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D35.1 Evaluation of the results and impacts on ESS of a flexible ASR system in Barcelona (ES) demo site. Guidelines and recommendations for transfer this innovative solution

Results of Tasks 35.2, 35.3 and 35.4

January (2018)

The research leading to these results has received funding from the European Union Seventh Framework Programme (FP7/2007-2013) under grant agreement no. 619039

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RESULTS OF TASKS 35.2, 35.3 AND 35.4

SUMMARY

Results of Tasks 35.2, 35.3 and 35.4 have been summarised in four separated reports, which are presented in this document for a comprehensive understanding. The reports present same structure, executive summary, background information and conclusions, so they can be read separately. Aquifer Storage and Recovery (ASR) is a site-specific technique which can be approached from several disciplines: hydrogeology, water quality regulations and recommendations, international experiences, clogging formation and evolution, potential pre-treatments, numerical modelling, etc. All of these issues have been studied and are presented in three main chapters.

Results of Tasks 35.2, 35.3 and 35.4 provides valuable background information to responsibly inject pre-potable water into Lower Llobregat alluvial aquifer at operative scale.

Chapter A:

Conditioning of existing network of observation wells: Hydrogeological information acquired during field works in Sant Joan Despi

This reports corresponds to the first hydrogeological information gathered at local scale by drilling works for the construction of the observation network in Sant Joan Despi Drinking Water treatment plant (DWTP). Well named P18 has been selected to carry out the demonstrative phase in the Llobregat area. This well was constructed in 1973 and rebuilt in 1987, so previous hydrogeological information allowed to design the network of 3 observation wells in the surroundings of the former well, located in the DWTP operated by Aigües de Barcelona.

The recovery of the unaltered sediments core in one of the piezometers (named Pz1) has permitted to characterise the upper and lower aquifer, the aquitard, and more important, to install automatic equipment for groundwater level monitoring during the project. Pumping and recovery tests have been used to calculate hydraulic transmissivity, which is key parameter. Hydraulic transmissivity will be used as indicator of changes occurring in aquifer, such physical and chemical clogging that potentially could appear during the injection of pre-potable water.

Chapter B:

Numerical model of flow and conservative transport: Evaluation of the impact of the injection and extraction regime in the ASR system in the aquifer of Lower Valley and Llobregat River Delta

The application of numerical modelling to the Llobregat Aquifer Storage and Recovery (ASR) system during the first phase of the project was focused on the impact assessment of ASR in terms of groundwater volume infiltrated in the aquifer and the improvements and/or impacts in groundwater quality. The work has been divided into two parts: (i) a MODFLOW-based numerical model to simulate the impact of injected water via ASR in the local piezometric network installed during the project (4 km2) (ii) a VISUAL TRANSIN-based numerical model to simulate the impact of ASTR at regional scale (129 km2).

The results of the simulations carried out for demonstration ASR project and application of ASTR at full scale are reported. Based on the former one, it is concluded that the demonstration phase of the project will have a limited impact in the aquifer, as the mixing ratio between injected water and native groundwater will be below 10% after 1.4 km of aquifer passage. Regarding regional model simulation, the obtained results correspond to a first approximation of the potential use of ASRT scenarios in Lower Llobregat alluvial aquifer. Based on the model, the aquifer has the sufficient storage capacity to regulate an infiltrated volume of 120 hm^3/year.

Chapter C:
Hydrogeochemical impact of ASR using pre-potable water in Barcelona

An exhaustive study of the impact of sand-filtered water on the hydrodynamic and hydrogeochemical characteristics of the Lower Llobregat alluvial aquifer near Sant Joan Despi DWTP was carried out. Different types of compounds, such as physico-chemical, organic and microbiological were analysed under natural, potable injection and sand-filtered water conditions. A comparison was made between the measured values and the threshold limits and revealed that none of these compound were above Spanish legal recommendations for drinking water quality and good chemical groundwater status. By analysing recorded groundwater levels, electrical conductivity values and temperature data at nearby piezometers, it was confirmed the injection periods resulted in groundwater quality improvement and significant piezometric rises. The water quality improvement upon aquifer recharge was verified statistically by applying multivariate statistical techniques (PCA and Heatmap), reducing the dimensionality of dataset and extracting the most relevant information.

Regarding organic compounds (BTEX and emerging contaminants), the observed concentrations in the injection water were, in most cases, below both the limit of detection and the threshold established for drinking water. This allows to conclude that there is no risk of organic contamination under the injection conditions that took place during the demonstration phase. With respect to microbiology, the obtained results have demonstrated the presence of indicative microorganisms already in both sediment and groundwater samples prior to injecting pre-potable water. Injection of sand-filtered water resulted in a slight increase, which was however attenuated during aquifer passage. The results obtained from cleaning cycles (short but high-rate abstraction to clean the injection wells) indicated that after injecting sand-filtered water, a good-quality groundwater could be recovered from the vicinity of the ASR-well. These cleaning cycles have also shown that there is no significant clogging processes at control piezometers.

Chapter D:
Guidelines and recommendations for ASR implementation using pre-potable water

The need to generate a methodological approach that could serve as a starting point to responsibly inject pre-potable water into the aquifer was raised. Therefore, it was decided to apply the existing methodology for risk management in drinking water and wastewater treatment plants (Water Safety Plans) to the managed aquifer recharge projects. In the case of the recharge with pre-potable water into the Lower Llobregat alluvial aquifer, the main hazards were, among others, the increase of chlorites and chlorates concentrations and potential EOCs bio-accumulation. A series of Critical Control Points and threshold values for the different variables were defined based on current legislation.

The implementation of these risk management plans at European level, which could be named as “Managed Aquifer Recharge Safety Plans”, will require specific studies, due to the different aquifer functioning depending on their nature, the variability of recharge water quality and the large differences observed in the legal thresholds values required in each Member State.

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D35.1(a) CONDITIONING OF EXISTING NETWORK OF OBSERVATION WELLS

Hydrogeological information acquired during field works in Sant Joan Despí (Barcelona)

CETaqua, February 2015

The research leading to these results has received funding from the European Union Seventh Framework Programme (FP7/2007-2013) under grant agreement no. 619039

CONDITIONING OF EXISTING NETWORK OF OBSERVATION WELLS

D35.1(a): CONDITIONING OF EXISTING NETWORK OF OBSERVATION WELLS
Hydrogeological information acquired during field works in Sant Joan Despí (Barcelona)

SUMMARY

This reports corresponds to the first hydrogeological information gathered at local scale by drilling works for the construction of the observation network in Sant Joan Despí Drinking Water treatment plant (DWTP). Well named P18 has been selected to carry out the demonstrative phase in the Llobregat area. This well was constructed in 1973 and rebuilt in 1987, so previous hydrogeological information allowed to design the network of 3 observation wells in the surroundings of the former well, located in the DWTP operated by Aigües de Barcelona.

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LEAD BENEFICIARY	**DELIVERABLE AUTHOR(S)**
CETaqua	Marta Hernández (CETaqua) Anna Castañeda (CETaqua)
QUALITY ASSURANCE	
CETaqua Andalucía Aigües de Barcelona	Bartolomé Andreo Navarro Jordi Martí
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List of Acronyms and Abbreviations

ACA	Catalan Water Agency (regional public entity)
ASR	Aquifer Storage and Recovery
CUADLL	Association of Users of The Llobregat Aquifer (non-profit organisation)
DWTP	Drinking Water treatment Plant
ICDD	International Centre for Diffraction Data
Pz1	Piezometer number 1 drilled in SJD
Pz2	Piezometer number 2 drilled in SJD
Pz3	Piezometer number 3 already existing in SJD
SJD	Sant Joan Despí facility of Drinking Water Treatment Plant (Barcelona)
TCD	Temperature, conductivity and water level sensors.
XRD	X-Ray Diffraction (technique used for the mineralogical identification

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Executive summary

This report is part of the Deliverable D35.1. The report summarises the findings obtained in the field instrumentation campaign carried out in July 2014 in Sant Joan Despí DWTP (Barcelona), corresponding to the demonstration site of Llobregat. Aquifer Storage and Recovery (ASR) techniques have been historically applied from the 70s in the area, using a dual system of injection – extraction in 12 wells near to the treatment plant.

Demonstration phase is intended to start in 2015. As preparative work of this phase, injection well P18 has been complemented with an observation network consisting in 3 piezometers (Pz1, Pz2 and Pz3). Drilling works allowed the recovery of the full geological core of 50 meters thickness, and the sampling of sediments at 5 different depths to perform mineralogical analysis. The results confirmed that alluvial aquifer is locally confined, having an upper aquifer and a deeper one, separated by a grey clay layer. The deep aquifer is called “main aquifer”, and the sediments are mainly coarse sand and gravels with high transmissivity. Temperature, conductivity and water level sensors (TCD) TCD have been installed in the piezometers, gathering automatic information about temperature, water level and electrical conductivity. Groundwater profiles have been represented, and no preferential pathways have been observed, as temperature and conductivity values were quite constant in depth.

Mineralogical analysis revealed quartz, carbonate phases (calcite and dolomite), clays (illite and clinochlore), and feldspars (microcline and albite) are the predominant minerals in the aquifer. This information will be useful for the hydrogeochemical evaluation along ASR cycles. No high mineral mobilisation or precipitation is expected.

P18 is currently used as pumping well for drinking water production. Pumping episodes have been analysed by pumping and recovery tests. Cooper-Jacob method was selected for the interpretation of pumping test, selecting a single pumping period. EPHEBO software was also applied using a large amount of data, including pumping and recovery episodes for the calculation of hydraulic transmissivity. The two methods of calculations determined a local transmissivity between 9,800 – 11,200 m^2/day, while historical data in the area reports higher values (35,000 m^2/day in a close well named P13).

Pumping tests are going to be periodically performed along the project, as it is an indirect indicator of well clogging. The complexity of the pumping regime in the aquifer puts an additional difficulty in the results interpretation in the demonstrative phase, so piezometers network monitoring is essential to better understand hydrogeochemical and hydrogeological changes caused by the ASR with pre-potable water.

1. Introduction

The deep aquifer recharge system of SJD (Sant Joan Despí, Barcelona) was installed in the middle 70's with the aim of increasing groundwater resources taking advantage of the surplus of water produced in the drinking water treatment plant[1]. This system is an example of Aquifer Storage and Recovery (ASR), which is a wide spread technology in scarce areas as Spain, while the main reported ASR experiences come from California, Australia and The Netherlands.

DESSIN site in Barcelona aims to demonstrate the advantages of the flexibilisation of the ASR system. Currently there is no water surplus in the drinking water treatment plant, as the analysis of the demand and the increased costs of drinking water production have optimized the quantity of water treated. Flexibilisation is understood as the possibility of perform ASR using pre-potable water coming from intermediate steps of the water treatment line. The project will test the response of the aquifer at local and regional scale with the injection of the effluent of sand filters, which represents the end of the conventional treatment of the DWTP.

The success of the demonstration phase will provide strong arguments for the application of ASR using pre-potable water, which nowadays is not totally accepted. Locally, the flexibilisation of the ASR system has a double advantage: (1) to increase groundwater resources and to reduce lack of supply risk in drought periods in the Llobregat aquifer and (2) to increase ecosystem services related to groundwater and aquifer replenishment.

Despite ASR application are very site-specific depending on the aquifer conditions, local regulations and water quality among others, DESSIN project will provide practical guidelines for further implementation of the technology, and will relate for first time aquifer recharge practices and their benefits for Ecosystem Services, which is one of the challenges of the project.

As a starting point of the demonstration phase to be performed in Barcelona from June 2015, preparatory work has been done in 2014. There were lots of historical documents describing the ASR system and constructive profiles and maps of the selected injection well (P18), which is located in the facility of SJD. This report aims at summarize them, integrating all the necessary data for hydrogeologists and outsiders to better understand the hydrogeological system. The deliverable compiles the information obtained in the field works carried out in July 2014 and the findings provided by the geological profiles, sediment analysis and first pumping test performed in P18. This information is crucial to set a basepoint for the interpretation and understanding of groundwater levels and chemical changes occurring during the injection phase.

All the data presented in the report corresponds to the hydrogeological information obtained in the surroundings of P18, which is the selected point for the demonstration phase due to the proximity to the effluent of filtered water, the location in the DWTP area and its capacity to be representative of the rest of injection wells. See location of P18 and spatial distribution of the pumping wells in the area in Figure 1.

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[1] More information of the hydrogeological context and the operation of this system has been described in DESSIN deliverable 22.4(a): http://dessin-project.eu/

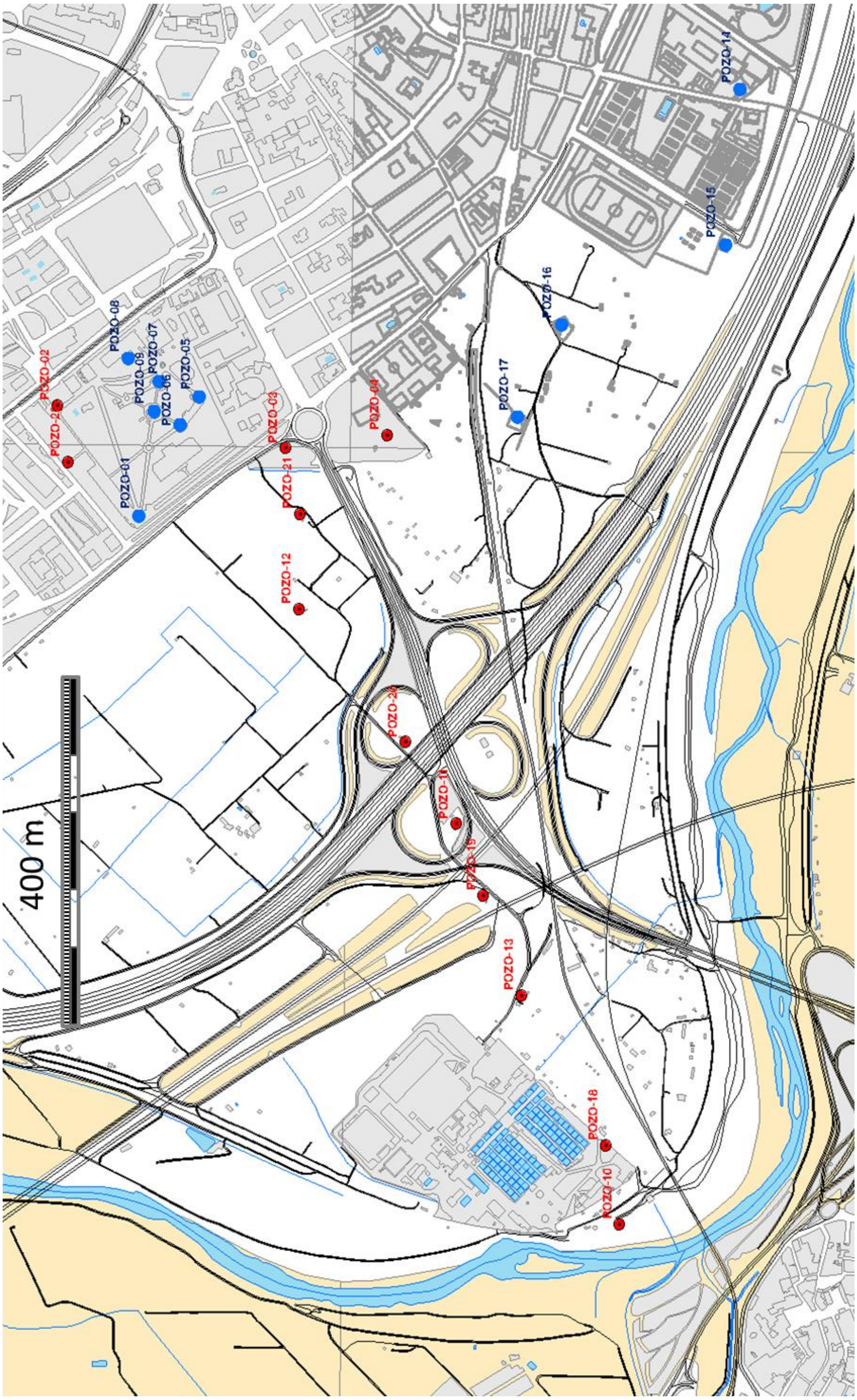


Figure 1: Map of location of extraction wells (blue) and reversible wells (red)

2. Objectives

The objectives of the field works are:

- **Construction of the monitoring network** to identify changes occurring in the aquifer due to injection in P18. Taking advantage of the drilling works, additional samples will be obtained with these specific objectives:
    - Construct a local geological profile
    - Mineralogical characterisation
    - Construction of conceptual model of aquifer configuration

- **Equipment of new and existing piezometers** with automatic sensors for the continuous monitoring of groundwater level, electrical conductivity and temperature during the project before demonstration phase implementation.

- **Calculation of local hydraulic transmissivity** and comparison with regional data. This parameter will be an indicator of potential physical and chemical clogging, and head loss.

3. Demonstration well description

P18 is an active well in the pumping system feeding the drinking water treatment plant. The selection of this well for the demonstration phase from the other 11 dual pumping-injecting wells fulfils the following criteria:

- Location in the facility of the treatment plant.
- Existence of geological profiles and detailed constructive schemes.
- Proximity to the sand filter effluent tank.
- Existence of an observation well 16 meters away.

This chapter compiles historical information and schemes compiled from Aigües de Barcelona Company. Originally, in 1973, the inner diameter was 950 mm. the well was rebuilt and in 1987 the inner diameter was reduced to 900 mm, according to the information obtained in Figure 3 and Figure 4.

Figure 5 summarises the equipment of P18, including the pumping tube and the injection tube. Some design data is reported in Table 5. Casing material is iron, and the filter presents a mesh size of 7 mm (see similar mesh in Figure 2

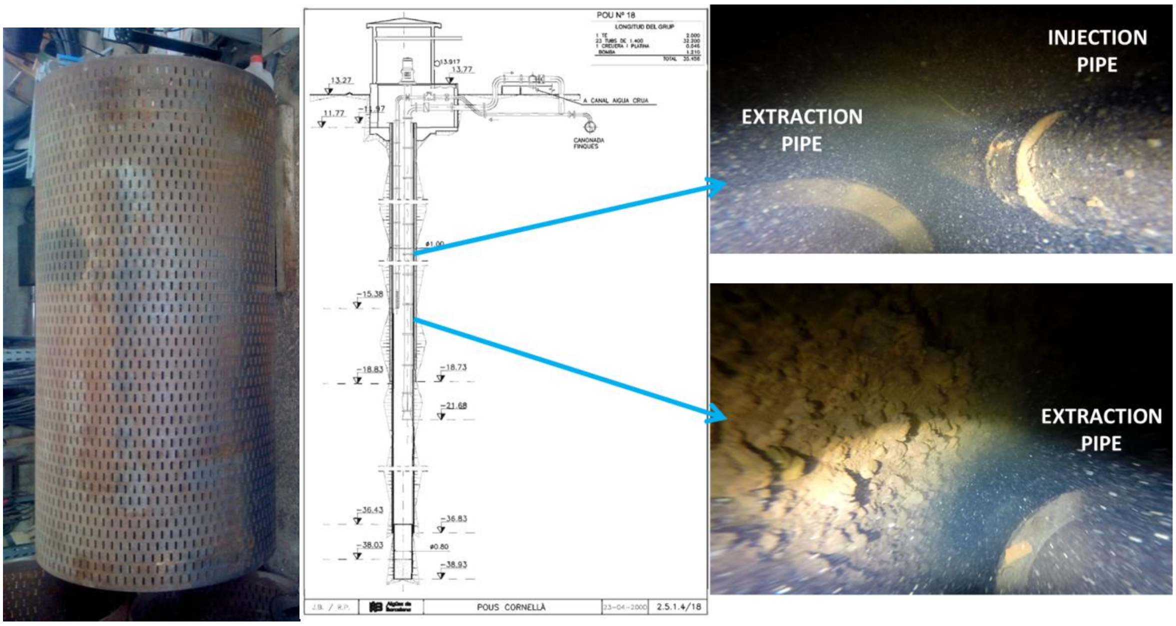


Figure 2: **Picture of real installation of filter and real status.**
Left: New filter aspect similar to the installed in P18.
Right: images of the P18 at different depths (See detailed scheme in Figure 5)

