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Treball Final de Grau

Evaluation of the distribution of salinity in the different recharge zones of the lower Llobregat River aquifer and its impact in groundwater.

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L'èxit és la suma de petits esforços, repetits dia rere dia.

Robert Collier

Aquest treball s'ha dut a terme a l'empresa Aigües de Barcelona per un període de temps de 4 mesos. Per això, vull donar les gràcies a la Meritxell i al Jordi, tutors de l'empresa, per donar-me un vot de confiança, dedicar-me tot el temps necessari i sobretot l'ajut que m'han proporcionat per fer aquest projecte en un àmbit més professional. També vull agrair a totes aquelles persones que hagin col·laborat amb una petita aportació fent que aquest treball sigui una mica millor.

En segon lloc, i no menys important, agrair-li al meu tutor de la Universitat de Barcelona, en Joan Mata, tota la implicació, dedicació i paciència que ha tingut en mi.

I finalment agrair a la meva família i als meus amics tot el suport que he rebut durant tota la carrera, sent una etapa tan important de la meva vida.

CONTENTS

SUMMARY

The salinity of surface water and groundwater of the Lower Valley of the Llobregat basin has experienced a significant decrease in the last decades.

This project aims to establish a traceability between the evolution of salinity in surface water and its impact on the aquifer, relating it with the structural modifications of the area, as well as the existing infrastructures and the natural evolution of the environment.

Historical information on the quality of surface and groundwater is available. Making a selection of wells and sampling points, we work in the analysis of the evolution of chloride concentrations (a clear indicator of salinity) and we use several tools such as Piper diagrams or the relationship of conservative parameters (chlorides / bromides), trying to find, through all this information, the impact of the different sources of recharge in the water of the left and right margins of the Lower Valley of the Llobregat.

Apart from the natural recharge with rainwater, the aquifer of the Lower Valley of the Llobregat River receives mostly contributions from the waters of the Llobregat River, of the Anoia River and of the Rubí Stream, affecting the two margins of the Llobregat River in different ways, that is: each margin is recharged with water of different origin and in different proportions. Using the methods mentioned above, it has been shown that the decrease in salinity in recent years has been caused by changes in the infrastructure of this system and for a higher rainfall regime, now reaching values below the established limit of 250 mg/L of chlorides. Other effects such as the saline intrusion produced during the drought period have also had a clear footprint which has lasted for a long time in specific areas of this system.

Keywords: Salinity, aquifer, Llobregat, recharge, surface and underground water.

RESUM

La salinitat de les aigües superficials i subterrànies de la Vall Baixa de la conca del Llobregat ha tingut una significant davallada en les últimes dècades.

Aquest projecte pretén establir una traçabilitat entre l'evolució de la salinitat en les aigües superficials i el seu impacte en l'aqüífer, relacionant-ho amb les modificacions estructurals de la zona, així com les infraestructures existents i la pròpia evolució natural del medi.

Es disposa d'informació històrica sobre la qualitat de les aigües superficials i subterrànies. Fent una selecció de pous i punts de mostreig, es treballa analitzant l'evolució de les concentracions de clorurs (un clar indicador de la salinitat) i utilitzant eines diverses com ara els diagrames de Piper o la relació de paràmetres conservatius (clorurs/bromurs), intentant en base a tota aquesta informació trobar l'impacte de les diferents fonts de recàrrega en l'aigua dels marges esquerre i dret de la Vall Baixa del Llobregat.

A part de la recàrrega natural amb aigua de pluja, l'aqüífer de la Vall Baixa del Llobregat rep aportacions majoritàriament de les aigües del riu Llobregat, del riu Anoia i de la riera de Rubí, afectant els dos marges del riu Llobregat de manera que cadascun recarrega amb aigua de diferent origen i en diferents proporcions. Mitjançant els mètodes citats anteriorment s'ha comprovat que la disminució de la salinitat en els darrers anys ha estat provocada per modificacions en les infraestructures d'aquest sistema i per un règim de precipitacions més elevat, arribant ara a uns valors inferiors al límit establert de 250 mg/L de clorurs. Altres efectes com la intrusió salina produïda durant els anys de sequera també han tingut una empremta clara durant anys en tot aquest sistema.

Paraules clau: Salinitat, aqüífer, Llobregat, recàrrega, aigua superficial i subterrània.

1. INTRODUCTION

The progressive salinization of the Llobregat River waters began at the late 20s, when the potash exploitations started their industrial activity in the locations of Súria, Cardona, Sallent and Balsareny, therefore producing residual brine. Then the salinity reached very high levels, which in turn made the “Law about salinity” arise in 1933. This law established that the Llobregat River should not exceed 250 mg Cl^-/l when reaching the municipality of Pallejà.

During the period of the Civil War, salinity levels decreased due to less industrial activities, which confirmed a cause-effect relation of the mining and the economic activity with the historical events that marked the country.

Due to the fact that both reduction of salinity in the river and the economic development needed to reach their aims, finally in 1989 the brine collector was built: a collecting canal that evacuates directly into the sea the highly salty water produced by potassium exploitations. In the years it has been working, it has enabled to reach considerably lower levels of salinity in the Llobregat River and this, in turn, has also had a positive impact on the decrease of salinity in groundwater.

In addition, over time, throughout the course of the River, other infrastructures have been built and improvements in the water treatment processes have been carried out (in water purification plants and in wastewater treatment plants), which have led to a change in the evolution and distribution of salinity in the basin.

To understand and explain the evolution of the salinity associated with this modification of infrastructures in the Lower Valley of the Llobregat basin, both in surface water and especially in the groundwater, it’s the object of this project.

2. EXPOSITION OF THE PROBLEM AND OBJECTIVES

In the last decades, the evolution of salinity in the surface resources of the Lower Valley of the Llobregat basin has had a clear decrease since the set-up of the brine collector in 1989 (see figure 32 of appendix 2). This decrease, however, isn't observed in groundwater, clearly in all wells, up to a few years later (from 2008 on). In this same way, the dispersion of chloride values in groundwater that there was years ago has diminished, with an obvious tendency to homogenize concentrations. This is clearly seen at Sant Joan Despí, where Aigües de Barcelona has its main treatment plant: the DWTP (Drinking Water Treatment Plant) of Sant Joan Despí (figure 1).

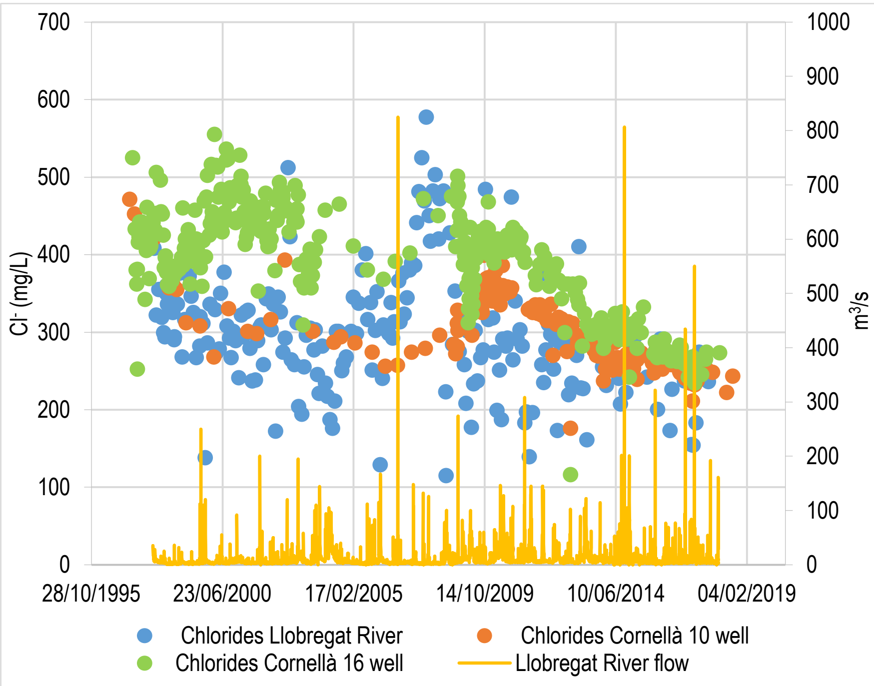

Figure 1. Evolution of chlorides in surface water and groundwater at the height of the Sant Joan Despí treatment plant and the Llobregat River flow at this same point.

The objective of this work is to explain why this evolution of salinity in the Lower Valley of the Llobregat River, both in surface water and groundwater.

All water inputs to the system will be taken into account: agriculture (irrigation surplus), WWTPs (Wastewater Treatment Plants), … Indeed, the crop surfaces of the left and right margins are watered with water of different origin and with also specific irrigation regimes for each margin. Thus, we must firstly try to find representative wells on both margins of the river and, secondly, to value, in the event that it’s feasible, the impact of surface waters of different origins in the aforementioned ground resources.

To do it, the chemical composition (relationship of cations and anions) of the surface water and groundwater of this system, the concentration of chlorides and the relation of conservative parameters will be analyzed. Along with this, the consideration of other aspects is necessary: the water regime or the exploitation of specific wells, as well as the changes in infrastructures that have been incorporated in this system.

3. CONTEXTUALIZATION

3.1. GEOGRAPHICAL DESCRIPTION OF THE STUDY AREA

The area analyzed in this work includes the surface and ground waters of the Llobregat basin from Martorell and down to the Delta zone (excluding the Delta itself).

So, on the one hand it covers about 16 Km of the river basin under analysis (with its contributions and derivations) and, on the other hand, the lower Llobregat River aquifer is located in the Baix Llobregat region, west of Barcelona, between the populations of El Papiol and Cornellà de Llobregat, with an area of 52 Km^2.

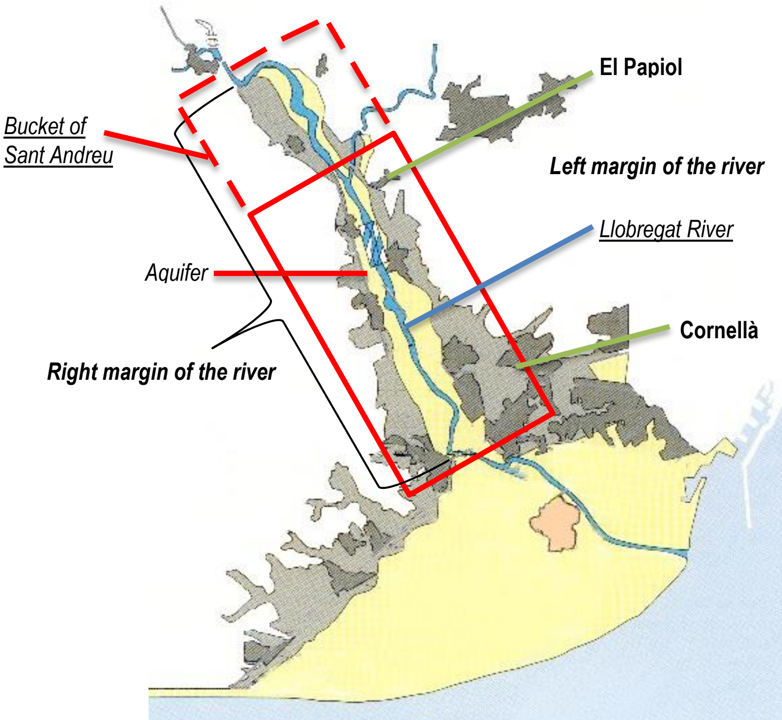

Figure 2. Geographical boundaries of the study area.

(Source: internal deposit of Aigües de Barcelona: La experiencia de Aguas de Barcelona en la recarga del Valle Bajo del río Llobregat).

It is an aquifer formed for gravels and sand, with areas where the substrate can be waterproof. It is a vulnerable system due to the possible intrusion of sea water. Its main source of recharge is the infiltration of river water, especially during periods of rain when the flow is much higher. Another source for recharging is the irrigation surplus and the losses of the irrigation canals, in addition to the infiltration of rain and the side water intake from the adjacent basins; the quality of these waters will condition that of the aquifer. The aquifer has a great strategic importance in the metropolitan area of Barcelona as an alternative or complementary resource to the surface water of the Llobregat River.

3.2. EXISTING INFRASTRUCRURES

The system that under study (figure 3) is made up of rivers, streams, water treatment plants, water purifiers, channels,... all of them affecting in one way or another the water quality of the aquifer.

In this way it should be noted that:

- The Rubí Stream, that receives the water outlet form the WWTPs of Rubí and Terrassa, is entirely derived by means of a wall of sand. When a flood occurs, this wall is easyly broken and then the waters of the Rubí Stream go to the Llobregat River.
- The Anoia River receives the waters outlet from the WWTP of Igualada and is partially derived towards the channel of Ferrer i Mora.
- The cultivation fields on the left margin of the Llobregat River are watered with the water of the derivations of Rubí and Anoia[1].
- The cultivation fields on the right margin of the Llobregat are mainly watered with the Llobregat River throught the Canal de la Dreta.

[1]The Anoia River and the Rubí Stream have waters of different origin and different quality, which are mixed at the height of El Papiol through a series of channels; in the first section the water circulates trough the Canal Capdevila, then passes through a second section called Canal Ferrer i Mora and finally, through the main channel that is the Canal de la Infanta, beginning at Molins de Rei and up to Cornellà.

- A small area on the right margin also receives water from a channel called Rec Vell, at the height of Sant Vicenç dels Horts, which brings water from the WWTP of Sant Feliu de Llobregat and of an agriculture well; nonetheless, this channel has low use.
- The system 7 is a sewage system that transports the rejected waters of the entire area to the WWTP at Sant Feliu de Llobregat, where there water is treated for better uses.

Figure 4 shows the geographic distribution of the aforementioned infrastructures, as well as the brine collector mentioned in the introduction of the project.

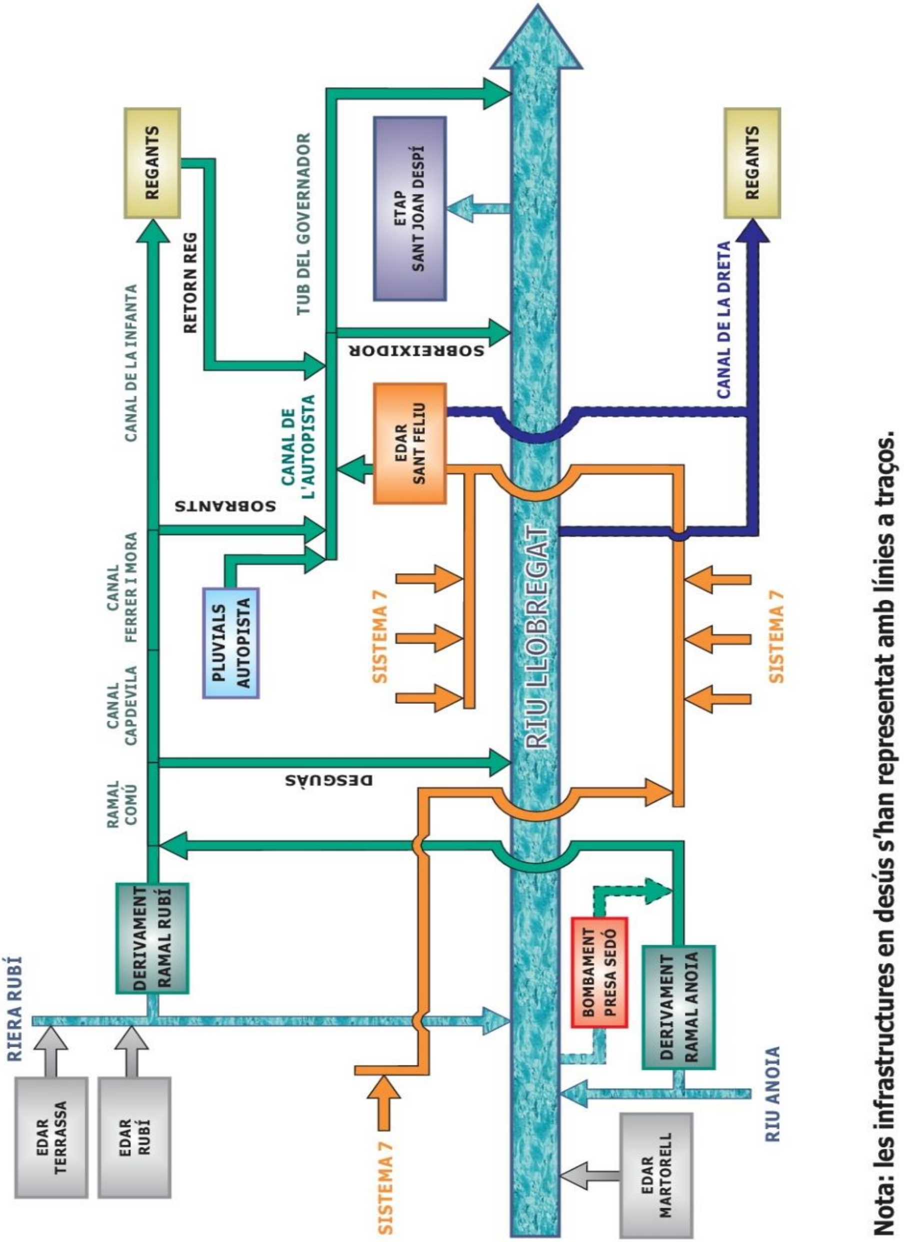

Figure 3. Nowadays infrastructures of the area of the Lower Valley of the Llobregat River (in Catalan).

(Source: Aigües de Barcelona).

