16.4	44.8	19.0	1.8	1,872.0	SS
B45	3	UA	O	<LD	<LD	25.0	7.5	0.0	490.0	2285.7	1100.0	1587.5	30.8	208.0	109.3	6.0	7,450.0	SB
B58	1	UA	A	<LD	<LD	3.0	8.0	0.0	432.5	181.8	85.7	313.5	12.0	37.6	11.2	60.0	1,202.0	SC
B59	1	UA	A	<LD	<LD	9.0	7.4	0.0	252.5	921.7	1714.3	843.3	23.4	464.0	170.7	28.0	6,100.0	SS
B60	2	UA	A/L	<LD	<LD	12.0	7.6	0.0	300.0	2897.6	1342.9	2321.5	48.4	224.0	156.1	17.6	7,925.0	SB
B63	3	UA	A	<LD	<LD	10.0	7.8	0.0	445.0	273.8	22.9	248.7	10.0	44.0	4.4	23.5	1,206.0	SS
B66	4	UA	A	<LD	<LD	270	7.8	0.0	205.0	981.4	51.4	299.3	12.9	176.0	29.3	3.0	2,031.0	SBS
B67	1	UA	A	<LD	<LD	150.0	8.2	0.0	875.0	102.0	45.7	455.0	10.0	8.0	3.9	24.0	1,804.0	SB.
B71	3	UA	A	<LD	<LD	100	8.0	0.0	415.0	67.1	28.6	181.0	6.2	25.6	6.3	13.0	807.0	SB
P59	-	Rain	A	**0.2**	<LD	0.0	6.8	0.0	25,0	1,6	5,7	1,5	2,6	7,2	1,5	-	53.1	CB

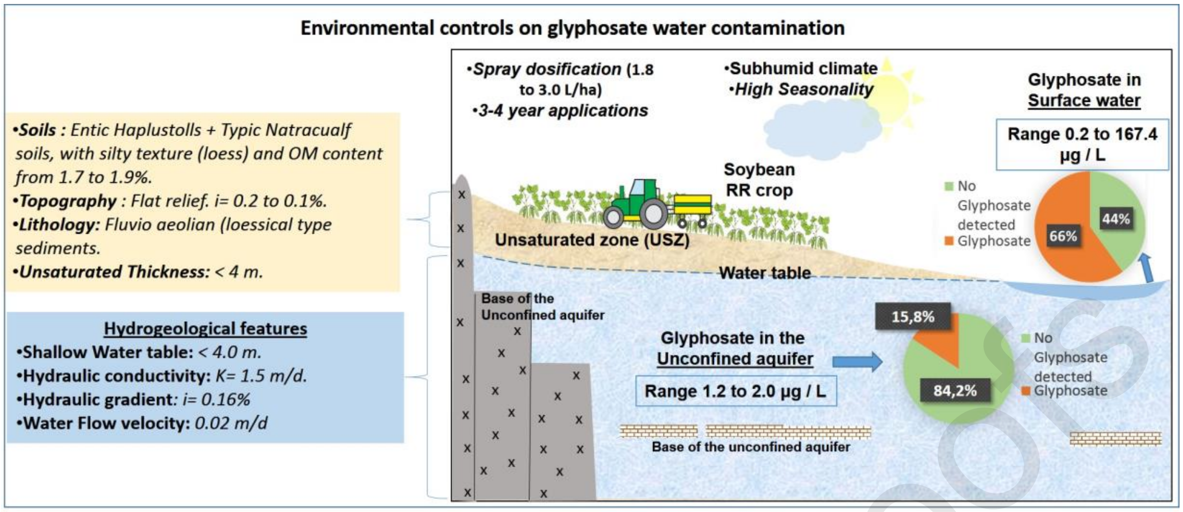
UH:Hidrogeological Unit. USZ: Unsaturated zone (meters). EC: Electric Conductivity[μS cm^{-1}]
U A : Unconfined Aquifer**Land Use: A:**Agricultural. **FL:** Feed Lot**. O:** Orchard. **A/L**: Agricultural and Livestock. **DF:** Dairy Farm.
LD: Limit detection [0.1 μg/L].
Geochemical type: **SB**: Sodium bicarbonate. **SS**: Sodium sulfate. **SC:** Sodium Chloride. **SBS**: Sodium bicarbonate sulfate. **SSC**: Sodium sulfate chloride **CB:** Calcium bicarbonate

Glyphosate and AMPA assessed in rain water, surface water and groundwater

Field application in wet season resulted in high surface-water glyphosate exposures

Glyphosate and AMPA detected in the unconfined aquifer (the primary water resource)

Concentrations were related to low hydraulic conductivity, gradient, and flow velocity


Environmental controls on glyphosate water contamination
•Soils : Entic Haplustolls + Typic Natracualf soils, with silty texture (loess) and OM content from 1.7 to 1.9%.
•Topography : Flat relief. i= 0.2 to 0.1%.
•Lithology: Fluvio aeolian (loessical type sediments.
•Unsaturated Thickness: < 4 m.
Hydrogeological features
•Shallow Water table: < 4.0 m.
•Hydraulic conductivity: K= 1.5 m/d.
•Hydraulic gradient: i= 0.16%
•Water Flow velocity: 0.02 m/d
•Spray dosification (1.8 to 3.0 L/ha)
•3-4 year applications
•Subhumid climate
•High Seasonality
Glyphosate in Surface water
Range 0.2 to 167.4 µg / L
Soybean RR crop
No Glyphosate detected
Glyphosate
44%
66%
Unsaturated zone (USZ)
Water table
Base of the Unconfined aquifer
15,8%
Glyphosate in the Unconfined aquifer
Range 1.2 to 2.0 µg / L
84,2%
Base of the unconfined aquifer

Lutri V.: Conceptualization, Methodology, Formal Analysis, Investigation, Writing – Original Draft, Writing – Review & Editing, Visualization. **Matteoda E**.: Investigation, Methodology, Review & Editing, Supervision. **Blarasin M**.: Investigation, Methodology, Writing – Original Draft and Review & Editing, Supervision. **Aparicio V:** Laboratory analysis. Review. **Giacobone D**: Investigation. Review**. Maldonado L**: Investigation. Review. **Becher Quinodoz F:**Investigation. Review. **Cabrera A**: Investigation. Review. **Giuliano Albo J:** Investigation. Review.