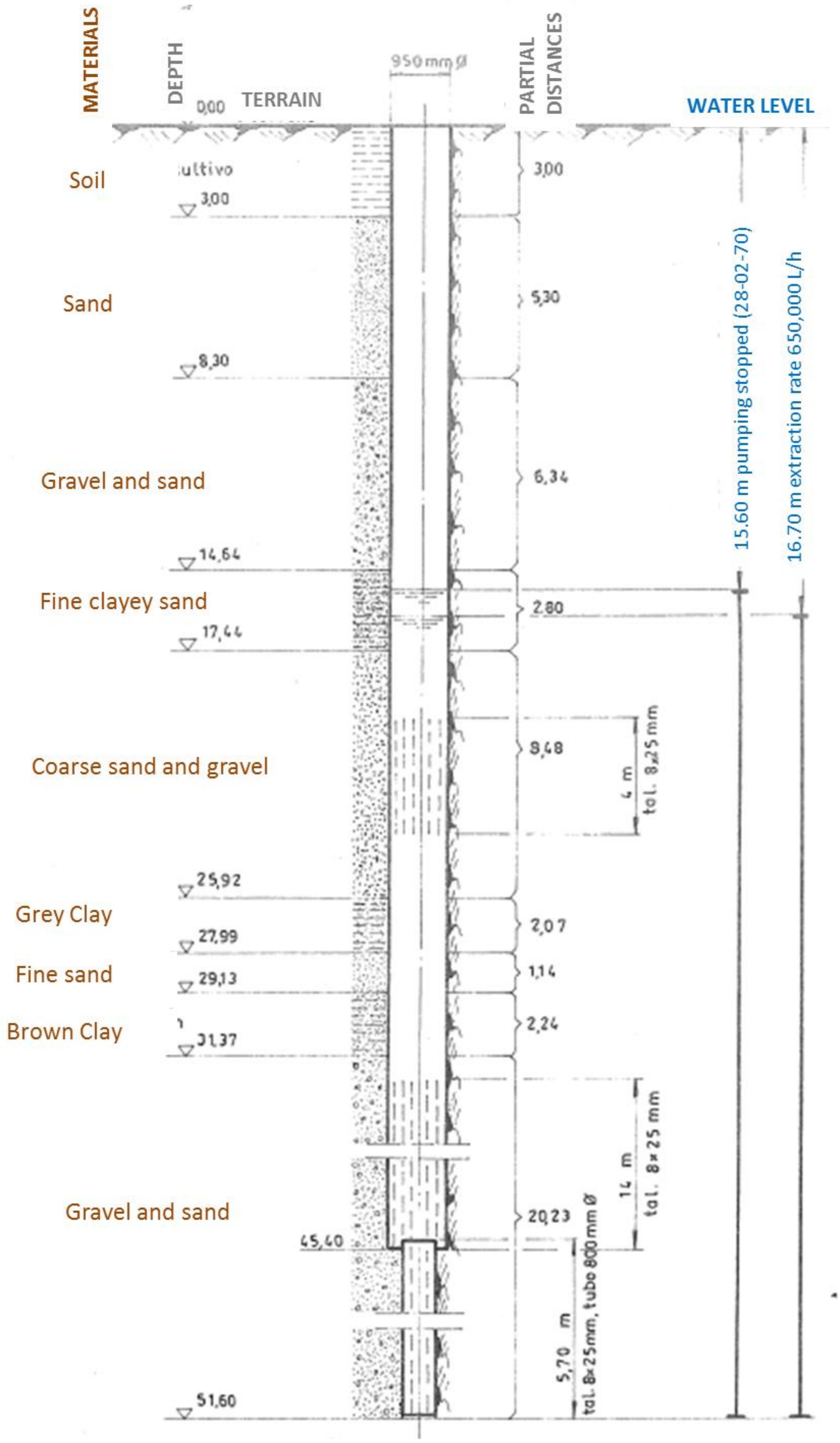
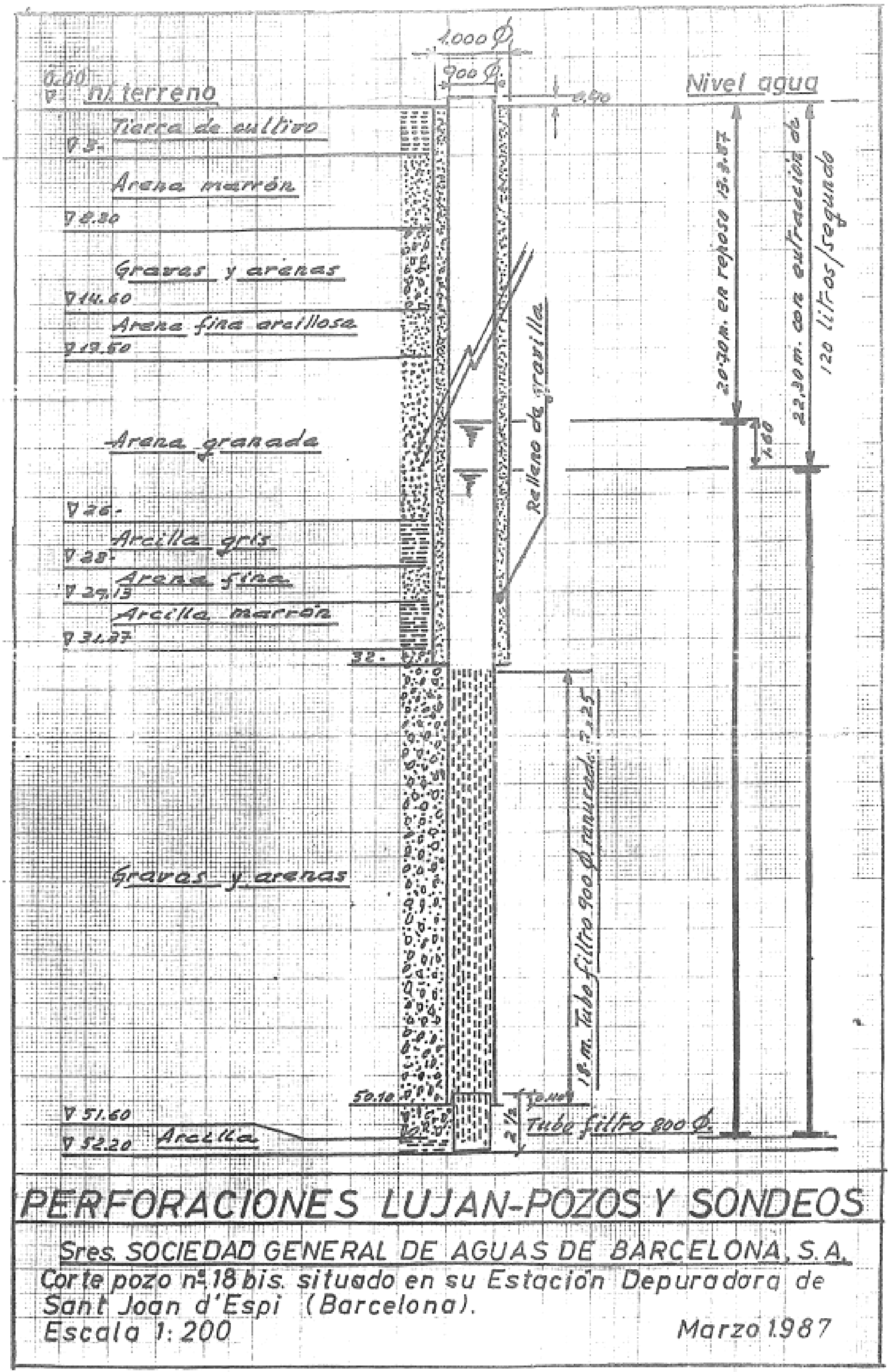


Figure 3: Original section of P18 (1973)



PERFORACIONES LUJAN-POZOS Y SONDEOS

Sres. SOCIEDAD GENERAL DE AGUAS DE BARCELONA, S.A.
Corte pozo nº 18 bis. situado en su Estación Depuradora de
Sant Joan d'Espí (Barcelona).
Escala 1:200
Marzo 1.987

Figure 4: Rebuilt section of P18 (1987)

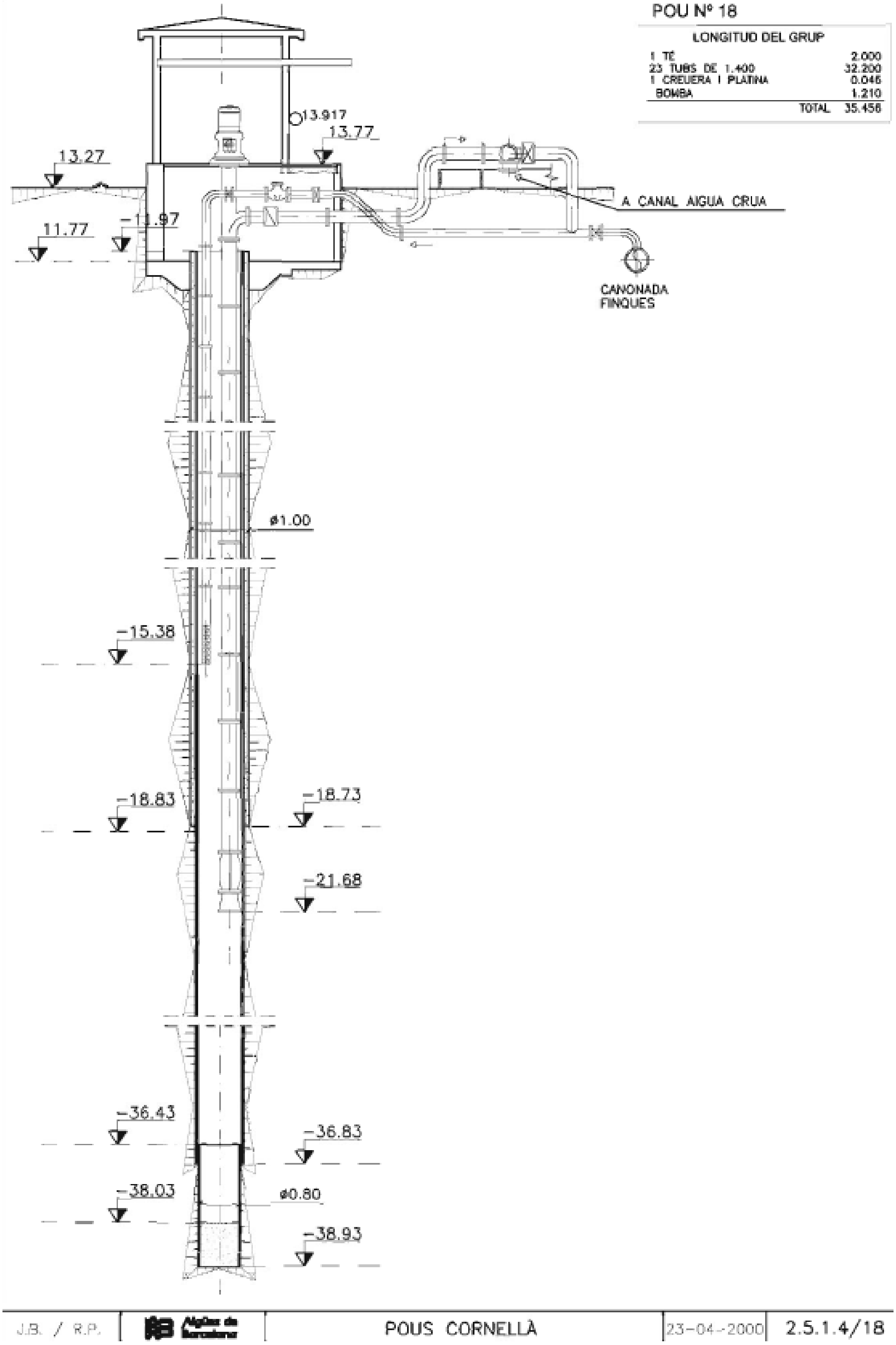


Figure 5: Section view of the equipment of P18

4. Implementation of the observation network

The existing piezometer “*Piezòmetre - E-2-4-B (Sant Joan Despí)*” has been renamed Pz3[2] in the DESSIN project. This piezometer is located at 16 meters of the P18 well and was considered not enough to follow the demonstration phase of the project. With the aim of increase the number of observation wells, Pz1 and Pz2 were constructed in July 2014. The purposes of the new observation wells (in order of priority) are:

- Control of water table evolution along the demo phase
- Knowledge of local lithology
- Execution of tracer tests

The considerations for the selection of the exact location of the observation wells are listed below:

- Inside DWTP facility (P18 is close to the fence of the plant)
- Avoiding underground installations (power, water pipes, underground tanks)

According to literature, the following values of transmissivity and storage coefficient were found:

Transmissivity values (m^2/day)

T = 13,000 – 60,000 m^2/day (AQUALOGY, 2012)
T = 30,000 m^2/day (Pérez Paricio, 1999a)
T= 5,000 – 20,000 m^2/day (Pérez Paricio, 1999b)
T = Max: 50,000 m^2/day; Min: 15,000 m^2/day; Average: 35,000 m^2/day (Azcon and Dolz, 1978)

Storage coefficient (no units)

S = 0.001 and 0.0002 (Pérez Paricio, 1999a)

S = Max: 0.005 ; Min: 0.0003 ; Average: 0.001 (Azcon and Dolz, 1978))

Injection flow (L/s) during the demonstration phase

Minimum = 10 L/s
Maximum = 50 L/s

Equation of Galofré: $\mathbf{T = \frac{100\,Q}{S}}$ **or** $\mathbf{s = \frac{100\,Q}{T}}$ attention in the use of units:

T = transmissivity in [m^2/day]
Q = pumping or injecting flow in [L/s]
s = drawdown[m]

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[2] Note than there is a well also named P03

Expected water level rise was calculated using the combination of transmissivity and injected flow. Results are shown in Table 1. Figure 6 represents the maximum rise of groundwater obtained with the combination of 50L/s and a hydraulic transmissivity of 20,000 m^2/d.

Table 1: Expected groundwater drawdown in P18 using literature data

Injection flow [L/s]	Transmissivity [m²/day]	Expected drawdown [m]
10	5,000	0.2
	20,000	0.05
	40,000	0.025
50	5,000	1.0
	20,000	0.25

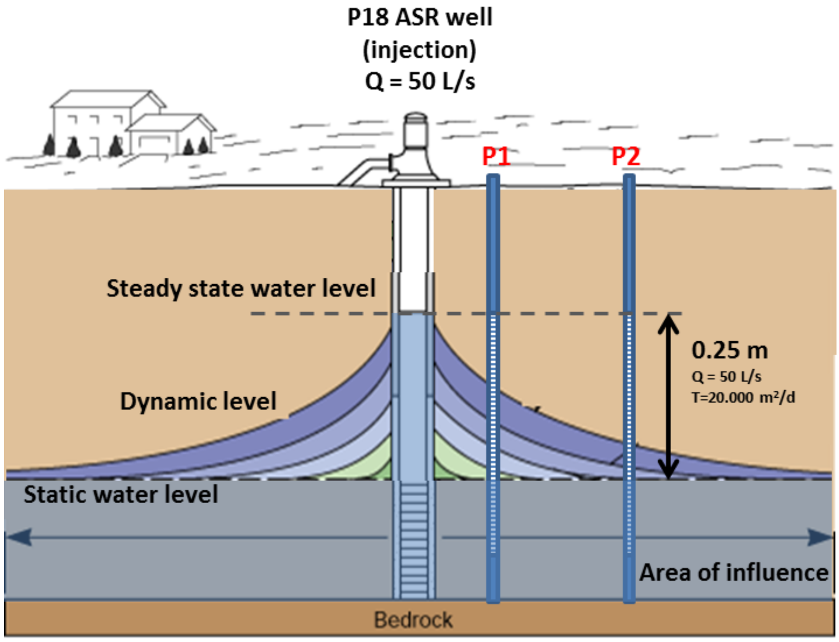


Figure 6: Scheme of expected groundwater rise in Pz1 and Pz2

As the calculated drawdown is equivalent to the groundwater rise in P18, it is possible calculate the expected groundwater rise in observation wells located at difference distances, applying the equation of Thiem (for confined aquifer and stationary conditions):

Equation of Thiem:

$$s = \frac{Q}{2\pi T} \cdot \frac{\ln R}{r}$$

s = drawdown[m]

Q = pumping or injecting flow in [m^3/day]

T = transmissivity in [m^2/day]

R = radius of influence. Value = 500 m (according to literature for confined aquifers)
r = distance to the observation well [m]

Table 2: Expected groundwater drawdown in observation wells

Injection flow [L/s]	Transmissivity [m²/day]	Distance of observation well [m]	Expected drawdown [m]
10 [L/s] **864 m³/d**	20,000	2	0.038
		5	0.032
		10	0.027
50 [L/s] **4,320 m³/d**	20,000	2	0.19
		5	0.16
		10	0.13

It is possible to calculate the arrival time of water injected in P18 to the observation wells considering conservative transport along the aquifer. Calculation of Darcy velocity:

$$\textbf{Darcy velocity} = \frac{\textbf{Pumping flow} \left[\frac{m^3}{d}\right]}{\textbf{Surface of the well filter } [m^2]}$$

Pumping flow = 4,320 m^3/d
Area of the surface of well filter = 2πr x Screen Length = 2π x 0.25 x 18 = 28.27 m^2
Inner diameter: 0.5 m → radius 0.25 m
Well filter length: 18 m

$$\textbf{Darcy velocity} = \frac{4320 \frac{m^3}{d}}{28.27\ m^2} = 152.81 \frac{m}{d}$$

Water velocity in the aquifer (V_w):
V_w = Darcy velocity / effective porosity = (152.81 m/d) / 0.2 = 764 m/d

Table 3: Expected travel time in observation wells

Distance of observation well [m]	Expected arrival time [min]
2	3.76 min
5	9.42 min
10	18.84 min

Tracer test performed by Perez-Paricio (1999b) having a constant pumping flow of 50 L/s revealed similar travel times in P13. See Figure 7 for specific values reported in the area:

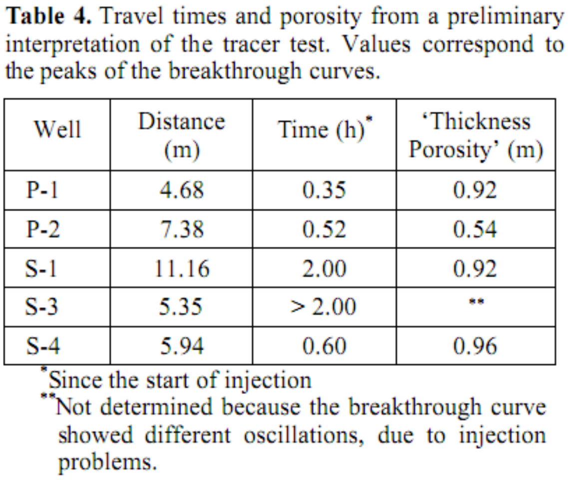


Table 4. Travel times and porosity from a preliminary interpretation of the tracer test. Values correspond to the peaks of the breakthrough curves.

Well	Distance (m)	Time (h)*	'Thickness Porosity' (m)
P-1	4.68	0.35	0.92
P-2	7.38	0.52	0.54
S-1	11.16	2.00	0.92
S-3	5.35	> 2.00	**
S-4	5.94	0.60	0.96

*Since the start of injection

**Not determined because the breakthrough curve showed different oscillations, due to injection problems.

Figure 7: Travel times reported in P13 and the observation network

Source: Perez-Paricio (1999)

These short travel times indicate that additional observation wells should be considered for chemical analysis to evaluate the fate and removal of pollutants, and the assessment of the hydrogeochemical impact in the aquifer. Additional observation wells for that purpose could be P10 and P13, which are relatively close to P18.

Table 4: Expected travel time to P10 and P13

Distance of observation well [m]	Expected arrival time [min]
P18-P10 → 137 meters	4.3 hours
P18-P13 → 294 meters	9.23 hours

Final configuration of observation well network has been established using the indicative values obtained in the previous calculations of this section (2, 5 and 10 meters from the injection well):

Figure 8: Aerial view of the distances of observation network to P18

3.1. Field works for the execution of piezometer P1

P1 was drilled using continuous core extraction and an inner diameter of 3’’. Sediment core was stored in standard core boxes, with 3 meter capacity each. Figure 27 (ANNEX A: Drilling works: storage boxes Pz1) shows pictures of the fresh sediments obtained in the continuous core.

Figure 9: Drilling works of Pz1 in Sant Joan Despí

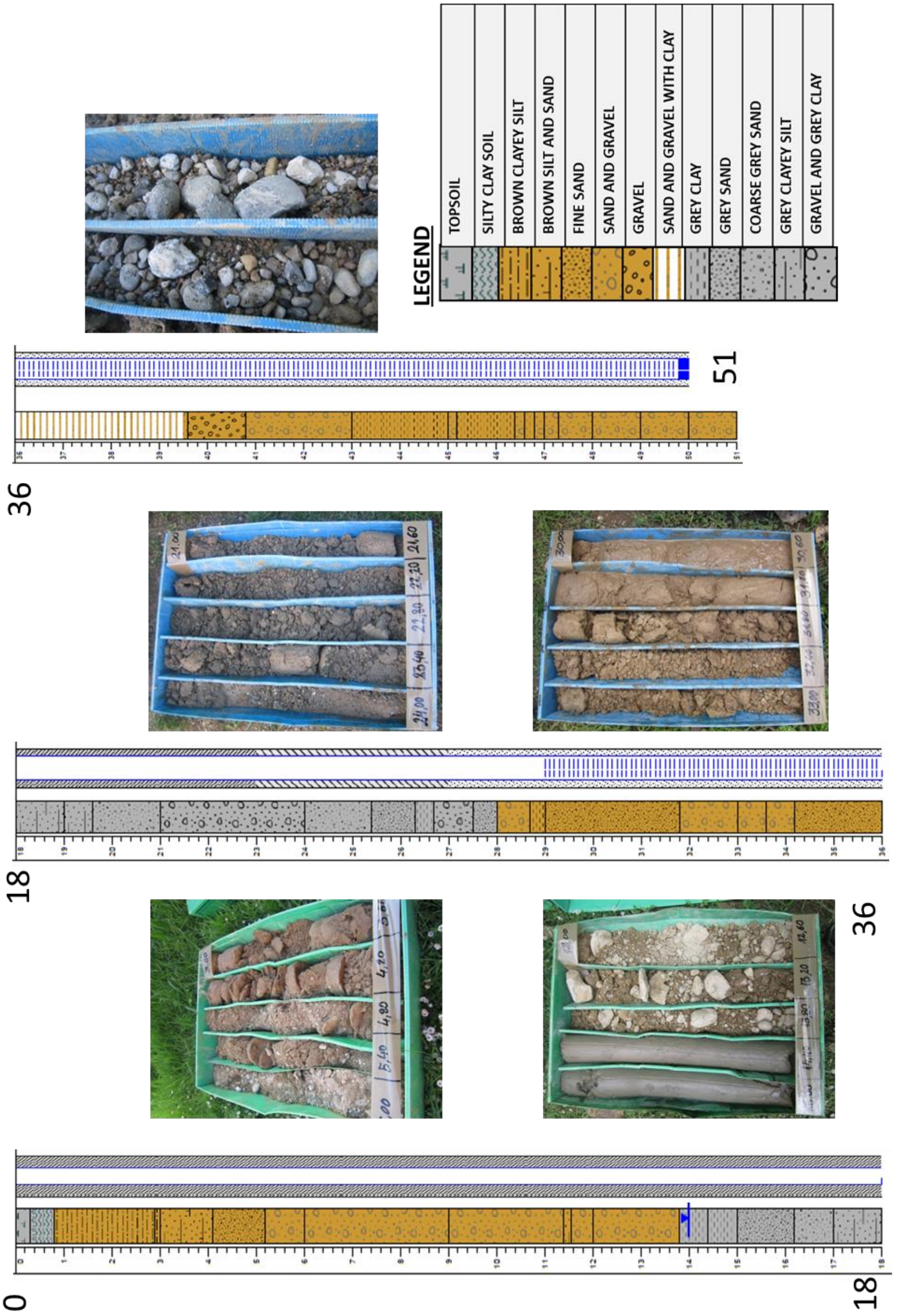


Figure 10: Geological profile Pz1 (see details in Annex C)

3.2. Field works for the execution of piezometer Pz2

Pz2 was drilled using a non-continuous core recovery method, as it is located very close to Pz1 and there was no need of additional geological information. Geological profile of Pz2 is attached in ANNEX D of the document.

Figure 11: Drilling works of Pz2 in Sant Joan Despí
(See in the middle details of pre-filter material)

3.3. Existing piezometer Pz3

An existing point has been identified close to the well P18. It is located in the DWTP facility, at 16 meters of the building of P18. It is one of the observation wells used for the Catalan Water Agency (ACA). The official name appearing in the registrations is "*Piezòmetre - E-2-4-B (Sant Joan Despí)*" and water level register exists at that point from 1973, corresponding to the construction of P18. There is no previous information about the depth and screen of the piezometer.

3.4. Summary of DESSIN observation network

Table 5: Summary of DESSIN observation network characteristics

Parameter	P18	Pz1	Pz2	Pz3
UTM coordinates	X=420498 Y=4578270	X=420406 Y=4578071	X=420411 Y=4578075	X=420411 Y=4578081
Distance to P18 [m]	0	3.5	8	16
Inner diameter	900 mm	3’’	2’’	2’’
Material	iron	PVC	PVC	PVC
Pre-filter	NONE	YES	YES	Unknown
Total depth	50	50	50	Unknown (35?)
Screen from surface	30 - 50	30 - 50	30 - 50	Unknown
Date of construction	1973	2014	2014	1973?

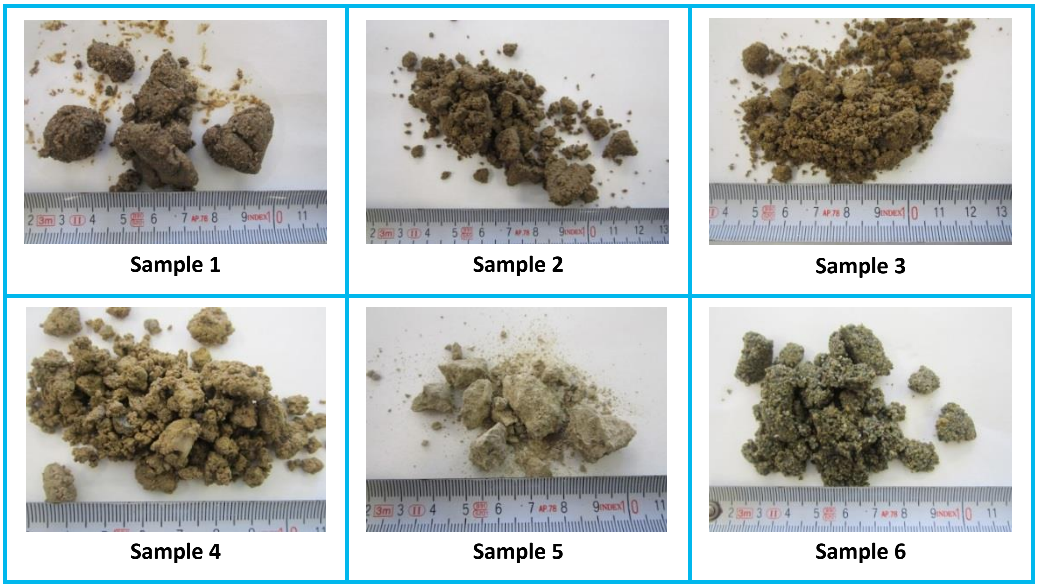
5. Mineralogical analysis

The aim of the analysis of minerals in the aquifer is to provide local information of the minerals and their chemical composition to do a more accurate interpretation of the hydrogeochemical changes occurring along the ASR process. This preliminary work consisted in the qualitative assessment of the minerals present in Pz1 recently drilled.