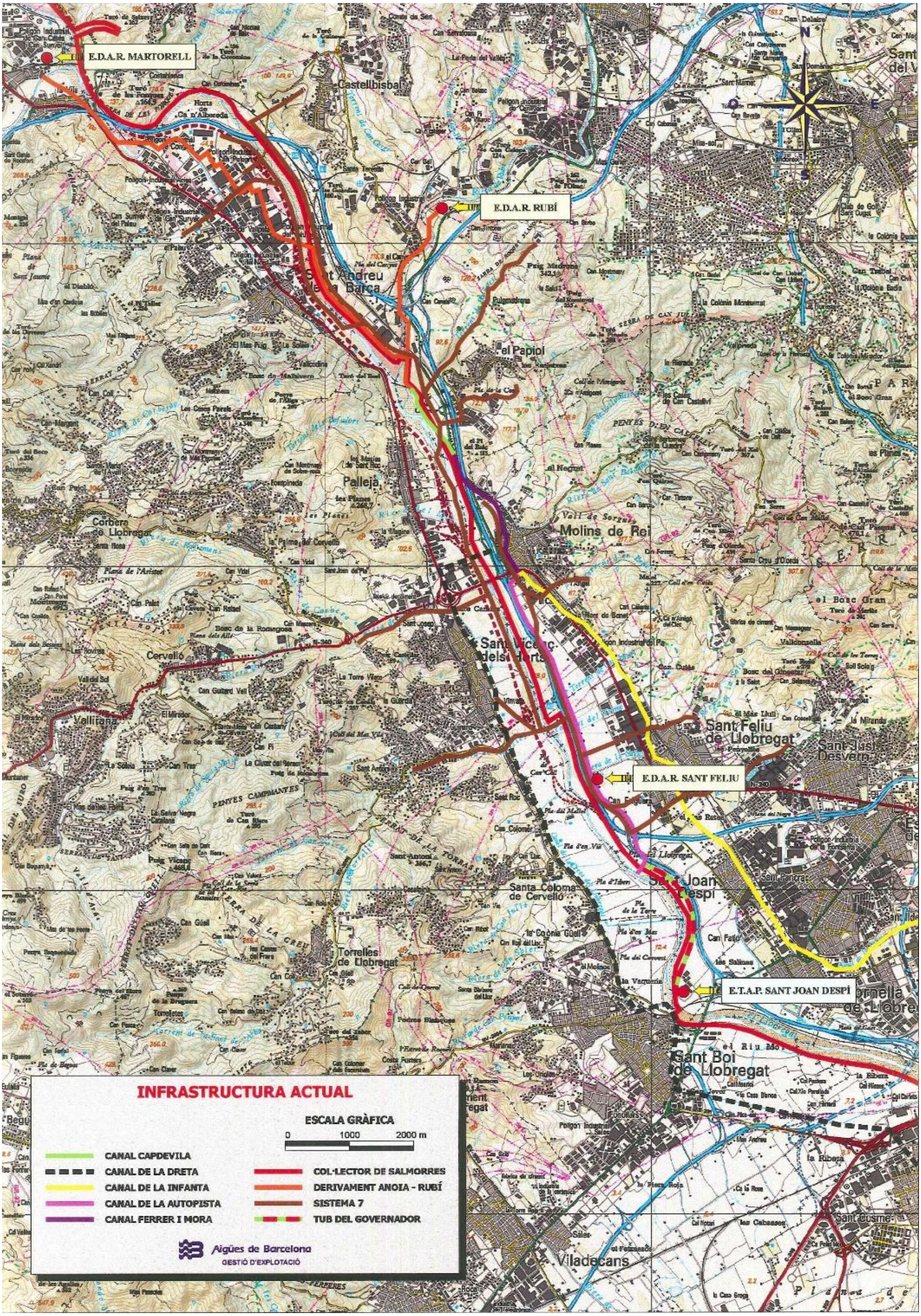

Figure 4. Geographic situation of the study area (in Catalan). *(Source: Aigües de Barcelona).*

4. WORKING METHODOLOGY

4.1. DATA COLLECTION AND GEOGRAPHICAL LOCATION OF THE SAMPLING POINTS

4.1.1. Surface water

In the Llobregat River basin, Aigües de Barcelona and the ACA have several sampling points to perform a monthly physical-chemical analysis of surface water. In the Lower Valley, samples are taken in 4 points, which are of interest in this study to evaluate the impact of the different surface waters of this system in the aquifer.

The points mentioned above are shown in table 1 and photos 5 and 6.

Table 1. Sample collection points along the basin of the Lower Valley of the Llobregat River.

Sampling point	Code	Township	Coordinates	
			UTM X	UTM Y
Anoia River	point 11	El Papiol	416152.62	4587842.44
The Llobregat River between the Anoia River and the Rubí Stream	point 12	El Papiol	415784.10	4587926.91
Rubí Stream	point 13	El Papiol	416152.62	4587842.44
The Llobregat from the confluence of the Rubí Stream to SJD	point 14	Molins de rei	417383.89	4584548.13

In all these 4 sampling points, two sources of information have seen used, with the same data frequency and the same parameters. Information has been extracted from the ACA website[2] and historical data from Aigües de Barcelona. Thus, there are 4 values per year and

[2] http://aca.gencat.cat/ca/laigua/consulta-de-dades/aplicacions-interactives/

per parameter from 1998 to 2018. The parameters analyzed are as follows: Cl^-, Br^-, HCO_3^-, CO_3^{2-}, SO_4^{2-}, Na^+, K^+, Ca^{2+} and Mg^{2+}.

Figure 5. Sampling points numbers 11, 12 and 13.

The points 11 and 13 have the same coordinates because both are located at the same point; a canal that is divided into two parts, respectively, canalizing the waters of the Rubí Stream and the Anoia River. Later, on this same channel, these two waters sources come together.

Figure 6. Sampling point number 14.

4.1.2. Groundwater

Throughout the course of the Lower Valley of the Llobregat, both on the left margin and on the right margin, there are a number of wells that should allow us to carry out the analysis proposed: from Martorell to Sant Boi/Cornellà de Llobregat. It should be mentioned that the wells located in the deltaic area of the Llobregat River are not considered in this study, because these wells may receive the influence of the sea intrusion, in other words, they will have more salts due to the incorporation of salt water into the basin.

From each one of them, periodic samples are taken with variable temporalities and a series of parameters are analyzed (not always the same for all wells).

The wells used in this study are those found in table 2, which shows a synthesis of the number of wells per municipality. The detailed information of the wells with their specific location, their name and coding, and the available data (parameters and historical) can be found in appendix 1 in the tables 3, 4, 5 and 6.

Table 2. Synthesis of all the wells that will be studied.

Right margin		Figure	Left margin		Figure
Township	**nº wells**		**Township**	**nº wells**	
Martorell	6	7	El Papiol	1	10
Castellbisbal	1	7	Molins de Rei	1	10
Sant Andreu de la Barca	2	7	Sant Feliu de Llobregat	6	10
Pallejà	1	8	Sant Joan Despí	1	11
Sant Vicenç dels Horts	17	8	Cornellà	25	11
Santa Coloma de Cervelló	2	9			
Sant Boi	4	9			

To have a better situation of the wells included in this study, they are geographically located in the following pictures on Google Earth (both for the left and right margins).

Right margin:

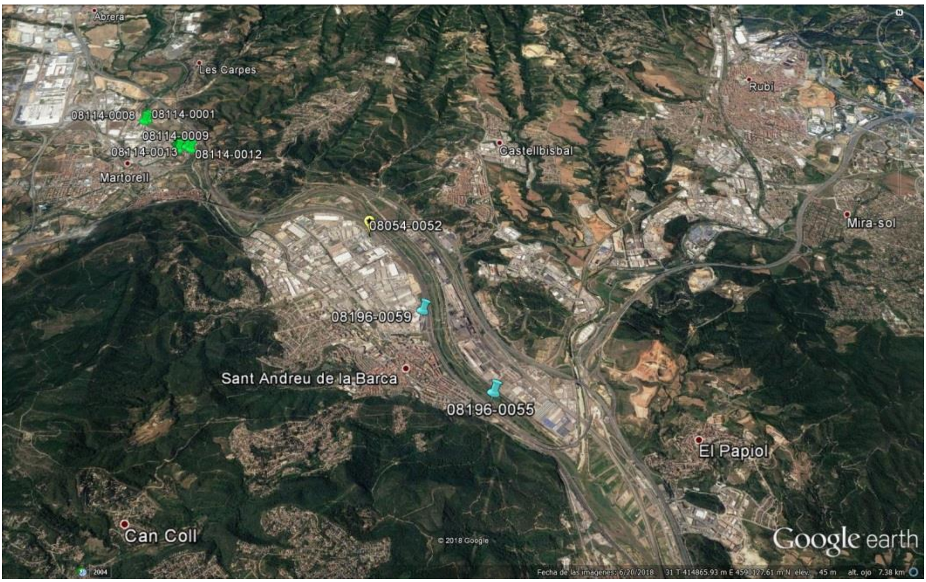

Figure 7. From Martorell to Sant Andreu de la Barca.

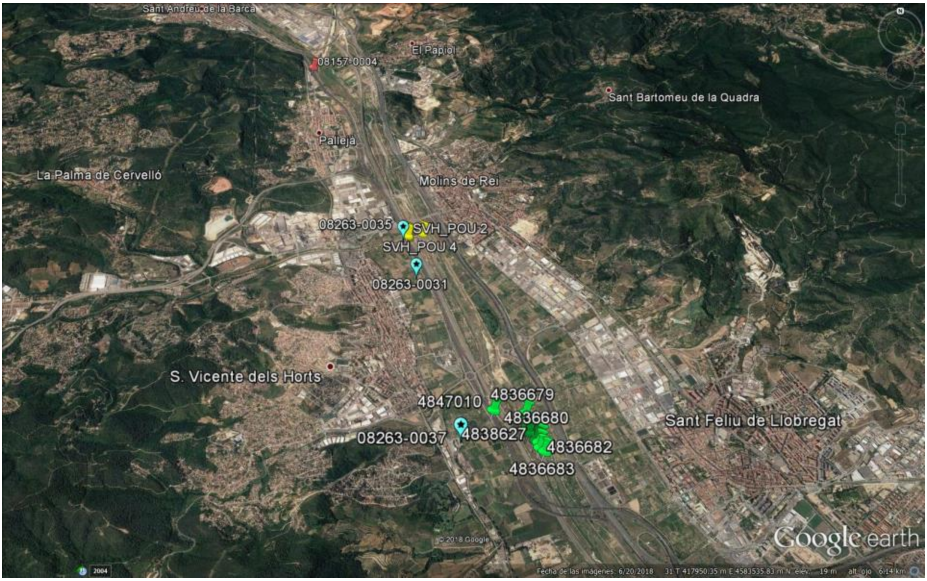

Figure 8. From Pallejà to Sant Vicenç dels Horts.

Figure 9. From Santa Coloma de Cervelló to Sant Boi.

Left margin:

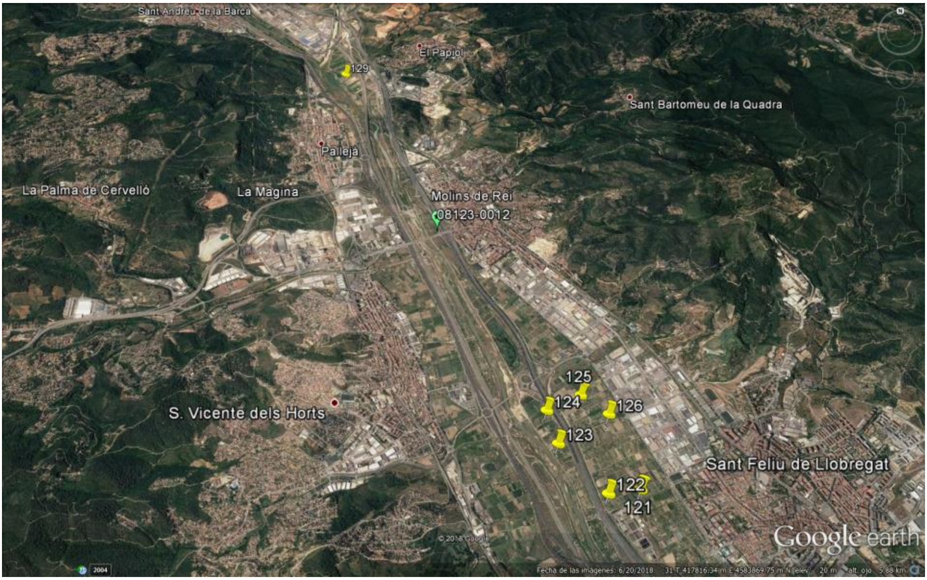

Figure 10. From El Papiol to Sant Feliu de Llobregat.

Figure 11. From Sant Joan Despí to Cornellà.

As it can been seen, in the whole lower Llobregat River aquifer there are many wells. However, as we will see, not all of them will turn out to be representative of the system for this specific study. The reasons for this can be wide: they can be influenced by the geography of the terrain, do not have a enough tracking control, having suffered occasional pollution events,...

The chlorides are one of the conservative parameters by means of which we can keep good track of salinity in the water and, in fact, they are one of the basic pillars of this study. For that reason, in appendix 1 in table 7, the averages, the maximum, the minimum of chlorides and the amount of data available for each well are indicated. In this same table, the wells that finally lay out of the scope of this study are pointed out, as well as the reason for its exclusion.

Thus, of the 67 existing wells with chemical data in the area, a first selection makes us work with 56 wells.

4.2. ANALYSIS TOOLS AND METHODS USED

To be able to analyze the evolution of salinity at the Lower Valley of the Llobregat River, both in groundwater and in surface water, different tools and resources have been used:

- Concentrations of salts (chlorides) and their graphic representation through the Surfer program, which generates surfaces with isoconcentration curves from various points, making interpolations. The figure of the aquifer is represented and the different chloride values of the entire area are shown with a color degradation scale. By means of this one can see the evolution of chlorides over the years.
- Relationships of conservative parameters (chlorides/bromides): parameters that do not degrade along the basin through the time, so therefore they can become a clear tracer of the origin of the recharging water.
- Proportions of elements through the Piper diagrams.

Piper diagrams are a graphic representation of the chemical composition of water. The cations and anions are shown in separate ternary diagrams. In the diagram of the cations the vertices are calcium, magnesium and sodium plus potassium; nevertheless, in the anion diagram the vertices are sulphate, chloride and carbonate plus bicarbonate (if considered appropriate, other combinations of cations and anions can be chosen to be represented). The two ternary diagrams are projected in a diamond; which is a transformation of the anions and cations graph. Piper diagrams are expressed percentage of meq/L.

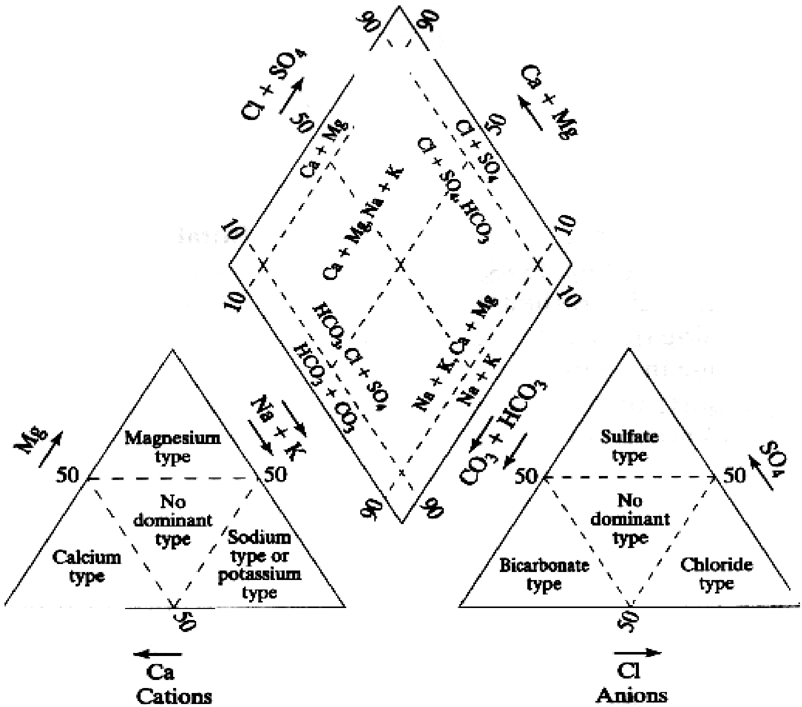

Figure 12. Generic representation of a Piper Diagram.

5. RESULTS AND DISCUSSION

Once introduced the geographic system to study, located all wells and the surface water sampling points and compiled all the necessary data, results are analyzed.

5.1. EVOLUTION OF SALINITY IN SURFACE AND UNDERGROUND WATER

This section analyzes the evolution of salinity in the Lower Valley of the Llobregat River based on chloride concentrations of the different wells of the two margins as well as on the surface water sources that feed the aquifer, being the chloride a key parameter indicating the salinity in the Llobregat basin[3].

5.1.1. Surface water

In the setting of the problem, it has been stated that, in this system, there has been a significant decrease in the concentration of chlorides in surface water throughout the years. This decrease can be seen in figure 13.

[3] The RD140/2003, of February 7, w*hich establishes the health criteria for the quality of water for human consumption* determines, in its Appendix 1, a limit of 250 mg/L of chlorides in treated water.[(10)]

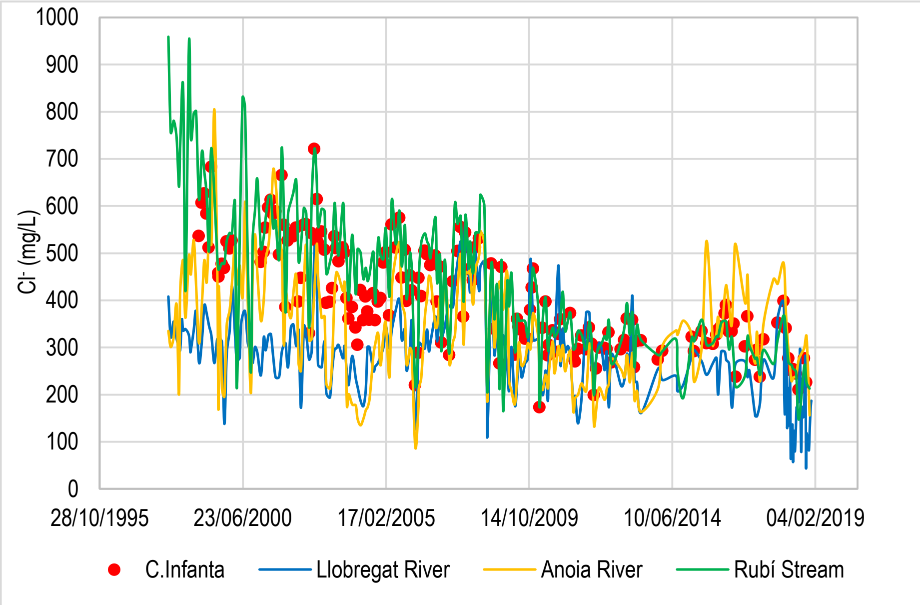

Figure 13. Chlorides evolution of surface water in the area of the Lower Valley.

(Note: The chlorides values of the Canal de la Infanta are found though a balance between the flows and the concentrations of chloride of the Anoia River and the Rubí Stream).

As mentioned above, there was a first decrease in chlorides due to the set-up of the brine collector. However, the sharpest decrease in the concentration of chlorides in surface water is attributed to another factor: the modifications of the water treatment facilities, both wastewater and drinking water (WWTPs and DWTPs); existing in this system.

Among these improvements, we can mention than at the DWTP Llobregat (Drinking water treatment plant of the Llobregat), located in the township of Abrera, in 2009 a reversible electrodialysis (EDR) installation was put into operation: a system that eliminates a high content of salts and pollutants in the water to prevent the formation of trihalomethanes in the water when the chlorination process occurs.

This DWTP supplies potable water to the townships of Terrassa, Rubí, Esparreguera, Collbató, Martorell, Abrera, Masquefa, Igualada and nearby towns. So, the wastewater of these municipalities, after its cycle of consumption, goes to the WWTPs of their area (Igualada, Martorell, Rubí and Terrassa). These two last ones go directly to the Rubí Stream, the Martorell WWTP discharges to the Llobregat River and the water outcome of Igualada is sent directly to the Anoia River. So, the Llobregat, the Anoia River and the Rubí stream see the effect of the EDR system since 2009.

With all this, there is a general decrease in chlorides due to an improvement in the quality of the water of origin. Other factors that have influenced this decrease have been an improvement in the salt rejection and, therefore, more quantity of salts sent to the brine collector.(1)

It should be noted that the Rubí Stream and the Anoia River in previous years transported a high content of chlorides. Now the saline load of potable water has decreased and, therefore, the residual water saline load too, thus improving the water that passes through the Canal de la Infanta and which uses the agricultural sector on the left margin of the river, getting close to the values of the River itself. In short, we could say that, with respect to chlorides, the waters with which the left and right margins of the Lower Valley of the Llobregat are watered, every time they look more like each other.

In the last years, chlorides of the Llobregat River had values around 300 mg/L, however now the value is sometimes nowadays around 100 mg/L. Nonetheless, despite the concentration is lower, the daily chloride tons that drags the river remain quite constant (see figure 14).