Figure 1

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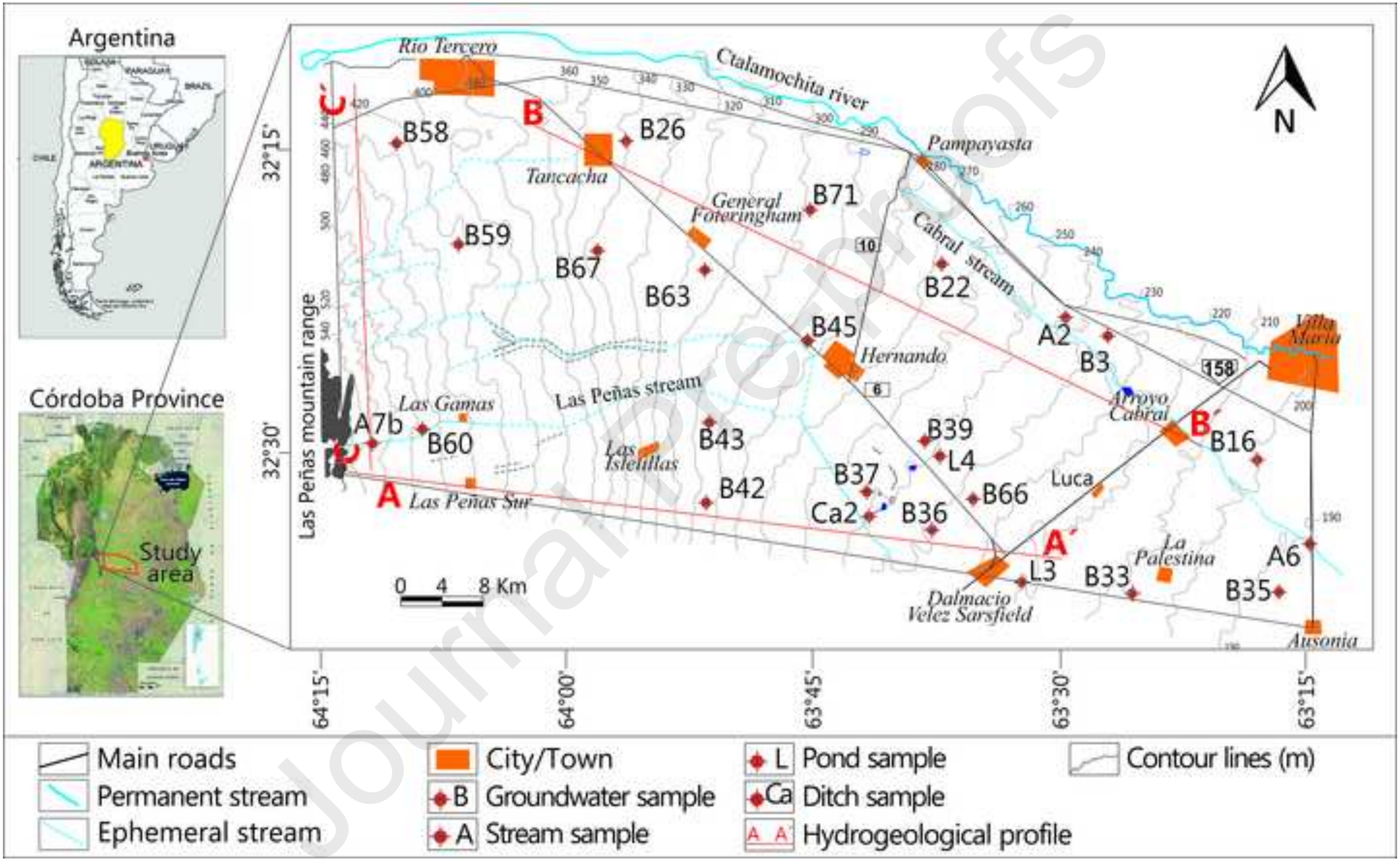

Figure 2
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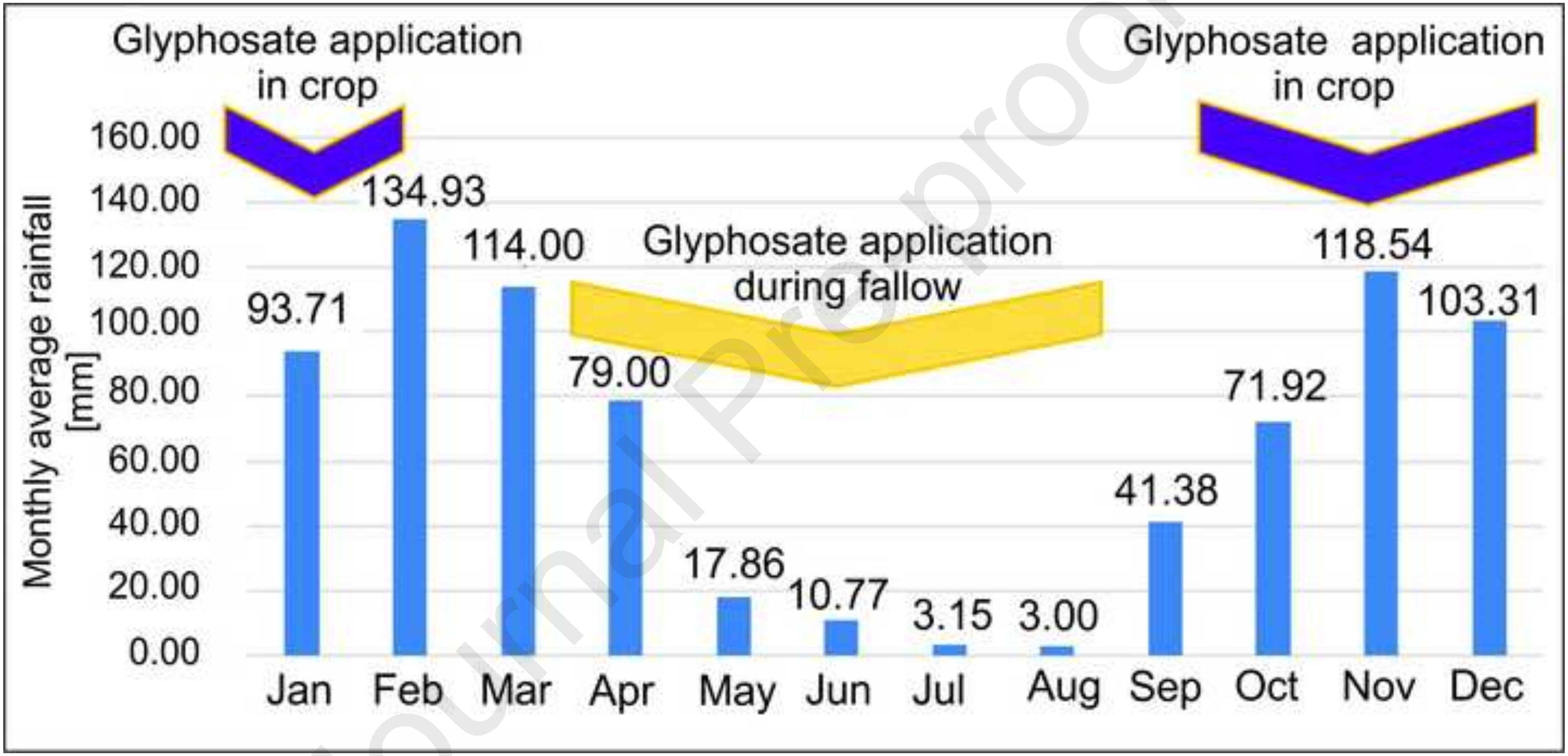