4.1. Methods and analytical conditions

A total of 6 samples from the unaltered core of Pz1 were collected to analyse the mineralogical composition. The depth of the samples and their characterisation are listed in Table 6. Samples were collected from the core boxes and stored in a plastic bag. After their identification were taken to ICTJA[3] Laboratory in Barcelona. Before milling the samples for the X-Ray Diffraction (XRD) measurements, the sediments were subject to a pre-heating stage (at around 45ºC) to remove remaining humidity in the material.

XRD measurements were performed with a state-of the-art Bruker D8-A25 diffractometer equipped with a Cu tube (ƛ=1.5405 Å) and an ultrafast position sensitive detector (PSD). XRD scans were collected over the 2θ range between 4° and 60° with steps of 0.035° and an equivalent integration time of 192 s per step. A voltage (current) of 40 kV (40 mA) was applied to the x-ray generator. The phases in the samples were identified with Bruker's software package Diffrac.Suite™ together with the PDF-2 database from the International Centre for Diffraction Data (ICDD).



Sample 1

Sample 2

Sample 3

Sample 4

Sample 5

Sample 6

Figure 12: Pictures of fresh sediments collected

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[3] ICTJA = Institut Ciències de la Terra Jaume Almera (Barcelona). CSIC Associated unit.

Table 6: Depth and description of Pz1 sediment samples

#	Depth (m)	Type	Box	#	Depth (m)	Type	Box
1	31.5 – 31.8	Fine sand	11	4	40.8 - 42	Gravel & Sand	14
2	34.2 – 35.4	Fine sand	12	5	12 – 13.8	Lime crust	5
3	35.4 - 36	Gravel (50%) & Sitty (50%)	12	6	25.4 – 26.5	Fine sand with yellow Clay	9

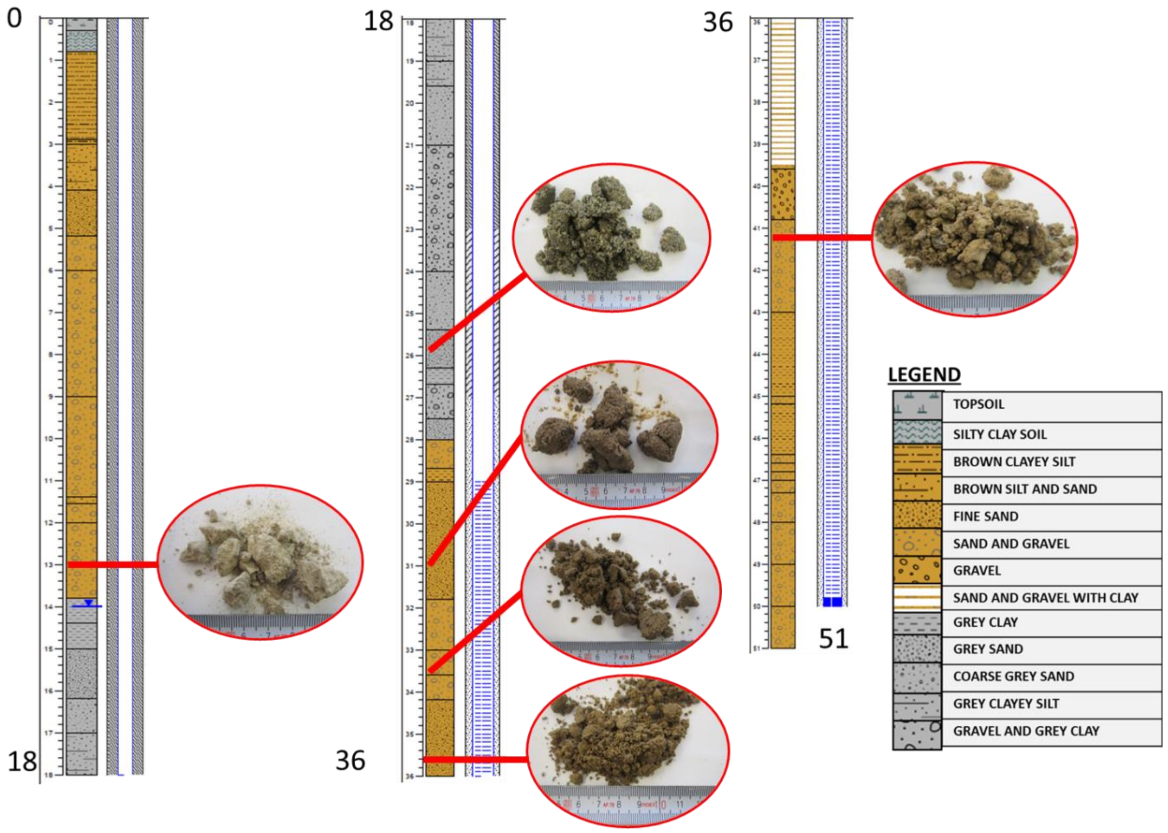

Figure 13: Location of sediment samples and correspondence to geological profile

4.2. Results: minerals identified

XRD scans from the 6 sediment samples investigated can be found in ANNEX B: Mineralogical XRD profiles. It can be seen that the spectra of all the samples are very similar, as only intensity differences between the XRD peaks corresponding to the different mineral phases in the samples are observed. The following phases have been identified in the six samples: Quartz, carbonate phases (calcite and dolomite), clays (illite and clinochlore), and feldspars (microcline and albite).

The following subsections details the minerals identified, as some of their components are going to be found in water along the injection and extraction of groundwater. The concentration of their components will mainly depend of the solubility of the minerals. Some minerals react fast upon contact with water. This is particularly the case for the more “soluble” minerals such as gypsum and halite, which were not identified in the mineralogical analysis. Carbonate minerals as calcite and dolomite reach the equilibrium, within a timespan that is short compared to the residence time of groundwater. Other minerals, typically silicates, react so sluggishly that equilibrium is never attained at low temperatures and therefore reaction kinetics has to be considered.

- Carbonates: Calcite and dolomite
- Silicates: Quartz, clinochlore, illite, microcline, albite

Figure 14: **Pictures of minerals identified in sediment samples**
Note: pictures were not obtained in the analysis (generic representation)

4.2.1. Calcite

Chemistry: $CaCO_3$, Calcium Carbonate
Class: Carbonates; Group: Calcite

Calcite is a carbonate mineral which is in equilibrium with Ca^{2+} in groundwater due to the reaction of calcite with carbon dioxide derived from respiration or oxidation of organic matter. Carbon dioxide reacts with H_2O to form carbonic acid (H_2CO_3). The acid provides proton (H+) which associate with the carbonate ion (CO_3^{2-}) from calcite to form bicarbonate (HCO_3-). The overall reaction between carbon dioxide and $CaCO_3$ is:

$$CO_2(g) + H_2O + CaCO_3 \rightarrow Ca^{2+} + 2HCO_3-$$

This reaction if fundamental for understanding the behavior of calcite dissolution and precipitation in nature. An increase of Co2 results in dissolution of $CaCO_3$. Removal of CO_2 causes $CaCO_3$ to precipitate (see more details in Appelo & Postma, 2009).

4.2.2. Dolomite

Chemistry: $CaMg(CO_3)_2$, Calcium Magnesium Carbonate
Class: Carbonates; Group: Dolomite

Dolomite differs from calcite, $CaCO_3$, in the addition of magnesium ions to make the formula, $CaMg(CO_3)_2$. The magnesium ions are not the same size as calcium and the two ions seem incompatible in the same layer. In calcite the structure is composed of alternating layers of carbonate ions, $CO_3{}^{2-}$, and calcium ions. In dolomite, magnesiums occupy one layer by themselves followed by a carbonate layer which is followed by an exclusively calcite layer and so forth.

4.2.3. Quartz

Chemistry: SiO_2 , Silicon dioxide
Class: Silicates; Subclass: Tectosilicates; Group: Quartz

Silica is an indicator of groundwater, as it comes from hydrolysis processes of feldspars and silicates. Quartz is a source of silica in groundwater. Dissolved silica is normally represented as SiO_2, while in natural waters it appears as H_4SiO_4 until pH value is above 9. Normally, the silica values in groundwaters are above 3 mg/L (UJI, 2014).

4.2.4. Clinochlore

Chemistry: $(Mg, Fe, Al)_6(Si, Al)4O_{10}(OH)_8$, Magnesium Iron Aluminum Silicate Hydroxide
Class: Silicates; Subclass: phyllosilicates; Groups: The Clays and The Chlorite Group.

It is an iron-bearing mineral corresponding to the chlorite group in the phyllosilicate minerals. Chlorites can be described by the following four end-members-based on their chemistry via substitution of the following four elements in the silicate lattice; Mg, Fe, Ni, and Mn.

- Clinochlore: $(Mg_5Al)(AlSi_3)O_{10}(OH)_8$
- Chamosite: $(Fe_5Al)(AlSi_3)O_{10}(OH)_8$
- Nimite: $(Ni_5Al)(AlSi_3)O_{10}(OH)_8$
- Pennantite: $(Mn,Al)_6(Si,Al)_4O_{10}(OH)_8$

4.2.5. Illite

Chesmistry: $(K, H)Al_2(Si, Al)4O10(OH)_2$ - xH2O
Class: Silicates; Subclass: Phyllosilicates; Group: Clay-Mica Group.

4.2.6. Microcline

Chemistry: $KAlSi_3\ O_8$ Potassium aluminum silicate.
Class: Silicates; Subclass: Tectosilicates; Group: Feldspars

4.2.7. Albite

Chemistry: $NaAlSi_3 O_8$, Sodium aluminum silicate.
Class: Silicates; Subclass: Tectosilicates; Group: Feldspars

Silicates as Albite, Microcline, Illite and Clinochlore are characterized by weathering processes. Weathering of silicate minerals is a slow process and the resulting changes in water chemistry will be gradual and less conspicuous than in carbonate aquifers. Silicate weathering is the most important pH-buffering mechanism in sediment without carbonate minerals. Apello & Postma (2009) use albite as an example to illustrate this transformation process:

$$\underset{albite}{3Na(AlSi_3)O_8} + Mg^{2+} + 4H_2O \rightarrow \underset{montmorillonite}{2Na_{0.5}(Al_{1.5}Mg_{0.5})Si_4O_{10}(OH)_2} + 2Na^+ + H_4SiO_4$$

$$\underset{albite}{2Na(AlSi_3)O_8} + 2H^+ + 9H_2O \rightarrow \underset{kaolinite}{Al2Si_2O_5(OH)_4} + 2Na^+ + 4H_4SiO_4$$

$$\underset{albite}{Na(AlSi_3)O_8} + H^+ + 7H_2O \rightarrow \underset{gibbsite}{Al(OH)_3} + Na^+ + 3H_4SiO_4$$

6. Temperature and conductivity profiles

5.1. Conductivity profiles

Conductivity and temperature profiles were obtained the 24th July 2014, using a submerged TCD with a continuous record of temperature, depth and conductivity (using data interval of 1 second). Figure 15 represents electrical conductivity profiles in Pz1, Pz2 and Pz3. Red line represents the starting point in depth of the screen of the piezometers Pz1 and Pz2. From 30 meters depth to the end of the screen (50 meters depth), conductivity levels are constant, around 2000 microS/cm.

Regarding P3, data the total length is undefined, as it was already constructed before DESSIN project. Conductivity values are stable from 20 to 35 meters depth.

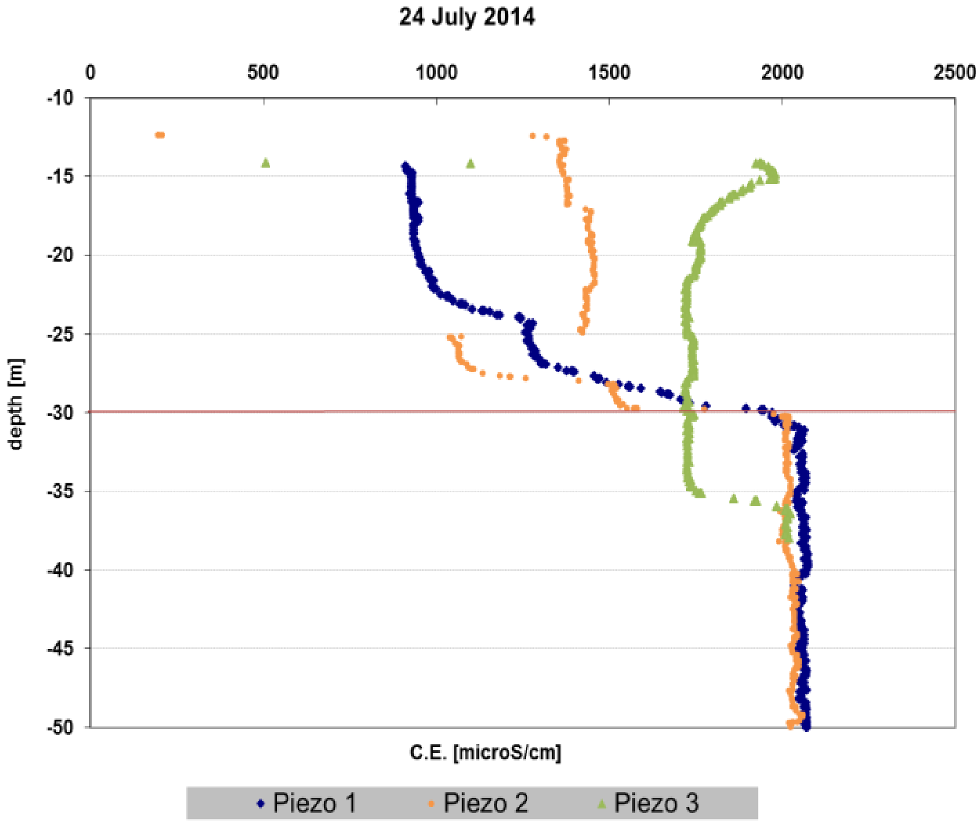

Figure 15: Conductivity profiles of piezometers Pz1, Pz2 and Pz3

5.2. Temperature profiles

Figure 16, represents temperature evolution along the piezometers. Constant temperatures below the screen stating point (red line) indicates no lateral flows are occurring in any observation well. Next figures (Figure 17, Figure 18 and Figure 19) shows the conductivity and temperature profiles in the piezometers separately and taking into account the phreatic level measured in the moment of the data acquisition.

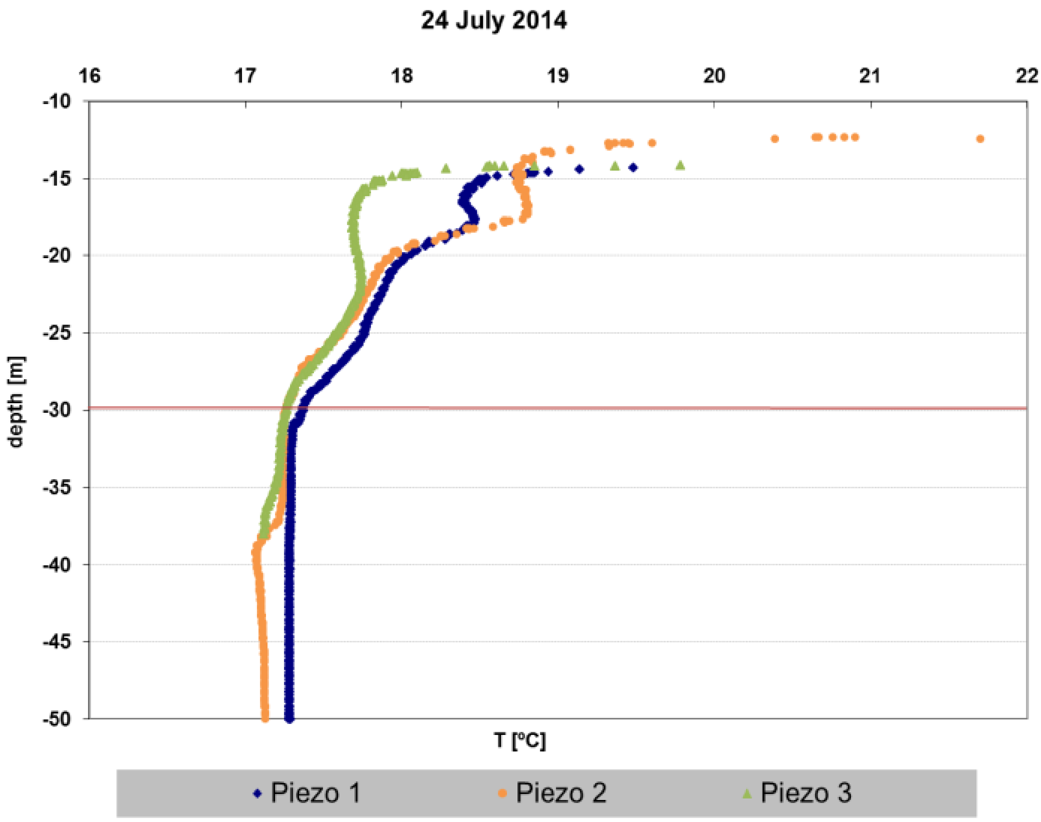

Figure 16: Temperature profiles of piezometers Pz1, Pz2 and Pz3

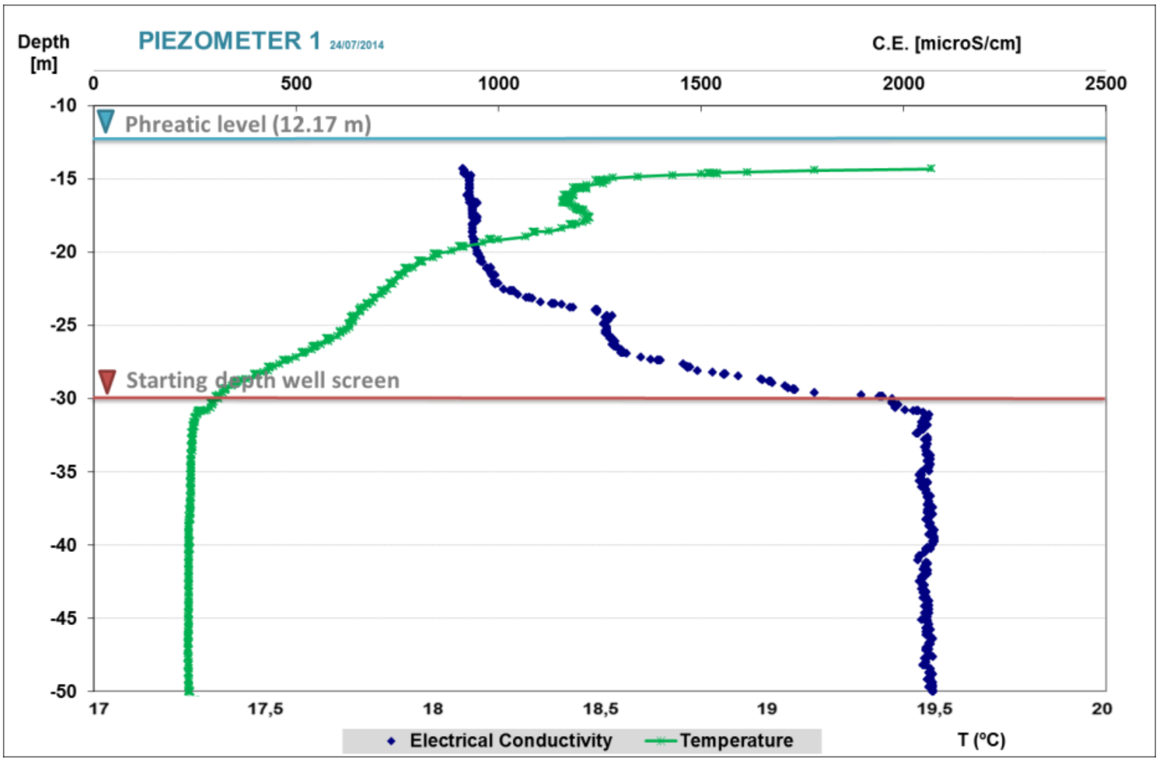

Figure 17: Temperature and conductivity profile in Pz1 (July 2014)

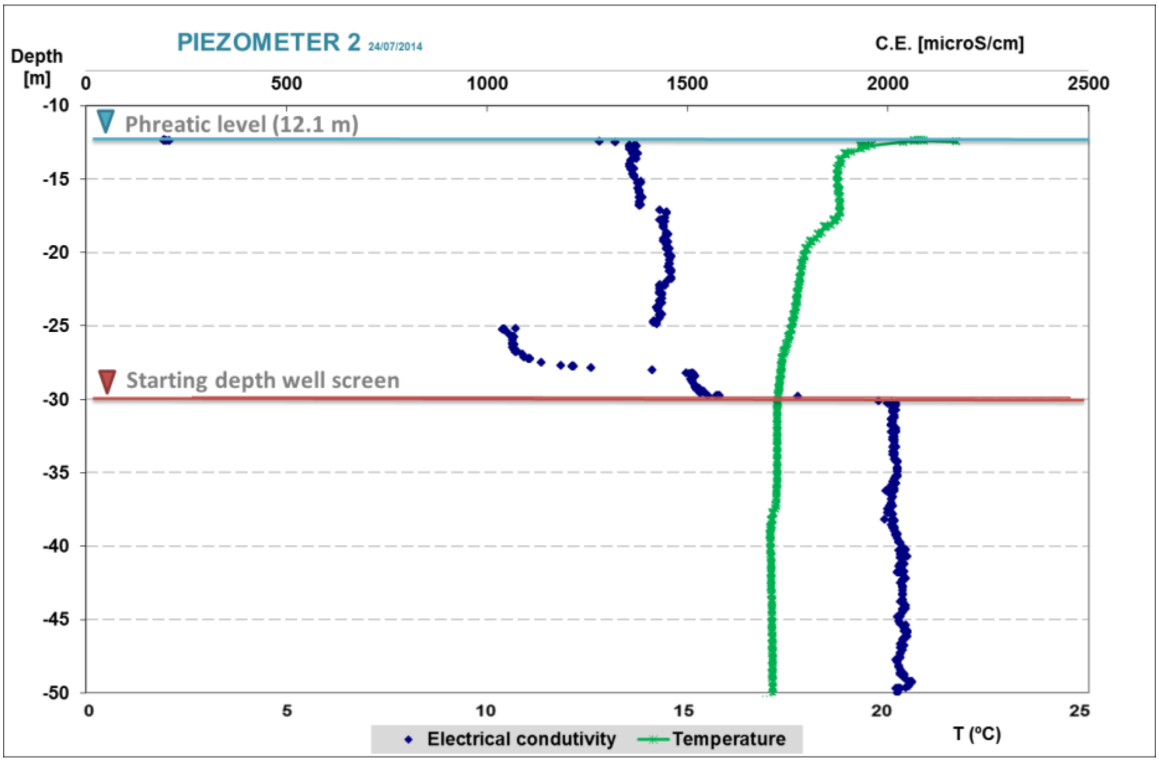

Figure 18: Temperature and conductivity profile in Pz2 (July 2014)

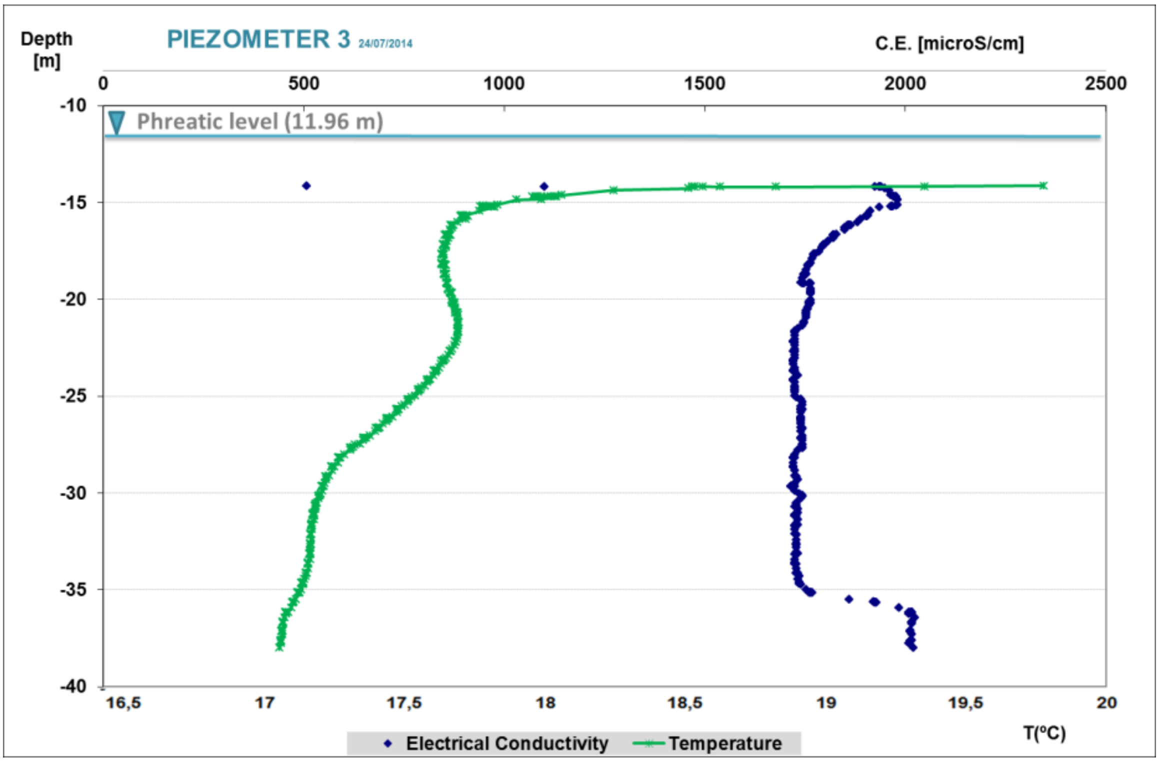

Figure 19: Temperature and conductivity profile in Pz3 (July 2014)

6.1. General considerations

P18 is a pumping well installed in the facility of the DWTP of SJD. Operational data of pumping episodes in September 2014 have been used as a pumping test. The response of the pumping in P18 has been observed in the drawdown in Pz1, Pz2 and Pz3 (automatic data loggers took depth data each 15 minutes). Figure 20 represents the conceptual scheme of the pumping test carried out.