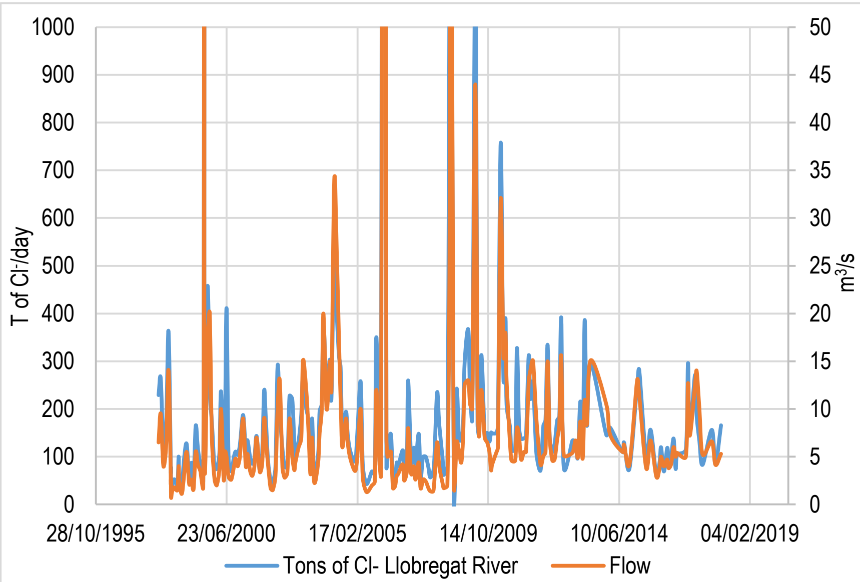

Figure 14. Tons of chlorine daily in the Llobregat River and the flow of the same river.

When the flow of the Llobregat River increases, the tons of chlorides also do it. This is because when it rains, the rainwater dissolves the salty mountains that are located in the Bages region: Based on this: the higher the flow, more tons of salt in the river.

Thus, if we compare tones with chloride concentration, as these last years have been a bit more humid, there has been a greater dilution and the concentrations have dropped. The graph of figure 33 of appendix 2 shows the historical evolution of the reservoirs at the Llobregat basin, with a clear evolution upwards in recent years.

5.1.2. Groundwater

To perform the analysis of the distribution of salinity in the aquifer, it has been considered appropriate to perform isoconcentration maps of chlorides made with Surfer program[4]. These maps have been created by the chloride concentrations (in mg/L) and the coordinates of the wells of the two margins of the river in 3 different years (2003, 2008 and 2017).

4 Note that the limitations of the graphic representation offered by the Surfer program makes the map scales different for each one year.

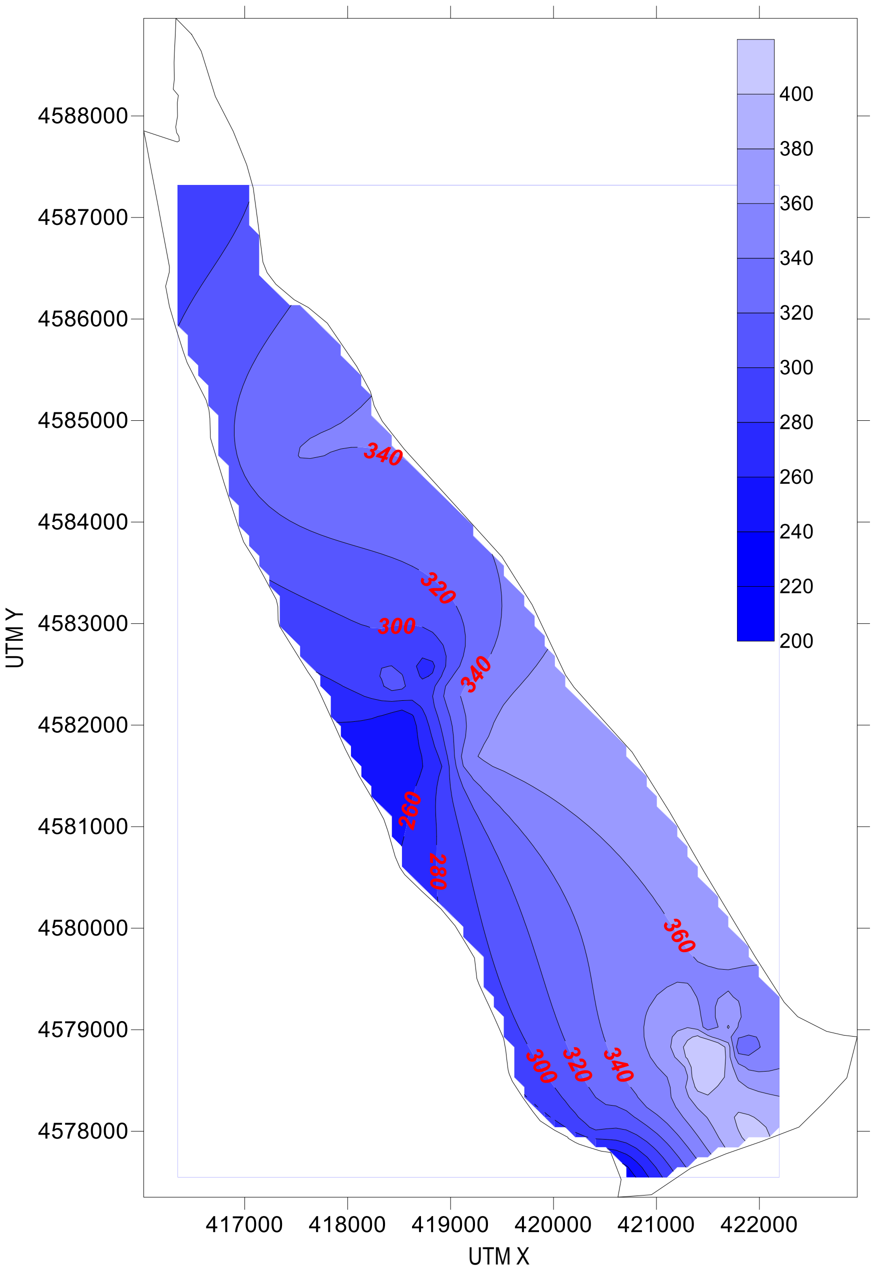

Figure 15. Map of isochlorides in the Lower Valley of the Llobregat River aquifer in 2003.

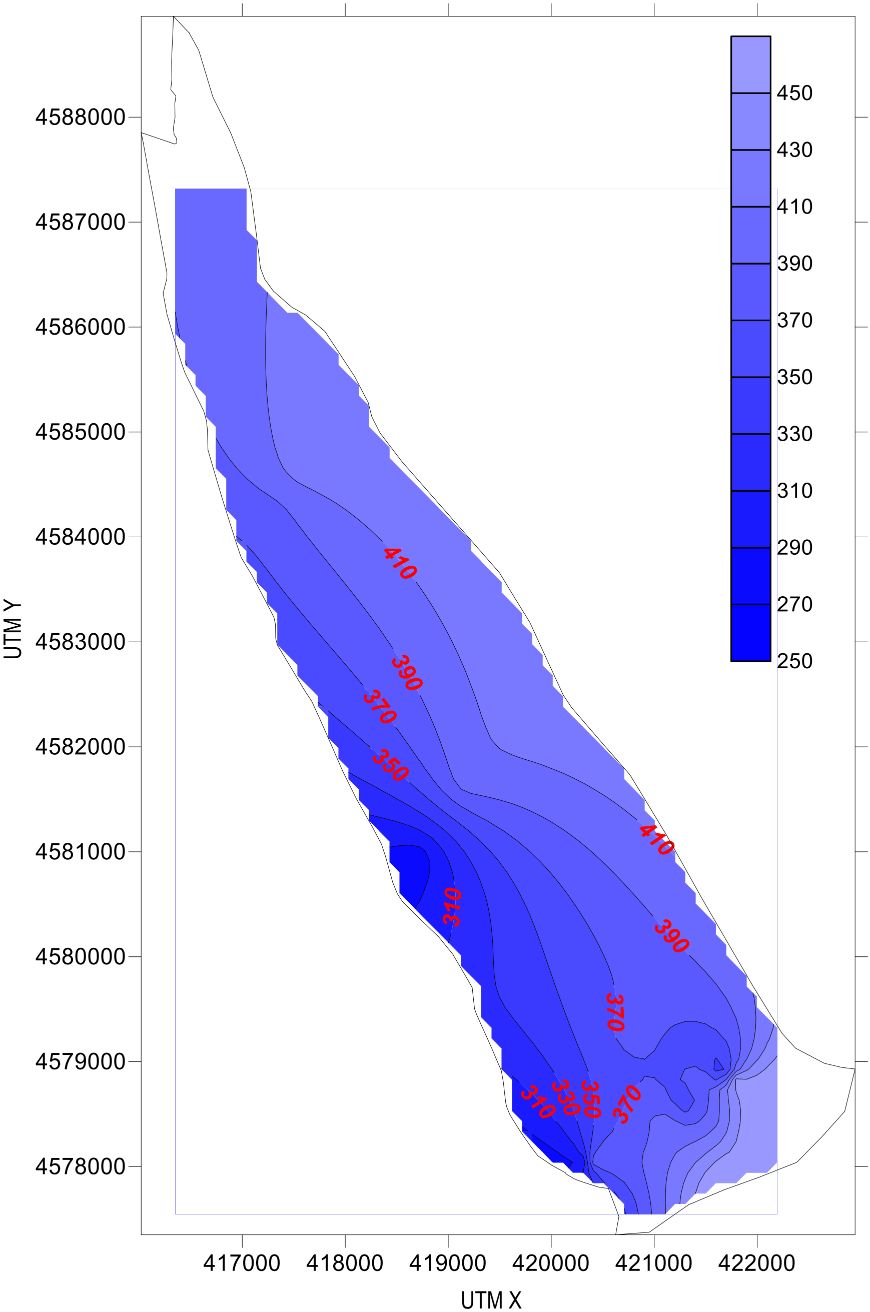

Figure 16. Map of isochlorides in the Lower Valley of the Llobregat River aquifer in 2008.

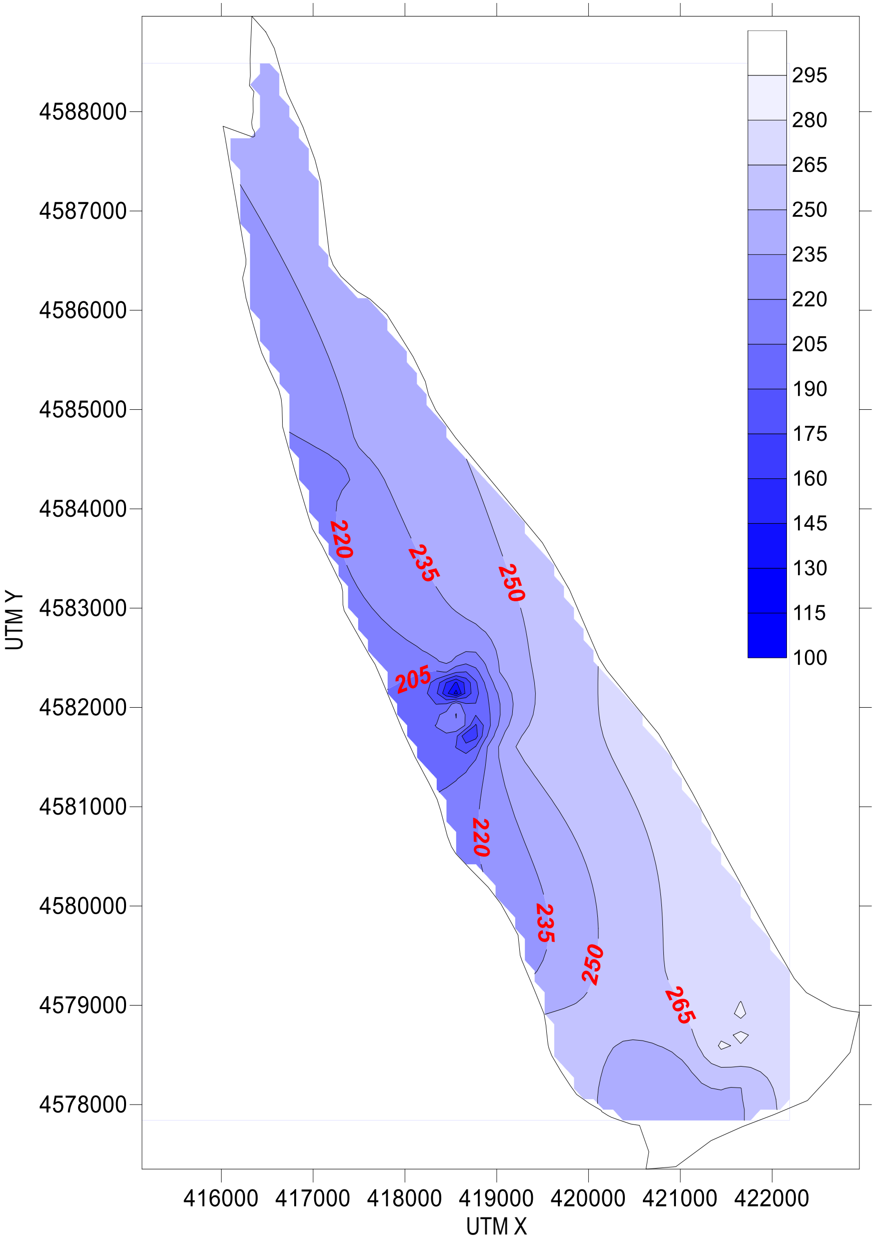

Figure 17. Map of isochlorides in the Lower Valley of the Llobregat River aquifer in 2017.

If one observes these three maps, it can be seen that chlorides are now considerably lower than years ago. In 2008 the values were higher than in 2003. This is explained by the fact that this year was a year of drought and the extraction of groundwater increased significantly, especially in the wells located in Cornellà (see this effect in figure 18). As there was more extraction than usual, in 2007-2008 it lowered the level of the aquifer and there was saline intrusion. This intrusion, depending on the location of the wells, will have more or less impact (see figure 34 in appendix 2).

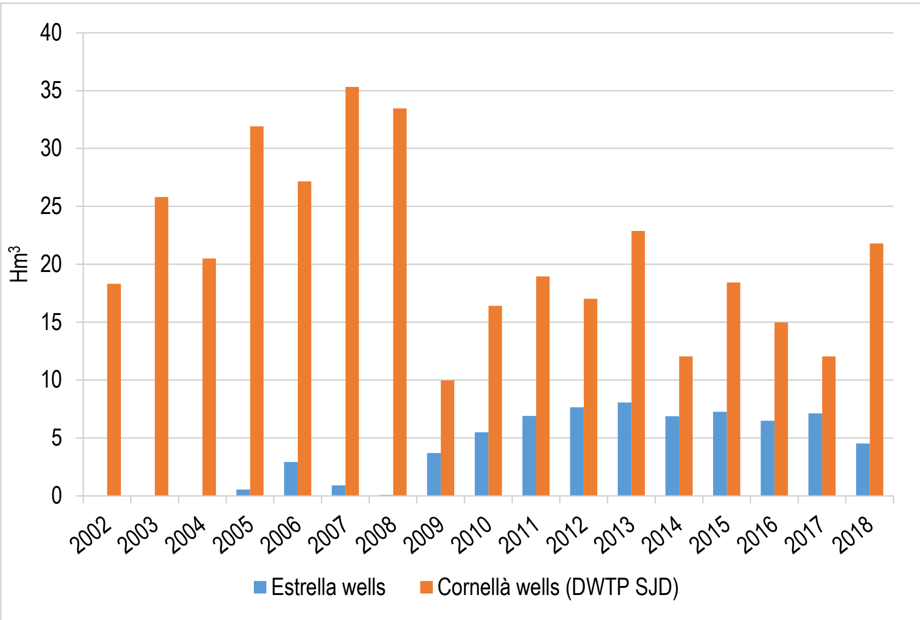

Figure 18. Hm^3/year extracted at the wells of Cornellà at the height of the DWTP of Sant Joan Despí and to the wells called Estrella.

And now in 2017 the chlorides values are lower again, below or around the limit of 250 mg/L.

If one compares one margin against the other, it can be seen that the left margin is where the maximum concentrations of chlorides are found, and as we move closer to the right margin, the concentrations are lower. To find a possible explanation for this fact, it is necessary to check with which water it is watered each one of the two margins. As it has been mentioned above, the fields on the right margin are mainly watered with Llobregat water, while those on the left margin receive the water flowing through the Canal de la Infanta (the flow that prevails in the channel is that of the Rubí Stream, because the average proportion derived of water of Rubí and Anoia is of 1:2., Figure 19).

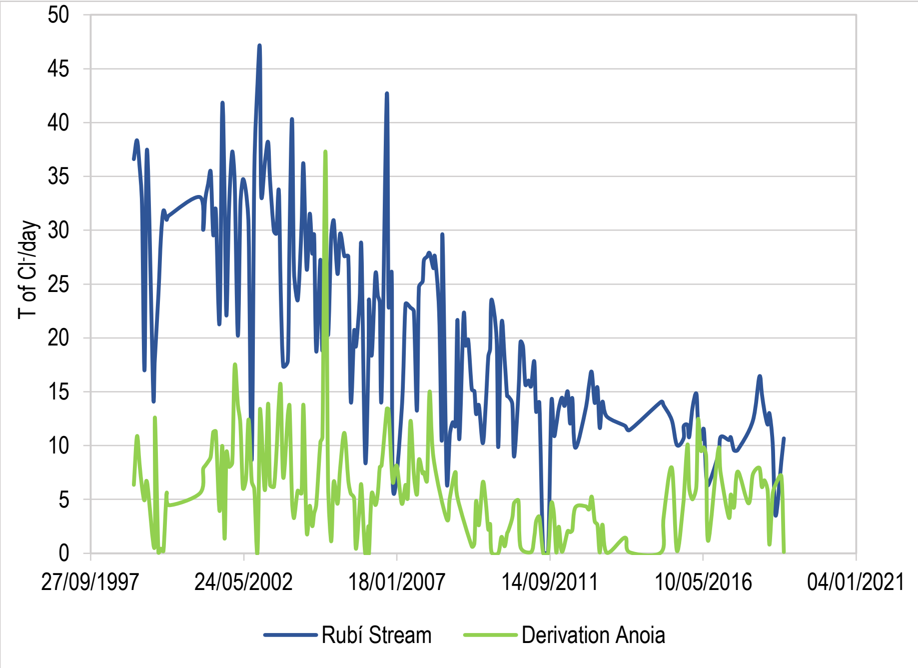

Figure 19. Evolution of the tons of chlorides by day of the Anoia River and the Rubí Stream.

The Canal de la Infanta historically had chloride values higher than the Llobregat River (figure 13). That is why on the left margin there are the highest concentrations of chlorides and on the right margin, the lowest. However, in recent years, the difference in chlorides between the river and the Canal de la Infanta is becoming smaller. A possible explanation for this fact is detailed later in this study.

In terms of groundwater, in all the maps it can be seen a point where the concentration is much lower than the rest; that is because at that point is located the well of Pallejà (well with code 08157-0004), a well with a very low chloride concentration due to the lateral contribution it receives from the mountain. Otherwise, as we approach the Delta area, especially in the years

2003 and 2008, the influence of saline intrusion is observed, with an increase in salinity. The effects of this amount of sea water disappear in the last map, that of 2017.

To sum up: the improvement on surface water has had a clear impact in the evolution of the chlorides of the different wells on the two margins of the Lower Valley of the Llobregat River Aquifer.