Figure 3a

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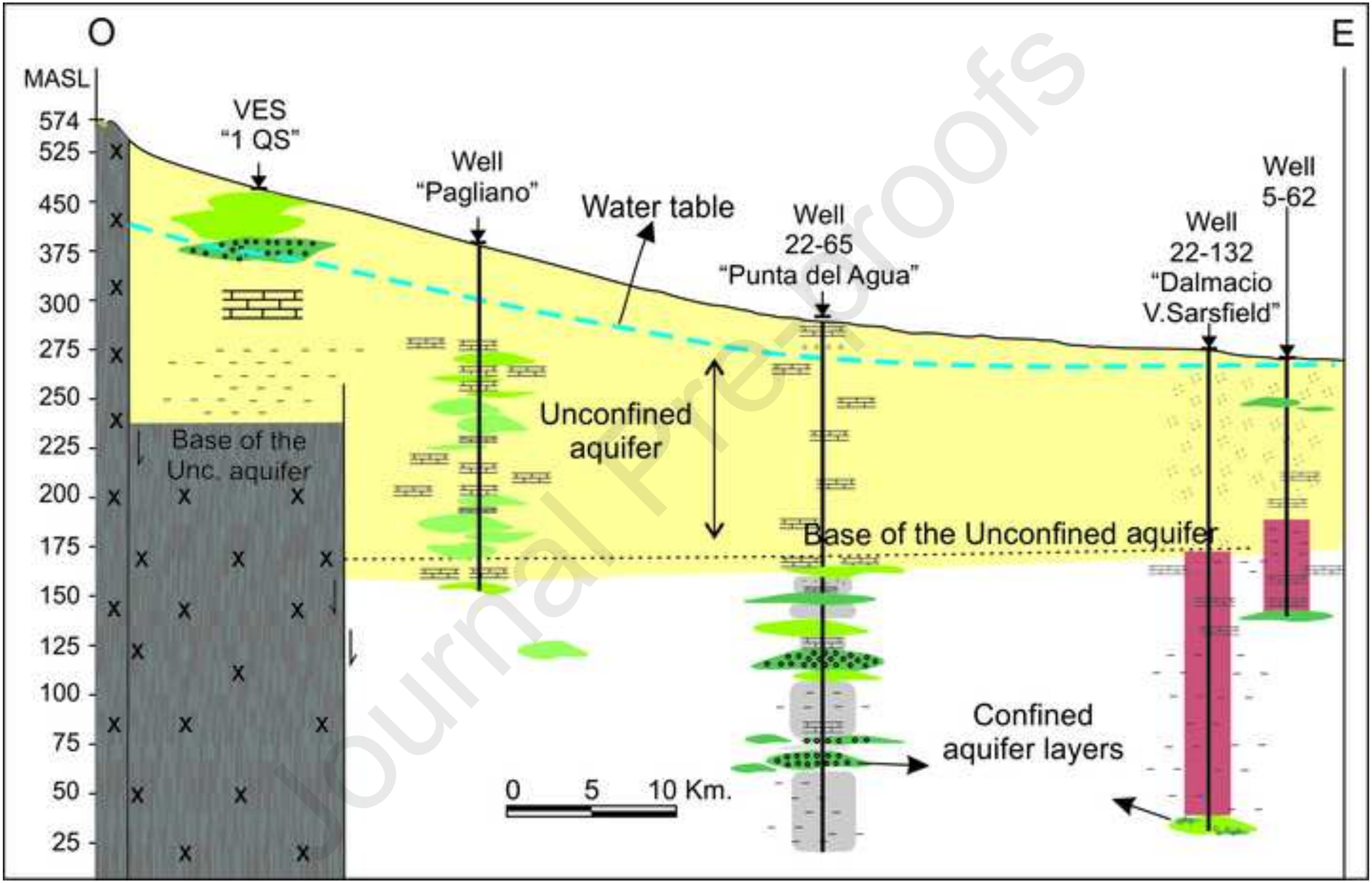

Figure 3b
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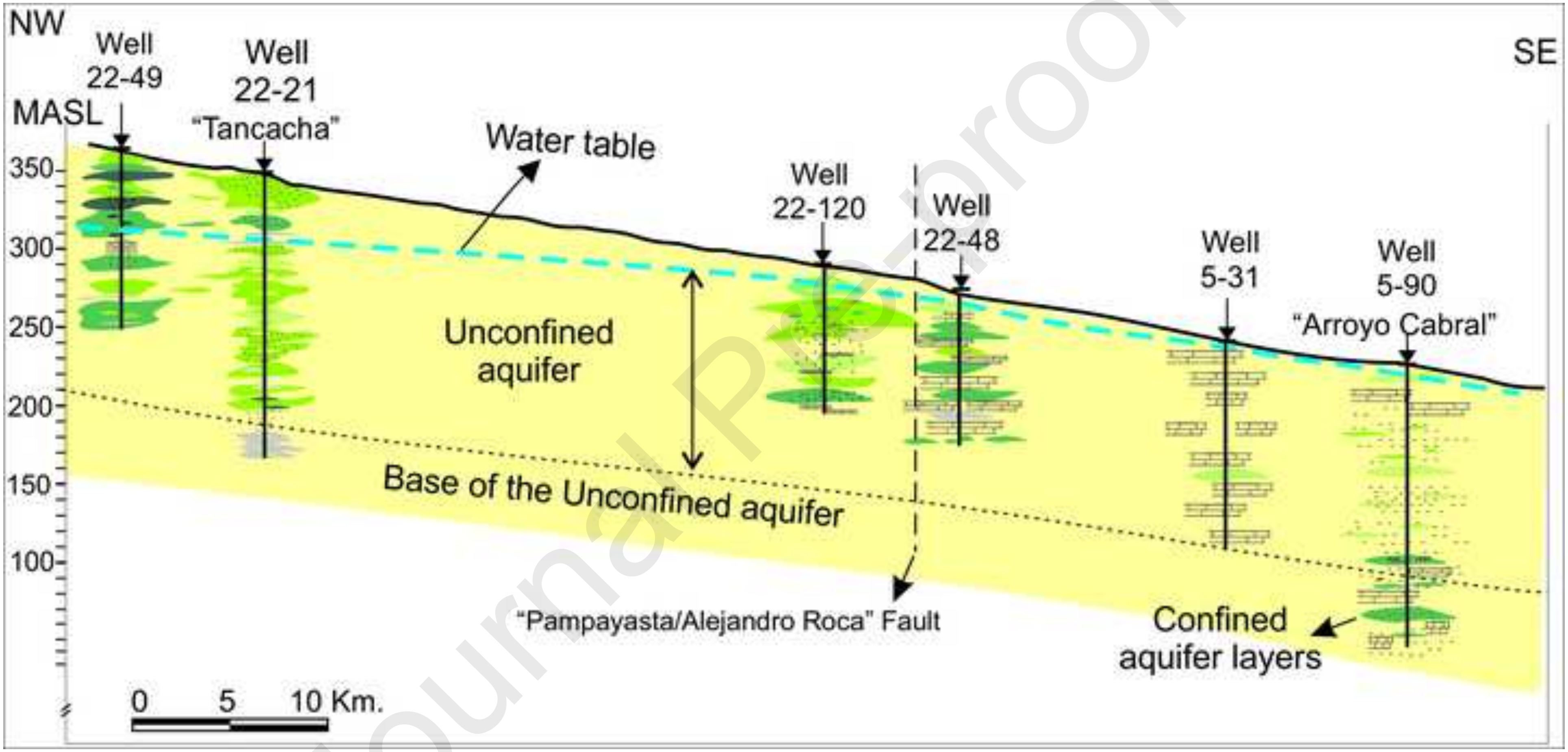