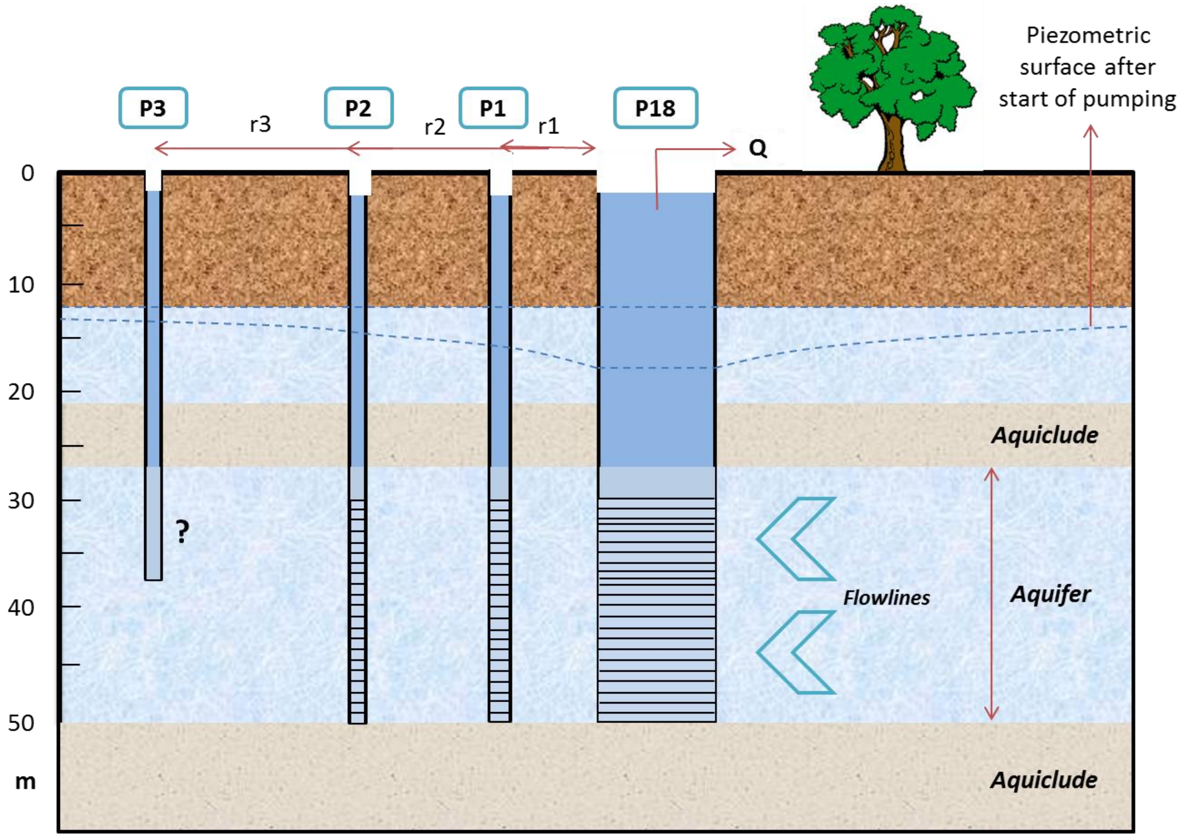

Figure 20: Conceptual scheme of pumping test at SJD P18

The selected methods for data interpretation are:

- **Cooper-Jacob solution:** The pumping test is characterized for its constant pumping flow and the unsteady-state in the drawdown. The method has been applied manually using MS EXCEL for a specific period of time.
- **EPHEBO Software:** The EPHEBO computer program allows estimating hydraulic parameters in pumping tests. It is directly applied with the introduction of the data series of pumping and recovery in Pz1, Pz2 and Pz3.

6.2. Interpretation using the method of Cooper-Jacob

4.2.8. Methodology: Numerical solution method

The problem of unsteady-state flow due to a constant pumping rate in a fully confined aquifer was solved by Theis (1935) but, the Cooper-Jacob (1946) method is a simplification of the Theis method valid for greater time values and decreasing distance from the pumping well (smaller values of "*u*" parameter). See an example of application in Chapuis, 1992. This method involves truncation of the infinite Taylor series that is used to estimate the well function W(u). Due to this truncation, not all early time measured data is considered to be valid for this analysis method. The decline, to anywhere and anytime has been expressed of simple form by Cooper-Jacob equation. The resulting equation is:

$$s = \left(2.\frac{3Q}{4\pi T}\right)\log_{10}\left(2.\frac{25Tt}{Sr^2}\right)$$

Where:

s= drawdown [m]
Q= pumping rate [m³/day]
T= transmissivity [m²/day]
r= radial distance from pumping well to observation well [m]
S= storage coefficient [unitless]
t= elapsed time since start of pumping [days]

Knowing the aquifer hydrogeological parameters S and T and the flow rate Q, one can calculate the decrease at any point located at a distance r from the well for any predetermined time (t). Also known data times-decrease pumping, may estimate the values of T and S, using the same expression or through a graph.

The Cooper-Jacob solution the following assumptions:

- The aquifer is confined and has an "apparent" infinite extent
- The aquifer is homo generous, isotropic, and of uniform thickness over the area influenced by pumping
- The piezometric surface was horizontal prior to pumping
- The well is pumped at a constant rate
- The well is full penetrating
- Water removed from storage is discharged instantaneously with decline in head
- The well diameter is small, so well storage is negligible
- The values of *u* are small (acceptable if $u<0.02$)

$$u = \frac{r^2 \cdot S}{4 \cdot T \cdot t}$$

Where:

u= control parameter
T= transmissivity [m²/day]
r= radial distance from pumping well to observation well [m]
S= storage coefficient [unitless]

t= elapsed time since start of pumping [days]

The Cooper-Jacob methodology corresponds in a graphical data interpretation, using a semi logarithmic plot, representing values of drawdown ("s" in meters or ft in American units) in the y-axis, and the time in days or minutes the x-axis, using logarithmic scale. Figure 21 represents the graphical.

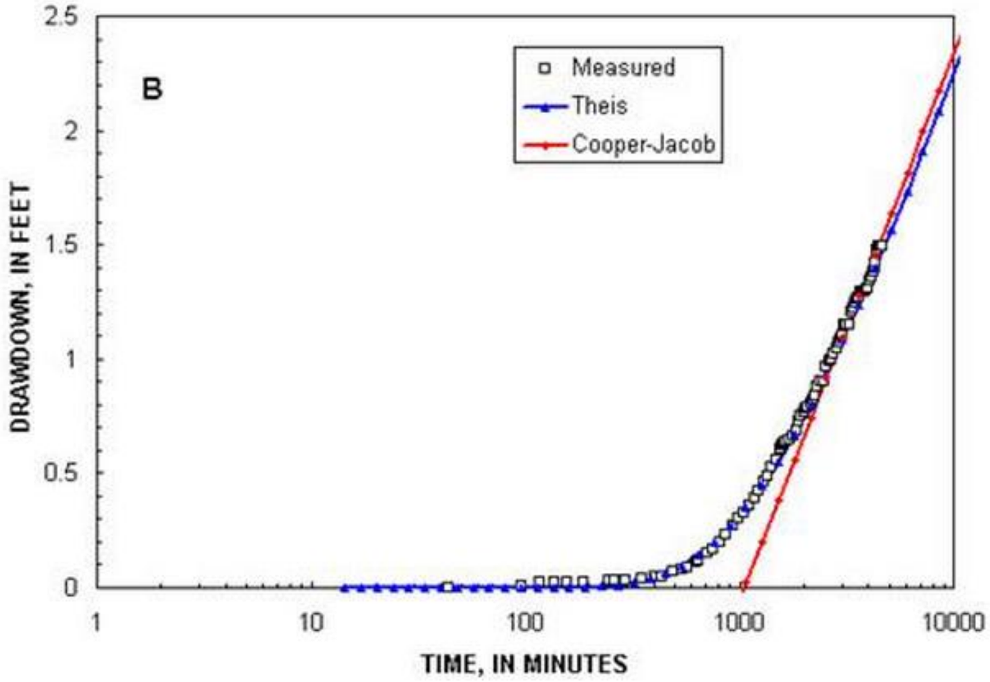

Figure 21: Example of Cooper-Jacob graphical interpretation
Source: USGS Nevada Water Science Centre (website)

Transmissivity of the aquifer can be directly calculated using the slope "m" of the regression line (see red line in Figure 21) and applying the formula:

$$\mathbf{T = 0.183\frac{Q}{m}}$$

Where:

Q= pumping rate [m^3/day]
T= transmissivity [m^2/day]
m= slope of the regression line

The intersection between the regression line with the x-axis (t_0) is considered the time when the drawdown would be zero in ideal conditions. In t_0 the following equation is fulfilled:

$$\mathbf{S = \frac{2.25Tt_0}{r^2}}$$

Where:

t_0= intersection between the regression line with the x-axis [days]
T= transmissivity [m^2/day]

r= radial distance from pumping well to observation well [m]
S= storage coefficient [unitless]

In pumping tests with multiple observation wells, the closer wells will meet the conditions before the more distant ones.

In September 2014, dataloggers of pressure (DIVERS) where installed in the boreholes Pz1, Pz2 and Pz3. From then to February 2016 six pumping episodes in P18 have been selected to do the interpretation and obtain hydrogeological parameters at local scale. The criteria to select pumping episodes are listed below:

- Continuous pumping without stops (more than 24 hours)
- Drawdown clearly observed in the observation Wells
- Not increase in groundwater level along the pumping test
- Stabilisation of groundwater level with large times (it indicates the stationary state)

Table 7: Selected time episodes for the pumping test

Parameter	Starting time	Finishing time	Total time pumping [h]	Comments
Pumping Test A	06/09/2014 4:30	06/09/2014 22:15	17.7	-
Pumping Test B	05/09/2014 20:00	07/09/2014 7:45	35.7	-
Pumping Test C	15/09/2014 22:30	16/09/2014 5:45	7.2	Highly influenced external pumping wells
Pumping Test D	14/04/2015 11:19	16/04/2015 10:34	47.2	Reliable information: not additional pumping wells
Pumping Test E	26/05/2015 15:19	27/05/2015 6:19	15.0	-
Pumping Test F	29/02/2016 10:48	02/03/2016 14:20	51.5	-

4.2.9. Analysis of the heterogeneity of the aquifer: normalized method

The degree of homogeneity of the aquifer can be analysed compared the value of the storage coefficient “S” obtained in the observation wells. “S” is sensitive to the homogeneity of the aquifer. A graphical method has been applied, dividing the pumping test by the values of drawdown by the radius squared “r^2” to normalize the value of the storage coefficient. Thus, this method considers same distance to the observation well, so I the aquifer is homogenous, the three curves should be overlapped in the following figure:

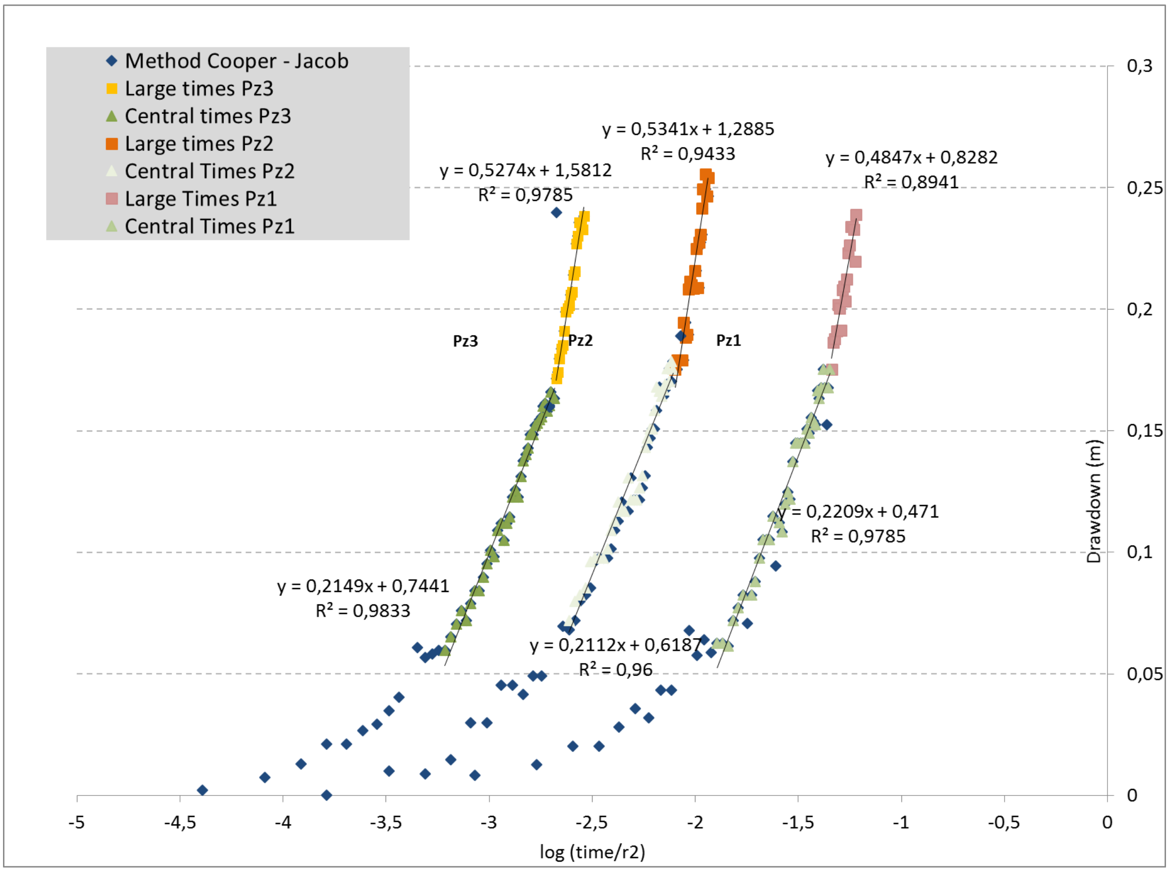

Figure 22: Analysis of heterogeneity using normalised method

The information obtained in this figure is very valuable in two senses:

- Slope of curves: Pz1, Pz2 and Pz3 presents similar slopes in the central times and large times of the pumping tests. This means that we can use indistinctly anyone of the three observation wells to determine transmissivity, as they present same trend.
- Not overlapping in the curves normalized: this means that the terrain presents some heterogeneity. This heterogeneity is easily observed in the values of the storage coefficient.

4.2.10. Results

The following figures (Figure 23), graphs are obtained by applying the method of Cooper-Jacob, for observation wells Pz1, Pz2, Pz3, in the pumping tests of 2014. The graphics appointed Range A, correspond to extraction date of September 6, 2014 and therefore appointed as Range B, the date of removal from 15 to 16 September 2014. The results of the Cooper-Jacob method are shown in Table 7.

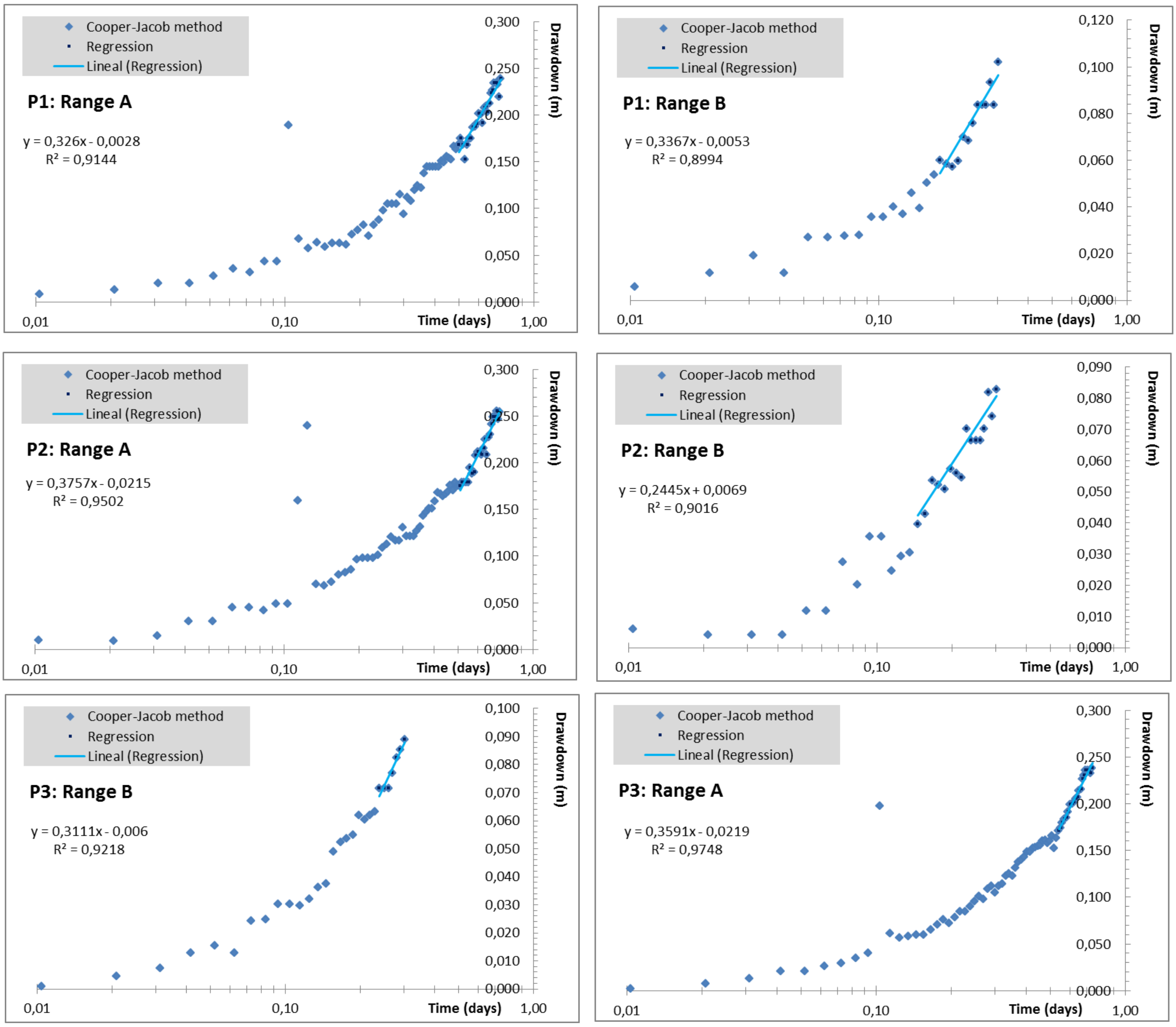

Figure 23: Graphical interpretation Cooper-Jacob using field data

Table 8: Results obtained from the Cooper-Jacob method of T and S

Parameter	Pz1		Pz2		Pz3		Average
	A	B	A	B	A	B	
u	0.002	0.010	0.016	0.013	0.017	0.011	**0.012**
T (m²/day)	10984	10633	9531	14642	9971	11510	**11212**
S*	5.65	10.35	7.20	33.55	1.92	0.61	**4.88**

(*) S represents the storage coefficient, which should be < 1. The storage coefficients have been listed in the table, but there have no physical coherence.

Same calculations were extended to the pumping tests identified in Annex E, corresponding. Following table presents single results of Transmissivity values using Galofré method:

$$T = \frac{100 * Q}{s}$$

Table 9: Results obtained from the Galofré method

Parameter	**Average T [m2/d] – Galofré method**			
	Pz1	**Pz2**	**Pz3**	**Average T [m2/d]**
Pumping Test A	94,358	89,157	95,151	**92,889**
Pumping Test B	14,013	15,134	17,875	**15,674**
Pumping Test C	-	-	-	**-**
Pumping Test D	19,663	23,877	-	**21,770**
Pumping Test E	19,149	-	-	**19,149**
Pumping Test F	19,561	24,388	31,828	**25,259**

6.3. Application of EPHEBO software

The EPHEBO computer program allows estimating hydraulic parameters in pumping tests. EPHEBO is mainly a user-friendly interface for MariaJ. This program, which allows interpreting pumping tests by means of automatic calibration, was developed for VAX/VMS environments and it is provided with a text-mode interface which makes it quite difficult to understand and manage. In order to solve all these problems and include new graphic functions, when transferring it to this platform, it was decided to stop developing the text-mode interface and create a new interface for Microsoft Windows, that is, EPHEBO. The new program also allows interpreting graphically (Diagnostic Plot, Theis Superposition, Hantush Superposition, Cooper-Jacob Solution, Neuman Solution), as well as generating charts and data with the results obtained. MariaJ code is only used for automatic methods, the rest of interpretation methods are all new (see more details in Carbonell *et al*, 1997).

The complete series of data have been introduced in the software, including pumping and recovery episodes. Theis method has been applied for the interpretation of data and automatic calculation of hydrogeological parameters (T, S).