Wells of the right margin of the Llobregat

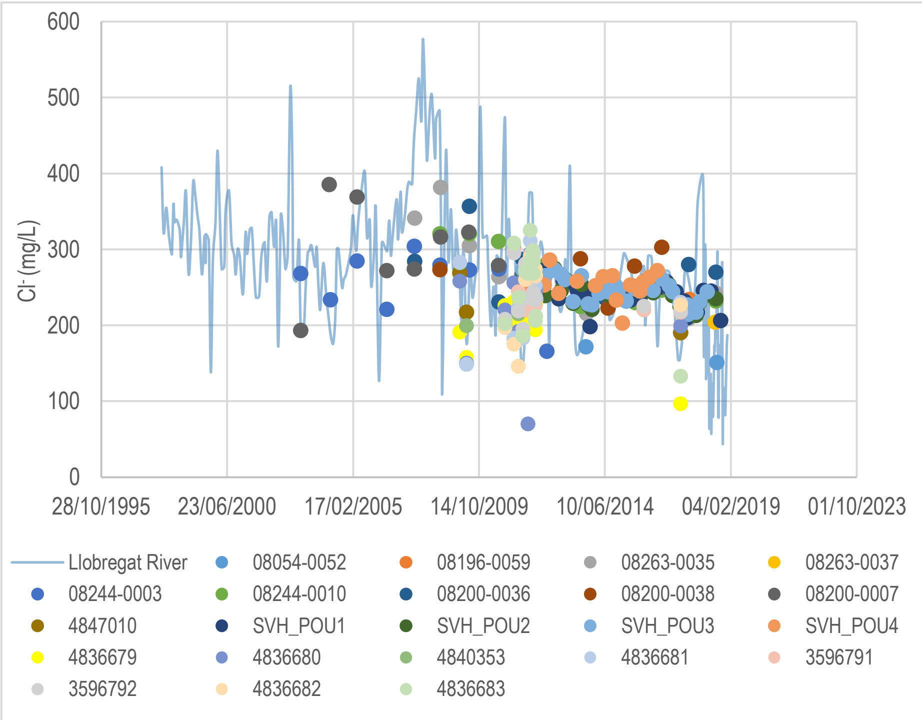

Figure 20. Evolution of the chlorides of the right margin wells and chlorides of the Llobregat River.

All the wells on the right margin (figure 20) have a direct relation with the Llobregat River water. In this area, the Canal de la Dreta elapses: a canal that is used for watering and that transports water derived from the Llobregat River. Therefore, the same pattern of behavior as the river should be expected. This relation of surface water with groundwater can be due to both the effect of the canal (going down the valley, this effect should be seen from Sant Vicenç dels

Horts/Molins de Rei on; 08263-0037 well is located right at this point (figures 4 and 8)) and also to the proximity of the well with the river.

A small part of the right margin is watered with the Canal del Rec Vell, but there is no impact of it in the wells due to its low and irregular ratio of use.

It can be seen that the wells with code 08200-0036 and 08200-0038, located in Sant Boi, since the drought period (2007-2008), they have slightly higher chloride values than those of the River (before the drought, the well 08200-0007 also has the same pattern). This is because these wells are somewhat influenced by the saline intrusion that occurred in these specific years, because they are the ones that are closer to the Llobregat delta, vulnerable zone due to the sea water intrusion.

<u>Wells of the left margin of the Llobregat</u>

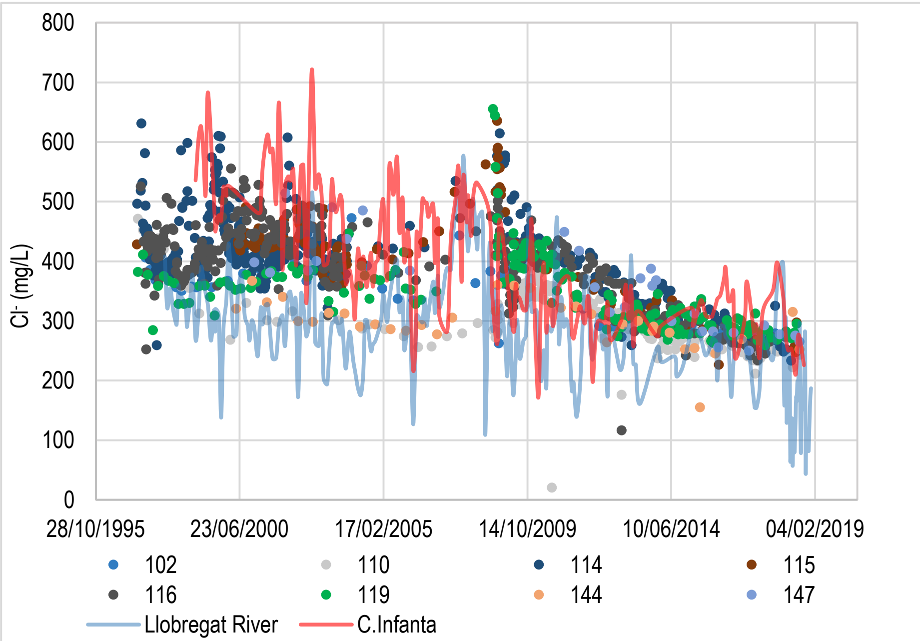

Figure 21. Evolution of the chlorides of the wells of the left margin in Cornellà and chlorides of the Llobregat River and the Canal de la Infanta.

On the left margin we have a well located in Papiol, another in Molins de Rei and one in Sant Joan Despí; the rest are in Sant Feliu de Llobregat and in Cornellà (table 2). Figure 21 shows only some wells that are located in Cornellà. These wells have been chosen among all based on 2 main reasons: they provide a clearer picture of the necessary information and there is plenty of data available. In the same way, both the nearest wells on the riverbed and the farthest ones have been depicted. The rest of Cornellà wells are an interpolation between the wells represented in figure 21. Nonetheless, the complete set of data of these wells can be found in appendix 2 figure 35.

It can be appreciated that the two nearest wells to the River (110 and 144) are the ones that follow the same trend as the Llobregat River. However, the rest of the wells represented have more input of the Canal de la Infanta, because they are located at a certain distance of the riverbed (see figure 11 for the wells situation).

In 2007 and 2008 there was a considerable period of drought. Intensive extraction of the wells was carried out (see figure 18), causing some of the wells located in Cornellà to be salinized, especially those that receive more directly the entrance of sea water. Thus, the peak seen in 2009 in groundwater (with a certain temporary delay with respect to the surface water, due to the own inertia of the system): a peak caused by this marine intrusion, increasing the chlorides.

Following the peak of drought, the values of chloride concentrations fall down for a few days. A shock action was carried out, starting up the barrier against saline intrusion(8). Moreover, it began to rain recurrently (figure 14) and progressively the level of the aquifer began to recover, while the chlorides of the groundwater started a slow decrease.

Even once this period was over, it can be seen that there are still wells that have a concentration of chlorides above the values of the River and the Canal de la Infanta. We attribute this to the fact that the saline intrusion still has an ongoing effect on these wells until 2015. Indeed, once the drought is over, the concentrations remain with the same values they had before this dry episode. These concentrations are kept until 2011, when the chlorides begin to descend until they achieve a stationary state.

Years ago, the concentrations of chloride in groundwater had a dispersion that in subsequent years has reached a homogenization. The different sources of surface water that recharge the aquifer (Llobregat River and derivations of the Rubí and Anoia) have concentrations of chlorides with more and more similar values as time goes by, impacting also in the groundwater with this same pattern.

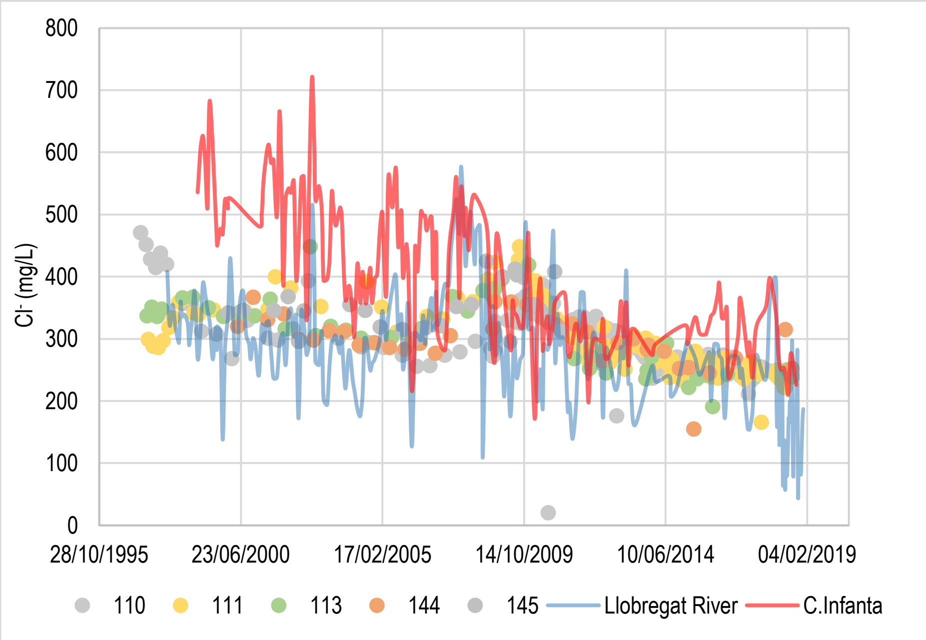

Figure 22. Evolution of the chlorides in the left margin wells closest to the River at Cornellà, together with chloride levels of the Llobregat River and Canal de la Infanta.

The figure 22 shows how all the wells located in Cornellà near the River have a direct contribution of the Llobregat River water, as it has been discussed before.

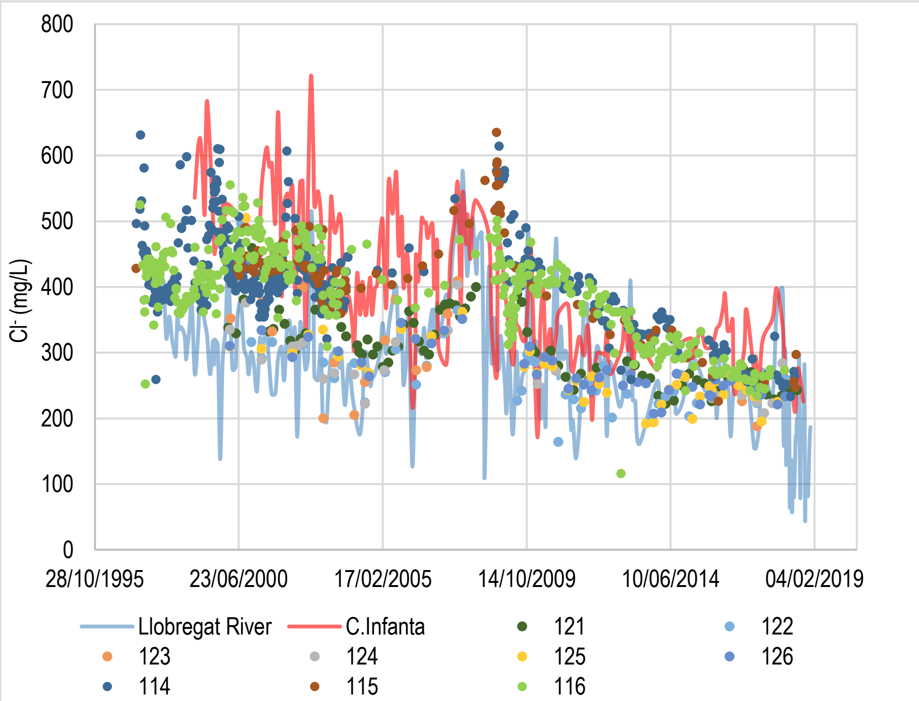

Figure 23. Chlorides evolution of the nearest and the farther left margin wells in the Llobregat delta with the evolution of the chlorides of the river and the channel.

Figure 23 shows the three wells that are located closer to the sea and to the left margin (114, 115 and 116), as well as all Estrella wells (121, 122, 123, 124, 125 and 126) located in the same margin, but in an upper region of the Valley. As it can be seen, all Estrella wells are mostly influenced by the Llobregat River and they do not have influence from the marine intrusion, because they are located at larger distance from the sea.

It can be also appreciated that Cornellà and Estrella wells showed years ago a remarkable difference in chloride values (having, nonetheless, a parallel evolution). Nonetheless, they do not show such a difference nowadays, since Cornellà wells seem not to be affected by saline intrusion anymore.

Finally, regarding chloride concentrations, there was an attempt to find, for each well of the left margin, the proportions of recharged water coming from the Llobregat River and of the

Canal de la Infanta, in order to try to find if there had been any change over the years. To do so, the following equation was used:

$$[Cl^-]_{well} = [Cl^-]_{Llobregat\ River} * x + [Cl^-]_{Canal\ Infanta} * (1-x)$$

x = proportion of the river

(1-x) = proportion of the channel

Since the values of the groundwater show a delay in concentration when compared to those of the surface water, the aforementioned equation was applied by using average values per year for each point. However, this calculation does not provide significant results because there are many values that lay below the values of both the River and the Canal, possibly due to an extra dilution (rain or lateral inputs). On the other hand, there are also many values that lay above the values of both the River and the Canal, mainly influenced by marine intrusion. As we have these two factors (water from the rain and from the sea) and moreover a temporary decalage in the values of groundwater with respect to the evolution of chlorides in surface waters, the proportions of recharge of each well during the last years could not be specified by means of a mass balance (further information should be required, which lays out of the scope of this project).

In the tables 8, 9, 10 and 11 of the appendix 1 there is the complete set of results regarding the aforementioned mass balance.

5.2. CONSERVATIVE PARAMETERS

Chlorides and bromides are conservative parameters, that is, parameters that do not degrade over time and can therefore be considered as tracers. By stablishing a relation between them, one should be capable of tracking the origin of the water that recharges each well [(11)]. Nonetheless, due to lack of bromide values for the wells on the right margin, the chloride/bromide (Cl^-/Br^-) ratio can only be analyzed for surface water points and for the left margin wells.

Surface water:

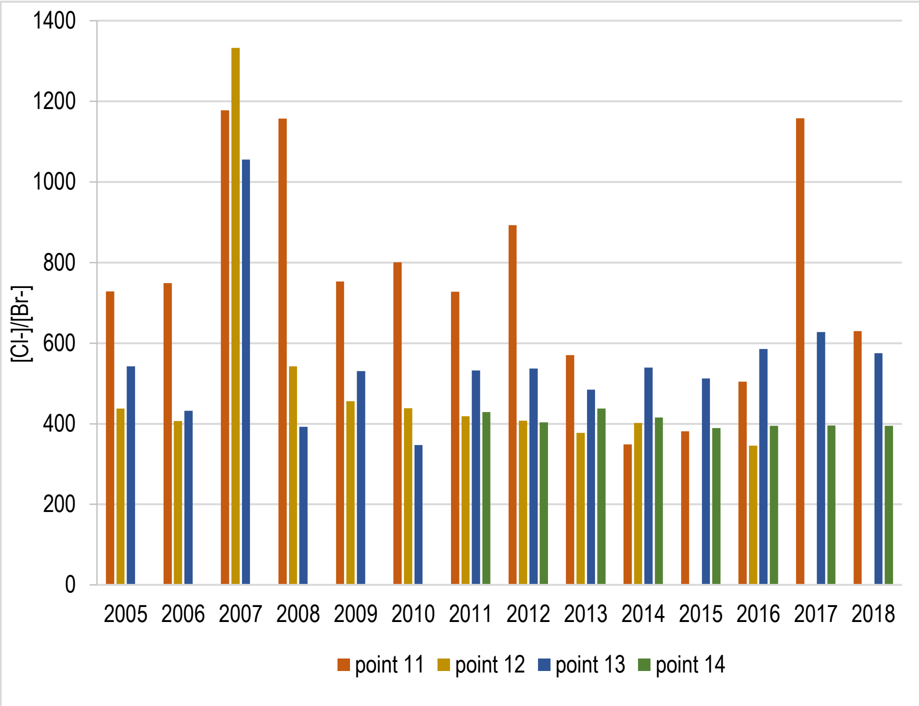

Figure 24. Cl^-/Br^- ratio of surface water from 2005 to 2018.

The point 12 (Llobregat River between the Anoia and the Rubí) and the point 14 (Llobregat River between the Rubí and SJD) have approximately the same values. This is because, in a normal situation (not heavy rain), they are practically the same water; in other words: the Rubí Stream is completely deviated to the Canal and has no influence on the Llobregat River.

In figure 24 one can also appreciate that the Anoia River (point 11) and the Rubí Stream (point 13) have slightly higher values if compared to the other points, although the Anoia River is the one with the highest values, because it is a River that carries a lower amount of bromides. With this one can see a small difference of the various surface waters that recharge the aquifer in relation to their proportion (Cl^-/Br^-).

<u>Groundwater:</u>

However, in figure 25 one can see that there is no virtually difference between the different wells on the left margin; in other words: all of them move in a very stable range of values, with the exception of the period of drought.

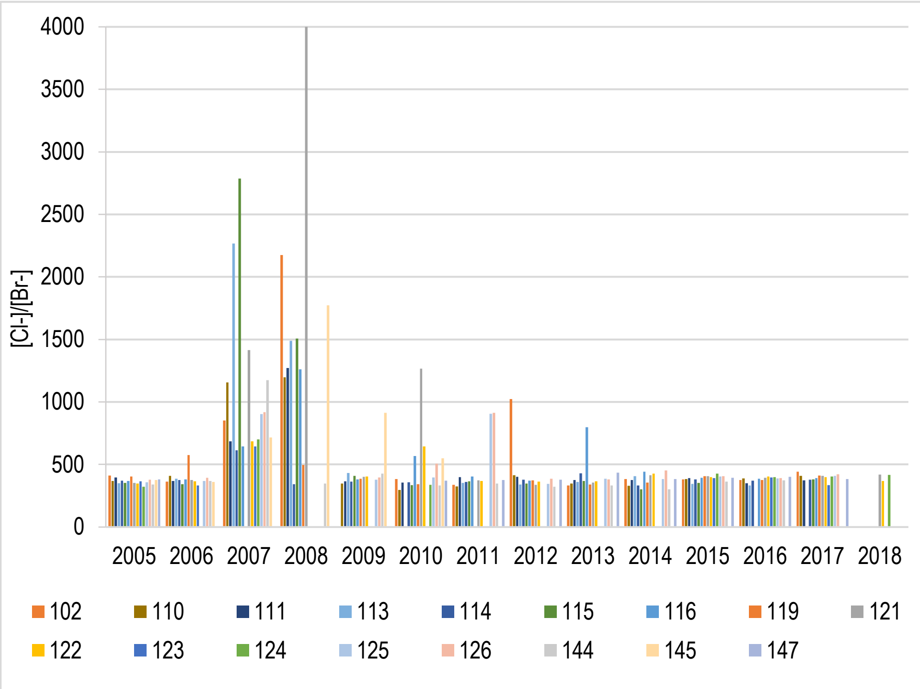

Figure 25. Cl^-/Br^- ratio of groundwater from 2005 to 2018.

In the two previous figures it can be observed that in the years 2007 and 2008 there are very high values, values that multiply up to 10 in the wells of the left margin and up to 3 in the points of the surface water if we compare to the rest of the years. Again, those years are the ones in which the area was punished with a severe drought. When there is shortage of water, the piezometric levels go down, the chlorides increase (the flow of the river decreases and there is not that much salt dilution transported by the river) but the bromides decrease. These last ones are reduced up to a level where they can be considered negligible. The rest of the years are quite stable regarding Cl^-/Br^-.

All these statements are complemented with tables 12, 13 and 14 of appendix 1.

Chloride concentrations continue to relatively high for a long time after the drought, whilst the relation Cl^-/Br^- immediately comes back to the values it had before this period. The hypothesis to give an explanation to this fact could not be found with the data available for this study. In fact, it would be necessary to get into detail on this point in further works.