Figure 3c

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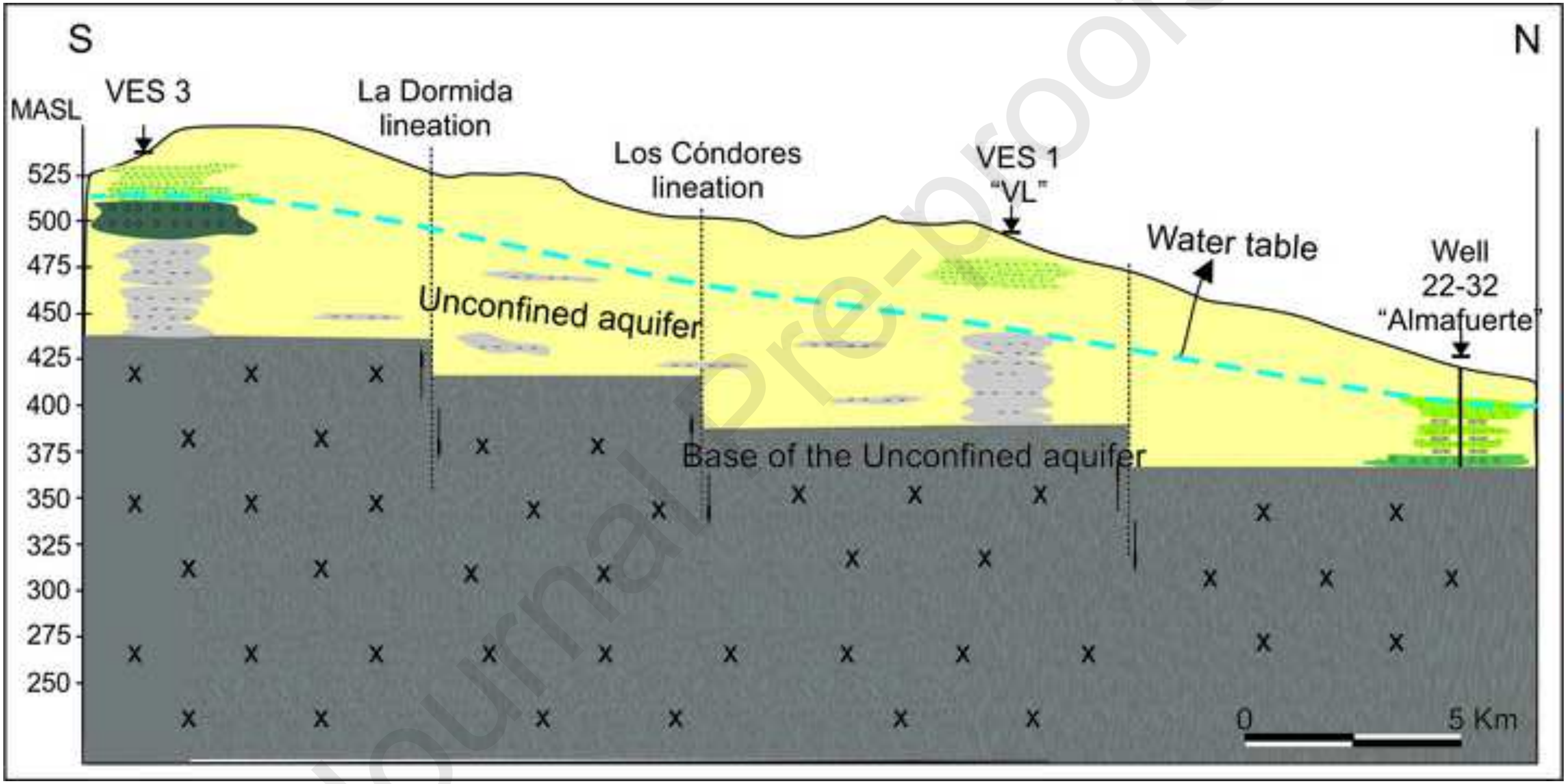

Figure 3d

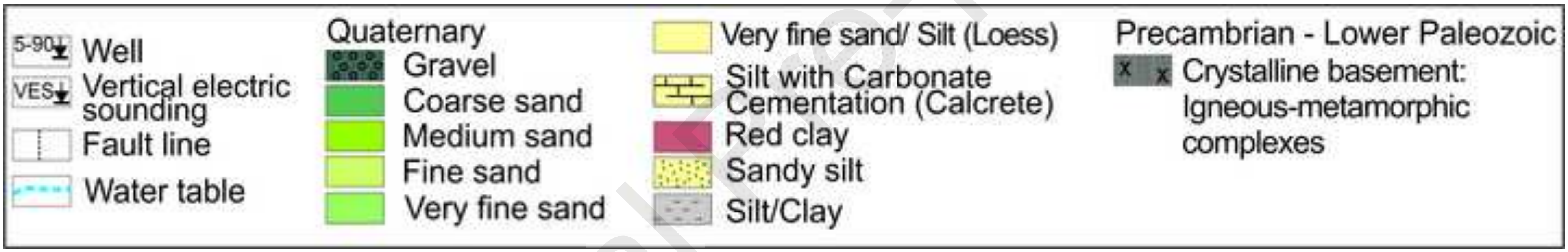
5-90 Well
VES Vertical electric sounding
Fault line
Water table
Quaternary
Gravel
Coarse sand
Medium sand
Fine sand
Very fine sand
Very fine sand/ Silt (Loess)
Silt with Carbonate Cementation (Calcrete)
Red clay
Sandy silt
Silt/Clay
Precambrian - Lower Paleozoic
Crystalline basement: Igneous-metamorphic complexes