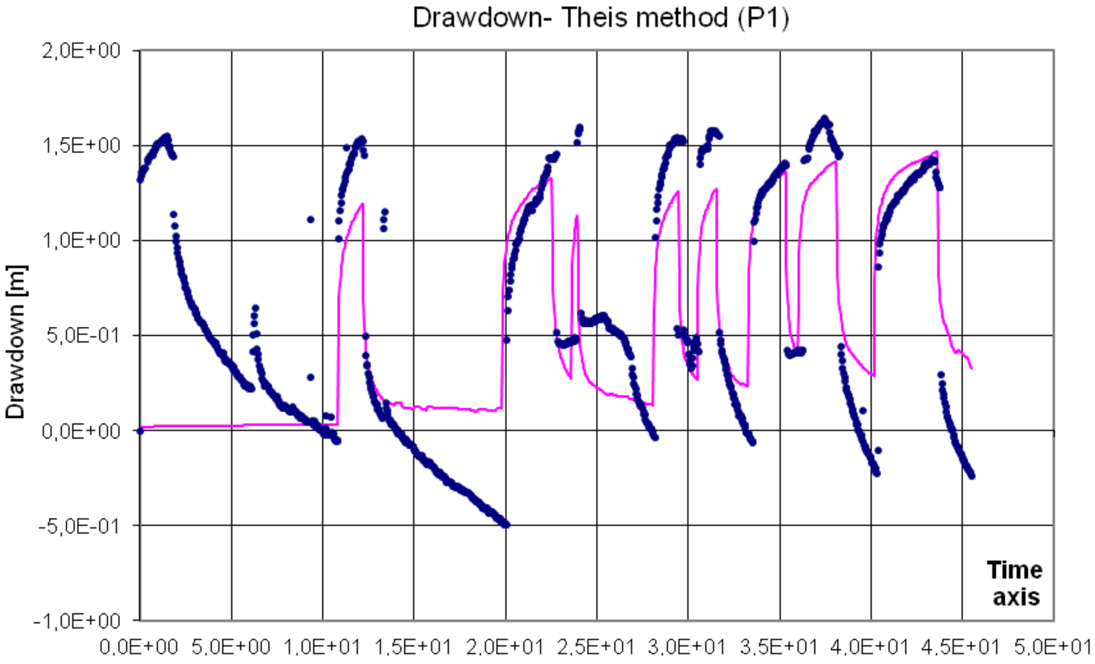

Figure 24: Theis method using EPHEBO software (Pz1)
NOTE: Blue points are measured data and Magenta line is simulated data

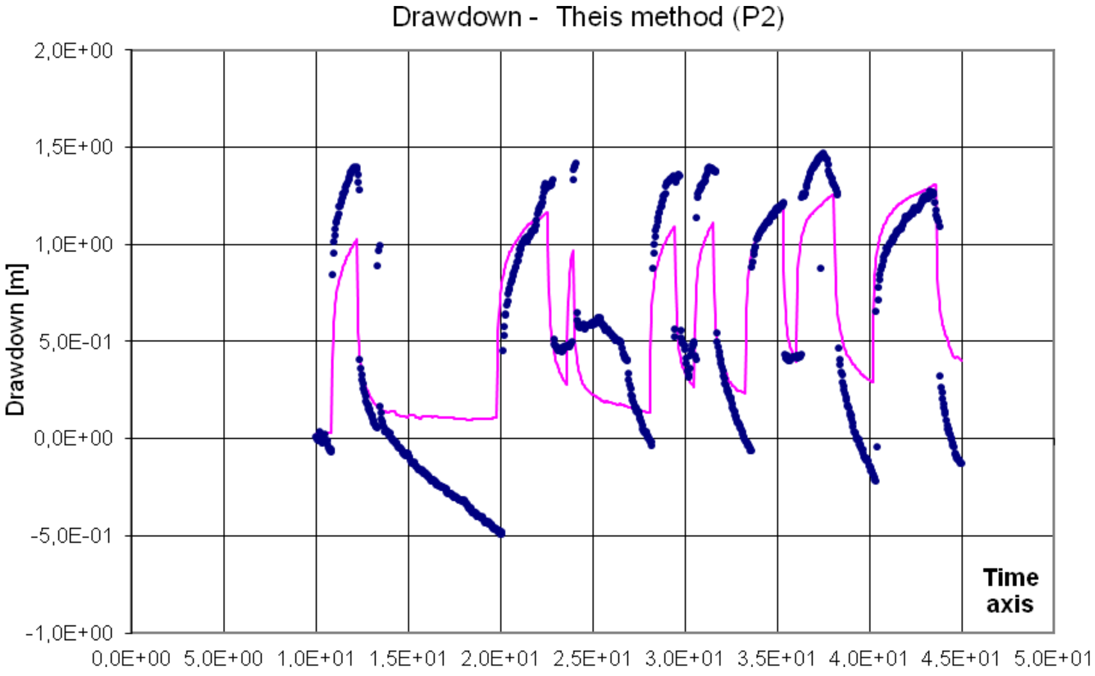

Figure 25: Theis method using EPHEBO software (Pz2)
NOTE: Blue points are measured data and Magenta line is simulated data

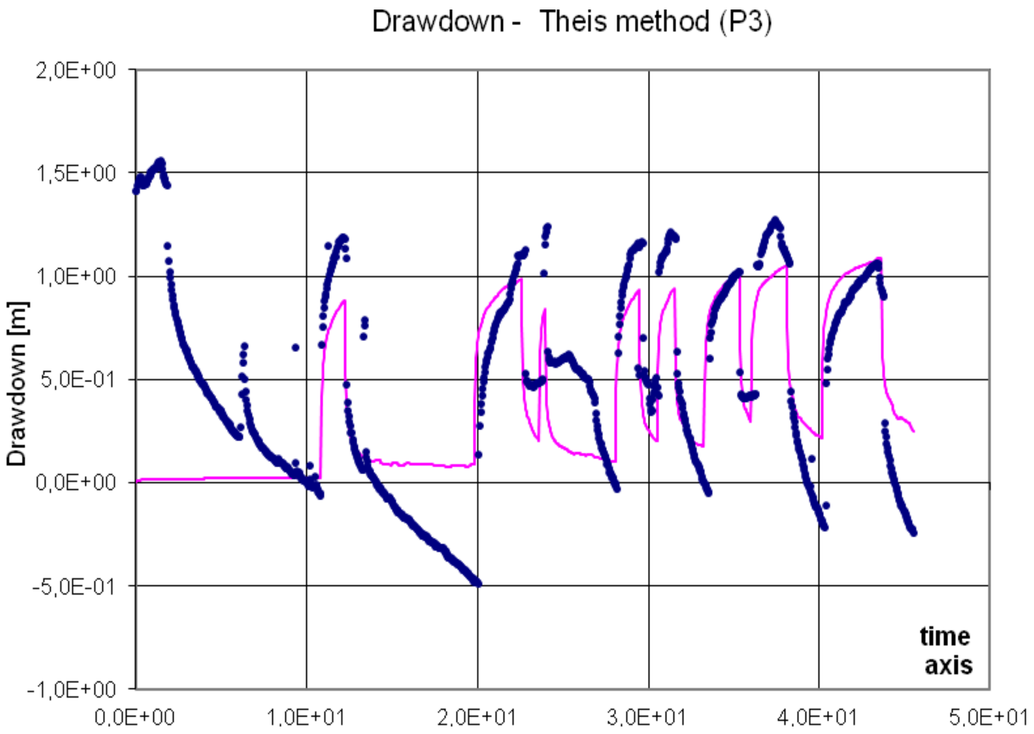

Figure 26: Theis method using EPHEBO software (Pz3)
NOTE: Blue points are measured data and Magenta line is simulated data

Table 10: Results obtained from the Theis method applying EPHEBO Software

Parameter	Pz1	Pz2	Pz3	Average
T (m^2/day)	8840	8870	11800	**9836**
S*	2.5	1.4	0.18	**1.36**

(*) S represents the storage coefficient, which should be < 1. The storage coefficients have been listed in the table, but they have no physical coherence.

6.4. Values of Transmissivity: comparison with regional data

Historically, have been performed several pumping tests in the aquifer using different pumping wells. The hydraulic parameters obtained have been compiled in Table 11

Table 11: Summary hydraulic parameters obtained in pumping tests in the study area

Well name	Year pumping test	T value (m^2/day)	Q pumping test (L/second)	S value	References
P13	1968	**35000**	145	$1x10^{-3}$	CIHS[4] 1968 (2)

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[4] CIHS: Hydrogeology postgraduate course carried out in Barcelona. Every year the students perform a pumping test, and sometimes SJD has been the selected study area.

P13	2002	**35000**			ACA 2002
P7	2002	**13000**	250		CIHS 2002
P9	2009	**65000**	125		CIHS 2009

Comparing transmissivity values obtained in the pumping test performed in P18, historical values are quite high than the obtained in P18 during DESSIN project, which is about 11,200 m^2/d. Some authors classify the aquifer material using hydraulic permeability, which is directly related to transmissivity according to the following equation:

$$K = \frac{T}{b}$$

Where:

K= permeability [m/day]

T= transmissivity [m^2/day]

b= thickness of the aquifer [m]

The thickness of the aquifer in SJD is 20 m, so the permeability obtained is 560 m/day. According to classifications (see Table 12 and Table 13) the aquifer consists mainly in clean coarse sand. Hazen classification identifies this permeability with a “very high permeability class” and the aquifer is classified as “very good” due to their hydraulic properties of storage and water circulation.

Table 12: Hazen Classification permeability to an aquifer
Source: Custodio and Llamas (2001)

Class	Permeability (cm/second)		Type of aquifer	Permeability class
1	3	Aquifer	Very good	Very high
2	0.7		**Very good**	**Very high**
3	0.1		Good	High
4	0.05		Regular	Medium
5	$9 \bullet 10^{-3}$		Poor	Small
6	$5 \bullet 10^{-3}$		Poor	Small
7	$2 \bullet 10^{-3}$		Very poor	Very small
8	$7 \bullet 10^{-4}$		Very poor	Very small
9	$7 \bullet 10^{-5}$		Impermeable	Practically impermeable
10	$1 \bullet 10^{-5}$	Aquiclude	Impermeable	Practically impermeable
11	$< 10^{-5}$		Impermeable	Practically impermeable
12	$<< 10^{-5}$		Impermeable	Practically impermeable

Table 13: Classification of texture and material according to an aquifer permeability

Source: Custodio and Llamas (2001)

Material	K (cm/seg)	K (m/day)
Clean gravel	> 1	> 1000
Clean coarse sand	1 to 10^{-2}	**1000 to 10**
Sand mixture	10^{-2} to $5 \bullet 10^{-3}$	10 to 5
Fine sand	$5 \bullet 10^{-3}$ to 10^{-3}	5 to 1
Silty sand	$2 \bullet 10^{-4}$ to 10^{-4}	2 to 0.1
Silt	$5 \bullet 10^{-4}$ to 10^{-5}	0.5 to 0.001
Clay	$< 10^{-6}$	< 0.001

8. Conclusions

Field works in the demo site of Llobregat have reported valuable data about local geology and hydrogeological parameters, which will be key information to understand the response of the aquifer in the demonstration phase.

Despite the Llobregat area is widely studied and lots of scientific papers and technical works have been published, the knowledge of the local parameters at very small scale is very important. Cornellà and Sant Joan Despí municipalities, when the injection – extraction system is located, is in the frontier between two clear configurations of the Llobregat aquifer: upstream there is an unique free aquifer with thicknesses from 40 – 20 metres, while downstream the aquifer is divided in two independent aquifers: upper and main aquifer, separated horizontally by a clay aquitard.

Geological profile obtained in Pz1 revealed that P18 is located in the divided configuration, which means that the aquifer receiving injection water is confined, with a thickness of 20 meters. This information agrees with the original sections of P18 done in 1973 and 1983. Now, the description of sediments has been accurately and mineralogical samples have been analysed to determine qualitatively the presence of minerals.

The work described in this report has been done in parallel with the conceptual model of the aquifer to apply the numerical modelling of flow and conservative transport (developed with VISUAL TRANSIN and MODFLOW by CUADLL. The results obtained in the field works will be applied in the interpretation of the hydraulic response (clogging) and the hydrogeological assessment (chemical mobilisation and changes in quality occurring along groundwater passage).

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ANNEX A: Drilling works: storage boxes Pz1

Figure 27: Total set of storage boxes Pz1 (continuous drilling)
Note: each box has a total storage of 3 meters of sediments

ANNEX B: Mineralogical XRD profiles

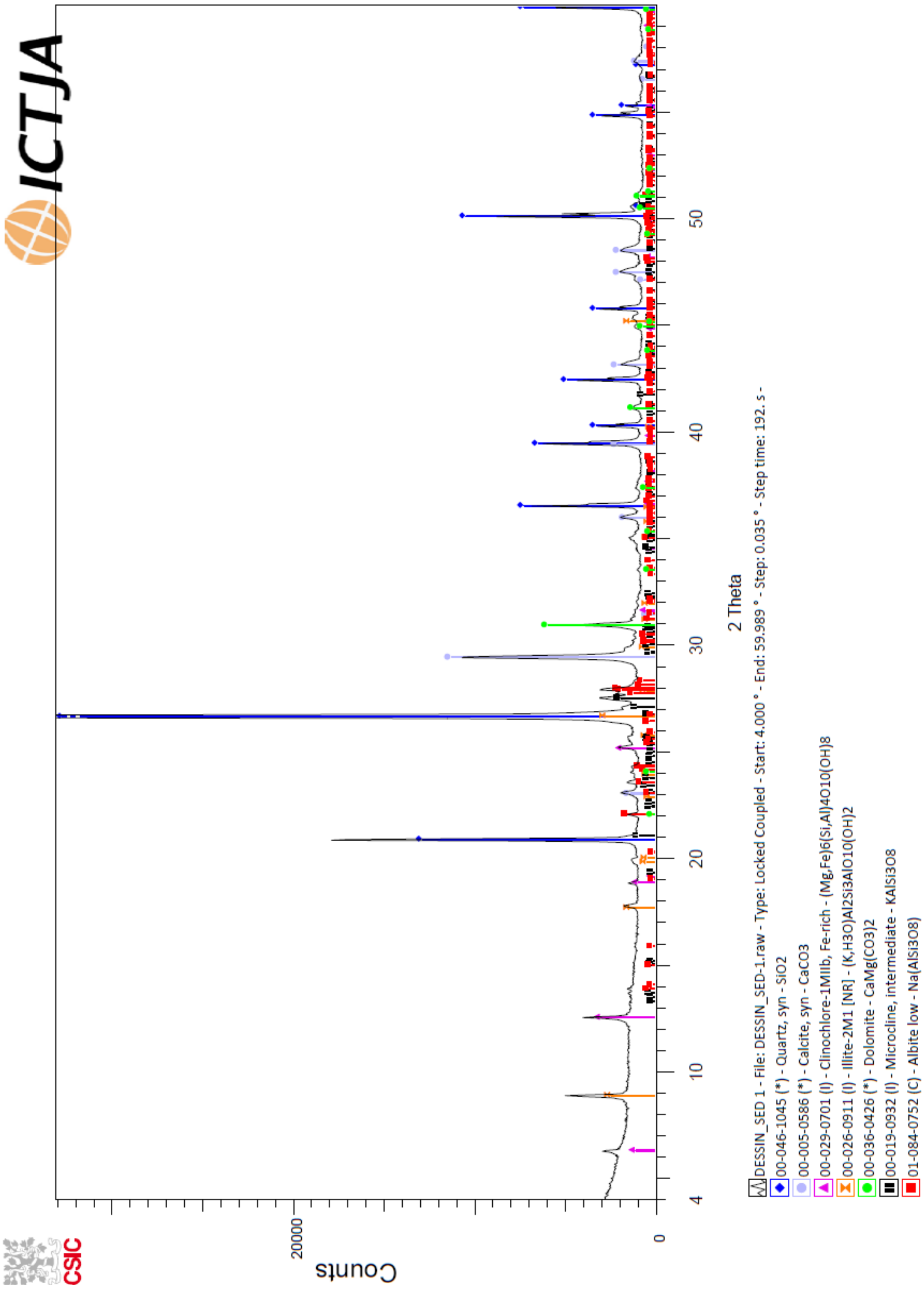


Figure 28: DESSIN_SED 1 - Mineralogical profile XR-Diffraction
Type: Locked Coupled - Start: 4.000 ° - End: 59.989 ° - Step: 0.035 ° - Step time: 192. S

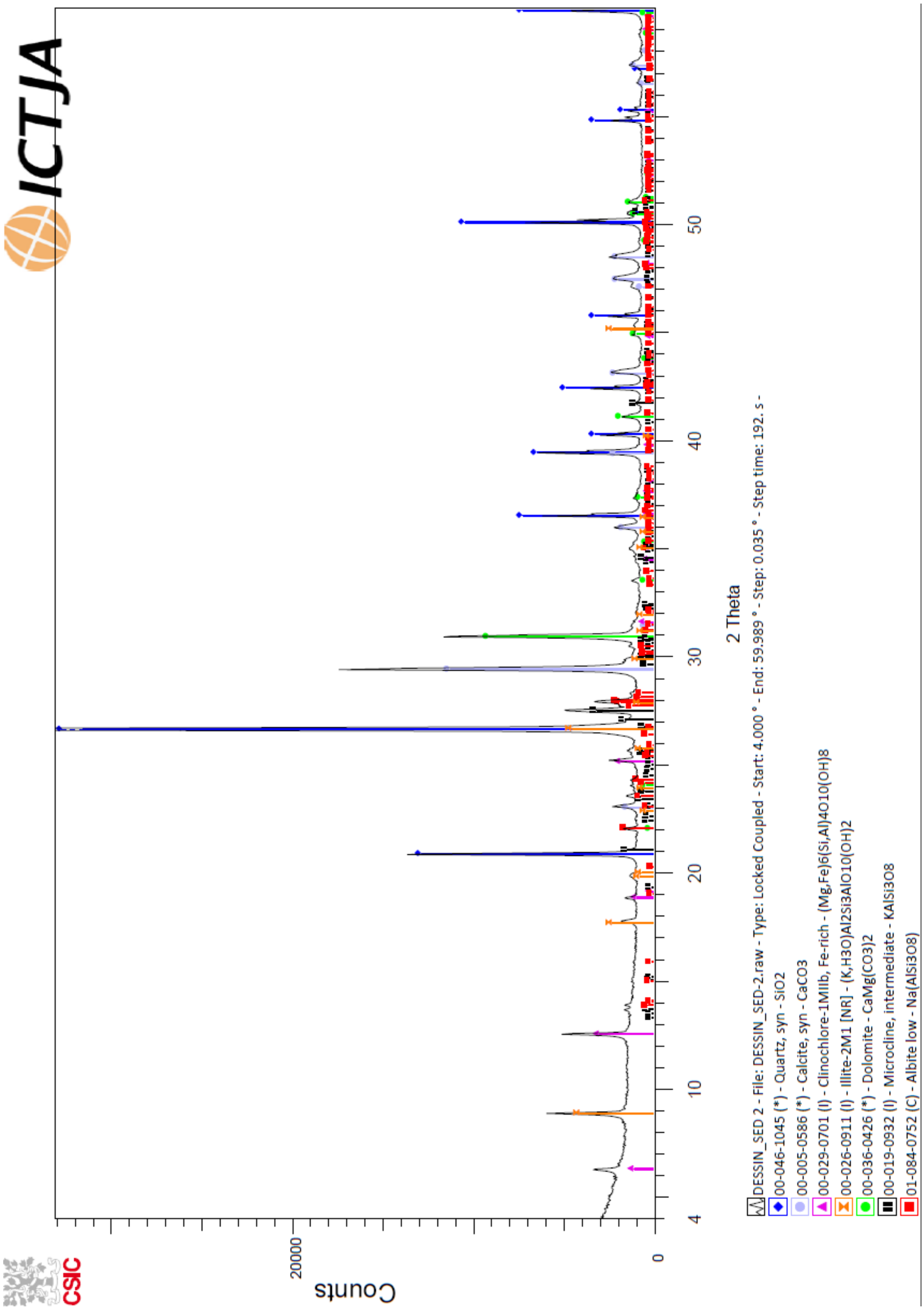


Figure 29: DESSIN_SED 2 - Mineralogical profile XR-Diffraction
Type: Locked Coupled - Start: 4.000 ° - End: 59.989 ° - Step: 0.035 ° - Step time: 192. s

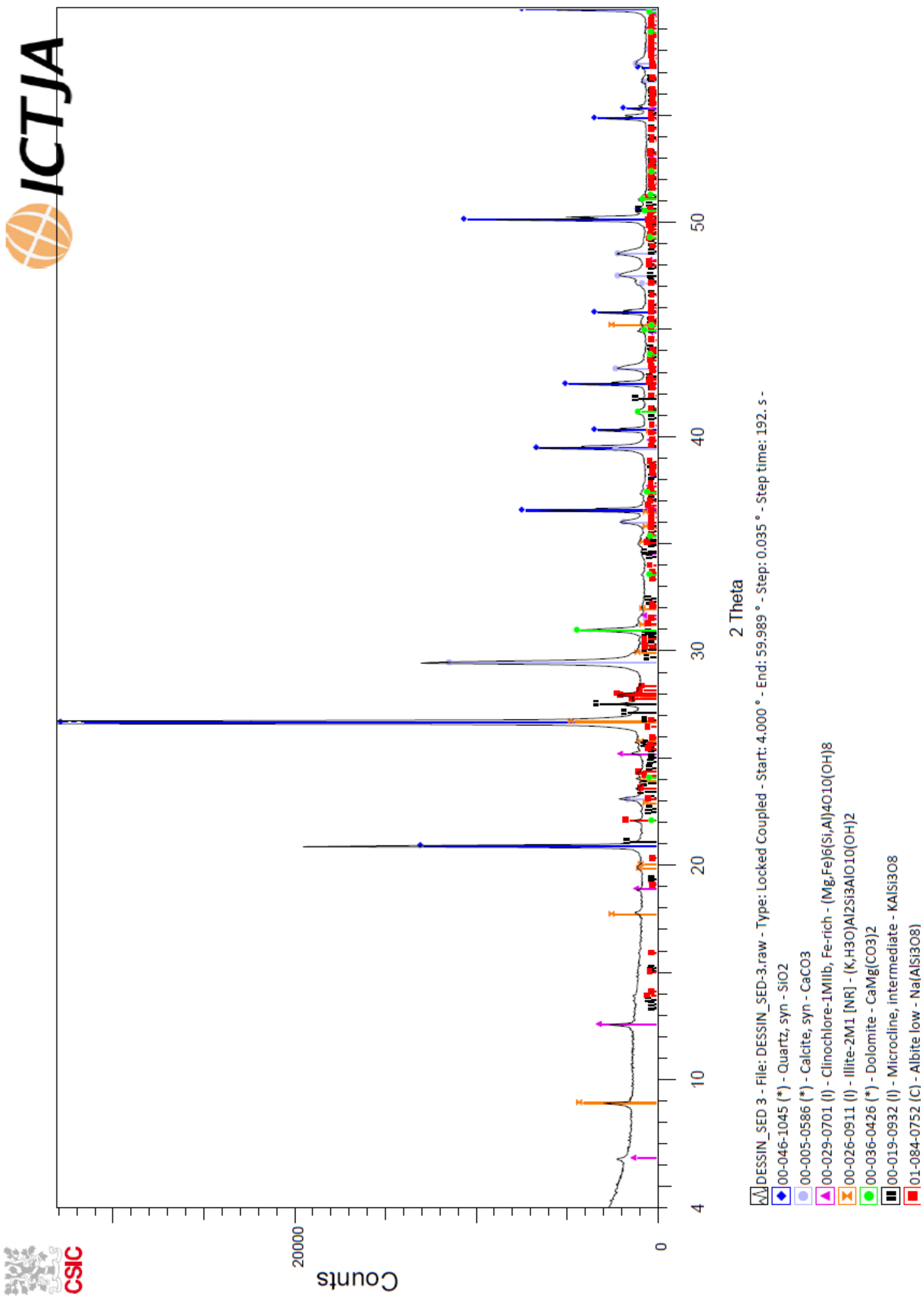


Figure 30: DESSIN_SED 3 - Mineralogical profile XR-Diffraction
Type: Locked Coupled - Start: 4.000 ° - End: 59.989 ° - Step: 0.035 ° - Step time: 192. s -