5.3. PIPER DIAGRAMS

The two previous sections (global salinity and relation of conservative parameters) have led us to an approach of how the system behaves and how the aquifer of the Lower Valley of the Llobregat is recharged. Nonetheless, in the way to try to corroborate the previously stated hypothesis and complement them, another tool should be tested.

Thus, in order to be able to analyze the composition of cations and anions in wells, rivers and streams, as well as to find a relation between them (both between wells and between groundwater and surface water), Piper diagrams have been used.

Surface water:

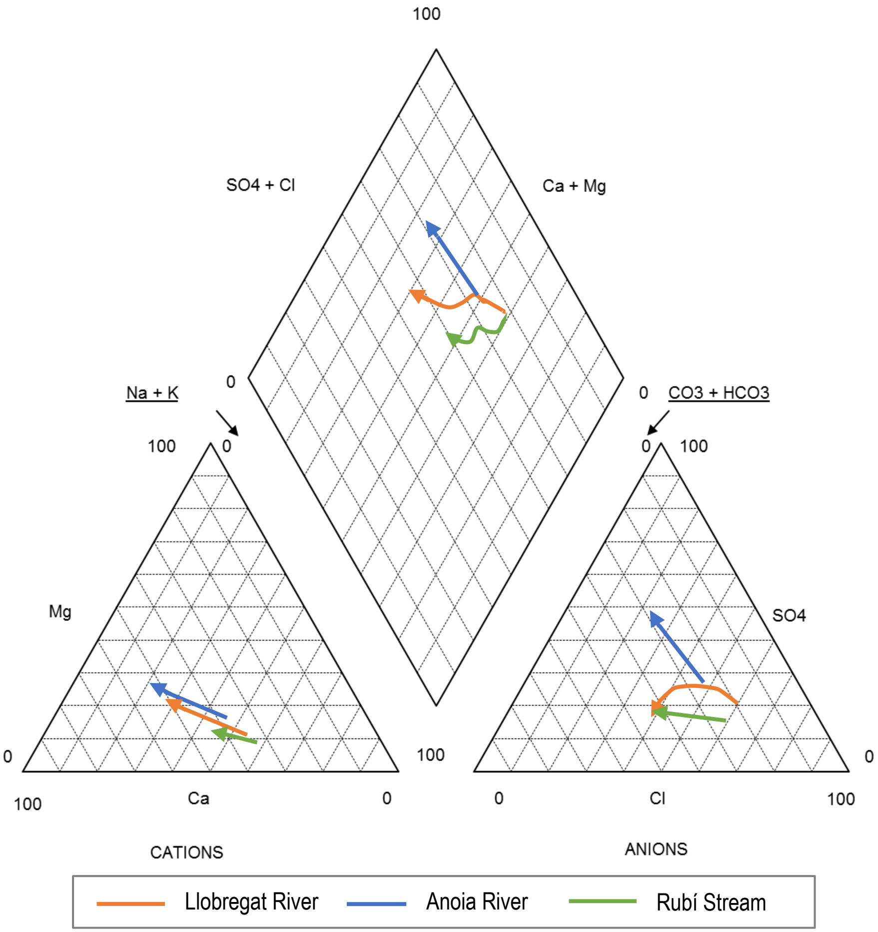

Figure 26. Piper diagram of surface water from 2007 to 2018.

In this diagram it can be seen that as the years pass by, there is an increase in calcium and bicarbonates, and a decrease in chloride and sodium plus potassium, due to the incorporation of the system of elimination of salts.

Moreover, if the different surface streams are compared among them, the Anoia River is the one that contains more sulphates, whilst the Rubí Stream carries a quantity of calcium lower than the rest, with a smaller dispersion.

In the appendix 2 in figures 36, 37 and 38, the Anoia River, the Rubí Stream and the Llobregat River are represented respectively, each with a diagram individually.

<u>Groundwater</u>:

In groundwater, different Piper diagrams for each one of the two margins have been considered in order to see the different affections of each well according to its location. The CUADLL wells will not be analyzed, due to lack of data (they are wells that are not used anymore nowadays and only samples are taken from time to time). Sorea wells are not analyzed neither due to lack of complete data from cations.

Right margin:

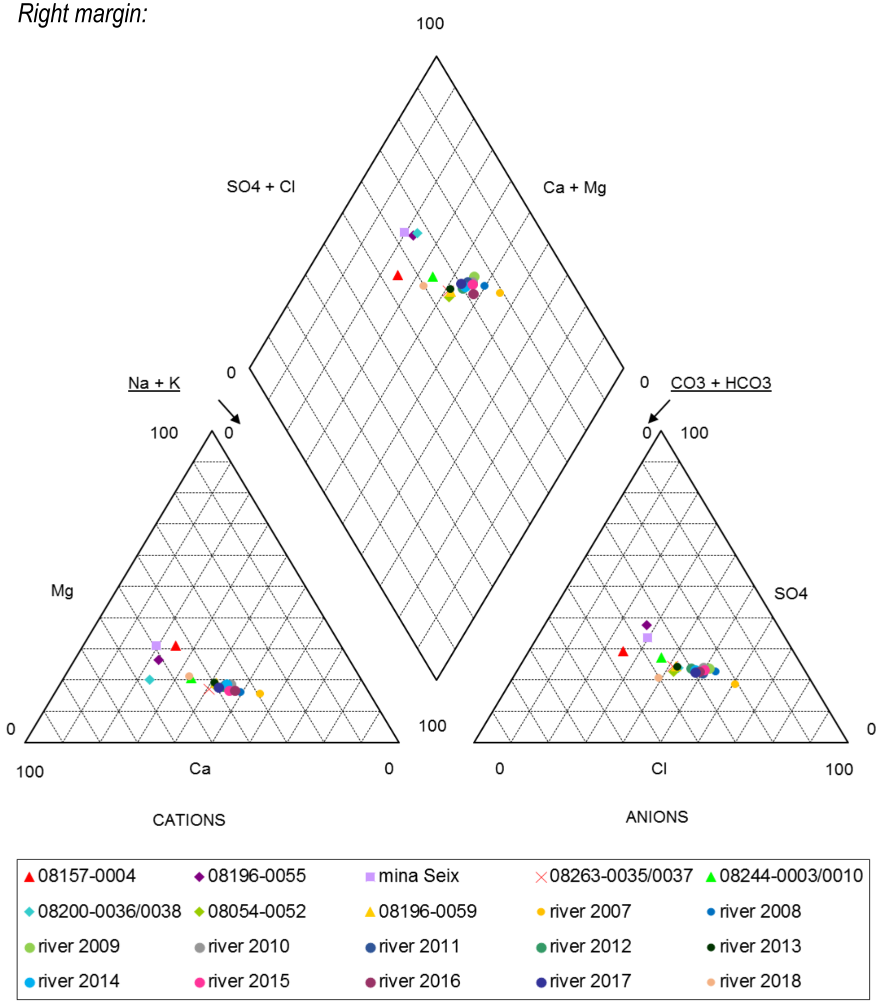

Figure 27. Piper diagram right margin and Llobregat River.

In the previous figure[5], the composition data of the Llobregat River and a water upwelling in the area (Mina Seix) are represented, together with the wells on the right margin. It is observed that:

- The wells 08196-0055 and 08157-0004 have a proportion of chlorides much lower than the rest. As already mentioned in section 4.1.2., this is attributed to the geography of the terrain, because 08196-0055 well is located next to a mountainous area (see figure 7) and, therefore, it receives water that comes from the mountain (water with less chlorides than that of the River).
- The well 08157-0004 also takes the water of the mountainous área, because it's located next to a stream that again receives water from the same mountain (figure 8). Indeed, in Pallejà there is a water upwelling called Mina Seix and operated by Aigües de Barcelona. It was wanted to compare the composition of well 08157-004 with the water of this Mine to see if they keep some type of relation, and it is observed that indeed it has many similar values.

So, these two wells are discarded because they experience a recharge of different origin to that of the other wells on the right margin; that is: these two wells have less influence of the Llobregat River water, and more of the side contributions of the area.

Once these wells are discarded, the wells 08054-0052 and 08196-0059 are representative wells of the recharge of the Llobregat River, because they are not yet influenced by the Rec Vell. In the diagram it can be seen how the two points of these wells remain on those of the River.

The rest of points are wells that are located in St. Vicenç dels Horts, in Sta. Coloma de Cervelló and in St. Boi. Regarding all these wells, as one goes down the River and towards the sea, there is a clear variation in cations: calcium is increasing and sodium plus potassium are decreasing. This is because they are strongly influenced by the limestone massif in the area (figure 28).

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[5] For surface water (the river), every point in the diagram is one year. For groundwater, each point is an average of the different years (2005-2018), since its variation over time is very small.

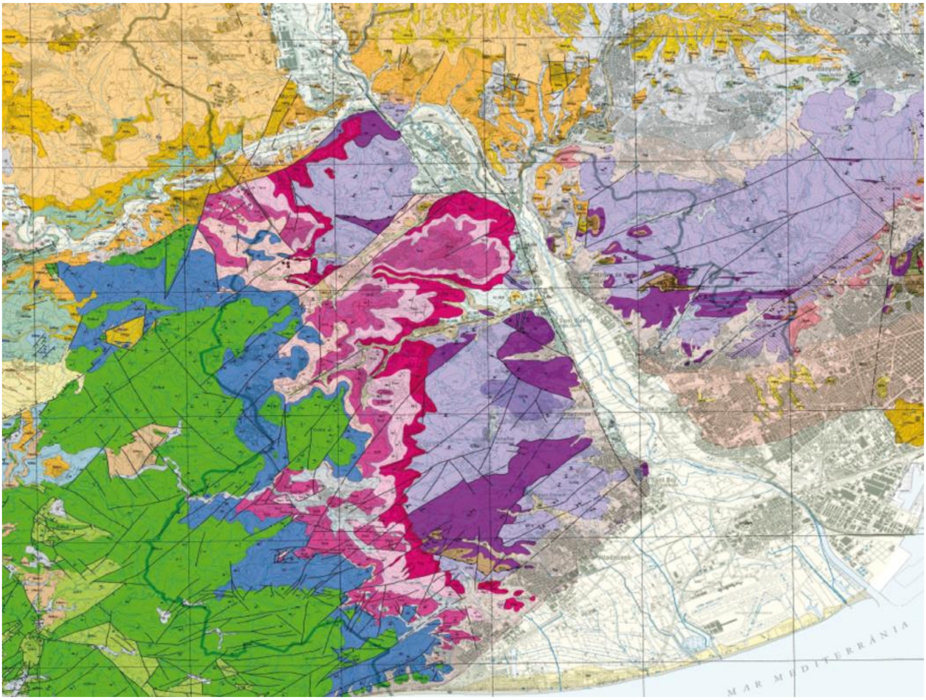

Figure 28. Geological composition of the area[6]. *(Image taken from the Institut Cartogràfic i Geològic de Catalunya – www.icgc.cat, 2015).*

In the area of the right margin of the River, the colors green, blue and pink identify a calcareous terrain. That is why, when water flows in a downward direction, it drags this type of material, making it visible in areas of different composition, such as that of the chalk-stone (purple color).

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[6] In appendix 2 in figures 39, 40 and 41 is the legend of the geological map.

Left margin:

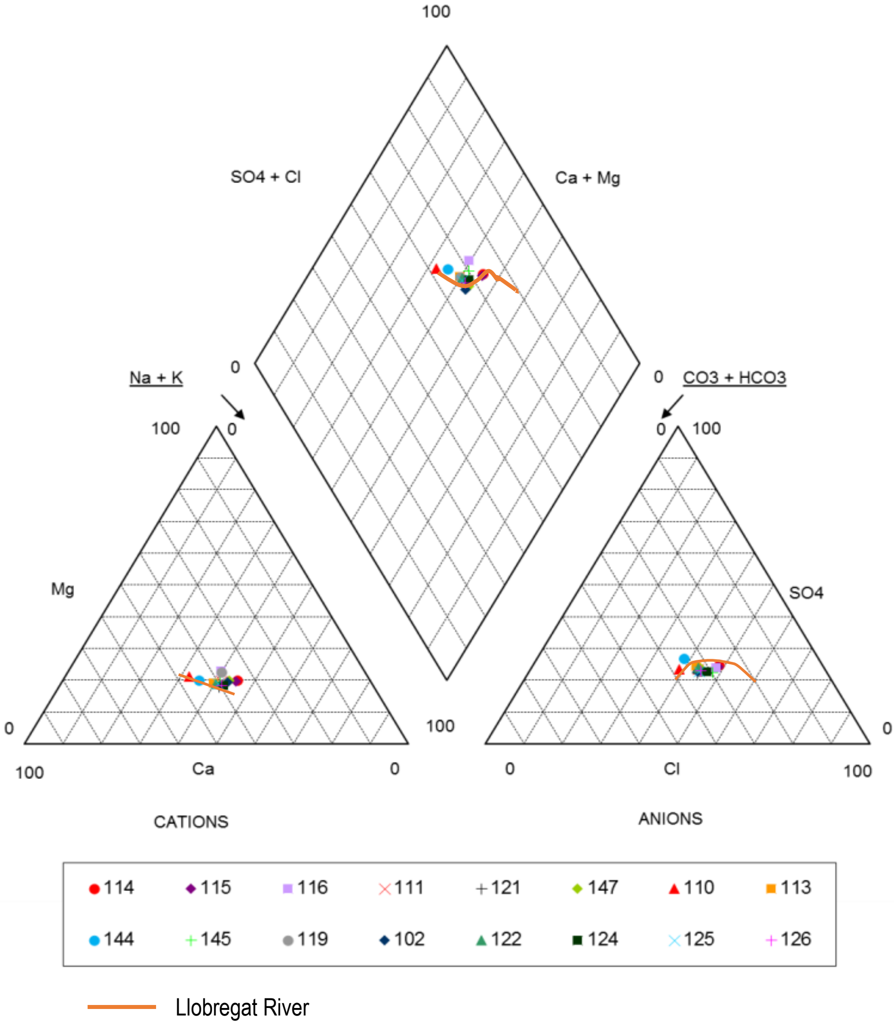

Figure 29. Piper diagram of the wells on the left margin of the Llobregat, representing the same wells that in the two previous sections.

As it can be seen in figure 29 all the wells are located at a constant point (their composition remains the same throughout the time), except for the wells 110 and 144. In fact, these two wells lay on the line that represents the River in the Piper diagram. Therefore, these two wells will be more influenced for the water of the River than for the water of the Canal, which is coherent with the fact that they are closer to the Llobregat River than the rest of the wells on the left margin (figure 11).

The wells 114, 115 and 116 are also placed at the constant point on the Piper diagram, something that surprises at a first sight, because during the drought period (2007 and 2008), these wells were affected by saline intrusion and it would be expected a difference based on chlorides concentration. However, a conclusion from this diagram is that despite the concentration of chlorides increases (section 5.1.2.), the proportion of cations and anions remains the same.

The wells called Estrella (from 121 to 126) allow to realize up to what point the proximity to the River can make the composition of relatively close wells vary among them.

The well 123 is analyzed separately because it shows a different trend from the rest of Estrella wells.

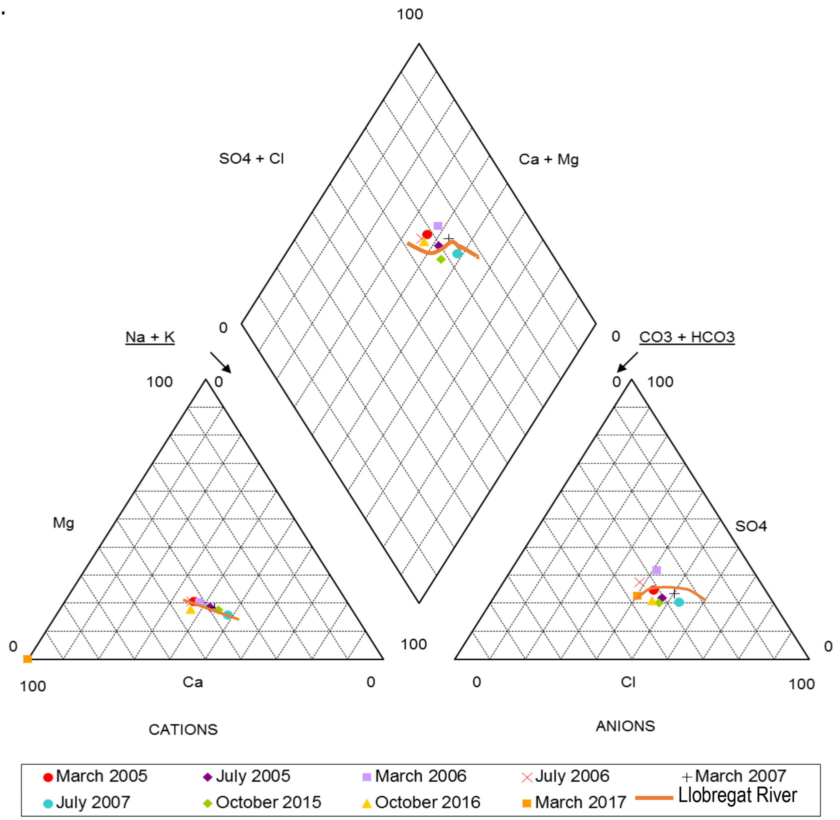

Figure 30. Piper diagram of well 123 and Llobregat River.

This well has a direct contribution of the Llobregat River, because it has the same dispersion and it's located just next to it.

In Molins de Rei there is the 08123-0012 well, which is not influenced by the Canal de la Infanta, since the Canal begins downwards of Molins de Rei. Therefore, it will be influenced by the Llobregat River water and not by irrigation water. In figure 31, the influence of the River on the well is perfectly seen.

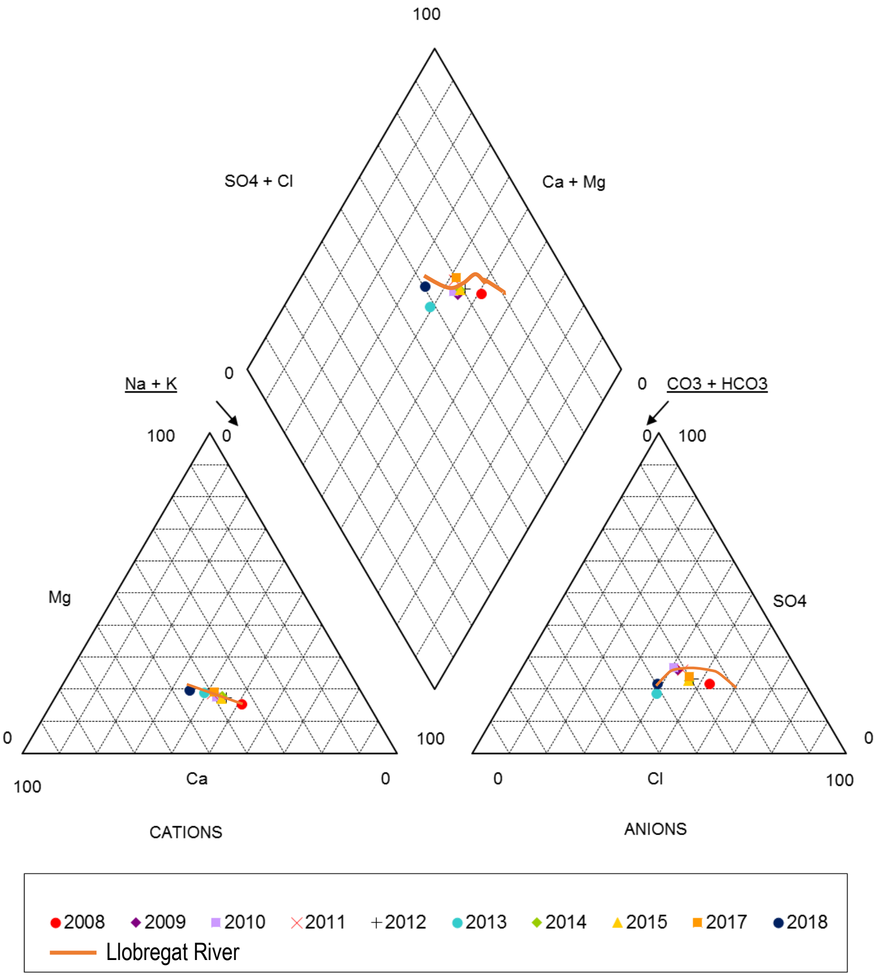

Figure 31. Piper diagram of well 08123-0012 and the river.