Figure 4
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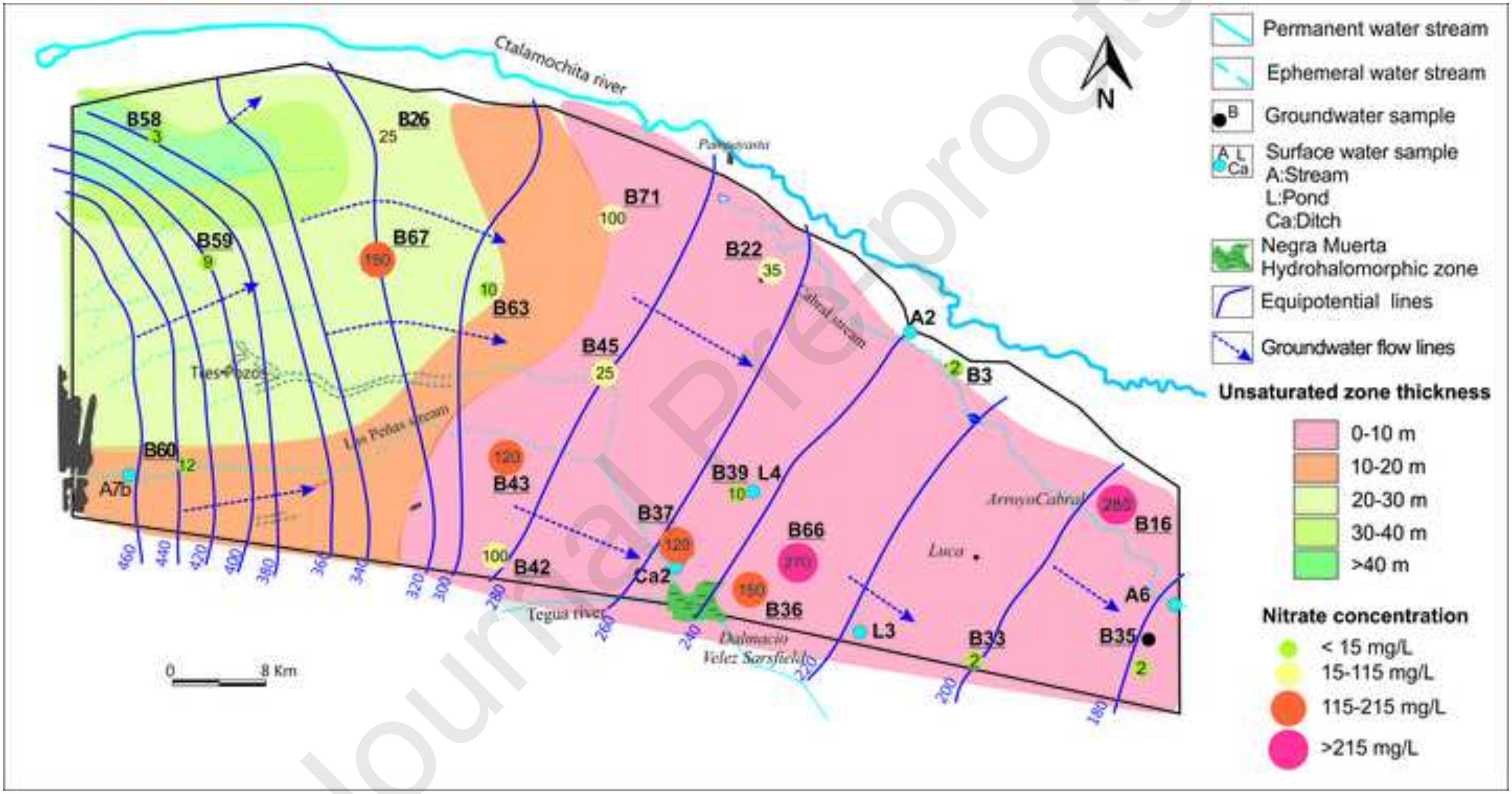

Figure 5

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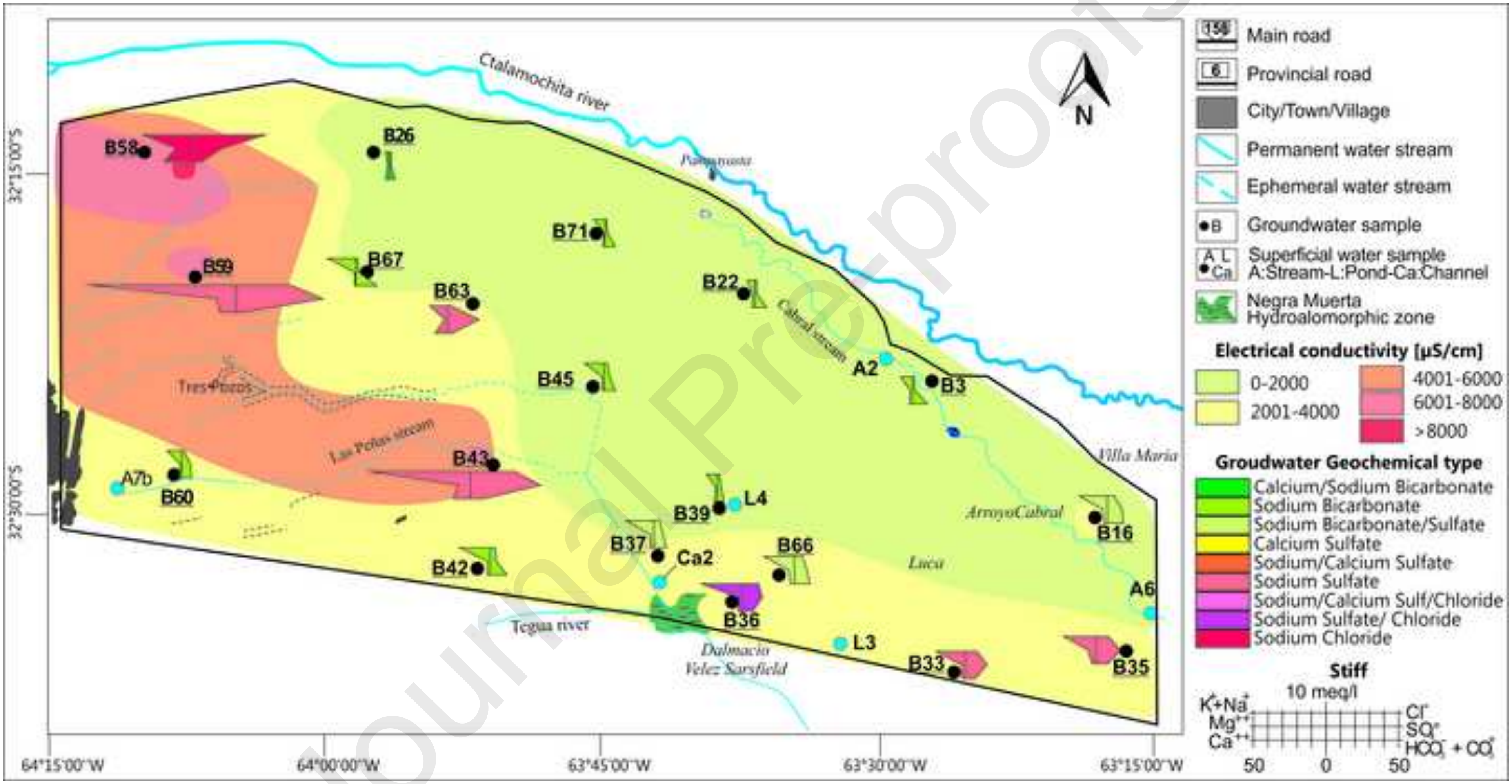