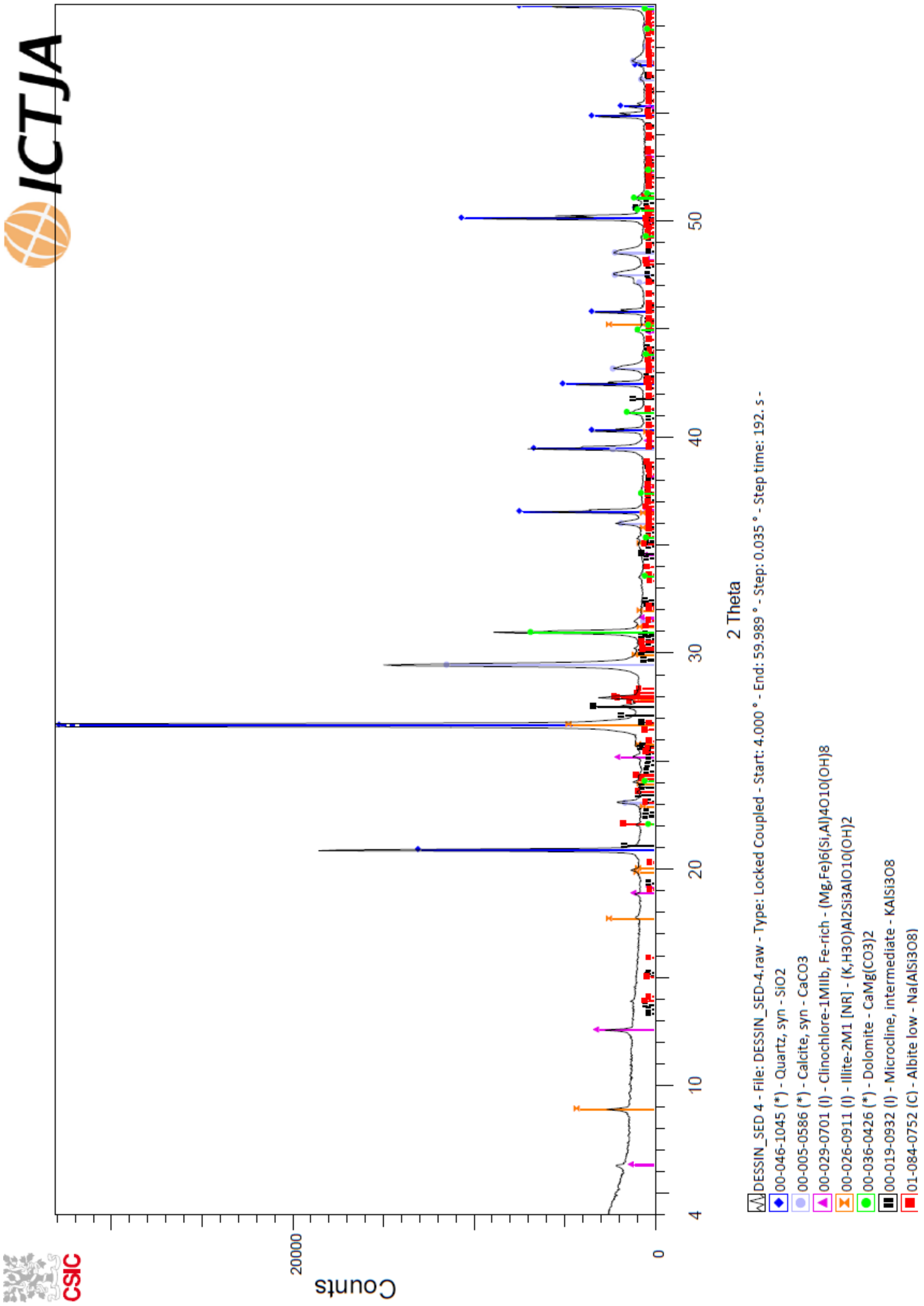


Figure 31: DESSIN_SED 4 - Mineralogical profile XR-Diffraction
Type: Locked Coupled - Start: 4.000 ° - End: 59.989 ° - Step: 0.035 ° - Step time: 192. s

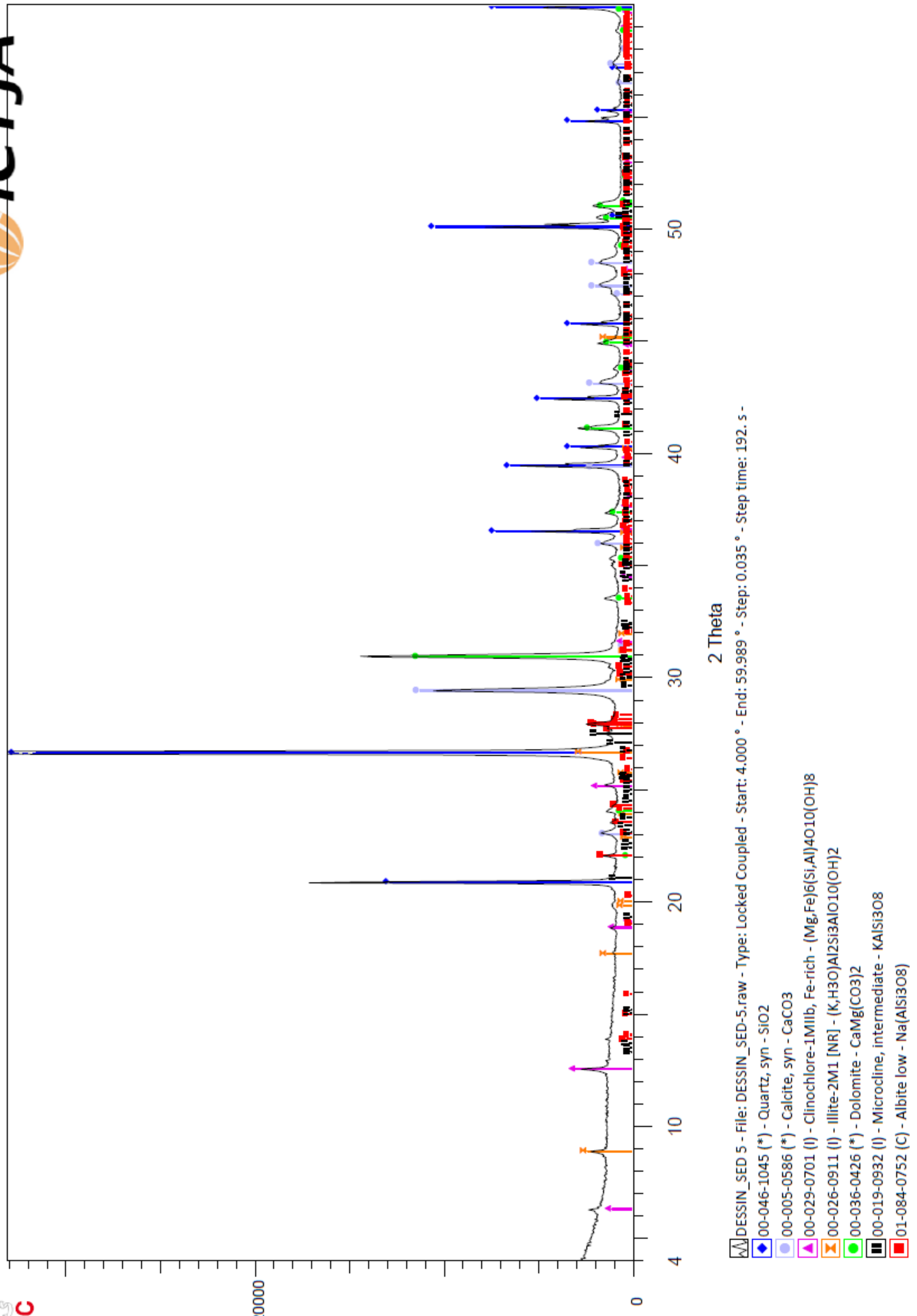


Figure 32: DESSIN_SED 5 - Mineralogical profile XR-Diffraction
Type: Locked Coupled - Start: 4.000 ° - End: 59.989 ° - Step: 0.035 ° - Step time: 192. s

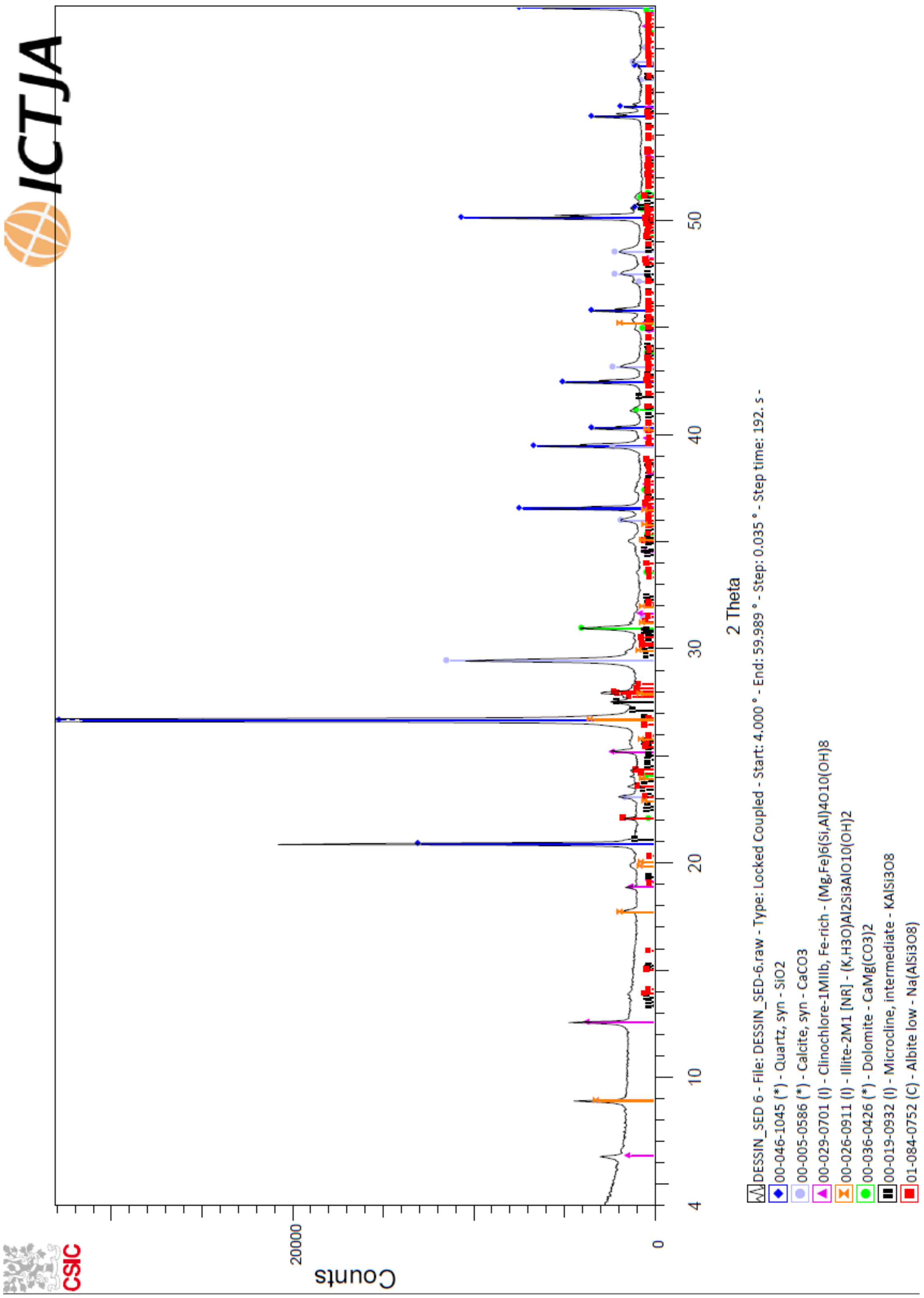
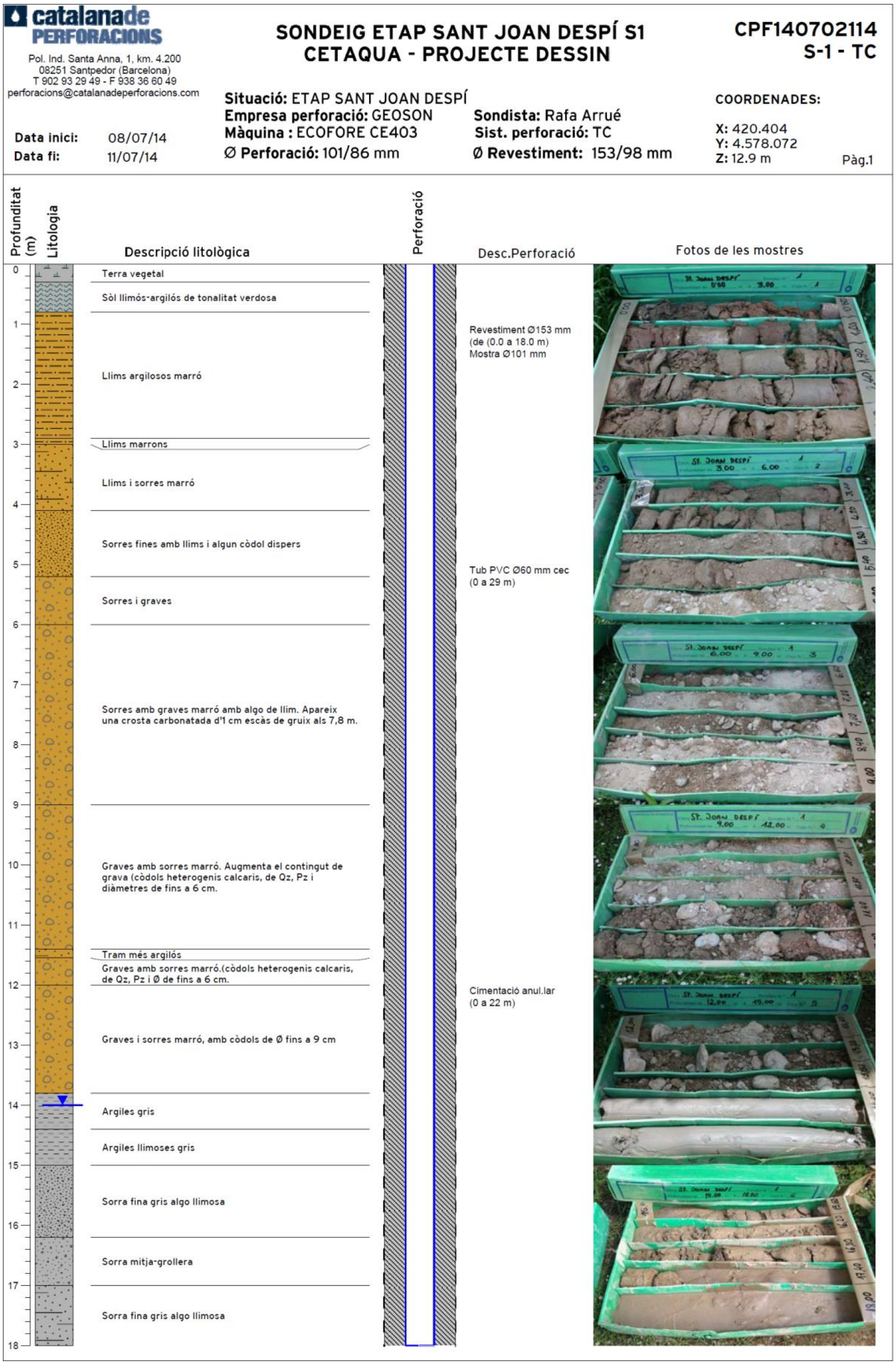


Figure 33: DESSIN_SED 6 - Mineralogical profile XR-Diffraction
Type: Locked Coupled - Start: 4.000 ° - End: 59.989 ° - Step: 0.035 ° - Step time: 192. s

ANNEX C: Pz1 Geological profile



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SONDEIG ETAP SANT JOAN DESPÍ S1
CETAQUA - PROJECTE DESSIN

CPF140702114
S-1 - TC

Data inici: 08/07/14
Data fi: 11/07/14

Situació: ETAP SANT JOAN DESPÍ
Empresa perforació: GEOSON
Màquina : ECOFORE CE403
Ø Perforació: 101/86 mm

Sondista: Rafa Arrué
Sist. perforació: TC
Ø Revestiment: 153/98 mm

COORDENADES:
X: 420.404
Y: 4.578.072
Z: 12.9 m

Pàg.1

Descripció litològica

Terra vegetal

Sòl llimós-argilós de tonalitat verdosa

Llims argilosos marró

Llims marrons

Llims i sorres marró

Sorres fines amb llims i algun còdol dispers

Sorres i graves

Sorres amb graves marró amb algo de llim. Apareix una crosta carbonatada d'1 cm escàs de gruix als 7,8 m.

Graves amb sorres marró. Augmenta el contingut de grava (còdols heterogenis calcaris, de Qz, Pz i diàmetres de fins a 6 cm.

Tram més argilós

Graves amb sorres marró.(còdols heterogenis calcaris, de Qz, Pz i Ø de fins a 6 cm.

Graves i sorres marró, amb còdols de Ø fins a 9 cm

Argiles gris

Argiles llimoses gris

Sorra fina gris algo llimosa

Sorra mitja-grollera

Sorra fina gris algo llimosa

Desc.Perforació

Revestiment Ø153 mm
(de (0.0 a 18.0 m)
Mostra Ø101 mm

Tub PVC Ø60 mm cec
(0 a 29 m)

Cimentació anul.lar
(0 a 22 m)

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SONDEIG ETAP SANT JOAN DESPÍ S1
CETAQUA - PROJECTE DESSIN

CPF140702114
S-1 - TC

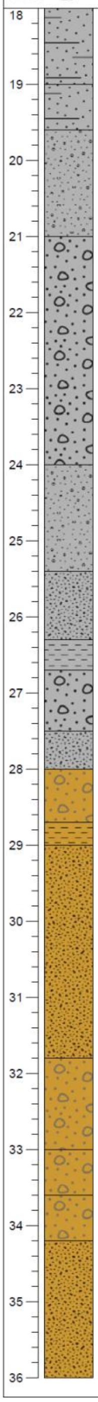
Data inici: 08/07/14
Data fi: 11/07/14

Situació: ETAP SANT JOAN DESPÍ
Empresa perforació: GEOSON
Màquina : ECOFORE CE403
Ø Perforació: 101/86 mm

Sondista: Rafa Arrué
Sist. perforació: TC
Ø Revestiment: 153/98 mm

COORDENADES:
X: 420.404
Y: 4.578.072
Z: 12.9 m

Profunditat (m) | **Litologia** | **Descripció litològica** | **Perforació** | **Desc.Perforació** | **Fotos de les mostres**



Sorra fina gris algo llimosa

Sorra fina a grollera amb algo de matriu llimosa

Sorra grollera força neta amb còdols de grava a la base.

Sorres grolleres amb gravetes força netes amb alguna passada de sorra més fina

Sorres grolleres-mitges amb alguna passada més llimosa i algun còdol

Sorra fina amb algun còdolet

Tram argilós-llimós

Graves amb matriu llimosa-argilosa

Sorra fina-mitja

Graves i sorres amb matriu més argilosa marró

Argila marró

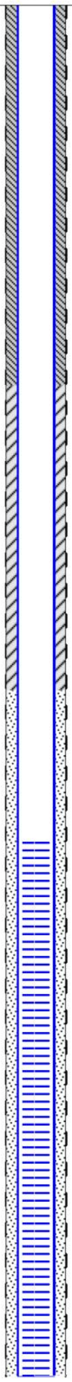
Sorres fines marró

Graves amb matriu sorrenca algo argilosa

Grava força neta (còdols de Ø2-3cm)

Graves amb sorres i algo de component argilós

Sorra fina algo argilosa amb graveta dispera. Alguna passada més argilosa



(0-50 m)
Mostra a Ø86 mm
(18.0 a 50.0m)

Tap bentonita
(22 a 27 m)

Tub PVC Ø60 mm filtre
(29 a 50 m) Ranura 1.5mm

Engravillat anul.lar Ø3-6mm
(27 a 50 m)

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SONDEIG ETAP SANT JOAN DESPÍ S1
CETAQUA - PROJECTE DESSIN

CPF140702114
S-1 - TC

Situació: ETAP SANT JOAN DESPÍ
Empresa perforació: GEOSON
Màquina : ECOFORE CE403
Ø Perforació: 101/86 mm

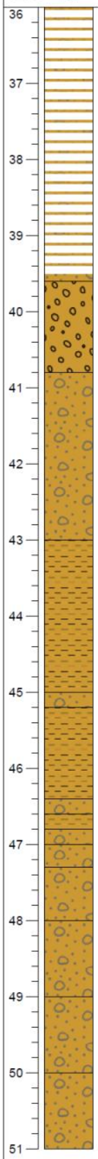
Sondista: Rafa Arrué
Sist. perforació: TC
Ø Revestiment: 153/98 mm

Data inici: 08/07/14
Data fi: 11/07/14

COORDENADES:
X: 420.404
Y: 4.578.072
Z: 12.9 m

Pàg.3

Profunditat (m) | **Litologia** | **Descripció litològica** | **Perforació** | **Desc.Perforació** | **Fotos de les mostres**



Graves amb sorres i amb component argilós

Grava neta amb còdols de Ø>4 cm

Sorres i graves amb matriu argilosa (amb algun còdol calcari de Ø fins a 5 cm)

Aglomerat argilós marró amb grava i sorra.

Sorres i graves amb matriu argilosa

Argiles amb graves

Graves més netes

Argiles amb graves

Grava amb sorres força neta

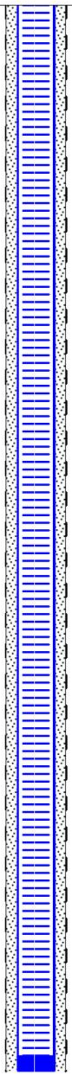
Grava i sorres amb matriu argilosa

Sorres i graves (tonalitat marronosa)

Sorres i graves amb algo d'argila

Graves i sorres amb matriu argilosa (còdol calcari de 10 cm)

Augmenta el component argilós



Tap de fons

ANNEX D: Pz2 Geological profile

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Població:	- SANT JOAN DESPÍ
Client:	- CETAQUA
Situació:	- ETAP - costat pou 18 S-2
Màquina:	- ECOFORE CE903
Sondista:	- Rafa Arrué
Sistema:	- ODE

CPF140702214

COORDENADES:

X: 420.406
Y: 4.578074
Z: 12.9 m

Data inici: 14-07-14
Data fi: 15-07-14

PERFORACIÓ:

·Unitat hidrogeològica:	- 405- Llobregat
·Aqüífer:	- Dipòsits al·luvials i delatics
·Fondària:	- 51 m
·Diàmetre perforació:	- 153/127 mm
·Diàmetre revestiment:	- 89 mm
·Tipus canonada:	- PVC-U
·Nivell estàtic:	- 14 m
·Cabal observat:	- Important
·Nivells aqüífers:	- Graves i sorres

Data inici:
Data fi:

ASSAIG DE BOMBAMENT:

·Realitzat per:	-
·Durada:	-
·Equip de bombeig:	-
·Resultats:	-
·Cabal específic:	-
·T, S:	-
·Observacions:	-

Analítica:	-
Conductivitat:	-

OBSERVACIONS:

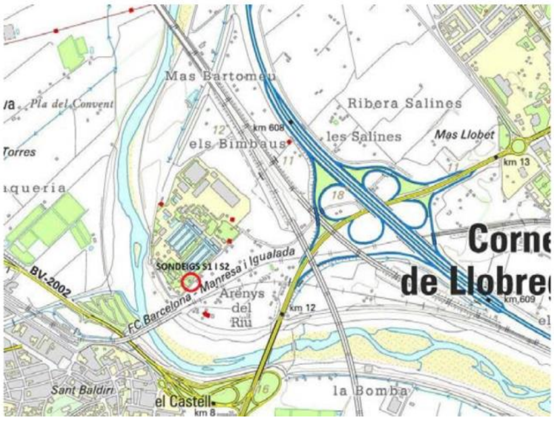
Perforació situada a uns 5 metres del pou 18 de l'ETAP, al costat del sondeig a TC.
Es mostreja fins els 39 m, però després, degut a l'elevat cabal, no s'agafen més mostres.