In appendix 1 there is the table 15 which compiles a synthesis of each well or surface water sampling point regarding the variation on all parameters of the diagrams.

Of all this section we can see that the relative proportions of cations and anions:

- Help to point which wells have a significant influence of side contributions (geography of the terrain).
- Do not show the differences related to the type of water with which the left and right margins are recharged.

6. CONCLUSIONS AND PROPOSALS FOR FUTURE STUDIES

From the analysis of the evolution of salinity data in the Lower Valley of the Llobregat River through different tools, it can be concluded that:

- The global salinity in the surface water of the Lower Valley of the Llobregat (Llobregat River, Rubí Stream and Anoia River) has a downward trend. This decrease in chlorides on surface water has 2 marked steps: the first one is attributed to the set-up of the brine collector (1989), and a second marked decrease years later (from 2009 on), associated with the improvements in the drinking water treatment plants (such is the case of the EDR in the DWTP of Abrera) as well as to the rainfall regime, which overall has increased during the last years.
- The improvement on salinity of the different surface waters has had a clear effect on the evolution of groundwater chlorides, also causing the concentrations to decrease throughout the years, with a marked trend to homogenize chlorides in the groundwater of the left and right margins of the Llobregat River.
- Based on the concentrations of chlorides in the wells of the left margin, the ones that are closer to the River have influence of the Llobregat; however, the rest of wells have more input of the Canal de la Infanta. On the contrary, the wells on the right margin have a direct relation with the Llobregat River water.
- The episodes of drought (2007-2008) have led to more intensive use of groundwater resources and this has caused episodes of marine intrusion. The effects of this salinity last up to 4-5 years after the drought is over. The wells that are located in Sant Boi and some wells of Cornellà are close to the Llobregat Delta, where this fact is clearly observed.
- The relation of conservative parameters (Cl^-/Br^-) also undergoes a marked variation during periods of drought: chlorides increase and bromides decrease as a result of higher extractions of water from the wells and the intrusion of seawater. In punctual years, bromides can be considered negligible; this fact sets a question on up to what point bromides can be considered a conservative parameter in this specific system.

- Piper diagrams for surface water present a greater dispersion of values (variation of the composition) than those of groundwater: although chlorides in groundwater suffer a drop over time, the relative composition of cations and anions in meq/L does not show significant variations in most wells.
- In the same way, Piper diagrams help to point out those wells that receive a more marked lateral influence (geography of the terrain) and for which salinity is almost not marked by chlorides in surface waters.
- The tools used in this work (Piper diagrams, relation of conservative parameters) based on the corresponding data available have not lead to find the right proportions of water with which the different wells of the two margins are recharged (only trends). Thus, the concentration of chlorides has been the only attribute that has enabled this differentiation in a qualitative way. To find quantitatively the proportions of the different sources of recharge for the wells, a new model of study should be proposed, focusing on making a more complex balance. For example, a balance including the detail of the kind of soil and types of crops for defined areas, with their corresponding irrigation endowments and he type of water that is used to irrigate in each one of the zones, together with the regime of historical rainfall, etc.
- In relation to the previous point and as a focus of improvement, it is suggested to incorporate in the sampling procedure an analysis of the bromides for the wells on the right margin of the Llobregat River. This should allow to highlight any difference between the Cl^-/Br^- ratio of the wells on both margins.
- The salinity data, both in surface water and groundwater, seems to have reached a stationary state around (or even lower) 250 mg/L of chlorides.
- In the future, it is expected that overexploitation of the aquifer and the effects of marine intrusion will be less likely, due to the fact that new infrastructures have been built in this system and they incorporate new water inputs to it. Among them, the new desalination plant built in El Prat de Llobregat (2009) or the reuse of regenerated water from El Prat WWTP.

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ACRONYMS

AB	Aigües de Barcelona
ACA	Agència Catalana de l'Aigua
Br^-	Bromide [mg/L]
Ca^{2+}	Calcium [mg/L]
Cl^-	Chloride [mg/L]
CO_3^{2-}	Carbonate [mg/L]
CUADLL	Comunitat d'Usuaris d'Aigua del Delta del Llobregat
DWTP	Drinking Water Treatment Plant
EDR	Reversible electrodialysis
HCO_3^-	Bicarbonate [mg/L]
K^+	Potassium [mg/L]
meq	Miliequivalent
Mg^{2+}	Magnesium [mg/L]
N	Number of data
Na^+	Sodium [mg/L]
RD	Reial Decret
SJD	Sant Joan Despí
SO_4^{2-}	Sulphate [mg/L]
T	Ton
WWTP	Wastewater Treatment Plant

APPENDICES

APPENDIX 1: TABLES

Right margin:

Table 3. Detailed information of the right margin wells (name, code, township and coordinates).

Name of the well	Code	Township	Coordinates	
			UTM X	UTM Y
Solvin Pou Radial	08114-0001	Martorell	410089.00	4593489.00
Solvin Pou Vinidor	08114-0008		410046.00	4593456.00
Aj. Martorell–La Torre 5	08114-0009		410709.00	4592774.00
Aj. Martorell–La Torre 1	08114-0012		410891.00	4592781.00
Aj. Martorell–La Torre 2	08114-0013		410825.00	4592835.00
Aj. Martorell–La Torre 3	08114-0014		410668.00	4592893.00
Stora Enso 1	08054-0052	Castellbisbal	413636.00	4591129.00
Aj. St. Andreu de la Barca	08196-0059	St. Andreu de la Barca	415136.07	4588486.75
Pz 38 st. Andreu de la Barca-1	08196-0055		414331.80	4589673.60
Benzinera Drac	08157-0004	Pallejà	415961.00	4587341.00
Joan Barcelò	08263-0031	St. Vicenç dels Horts	417460.15	4583684.58
St. Vicenç P3	08263-0035		417302.00	4584237.00
ES Les Palmeres P2	08263-0037		417901.66	4581768.15
Pou 1	SVH_POU 1		417334.87	4584160.07
Pou 2	SVH_POU 2		417323.12	4584187.97
Pou 3	SVH_POU 3		417311.83	4584216.10
Pou 4	SVH_POU 4		417475.40	4584224.47
BSV-0	4847010		418260.00	4582196.00
BSV-1	4836679		418446.00	4581955.00
BSV-2	4836680		418552.00	4581713.00
BSV-3	4840353		418466.00	4581823.00
BSV-5	4836681		418522.00	4581677.00
BSV-8.1	3596791		418462.00	4581764.00
BSV-8.3	3596792		418462.00	4581764.00
BSV-9	4836682		418553.00	4581606.00
BSV-10	4836683		418591.00	4581572.00
BSV-pou	4838627		418546.00	4581658.00
Àrids Garrigosa P1	08244-0003	Sta. Coloma de Cervelló	418721.00	4580966.00
Colònia Güell	08244-0010		419020.00	4579473.00
Benzinera Oasis	08200-0007	St. Boi	420540.84	4577545.72
Expafruit	08200-0021		420376.00	4576223.00
Benito Menni	08200-0036		419356.91	4578248.27
Benito Menni P2	08200-0038		419259.32	4578258.49

Table 4. Detailed information of the right margin wells (name, source of information, data frequency and used parameters).

Name of the well	Source of information	Data frequency	Parameters [mg/L]
Solvin Pou Radial	web ACA	1 data per year from 1999 to 2012	Chlorides
Solvin Pou Vinidor		1 data per year from 1996 to 2017	
Aj. Martorell–La Torre 5		1 data per year from 2002 to 2017	
Aj. Martorell–La Torre 1		1 data per year from 1996 to 2017	
Aj. Martorell–La Torre 2		1 data per year from 1999 to 2012	
Aj. Martorell–La Torre 3		1 data per year from 1996 to 2012	
Stora Enso 1		1 data per year from 2012, 2013, 2014, 2018	Cl^-, HCO_3^-, CO_3^{2-}, SO_4^{2-}, Na^+, K^+, Ca^{2+}, Mg^{2+}
Aj. St. Andreu de la Barca		1 data in 2017	
Pz 38 st. Andreu de la Barca-1		1 data in 2017 and 2018	
Benzinera Drac		1 data per year from 1999 to 2018	
Joan Barcelò		1 data in 2012	Chlorides
St. Vicenç P3		1 data per year from 2007 to 2018	Cl^-, HCO_3^-, CO_3^{2-}, SO_4^{2-}, Na^+, K^+, Ca^{2+}, Mg^{2+}
ES Les Palmeres P2		1 data in 2018	
Pou 1	Sorea	4 data per year from 2011 to 2018	Cl^-, HCO_3^-, CO_3^{2-}, SO_4^{2-}
Pou 2			
Pou 3			
Pou 4			
BSV-0	CUADLL	2 data in 2009 and 1 data in 2017	Cl^-, HCO_3^-, CO_3^{2-}, SO_4^{2-}, Na^+, K^+, Ca^{2+}, Mg^{2+}
BSV-1		1 data per year in 2009, 2010 and 2017. In 2011 1 data per month	
BSV-2			
BSV-3			
BSV-5			
BSV-8.1		1 data per year in 2009, 2010, 2015 and 2017. In 2011 1 data per month	
BSV-8.3			
BSV-9		1 data per year in 2009, 2010 and 2017. In 2011 1 data per month	
BSV-10		1 data per year in 2009, 2010, 2015 and 2017. In 2011 1 data per month	
BSV-pou		1 data in 2017	Chlorides
Àrids Garrigosa P1	web ACA	1 data per year from 2003 to 2012	Cl^-, HCO_3^-, CO_3^{2-}, SO_4^{2-}, Na^+, K^+, Ca^{2+}, Mg^{2+}
Colònia Güell		1 data per year from 2008 to 2018	
Benzinera Oasis		1 data per year from 2003 to 2011 and 1 dada al 2016	
Expafruit		1 data in 2013	Chlorides
Benito Menni		1 data per year from 2007 to 2018	Cl^-, HCO_3^-, CO_3^{2-}, SO_4^{2-}, Na^+, K^+, Ca^{2+}, Mg^{2+}
Benito Menni P2		1 data in 2008 and 1 data per year from 2013 to 2016	

Left margin:

Table 5. Detailed information of the left margin wells (name, code, township and coordinates).

Name of the well	Code	Township	Coordinates	
			UTM X	UTM Y
Papiol I	129	Papiol	416348.71	4587319.87
Urgellet	08123-0012	Molins de Rei	417546.00	4584666.00
Estrella 1	121	St. Feliu de Llobregat	419159.00	4581655.00
Estrella 2	122		418900.00	4581620.00
Estrella 3	123		418546.00	4582073.00
Estrella 4	124		418780.00	4582540.00
Estrella 5	125		418476.00	4582390.00
Estrella 6	126		418999.00	4582347.00
Gallina Blanca	08217-0004	St. Joan Despí	420723.00	4579266.00
Cornellà 1	101	Cornellà	421466.92	4578858.80
Cornellà 2	102		421650.71	4579002.47
Cornellà 3	103		421582.07	4578611.31
Cornellà 4	104		421604.31	4578438.17
Cornellà 5	105		421669.34	4578757.73
Cornellà 6	106		421624.21	4578790.31
Cornellà 7	107		421695.00	4578823.00
Cornellà 8	108		421736.47	4578877.28
Cornellà 9	109		421646.96	4578835.40
Cornellà 10	110		420333.14	4578060.04
Cornellà 11	111		420948.52	4578319.84
Cornellà 12	112		421304.91	4578588.84
Cornellà 13	113		420658.26	4578210.43
Cornellà 14	114		422192.97	4577840.31
Cornellà 15	115		421929.96	4577865.17
Cornellà 16	116		421794.77	4578142.18
Cornellà 17	117		421633.89	4578216.21
Cornellà 18	144		420403.39	4578066.42
Cornellà 19	145		420827.06	4578275.05
Cornellà 20	146		421084.70	4578409.49
Cornellà 21	147		421462.40	4578560.97
Cornellà 22	148		421557.24	4578980.15
Llobregat I	118		421761.54	4578786.04
Llobregat II	119		421755.56	4578800.89
Llobregat III	120		421668.93	4578880.17

Table 6. Detailed information of the left margin wells (name, source of information, data frequency and used parameters).

Name of the well	Source of information	Data frequency	Parameters [mg/L]
Papiol I	AB	2 data per year from 1997 to 2012	Cl^-, Br^-, HCO_3^-, CO_3^{2-}, SO_4^{2-}, Na^+, K^+, Ca^{2+}, Mg^{2+}
Urgellet	web ACA	1 data per year from 1996 to 2018	Cl^-, HCO_3^-, CO_3^{2-}, SO_4^{2-}, Na^+, K^+, Ca^{2+}, Mg^{2+}
Estrella 1	AB	5 data per year from 2000 to 2018	Cl^-, Br^-, HCO_3^-, CO_3^{2-}, SO_4^{2-}, Na^+, K^+, Ca^{2+}, Mg^{2+}
Estrella 2		3 data per year from 2000 to 2018	
Estrella 3		2 data per year from 2000 to 2017	
Estrella 4		2 data per year from 2000 to 2018	
Estrella 5		3 data per year from 2000 to 2018	
Estrella 6			
Gallina Blanca	web ACA	1 data per year from 2003 to 2018	Cl^-, HCO_3^-, CO_3^{2-}, SO_4^{2-}, Na^+, K^+, Ca^{2+}, Mg^{2+}
Cornellà 1	AB	3 data per year from 1997 to 2018	Cl^-, Br^-, HCO_3^-, CO_3^{2-}, SO_4^{2-}, Na^+, K^+, Ca^{2+}, Mg^{2+}
Cornellà 2		2 data per year from 1997 to 2018	
Cornellà 3			
Cornellà 4		3 data per year from 1997 to 2016	
Cornellà 5		2 data per year from 1997 to 2018	
Cornellà 6			
Cornellà 7		3 data per year from 1997 to 2018	
Cornellà 8			
Cornellà 9		2 data per year from 1997 to 2018	
Cornellà 10		3 data per year from 1997 to 2018	
Cornellà 11		3 data per year from 1997 to 2017	
Cornellà 12		2 data per year from 1997 to 2016	
Cornellà 13		2 data per year from 1997 to 2018	
Cornellà 14		4 data per year from 1997 to 2018	
Cornellà 15		2 data per year from 1997 to 2018	
Cornellà 16		4 data per year from 1997 to 2017	
Cornellà 17		3 data per year from 1997 to 2017	
Cornellà 18		2 data per year from 2000 to 2018	
Cornellà 19		2 data per year from 2000 to 2011, and from 2014 to 2016 1 data per year	
Cornellà 20		2 data per year from 2000 to 2018	
Cornellà 21		2 data per year from 2000 to 2005, and from 2010 to 2018	
Cornellà 22		1 data per year from 2000 to 2005 and 1 data in 2010	
Llobregat I		3 data per year from 1997 to 2018	
Llobregat II			
Llobregat III		2 data per year from 1997 to 2017	

Table 7. Concentration of chlorides for wells of both margins.

Code well	Average [mg/L]	Maximum [mg/L]	Minimum [mg/L]	N	Discarded wells
08114-0001	335,59	443,70	267,30	10,00	*
08114-0008	331,09	492,50	228,10	28,00	*
08114-0009	267,08	366,80	157,50	18,00	*
08114-0012	325,19	568,90	196,70	31,00	*
08114-0013	383,75	579,30	209,30	11,00	*
08114-0014	326,11	647,10	184,20	24,00	*
08054-0052	214,23	275,10	151,00	4,00	
08196-0055	174,50	204,00	145,00	2,00	Average chloride values too low
08196-0059	234,10	234,10	234,10	1,00	
08157-0004	168,04	277,90	106,40	21,00	Average chloride values too low
08263-0031	162,60	162,60	162,60	1,00	1 isolate sample
08263-0035	273,44	381,70	208,70	11,00	
08263-0037	204,00	204,00	204,00	1,00	
SVH_POU 1	240,97	272,00	198,00	36,00	
SVH_POU 2	239,12	275,00	213,00	33,00	
SVH_POU 3	242,00	273,00	214,00	33,00	
SVH_POU 4	251,88	286,00	203,00	17,00	
4847010	225,33	269,00	190,00	3,00	
4836679	205,68	231,00	96,60	18,00	
4836680	240,48	298,00	70,00	19,00	
4840353	236,73	302,00	199,00	6,00	
4836681	250,71	311,00	148,40	19,00	
3596791	247,73	298,00	202,00	15,00	
3596792	251,13	299,00	195,00	15,00	
4836682	250,69	290,00	146,00	13,00	
4836683	256,00	325,00	133,00	17,00	
4838627	221,00	221,00	221,00	1,00	1 isolate sample
08244-0003	251,04	304,00	165,80	12,00	
08244-0010	262,99	320,60	216,10	10,00	
08200-0007	291,44	385,50	193,00	10,00	
08200-0021	482,40	482,40	482,40	1,00	1 isolate sample
08200-0036	276,68	356,80	230,70	8,00	
08200-0038	272,78	302,50	222,70	5,00	
129	301,90	404,00	150,00	29,00	
08123-0012	326,81	1290,50	141,00	27,00	
121	309,15	459,00	222,00	82,00	
122	263,64	496,00	164,00	44,00	
123	306,21	435,00	188,00	19,00	
124	282,19	403,00	208,00	22,00	
125	273,22	505,00	192,00	46,00	
126	274,91	438,00	207,00	47,00	

Code well	Average [mg/L]	Maximum [mg/L]	Minimum [mg/L]	N	Discarded wells
08217-0004	297,26	396,60	226,00	12,00	
101	406,30	524,00	267,00	142,00	
102	353,27	472,00	262,00	51,00	
103	373,90	476,00	261,00	50,00	
104	536,47	1140,00	186,00	147,00	
105	386,51	524,00	277,00	74,00	
106	384,00	497,00	266,00	70,00	
107	346,36	499,00	178,00	190,00	
108	335,68	462,00	224,00	216,00	
109	367,57	486,00	257,00	74,00	
110	300,83	471,00	20,00	152,00	
111	302,18	448,00	166,00	136,00	
112	356,12	498,00	276,00	41,00	
113	316,22	448,00	191,00	41,00	
114	422,40	1300,00	233,00	384,00	
115	422,22	635,00	226,00	115,00	
116	395,83	555,00	116,00	332,00	
117	391,87	665,00	229,00	197,00	
144	297,37	367,00	155,00	35,00	
145	350,04	425,00	296,00	26,00	
146	317,33	471,00	209,00	39,00	
147	354,69	514,00	250,00	29,00	
148	379,29	485,00	193,00	7,00	
118	351,60	572,00	37,00	199,00	
119	345,69	655,00	259,00	181,00	
120	379,26	484,00	268,00	50,00	

*All the wells located in Martorell will not be analyzed because until 2012 there was the effect of the breakage of the brine collector that occurred years before, causing a severe increase in chlorides which affected the whole area of Martorell. Therefore, downstream, the first wells to be analyzed will be the ones from the Congost of Martorell on.