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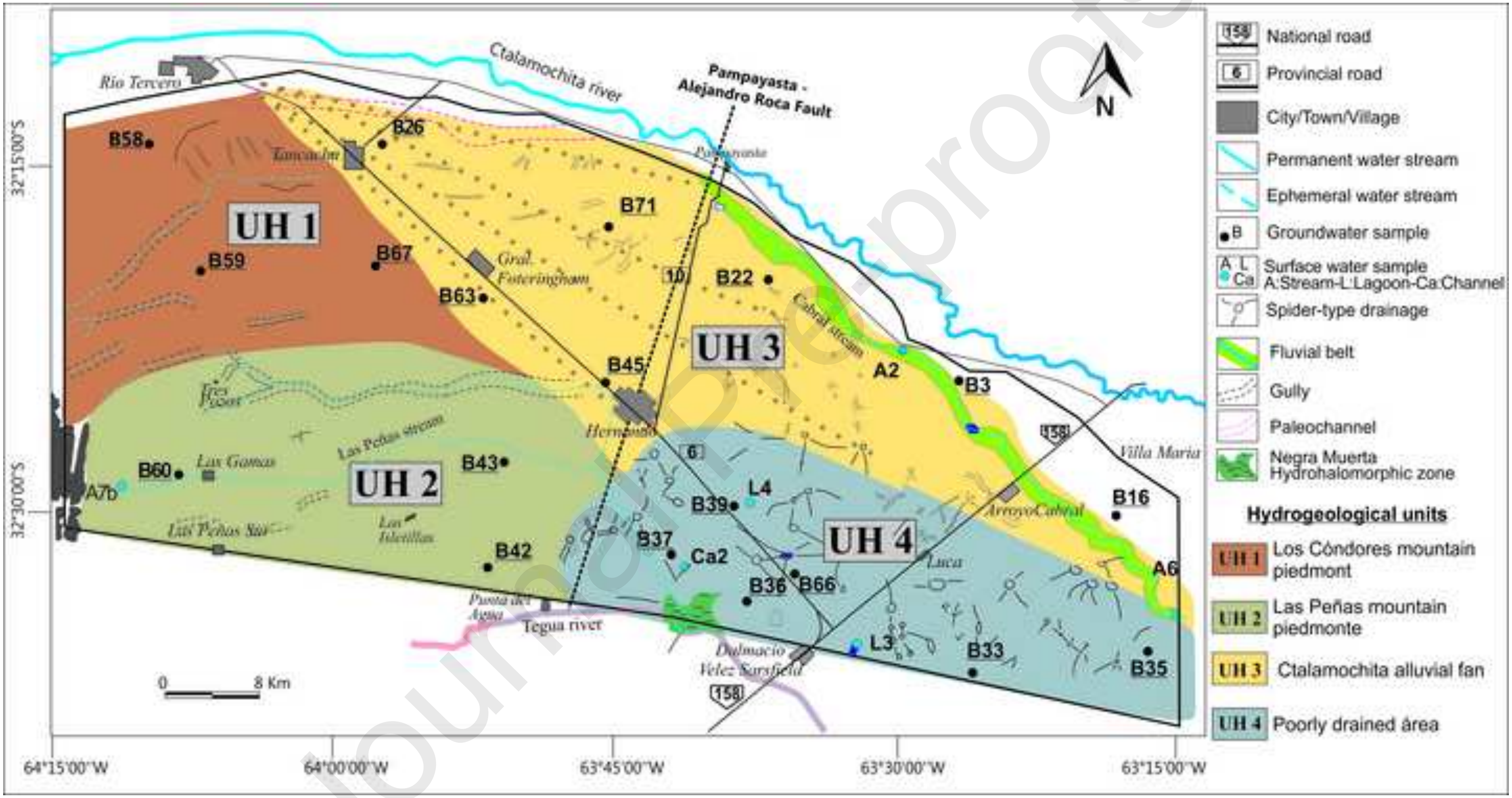