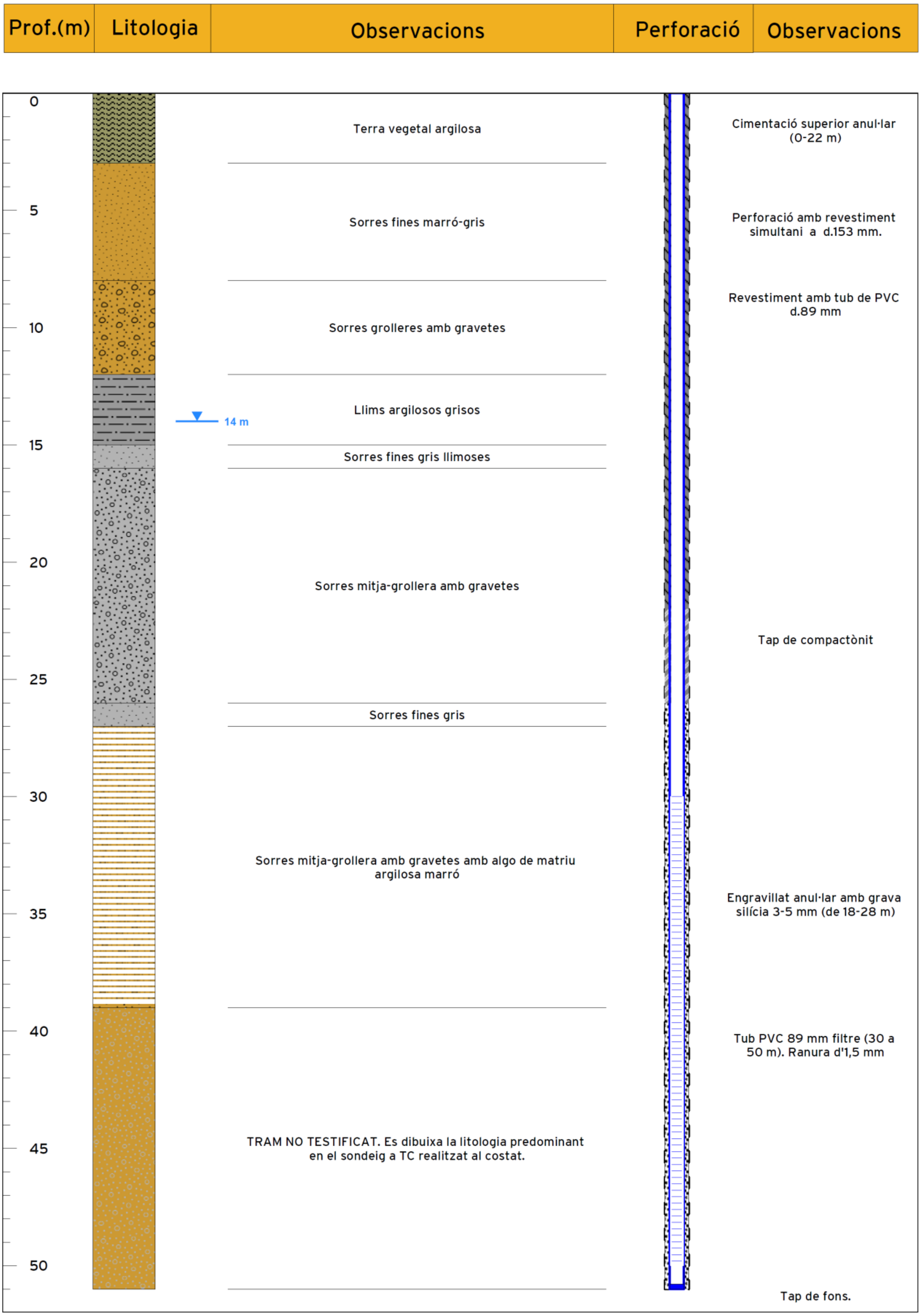
EQUIPAMENT POU:

·Model bomba:	-
·Potència:	-
·Cabal instantàni:	-
·Situat a:	-
·Tub impulsió:	-
·Empresa instal·ladora:	-

Expedient legalització:

Tramitat per Catalana: ☐




Prof.(m)
Litologia
Observacions
Perforació
Observacions
0
5
10
15
20
25
30
35
40
45
50
Terra vegetal argilosa
Sorres fines marró-gris
Sorres grolleres amb gravetes
Llims argilosos grisos
14 m
Sorres fines gris llimoses
Sorres mitja-grollera amb gravetes
Sorres fines gris
Sorres mitja-grollera amb gravetes amb algo de matriu argilosa marró
TRAM NO TESTIFICAT. Es dibuixa la litologia predominant en el sondeig a TC realitzat al costat.
Cimentació superior anul·lar (0-22 m)
Perforació amb revestiment simultani a d.153 mm.
Revestiment amb tub de PVC d.89 mm
Tap de compactònit
Engravillat anul·lar amb grava silícia 3-5 mm (de 18-28 m)
Tub PVC 89 mm filtre (30 a 50 m). Ranura d'1,5 mm
Tap de fons.

ANNEX E: Pumping tests – additional information

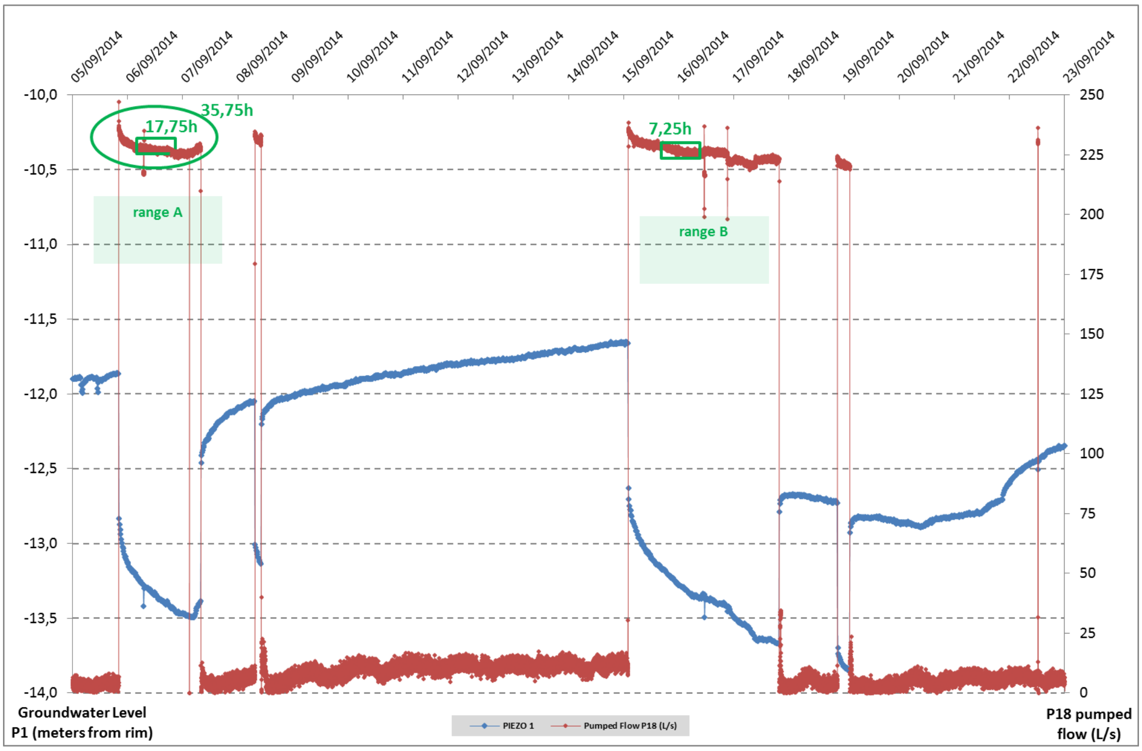


Figure 34: Identification of interval pumping test “A”, “B” and “C” using graphical data

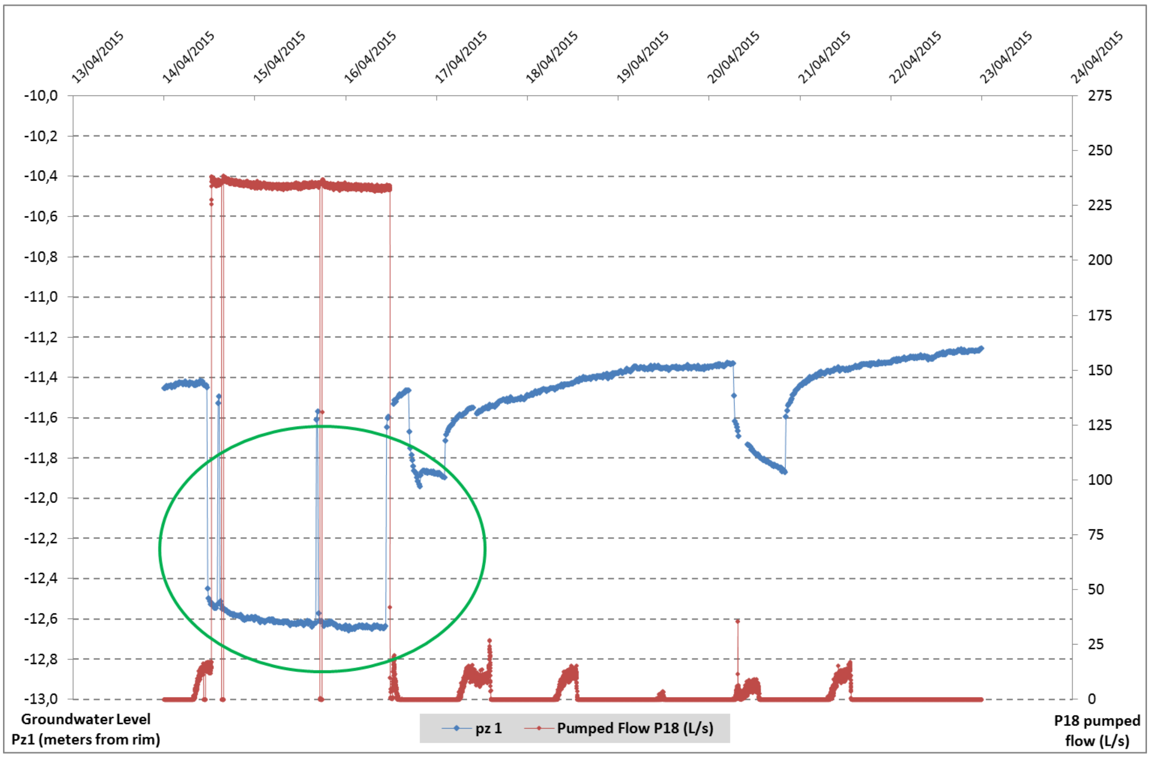


Figure 35: Identification of interval pumping test “D” using graphical data

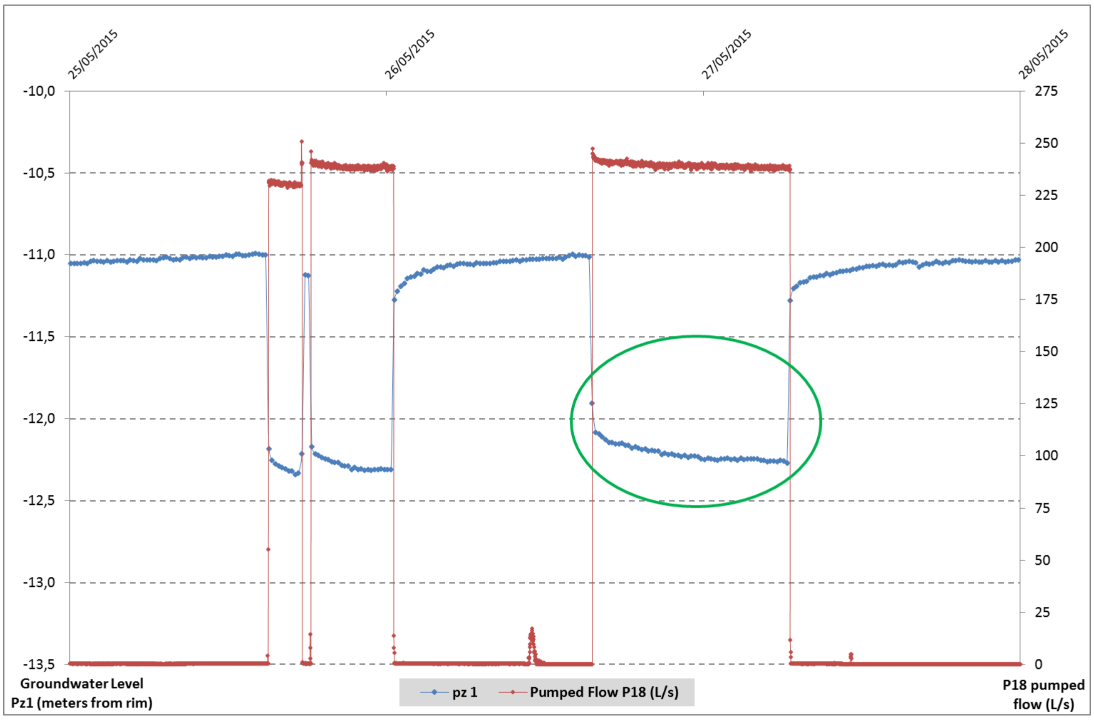


Figure 36: Identification of interval pumping test “E” using graphical data

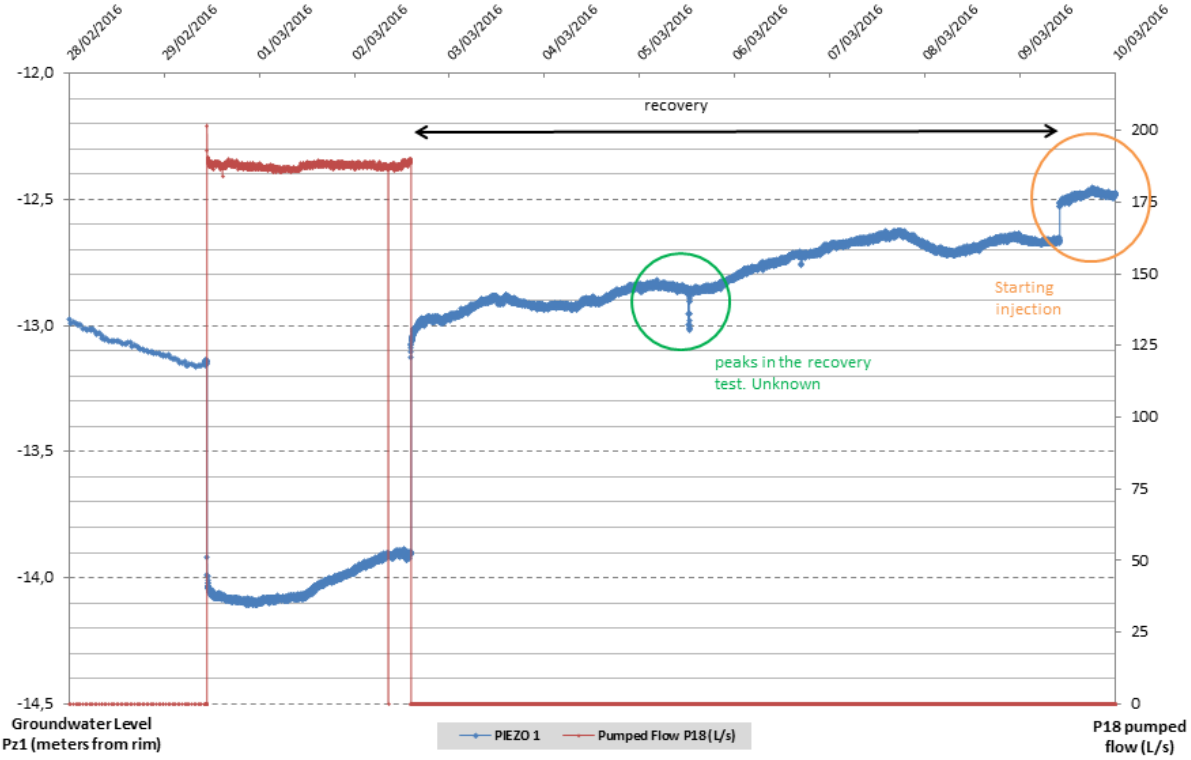


Figure 37: Identification of interval pumping test “F” using graphical data

The research leading to these results has received funding from the European Union Seventh Framework Programme (FP7/2007-2013) under grant agreement no. 619039

DESSIN

DEMONSTRATE ECOSYSTEM
SERVICES ENABLING INNOVATION
IN THE WATER SECTOR

www.dessin-project.eu

D35.1 (b) NUMERICAL MODEL OF FLOW AND CONSERVATIVE TRANSPORT

Evaluation of the impact of the injection and extraction regime in the ASR system in the aquifer of Lower Valley and Llobregat River Delta

CUADLL, December 2017

The research leading to these results has received funding from the European Union Seventh Framework Programme (FP7/2007-2013) under grant agreement no. 619039

SIMULATION OF ASR OPERATION AT DEMONSTRATION SCALE: NUMERICAL MODELLING

D35.1(b) SIMULATION OF ASR OPERATION AT DEMONSTRATION SCALE AND FULL-SCALE: NUMERICAL MODELLING
Regional and local numerical modeling to simulate the flow and conservative transport in the Llobregat demo site

SUMMARY

The application of numerical modelling to the Llobregat Aquifer Storage and Recovery (ASR) system during the first phase of the project was focused on the impact assessment of ASR in terms of groundwater volume infiltrated in the aquifer and the improvements and/or impacts in groundwater quality. The work has been divided into two parts: (i) a MODFLOW-based numerical model to simulate the impact of injected water via ASR in the local piezometric network installed during the project (4 km^2) (ii) a VISUAL TRANSIN-based numerical model to simulate the impact of ASTR at regional scale (129 km^2).

The results of the simulations carried out for demonstration ASR project and application of ASTR at full scale are reported. Based on the former one, it is concluded that the demonstration phase of the project will have a limited impact in the aquifer, as the mixing ratio between injected water and native groundwater will be below 10% after 1.4 km of aquifer passage. Regarding regional model simulation, the obtained results correspond to a first approximation of the potential use of ASRT scenarios in Lower Llobregat alluvial aquifer. Based on the model, the aquifer has the sufficient storage capacity to regulate an infiltrated volume of 120 hm^3/year.

DELIVERABLE NUMBER	WORK PACKAGE
D35.1 (b)	WP35
LEAD BENEFICIARY	**DELIVERABLE AUTHOR(S)**
Cetaqua	Enric Queralt (CUADLL - Subcontractor) Jordi Massana (CUADLL- Subcontractor)
QUALITY ASSURANCE	
AB (Aigües de Barcelona) KWR (Watercycle Research Institute)	Jordi Martín Koen Zuurbier
PLANNED DELIVERY DATE	**ACTUAL DELIVERY DATE**
31/12/2017 (M48)	19/01/2018
DISSEMINATION LEVEL	PU = Public

The research leading to these results has received funding from the European Union Seventh Framework Programme (FP7/2007-2013) under grant agreement no. 619039

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The research leading to these results has received funding from the European Union Seventh Framework Programme (FP7/2007-2013) under grant agreement no. 619039

List of Acronyms and Abbreviations

AB	Aigües de Barcelona Drinking Water Supply company
ASR	Aquifer Storage and Recovery
ASTR	Aquifer Storage Transfer and Recovery
CUADLL	Association of groundwater users in the Llobregat aquifer
DWTP	Drinking Water Treatment Plant
ICC	Catalan Cartographic Institute (http://www.icc.cat/)
Pz-1	Piezometer number 1 drilled in SJD
Pz-2	Piezometer number 2 drilled in SJD
Pz-3	Piezometer number 3 already existing in SJD
RFD	Real Full Demonstration (simulation of demonstration phase of the project, injecting 50 L/s in P18, corresponding to 1.57 Mm^3/year)
SJD	Sant Joan Despí facility of Drinking Water Treatment Plant (Barcelona)

The research leading to these results has received funding from the European Union Seventh Framework Programme (FP7/2007-2013) under grant agreement no. 619039
This publication reflects only the author's views and the European Union is not liable for any use that may be made of the information contained therein.

Executive summary

This report summarises results of the application of numerical modelling to the Llobregat ASR system. The work corresponds to the first phase of the project, focused on the impact assessment of ASR in terms of groundwater volume infiltrated in the aquifer and the improvements and/or impacts in groundwater quality. To this end, numerical modelling offers an incomparable opportunity of estimating the arrival plume of the demonstration phase, and what is more, to evaluate future scenarios considering the application of ASR technology to the full system.

The work has been carried out by CUADLL (Association of Users of Llobregat Aquifer). This public entity has developed a MODFLOW model of the Lower Llobregat alluvial aquifer, focused on the area subject of pre-potable water injection. The model simulates the changes occurring at local scale, using a mesh of 2 km x 2 km to assess the impact of injection in P18 in the local network of piezometers (Pz-1, Pz-2 and Pz-3). Geological information gathered in drilling works and pumping tests allowed to create the conceptual model. The main results are the estimation of the rise of groundwater level during the injection phase and the estimation of the arrival time of the injected water to Pz-1, Pz-2 and Pz-3.

The obtained results from MODFLOW model permit to conclude that the demonstration phase of the project will have a local impact in the aquifer, as the mixing ratio between injected water and native groundwater will be below 10% after 1.4 km of aquifer passage.

VISUAL TRANSIN regional model has been applied to simulate the injection and recovery of pre-potable water in different wells. This is the so called ASTR (Aquifer Storage Transfer and Recovery)

Local and regional model has provided key information for the establishment of local control network (Pz-1, Pz-2 and Pz-3) and the selection of external control points in the aquifer (P10, P13) to verify the impact in groundwater quality during the demonstration phase.

1. Introduction

This report aims the presentation of the numerical models to simulate and study the local impact of artificial recharge in the Lower Llobregat alluvial aquifer. The framework of this work corresponds to DESSIN project "Demonstrate Ecosystem Services Enabling Innovation in the Water Sector". DESSIN demo site in Barcelona will study and test the flexibilisation of ASR system of Sant Joan Despi Drinking Water Treatment Plant (SJD, DWTP). For this purpose, the last phase of the project has consist in a demo phase using an existing injection well located in the DWTP, operated by Aigües de Barcelona (AB). The well named P18 has been selected to carry out the demonstration phase of the project, with an injection flow of 50 L/s during at least one year of continuous operation. More information about the hydrogeology and the history of this ASR system can be found in DESSIN deliverables: D22.4 (a) and D35.1 (a).