All those wells that do not have sufficient data to be able to do an appropriate analysis will not be analyzed neither. Wells with code: 08263-0031, 08200-0021 and 4838627 they will be discarded due to lack of data, since only one value was found from them.

The wells with code 08196-0055 and 08157-0004 have an average value of chlorides very low compared to the rest of wells, and this is because they have a stronger lateral contribution from the area.

The well 08263-0037 has one data, but it is not ruled out because the Canal de la Dreta begins approximately in this well, and therefore there is an attempt sees its influence. Another reason not to rule it out is that when the well 08244-0003 stops working in 2012, this well is used instead.

The well 08196-0059 also has one data, but it will be a representative well of the origin of the Llobregat River, as mentioned in the section 5.3.

Table 8. Mass balance results of the recharge proportions of the wells on the left margin (1).

	121		122		123		124		125	
[%]	R. Llobregat	C. Infanta	R. Llobregat	C. Infanta	R. Llobregat	C. Infanta	R. Llobregat	C. Infanta	R. Llobregat	C. Infanta
1999	-	-	-	-	-	-	-	-	-	-
2000	71	29	56	44	63	37	82	18	56	44
2001	73	27	93	7	74	26	99	1	74	26
2002	100	0	0	0	89	11	0	0	0	0
2003	53	47	96	4	0	0	100	0	75	25
2004	54	46	93	7	0	0	99	1	77	23
2005	0	0	0	0	86	14	0	0	95	5
2006	78	22	0	0	0	0	-	-	80	20
2007	0	0	0	0	0	0	0	0	0	0
2008	38	62	-	-	-	-	-	-	-	-
2009	12	88	0	0	-	-	-	-	99	1
2010	76	24	0	0	-	-	0	0	0	0
2011	96	4	0	0	-	-	-	-	0	0
2012	66	34	0	0	-	-	-	-	0	0
2013	67	33	0	0	-	-	-	-	0	0
2014	88	12	77	23	-	-	-	-	70	30
2015	0	0	0	0	0	0	0	0	0	0
2016	86	14	0	0	0	0	0	0	0	0
2017	59	41	0	0	0	0	0	0	0	0

Table 9. Mass balance results of the recharge proportions of the wells on the left margin (2).

	126		110		111		113		144	
[%]	R. Llobregat	C. Infanta	R. Llobregat	C. Infanta	R. Llobregat	C. Infanta	R. Llobregat	C. Infanta	R. Llobregat	C. Infanta
1999	-	-	97	3	83	17	83	17	-	-
2000	72	28	0	0	88	12	90	10	88	12
2001	81	19	95	5	66	34	79	21	81	19
2002	0	0	87	13	73	27	76	24	0	0
2003	64	36	82	18	56	44	74	26	76	24
2004	77	23	65	35	0	0	57	43	64	36
2005	89	11	0	0	99	1	0	0	0	0
2006	85	15	0	0	85	15	85	15	0	0
2007	0	0	0	0	0	0	0	0	0	0
2008	-	-	0	0	52	48	64	36	0	0
2009	90	10	17	83	0	0	0	0	3	97
2010	0	0	0	0	0	0	-	-	0	0
2011	0	0	0	0	0	0	79	21	0	0
2012	98	2	21	79	55	45	0	0	62	38
2013	0	0	38	62	42	58	0	0	28	72
2014	78	22	43	57	42	58	0	0	39	61
2015	0	0	0	0	0	0	0	0	0	0
2016	92	8	94	6	0	0	0	0	82	18
2017	87	13	74	26	76	24	-	-	-	-

Table 10. Mass balance results of the recharge proportions of the wells on the left margin (3).

	145		102		114		115	
[%]	R. Llobregat	C. Infanta	R. Llobregat	C. Infanta	R. Llobregat	C. Infanta	R. Llobregat	C. Infanta
1999	-	-	77	23	9	91	-	-
2000	88	12	73	27	46	54	42	58
2001	77	23	62	38	56	44	41	59
2002	96	4	73	27	36	64	39	61
2003	-	-	32	68	35	65	29	71
2004	20	80	0	0	0	0	0	0
2005	0	0	89	11	24	76	46	54

	145		102		114		115	
[%]	R. Llobregat	C. Infanta	R. Llobregat	C. Infanta	R. Llobregat	C. Infanta	R. Llobregat	C. Infanta
2006	91	9	71	29	0	0	0	0
2007	0	0	0	0	0	0	0	0
2008	49	51	0	0	0	0	0	0
2009	0	0	0	0	0	0	0	0
2010	0	0	0	0	0	0	0	0
2011	0	0	0	0	0	0	0	0
2012	-	-	37	63	0	0	0	0
2013	-	-	25	75	0	0	0	0
2014	-	-	0	100	0	0	0	0
2015	-	-	59	41	46	54	81	19
2016	-	-	68	32	63	37	-	-
2017	-	-	0	0	8	92	48	52

Table 11. Mass balance results of the recharge proportions of the wells on the left margin (4).

	116		119		147	
[%]	R. Llobregat	C. Infanta	R. Llobregat	C. Infanta	R. Llobregat	C. Infanta
1999	52	48	82	18	-	-
2000	22	78	79	21	60	40
2001	36	64	66	34	38	62
2002	39	61	72	28	68	32
2003	30	70	66	34	0	100
2004	0	0	0	0	0	0
2005	54	46	66	34	62	38
2006	32	68	65	35	-	-
2007	0	0	-	-	-	-
2008	0	0	0	0	-	-
2009	0	0	0	0	-	-
2010	0	0	0	0	0	0
2011	0	0	0	0	0	0
2012	0	0	5	95	0	0

	116		119		147	
[%]	R. Llobregat	C. Infanta	R. Llobregat	C. Infanta	R. Llobregat	C. Infanta
2013	0	0	0	0	0	0
2014	0	0	0	0	0	0
2015	39	61	39	61	62	38
2016	80	20	59	41	87	13
2017	46	54	2	98	0	0

	Values below surface waters		Values above surface waters	----	No data

Table 12. Averages per year of the conservative parameters of surface water.

	Anoia River			**Rubí Stream**			**Llobregat River**		
Year	Cl^- [mg/L]	Br^- [mg/L]	$[Cl^-]/[Br^-]$	Cl- [mg/L]	Br- [mg/L]	$[Cl^-]/[Br^-]$	Cl- [mg/L]	Br- [mg/L]	$[Cl^-]/[Br^-]$
2005	360,82	0,53	728,77	506,55	0,97	542,55	329,50	0,77	437,83
2006	316,42	0,44	749,08	448,50	1,09	432,17	300,00	0,74	407,08
2007	380,00	0,38	1178,12	481,33	0,76	1055,51	409,70	0,89	1332,70
2008	405,33	0,46	1157,28	355,00	0,80	542,62	355,00	0,80	542,62
2009	290,83	0,45	753,35	389,67	0,87	445,15	287,75	0,65	455,98
2010	263,09	0,36	800,64	337,67	1,19	347,38	297,67	0,69	438,65
2011	224,27	0,34	727,81	311,64	0,63	532,05	261,50	0,67	404,70
2012	236,25	0,35	893,07	324,89	0,61	537,04	261,36	0,67	404,45
2013	214,50	0,38	570,65	317,67	0,67	484,86	260,44	0,66	405,06
2014	330,75	1,67	348,91	263,25	0,50	539,37	252,83	0,63	414,17
2015	339,86	1,04	381,09	322,29	0,63	512,31	262,00	0,67	389,57
2016	407,90	0,83	504,78	303,30	0,53	585,72	255,62	0,65	405,17
2017	342,67	0,56	1157,76	278,67	0,45	627,78	227,33	0,58	395,36

Table 13. Average of the chloride/bromide ratio of the left margin wells (1).

Year	121	122	123	124	125	126	110	111	113
2005	353,43	346,37	364,58	322,10	357,45	379,12	369,03	396,10	351,16
2006	375,69	365,92	331,55	0,00	367,64	394,40	408,11	366,93	386,59
2007	1414,63	685,71	644,56	701,43	903,10	918,00	1155,56	684,06	2266,18
2008	4000,00	0,00	0,00	0,00	0,00	0,00	1196,18	1271,96	1489,03
2009	401,94	402,63	0,00	0,00	377,80	396,47	348,21	364,23	431,96
2010	1266,06	643,86	0,00	338,17	396,64	506,77	295,41	354,46	0,00
2011	372,99	368,72	0,00	0,00	904,39	911,84	324,00	398,64	351,27
2012	337,80	363,76	0,00	0,00	344,70	385,40	414,62	401,33	340,28
2013	354,17	366,28	0,00	0,00	386,11	379,60	348,15	374,63	361,33
2014	413,08	425,86	0,00	0,00	382,33	451,27	329,91	374,68	406,94
2015	407,34	399,32	391,94	427,78	402,74	407,34	383,02	391,58	345,52
2016	393,65	404,92	396,49	398,31	387,10	391,51	387,57	350,72	332,88
2017	408,41	398,21	335,71	402,44	408,62	421,92	407,64	372,06	0,00

Table 14. Average of the chloride/bromide ratio of the left margin wells (2).

Year	102	114	115	116	119	144	145	147
2005	411,31	369,75	353,25	367,83	404,62	340,30	376,34	380,20
2006	363,04	374,34	343,18	379,65	574,62	367,68	360,44	0,00
2007	851,92	613,79	2787,14	644,17	0,00	1173,08	716,98	0,00
2008	2176,32	341,27	1505,71	1261,48	497,04	347,25	1774,04	0,00
2009	0,00	363,08	409,27	379,98	386,60	427,04	914,23	0,00
2010	382,31	357,66	335,65	567,57	342,61	331,96	548,59	371,07
2011	336,84	361,48	364,40	403,58	0,00	346,97	0,00	375,98
2012	1022,55	379,00	346,62	370,67	373,34	322,70	0,00	376,95
2013	332,56	428,24	368,96	796,81	339,61	332,59	0,00	433,37
2014	383,29	332,00	302,27	440,94	354,79	302,17	0,00	383,33
2015	380,52	381,66	352,03	394,20	406,50	363,07	0,00	394,56
2016	374,98	369,44	0,00	386,91	376,45	373,61	0,00	401,31
2017	442,69	379,15	380,60	390,31	411,76	0,00	0,00	384,21

Table 15. Summary table of the Piper diagram of all sampling points from 2005 to 2018.

	PARAMETERS							
	ANIONS			*CATIONS*			*ANIONS + CATIONS*	
	SO_4^{2-}	Cl^-	CO_3^{2-} + HCO_3^-	Mg^{2+}	Ca^{2+}	Na^++K^+	Ca^{2+}+Mg^{2+}	SO_4^{2-}+Cl^-
Point 12	≈ =15-25%	↓ 60-40%	↑ 20-40%	≈ =15-20%	↑ 30-45%	↓ 55-30%	↑ 40-65%	↓ 80-60%
Point 14	≈ =20-30%	↓ 60-35%	↑ 20-45%	≈ =15-20%	↑ 30-50%	↓ 60-30%	↑ 40-70%	≈ =70-80%
Point 13	≈ =15-25%	↓ 60-45%	↑ 25-40%	≈ =10-15%	↑ 25-40%	↓ 65-45%	≈ =40-50%	≈ =60-75%
Point 11	rank 15%	↓ 40-25%	≈ =25-30%	rank 15%	rank 15%	↓ 50-25%	↑ 50-75%	≈ =70-80%
121, 122	≈ =			≈ =			≈ =	
123	≈ =	rank 15%	rank 15%	≈ =	rank 10%	rank 15%	rank 15%	≈ =
124, 125, 126	≈ =			≈ =			≈ =	
8054	≈ =			≈ =			≈ =	
8123	≈ =	↓ 55-35%	↑ 25-40%	≈ =	↑ 33-45%	↓ 50-35%	≈ =50-65%	≈ =60-75%
8196	there are only two samples from well 55 and one from well 59							
8157	≈ =			≈ =			≈ =	
8200								
8217								
8244								
8263	≈ =			≈ =	↑ 35-42%	↓ 45-38%	≈ =	
129, 103	≈ =			≈ =			≈ =	
111, 112								
146, 147								
110, 113								
144, 145								
101	≈ =			≈ =			≈ =	
102	≈ =			≈ =	rank 12%	rank 14%	rank 15%	≈ =

	PARAMETERS							
	ANIONS			***ANIONS***			***ANIONS***	
	SO_4^{2-}	Cl^-	CO_3^{2-} + HCO_3^-	Mg^{2+}	Ca^{2+}	Na^++K^+	Ca^{2+}+Mg^{2+}	SO_4^{2-}+Cl^-
106	≈ =			≈ =			≈ =	
148	there are only two samples							
105, 107	≈ =			≈ =			≈ =	
108, 109								
118, 119								
120	≈ =	↓ 52-40%	↑ 27-36%	≈ =			≈ =	
104	≈ =			≈ =			≈ =	
114	≈ =	↓ 52-40%	↑ 25-37%	≈ =			≈ =	↓ 75-60%
115	≈ =	↓ 50-40%	↑ 26-40%	≈ =			≈ =	
116, 117	≈ =			≈ =			≈ =	

APPENDIX 2: GRAPHICS

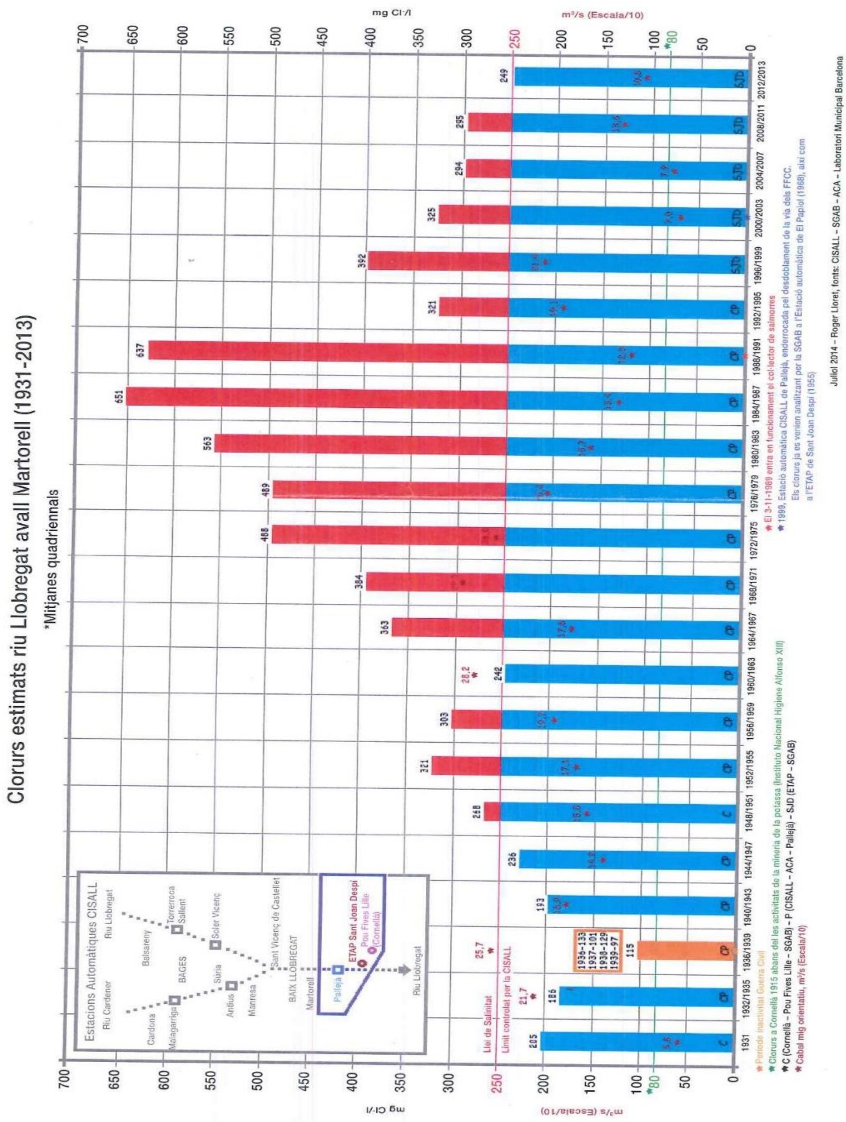

Figure 32. Historical graph of chlorides in the Llobregat basin (in Catalan).
(Source: Rius de sal, Lloret R. (2015)).

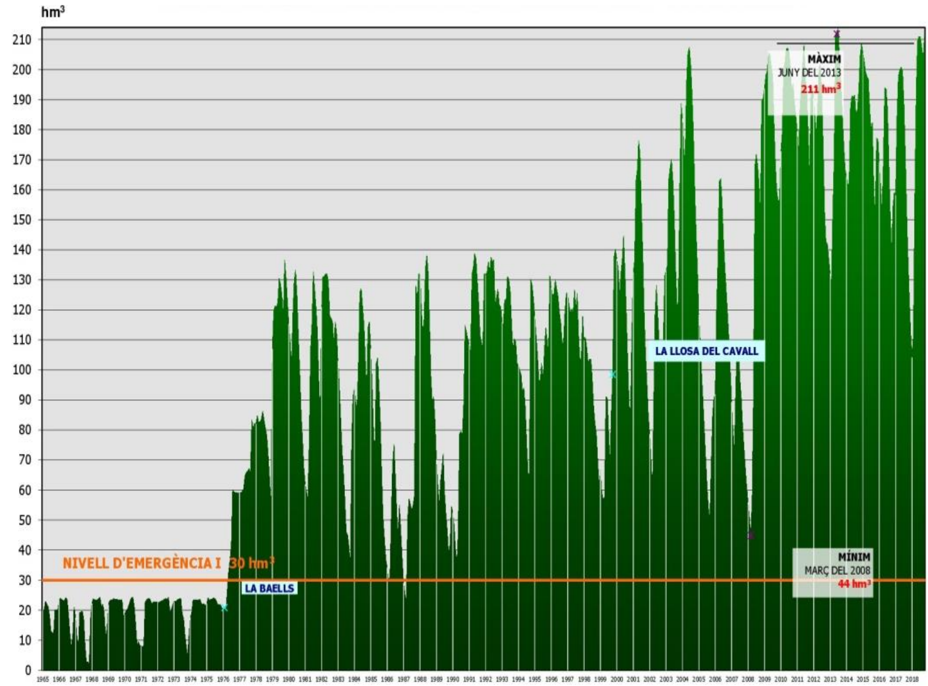

Figure 32. Historical evolution of the reservoirs in the Llobregat basin (in Catalan).
(Source: Aigües de Barcelona).

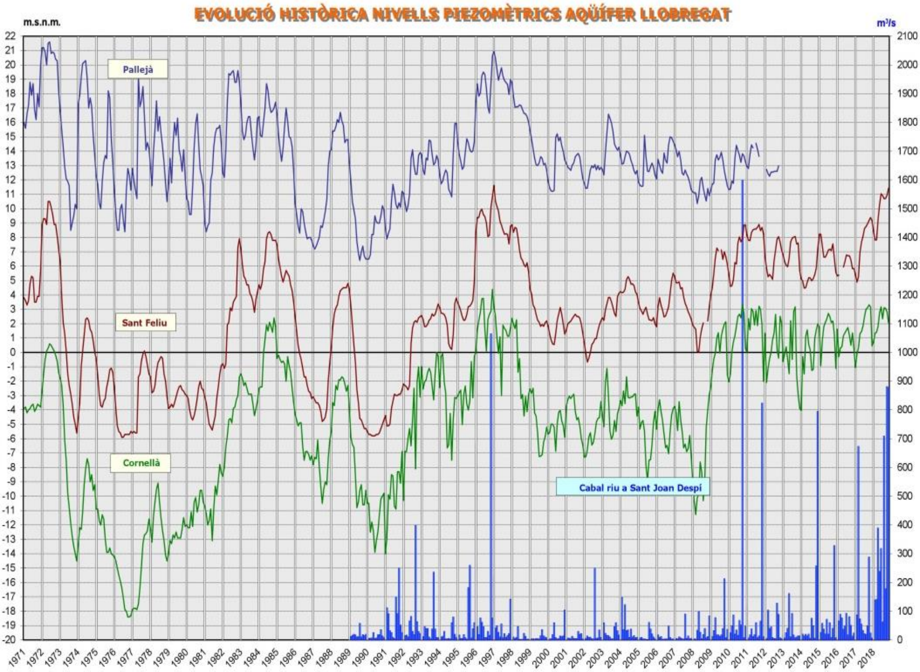

Figure 34. Evolution of the different levels of the Llobregat aquifer (in Catalan).
(Source: Aigües de Barcelona).