Figure 7a
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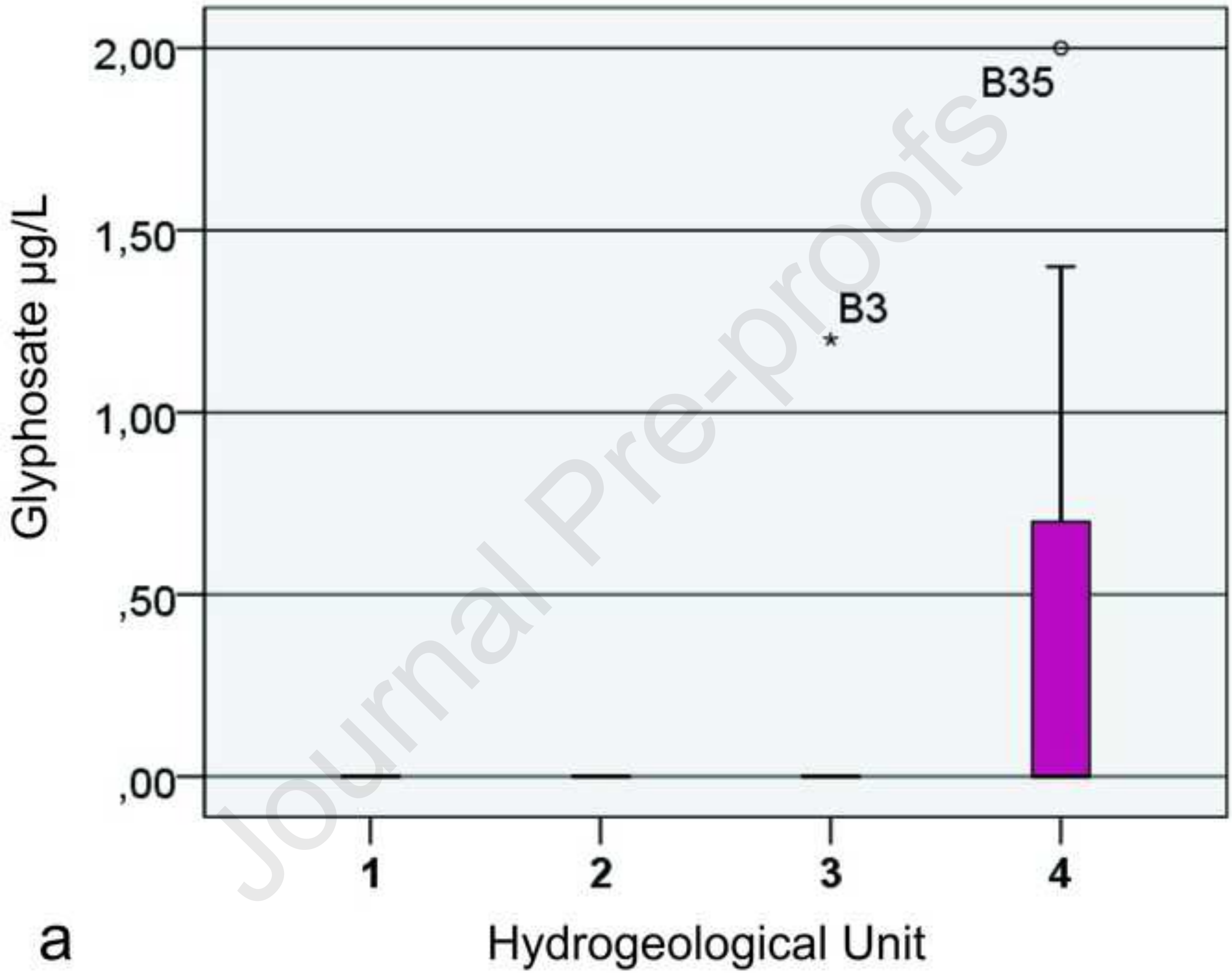

Figure 7b
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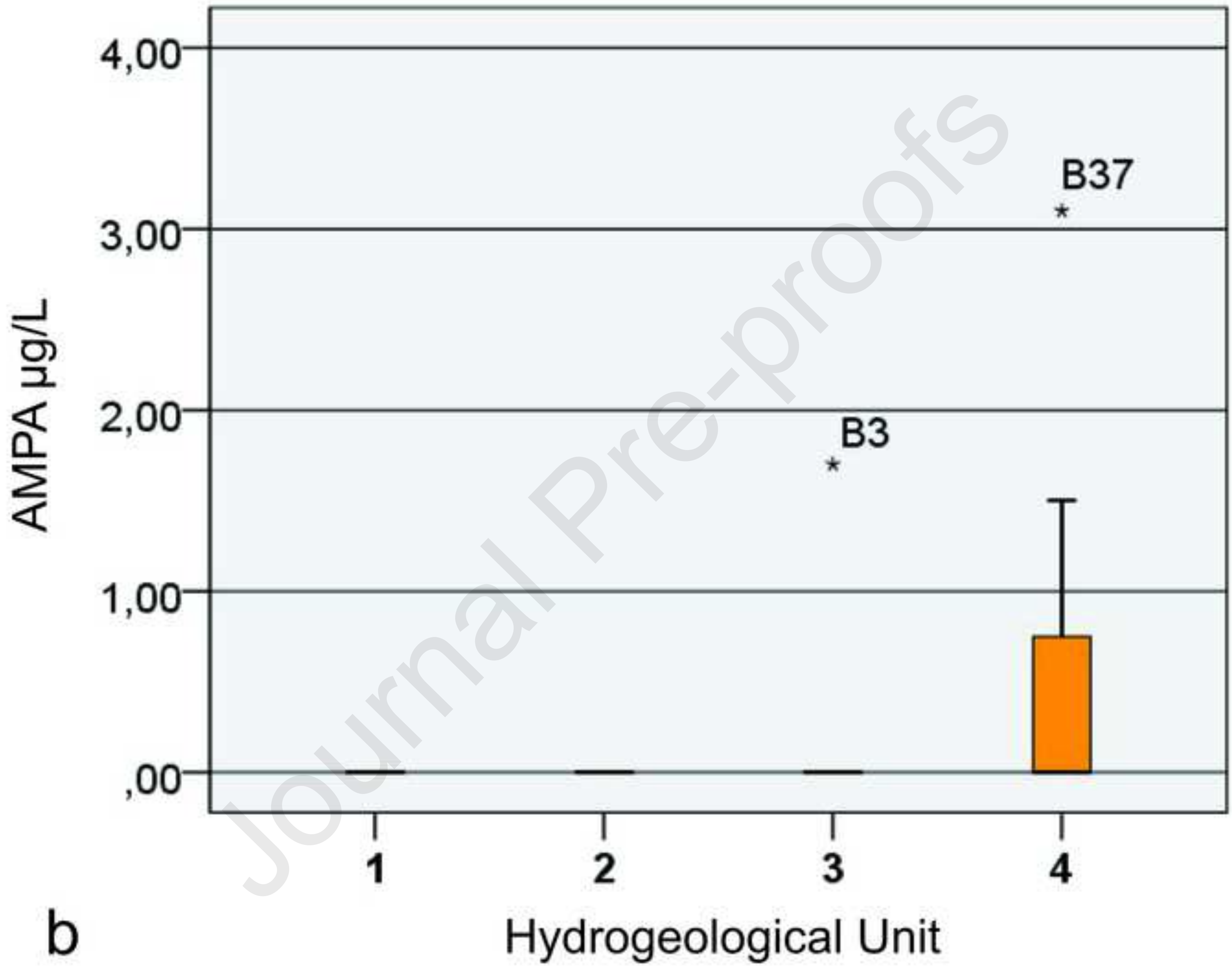