The green, red and blue lines are 3 levels in different points of the Llobregat aquifer.

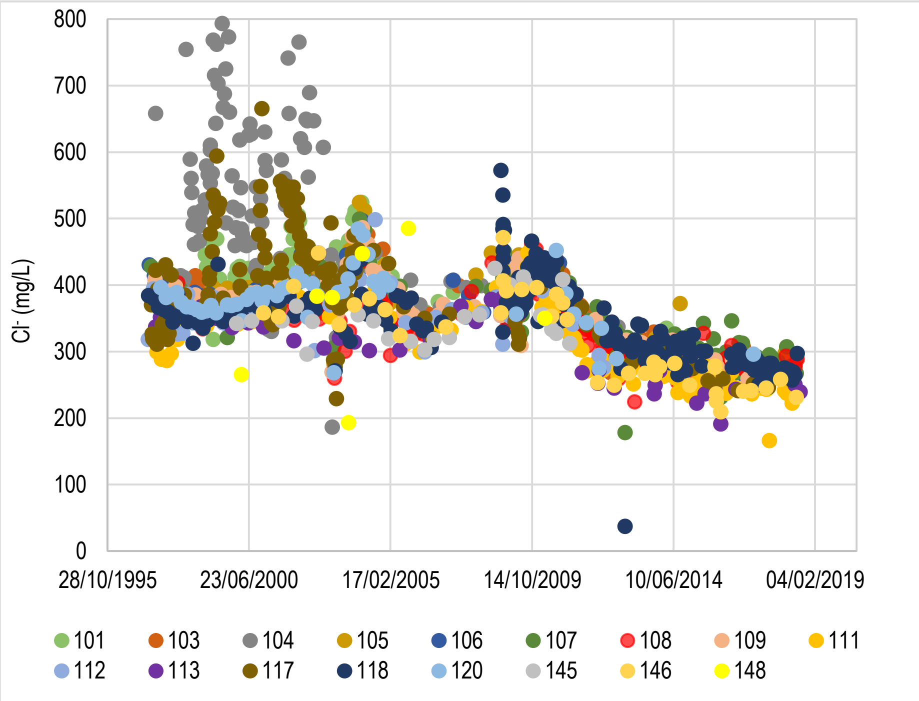

Figure 35. Evolution of the chlorides of the wells on the left margin of the Lower Valley of the Llobregat.

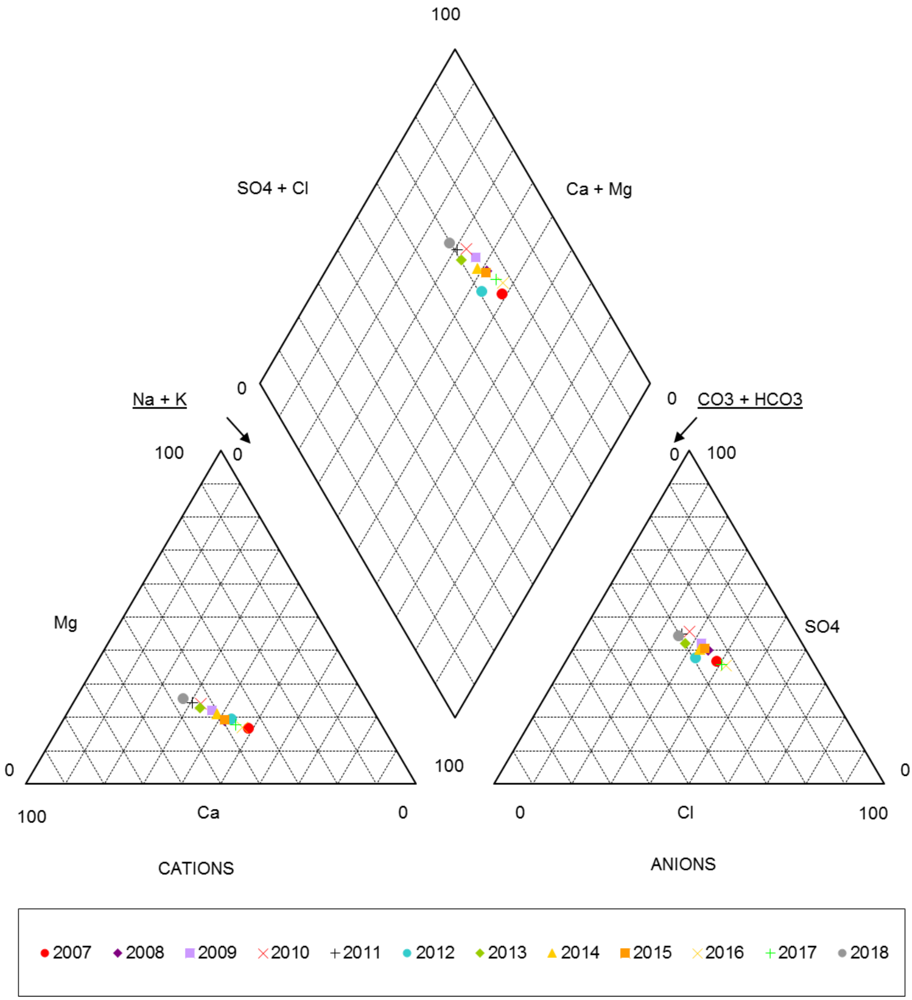

Figure 36. Piper diagram of Anoia River.

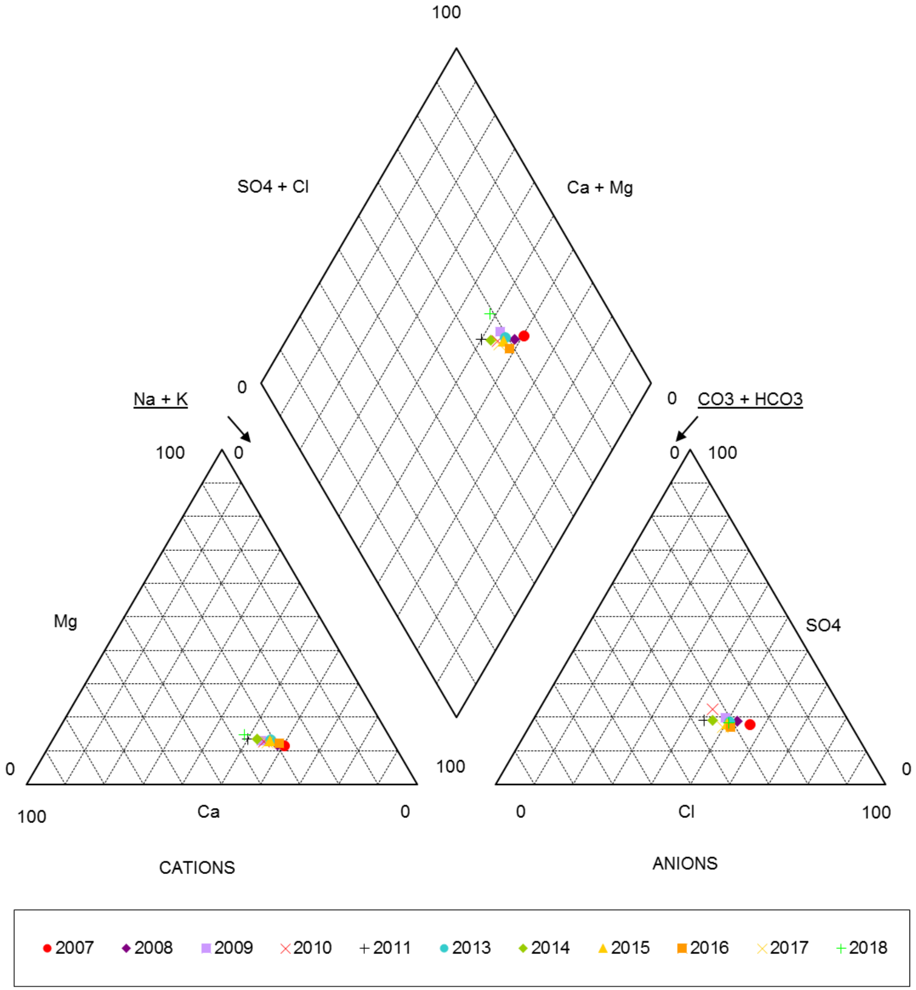

Figure 37. Piper diagram of Rubí Stream.

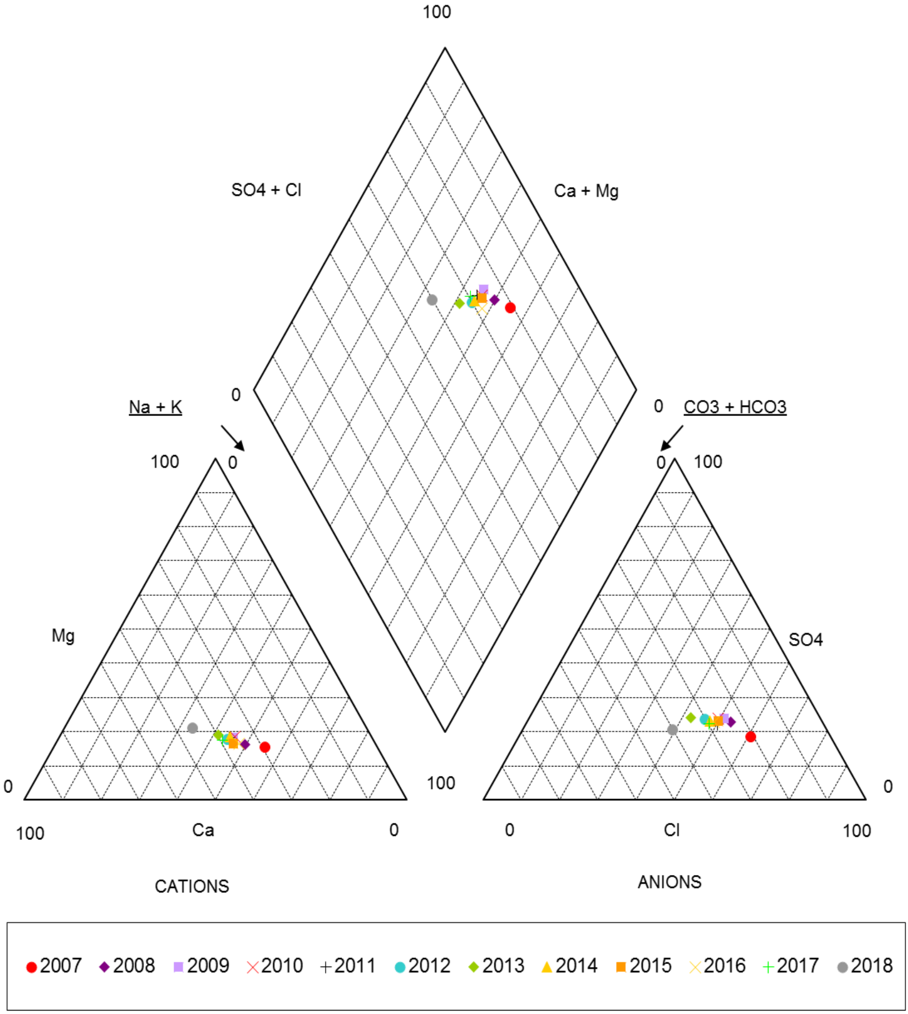

Figure 38. Piper diagram of Llobregat River.

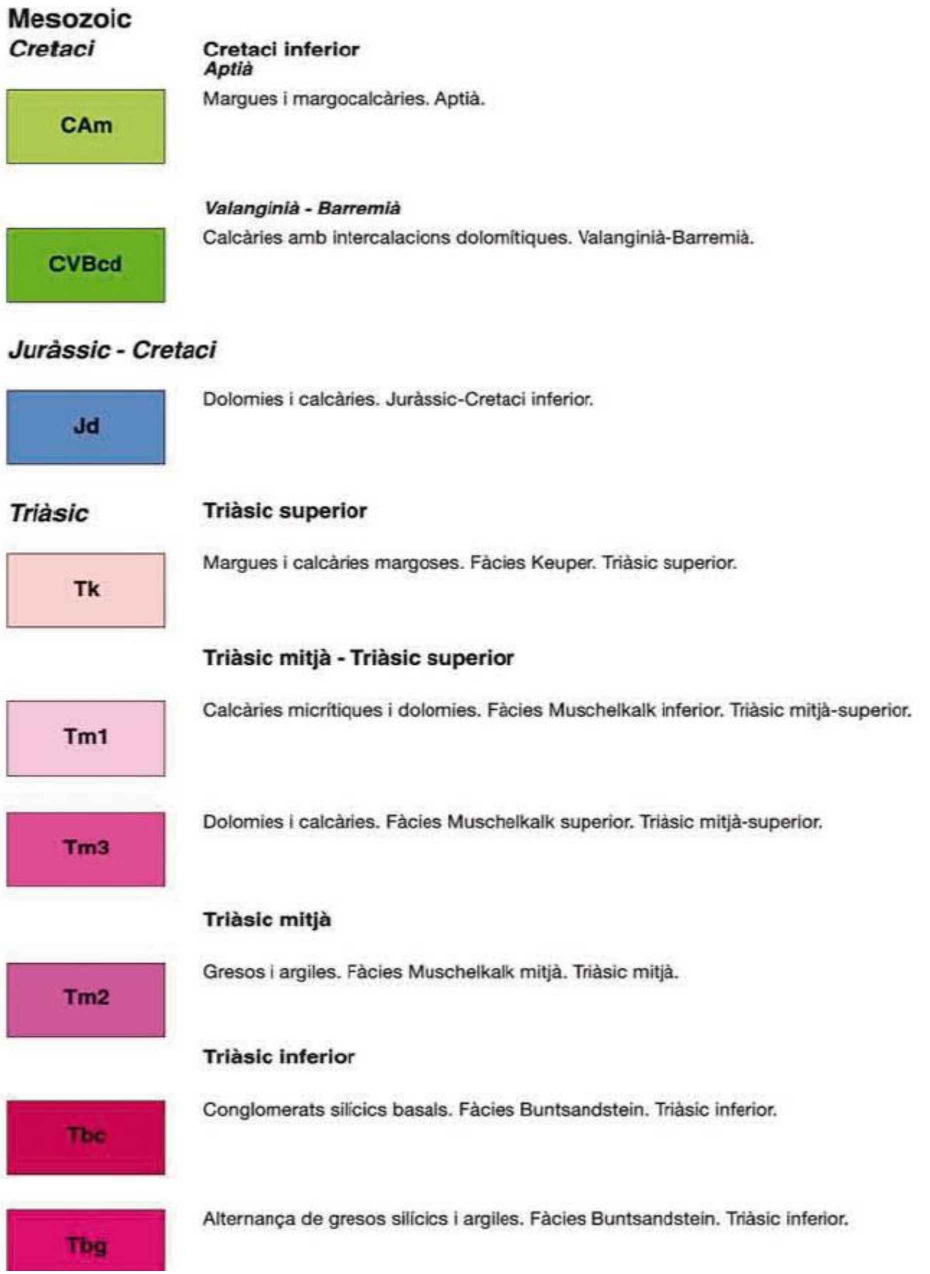

Figure 39. Legend of he geological map of the Llobregat basin (in Catalan) (1). *(Source: Institut Cartogràfic i Geològic de Catalunya).*

Paleozoic
Carbonífer - Permià

Fd	Dics de possible diàbasi. Carbonífer-Permià.
Ggd	Granodiorites i granits alcalins. Carbonífer-Permià.
Gpg	Pòrfirs àcids. Carbonífer-Permià.
mc_ÇOrp	Fil·lites i cornubianites. Materials de la unitat ÇOrp afectats per metamorfisme de contacte. Edat del metamorfisme: Carbonífer-Permià.
mc_ÇOrpc	Cornubianites i esquists. Materials de la unitat ÇOrpc afectats per metamorfisme de contacte. Edat del metamorfisme: Carbonífer-Permià.
mc_Sf	Fil·lites i cornubianites. Materials de la unitat Sf afectats per metamorfime de contacte. Edat del metamorfisme: Carbonífer-Permià.

Carbonífer

Capc	Pissarres, calcàries i calcosquists. Carbonífer.
Capl	Lidites i pissarres silíciques. Carbonífer.
Caps	Pissarres sorrenques, grauvaques i conglomerats. Carbonífer.

Devonià **Devonià mitjà**

Dc	Calcosquists i calcàries argiloses. Devonià mitjà.

Figure 40. Legend of he geological map of the Llobregat basin (in Catalan) (2). (*Source: Institut Cartogràfic i Geològic de Catalunya).*

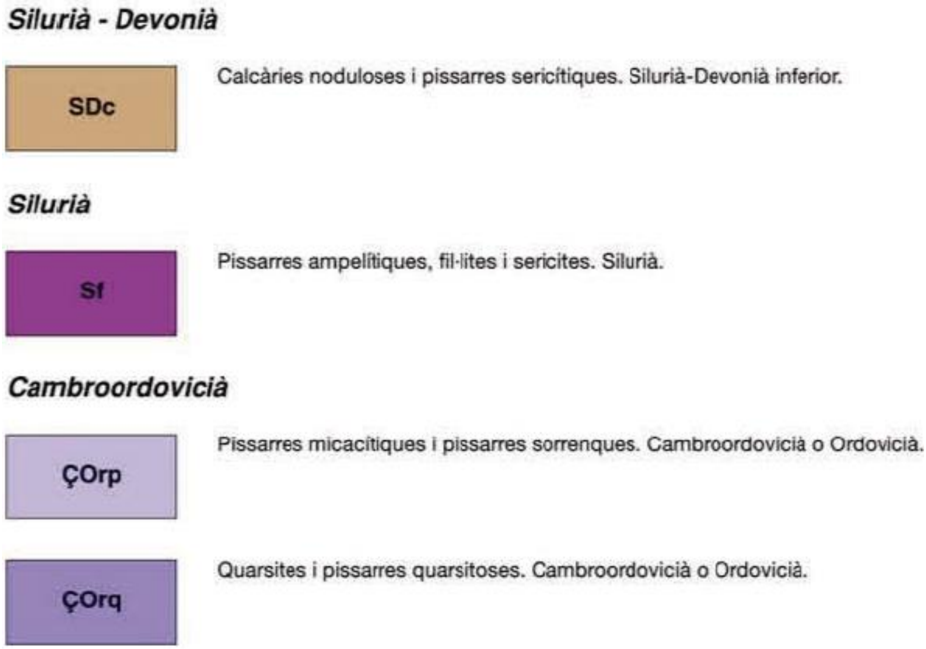

Figure 41. Legend of he geological map of the Llobregat basin (in Catalan) (3). *(Source: Institut Cartogràfic i Geològic de Catalunya).*