Figure 7c

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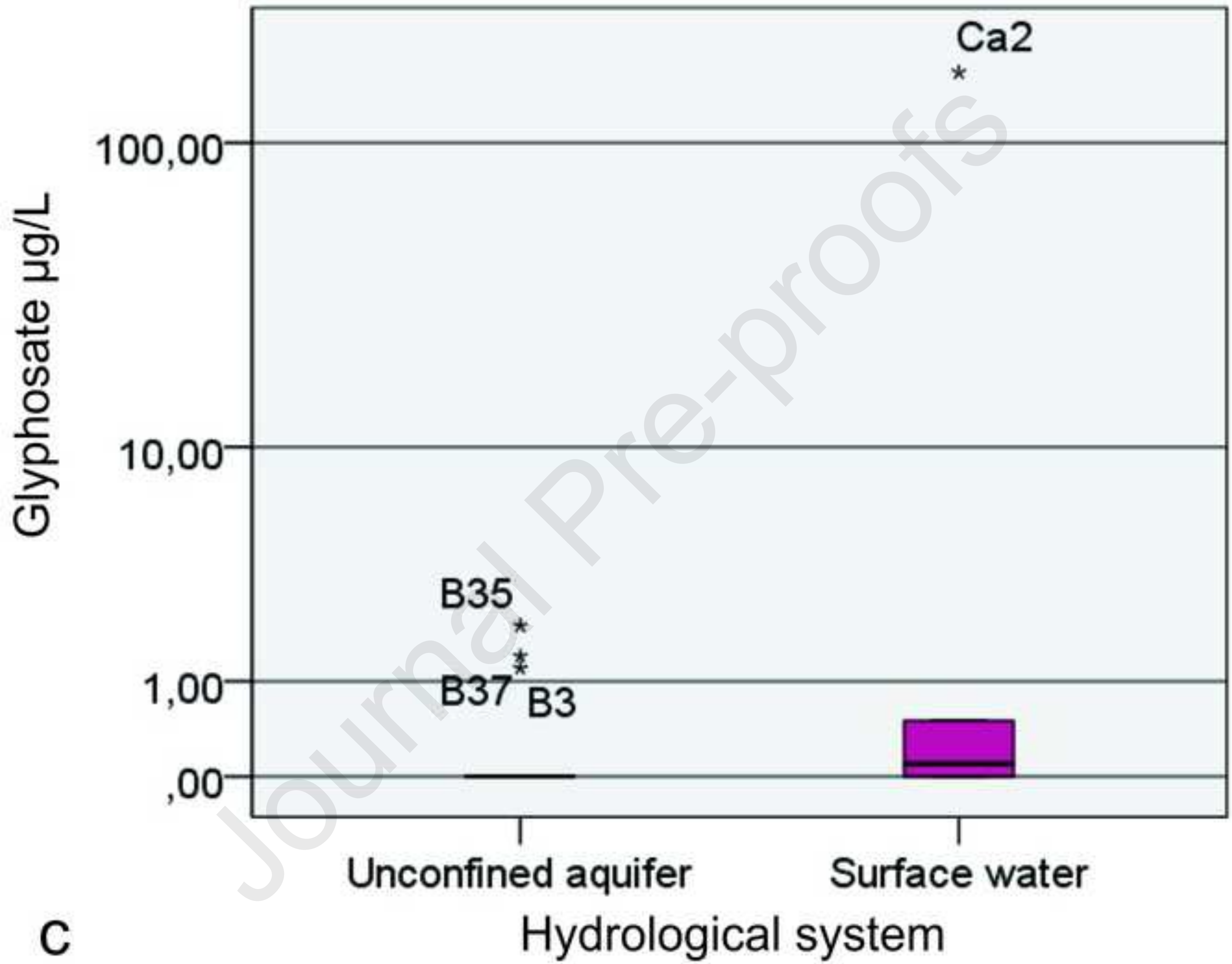

Figure 7d
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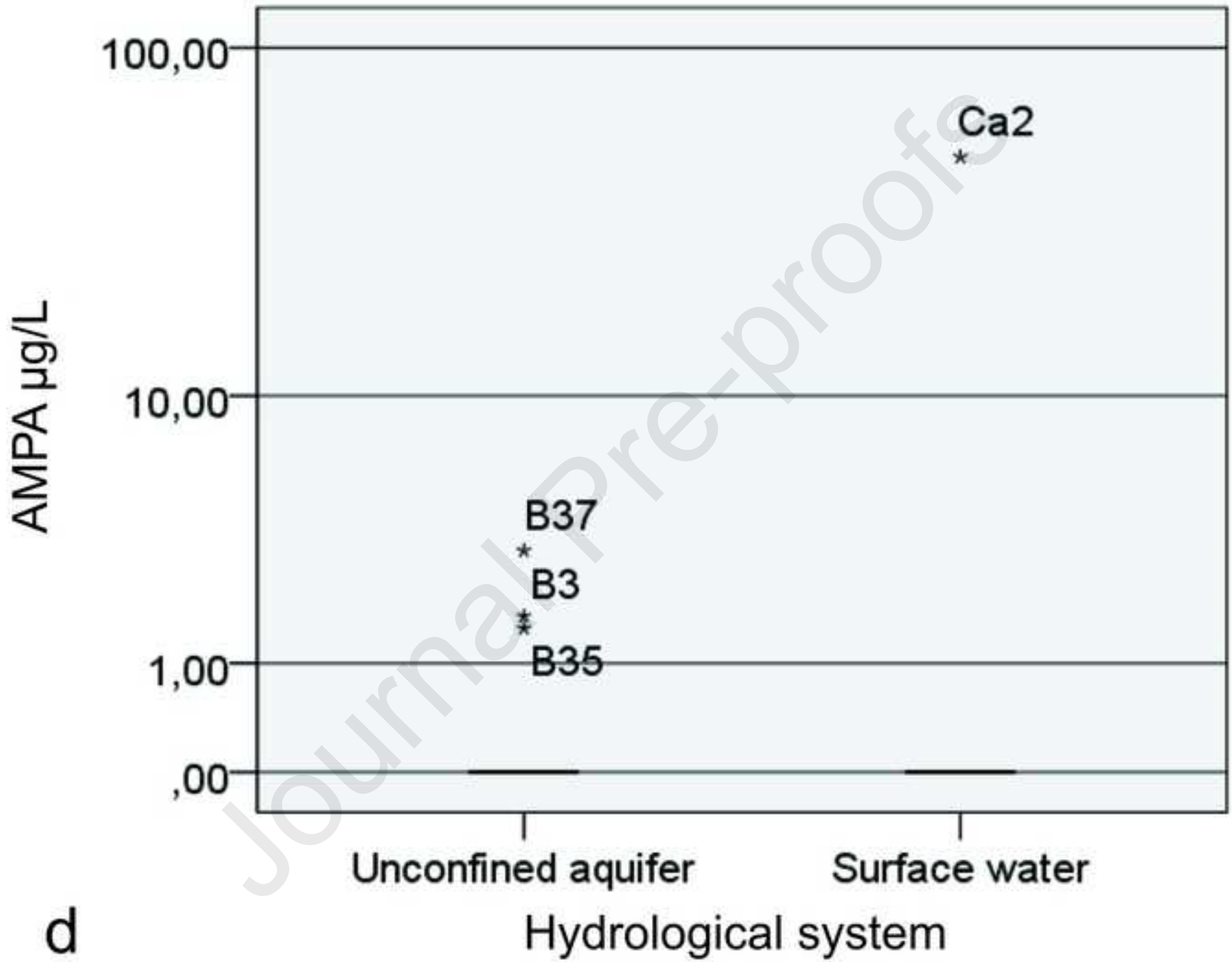

Figure 8
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