Numerical modelling is a useful tool in hydrogeology to simulate groundwater flow in the aquifer and predict impact of extraction and injection regimes. The main constraint of using numerical models is the uncertainty of the aquifer configuration and hydrogeological parameters governing water transport. The knowledge of the aquifer is limited to the observation points (geological profiles obtained normally during the recuperation of geological sediments in well excavations), historical pumping tests performed in wells and boreholes, or geophysical techniques applied in the surface. In the specific case of the demonstration site in Barcelona, the Lower Llobregat alluvial aquifer has been constantly studied, due the large tradition of hydrogeologists in the area. Nonetheless, the small scale of the injection in P18 represents a challenge. Throughout the project, hydrogeologists will deal with local scale for the interpretation of changes occurring in the observation network, and regional scale to simulate the impact of ASR system operating at full-scale (this is out of the scope of the demonstration phase, but should be assessed theoretically as well).

To fulfil all the needs of the project, two different numerical models have been developed:

- **Local model:** has been developed using MODFLOW. The objective is the simulation of groundwater level variations caused by the injection in P18 of 50 L/s. This injection flow corresponds to the demonstration phase that was carried out along the project, so it is expected to have two phases in the model development: (i) simulation and (ii) calibration with real data.

- **Regional model:** has been developed by using VISUAL TRANSIN. The existing numerical model of "Vall Baixa" (Lower Valley) and Llobregat Delta has been adapted to simulate the impact of ASR operation not only at project scale, but also at full scale.

Local model was built in the phase of simulation and explained in deliverable 22.4(b). In this deliverable is exposed the second phase, the introduction of real data for model calibration to achieve a good agreement between measured and calculated data. The global goal is to obtain a good model to satisfactorily describe hydrogeological processes at local scale.

2. Objectives

The objective of the groundwater model (MODFLOW) applied to the Llobregat demo site is to understand the response of the aquifer at local scale by using a very detailed numerical model located nearby injection well P18. Specifically, the response of the aquifer will be assessed replying the following questions:

- The increase of local piezometric level due to injection
- The influence on water quality due to the injection
- The residence time of injected water at the observation piezometers
- The validation of mixture percentage in the sampled piezometers, calculated in deliverable D35.1.C

With respect to the regional groundwater model (VISUAL TRANSIN), the objective has been to evaluate the feasibility of managed aquifer recharge by infiltrating 120 hm^3 via ASTR, similar to the production capacity of the SJD DWTP. Such a suitability has been assessed in terms of expected piezometric increases and travel time of injected water.

3. Local model simulation

3.1. Main characteristics

The local model was built in December 2014 and the main characteristics were explained in deliverable D22.4.C, written in February 2015. The local model consists in a mesh of 2 x 2 kilometres. The plane inclination angle is 325° with respect to the North and the model has the same amplitude than the alluvial. The implementation of the studied area has been done by the interpolation and rotation of terrain digital model (originally from Geological Institute of Catalonia with a cells of 5 x 5 m).The predominant cell size usually is 25 x 25 m and around the injection point corresponds to 2 x 2 m. The initial model had included three horizontal layers (upper aquifer, aquitard and deep aquifer). Due to all studied processes occur in the third layer, the first and the second ones have been deactivated.

3.2. Hydraulic Parameters

The hydraulic parameters implemented come from the regional model (UPC, 2004; Perez-Paricio, 1999), although it has been gathered more accurate information from pumping tests carried out at Llobregat demo site in July 2014. The spatial distribution of hydraulic conductivity values is shown in Figure 1.

Table 1: Hydraulic parameters implemented on the numerical model

Parameter	Deep Aquifer
Hydraulic conductivity (m/d)	747 3254 51 170
Porosity (%)	0.1
Storage Coefficient	0.0001

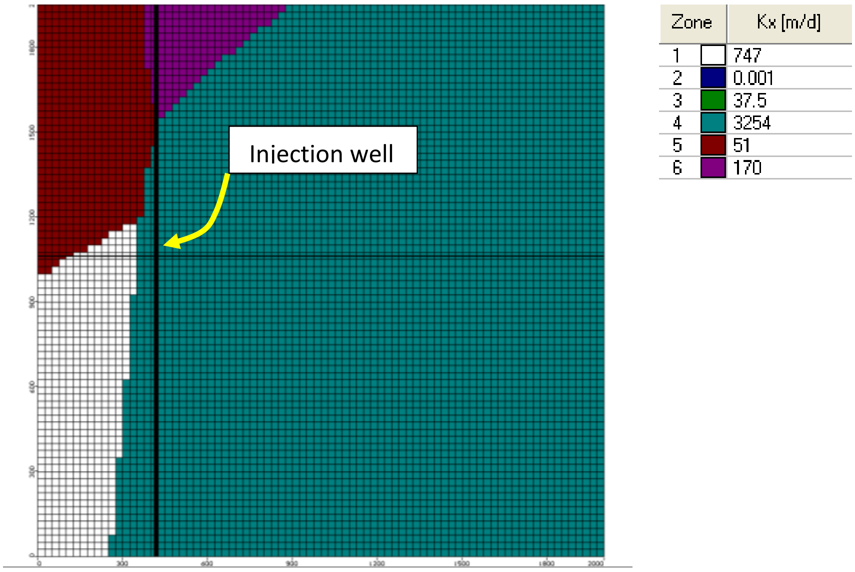


Figure 1: Distribution of hydraulic conductivity

3.3. Temporal treatment

The time domain is referred to demonstrative phase, from July 2015 to August 2016, when the water injection ends. Most of data are obtained from data-loggers with a frequency less than an hour, which correspond to a big data storage in a period of more than 400 days. In this sense, all measures were transformed into daily data in order to compare the observed values and the simulated ones.

3.4. Boundary conditions

3.4.1. Prescribed Head

Given the boundary definition, the flow direction is vertical. Therefore, conditions must only be defined in upper and bottom boundaries. Two pressure sensors are installed in piezometers SC-35 and AVE-1, which are located near the boundaries, with daily available data. Due to piezometers are close to each other, but not exactly at the same place that the boundaries, data have been analysed and correctly modified to build the conditions.

3.4.2. Prescribed flow (pumping and injection)

Pumping data was provided by AB. The pumping wells were grouped according to their proximity to grid's nodes (due to the size of the elements, several wells belong to the same node), and then implemented in the model. A pumping function is associated with every well group. The time function of the injection is provided by AB too.

3.4.3. Concentrations

Regarding water quality, data from injected water and groundwater are needed, but there are not enough concentration data, as far as frequency is concerned, to be implemented in the model. The first step was to transform electrical conductivity (from sensors) into concentration data (mg/L of chloride). Based on collected data throughout years in the Llobregat basin, this conversion was done. This information is implemented into the model by using a Point Source Boundary, which specifies the concentration of each species entering or leaving the model through a flow boundary condition grid cell.

Data characterising injected water are obtained from the electrical conductivity of the Llobregat River, provided by AB. Injected water comes from river and passes through conventional treatment in four hours, approximately. During this process it is assumed that electrical conductivity does not change.

The information about upper boundary, related to prescribed head zone, were obtained from a sensor located 3 km upstream this boundary, in a piezometer called BSV10. It was calculated from hydraulic conductivity and the piezometric gradient of the aquifer in this area, in which water takes three months to move from the sensor location to the upper model boundary.

3.4.4. Initial Conditions

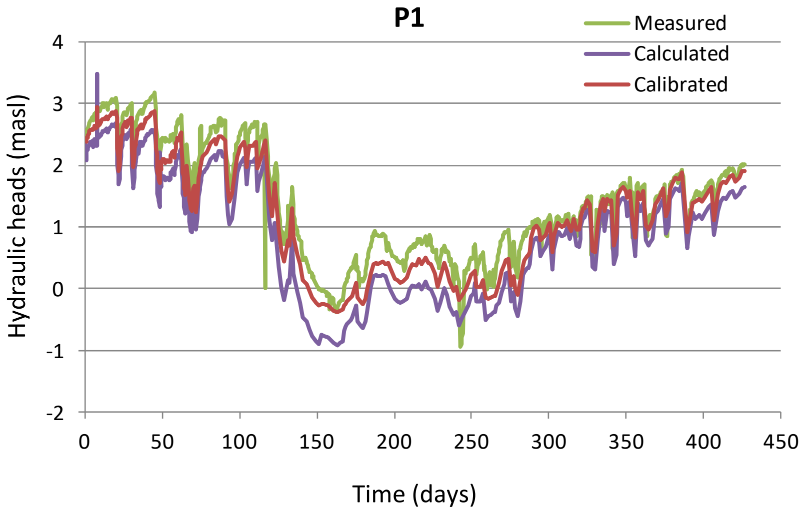
Regarding initial level conditions, a scale from the first level on upper boundary to the bottom boundary is done. For the initial concentration condition, the same value is applied to the boundary condition at the beginning of the period.

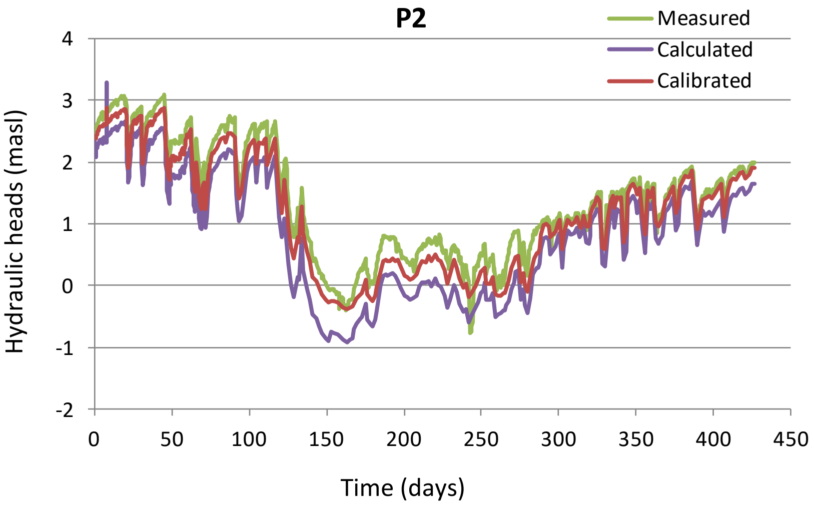
3.5. Running and calibration

3.5.1. Level agreement

In Figure 2 a comparative analysis between the observed and simulated piezometric levels is done. This analysis shows the obtained results with respect to groundwater flow. It is observed that calculated hydraulic heads are lower than the observed ones, because local model is calibrated to better find agreement between hydraulic heads. The changes in order to do so are only referred to hydraulic conductivity, and these, as it can be seen in Table 2, are limited.

The results of calibrated model provide better goodness-of-fit in terms of piezometric levels in comparison with concentration, as it can be observed in Figure 3. The reasons explaining that situation are presented in section 3.5.2.





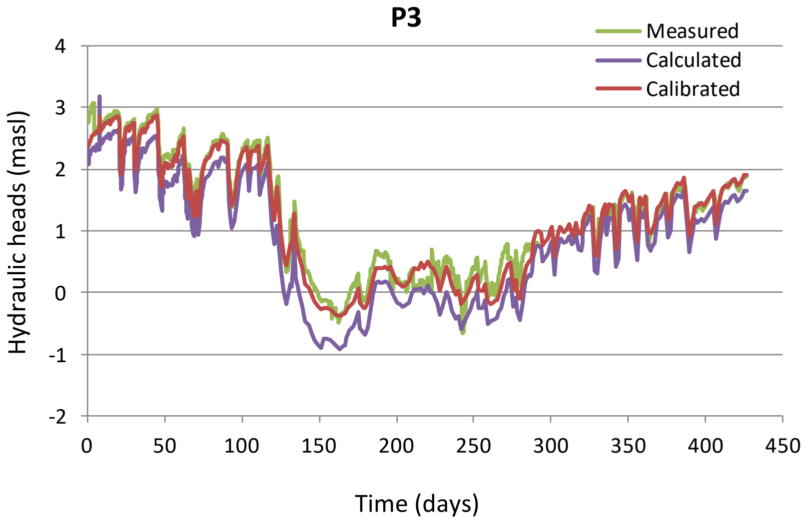


Figure 2: A comparison between simulated and observed piezometric levels in control points P1, P2, and P3

Table 2: Differences between hydraulic conductivity before and after calibration period

Parameter	Initial	Calibrated
Hydraulic conductivity (m/d)	747 3254 51 170	750 5500 1500 1700

3.5.2. Conservative transport modelling

Figure 3 shows the simulated chloride concentrations (mg/L) in comparison with the observed ones. It is known that water increases its concentration from the site where data was taken to the upper boundary. The best fit between observed and the simulated values is achieved from the day 250. After that, there is a period characterised by a good calibration concerning minimum values at piezometer 1, with a worse goodness-of-fit at piezometers 2 and 3, and a bad calibration concerning maximum values.

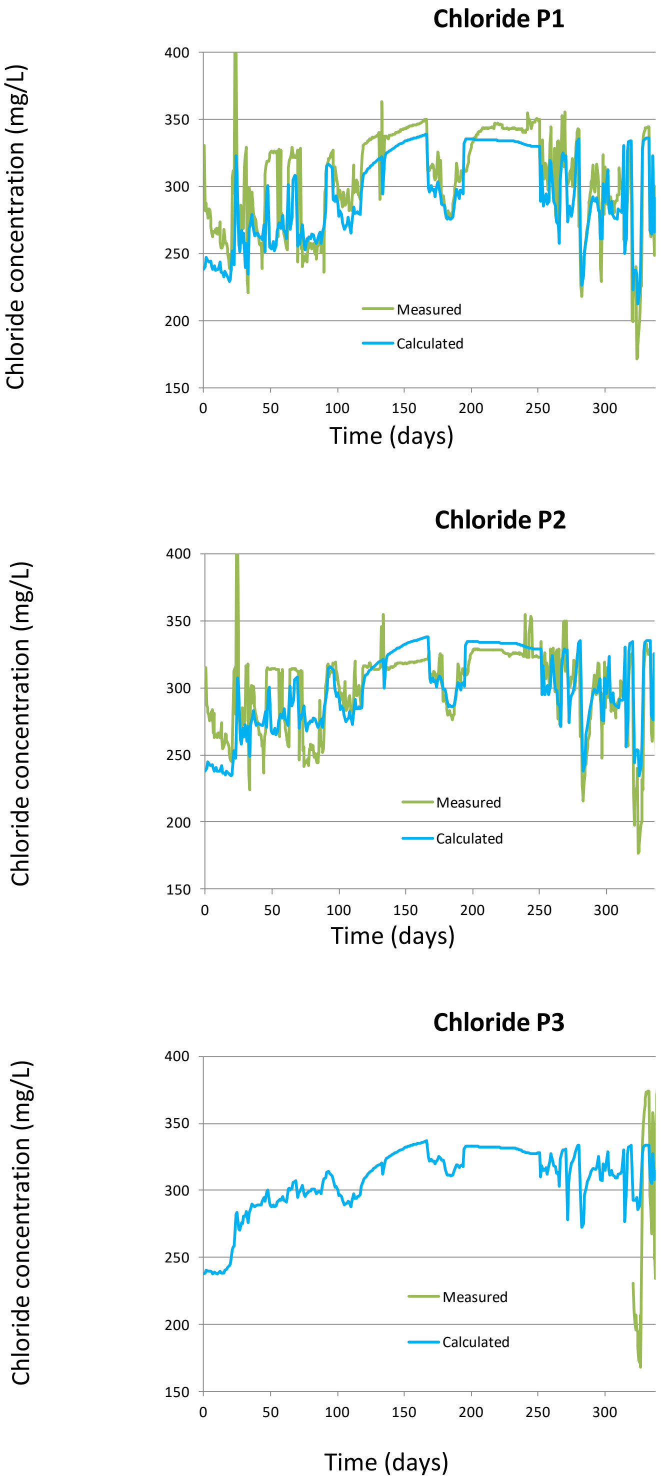


Figure 3: A comparison between simulated and observed chloride concentration in control points

3.6. Objectives' observance

3.6.1. Increase of piezometric levels

To assess the increase of piezometric levels due to water injection, several observation points are implemented in the model. Figure 4 shows their location with respect to injection point (P18). The nomenclature of points means: D 100, 100 meters Downstream from injection point; VU 300, 300 meters Upstream from injection point; HR 100, 100 meters Right from injection point; HL 300, 300 meters Left from injection point.

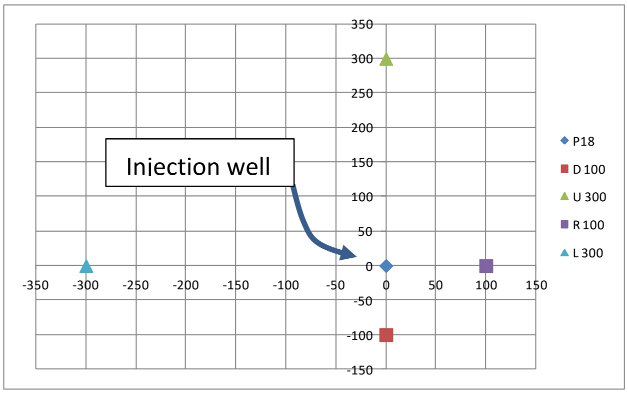


Figure 4: Location map of the different observation points implemented in the model

The simulated piezometric levels are represented in Figure 5, in which the evolution of piezometer SC-35 are represented as well. As it can observed the evolution of simulated hydraulic heads is mostly influenced by the evolution of aquifer representative level (piezometer SC-35), highly conditioned by pumping regime. That is probably because the mean injection flow rate (with an average around 36 L/s) is irrelevant with respect to extraction rate (average value of 550 L/s).

It is important to note that in the regional model simulation termed as "real full demonstration" (RFD, with an injection rate of 50 L/s), the piezometric level increase was 0.5 m close to the injection well (P18). In fact, in the deliverable D22.4.C, water levels differences were not shown due to their insignificant values.

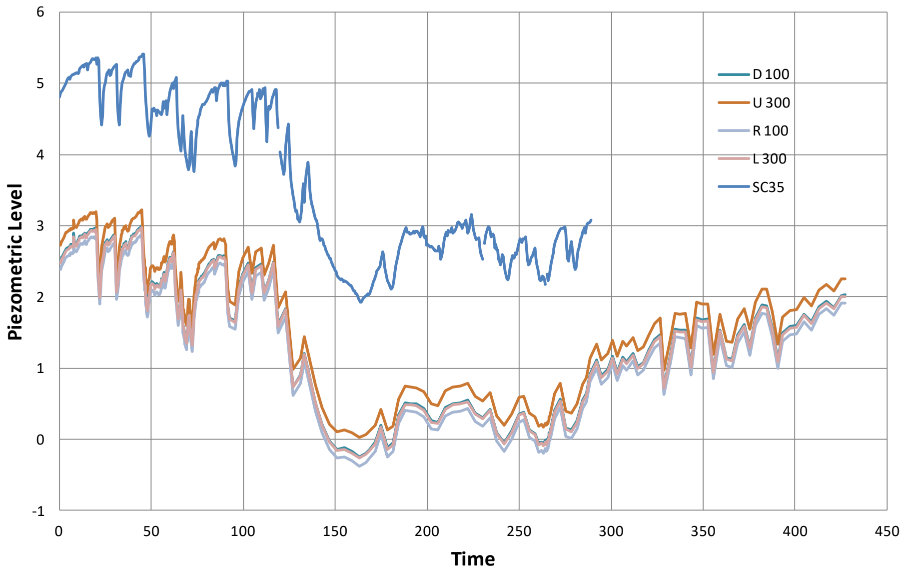


Figure 5: Assessment of piezometric level increases at observation points near injection well

3.6.2. Influence of injected water in groundwater quality

In deliverable D.22.4.C, the influence of injecting water into the aquifer was assessed by means of regional simulation. As it was done in section 3.6.1, a control network was defined in MODFLOW model. In this case, the number of control points was higher than that used for piezometric assessment. The nomenclature of these points is referred to the same rule explained in section 3.6.2.

In Figure 6 is represented the observation points located downstream the injection point. It is also shown the chloride concentration through the injection well (named as INJ CL), via upper boundary (Conc001), and the injection flow rate (INJ_18). It can be observed that chloride concentration of control piezometers decreases more effectively as they are closer to the injection point (P18). On the other hand, the chloride concentration increases reaching the upper boundary concentration (Conc001) as water injection stops.

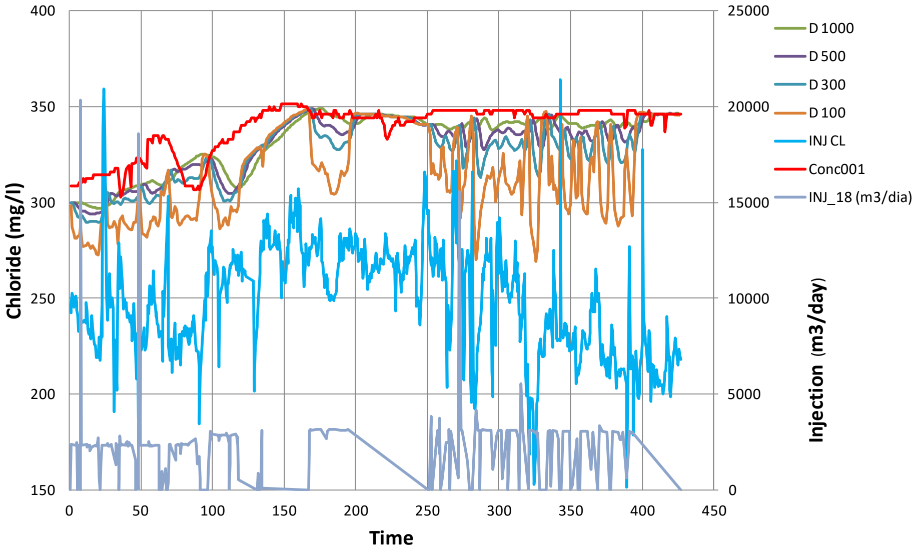


Figure 6: Assessment of chloride concentration at observation points downstream injection well

In Figure 7 the control piezometers are those located upstream the injection well. They show an evolution very similar to upper boundary control point, although with a certain delay. Therefore, it can be concluded that there is no influence of injected water over the upstream control points.

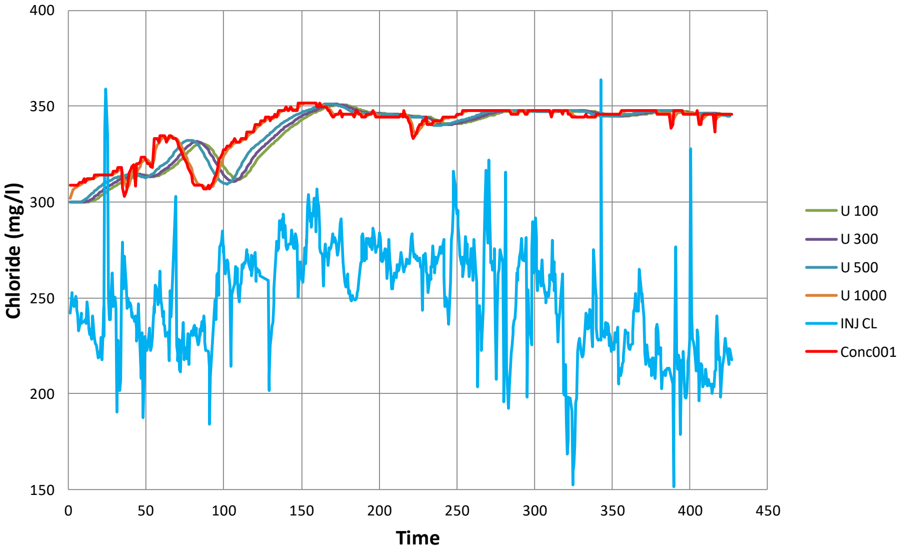


Figure 7: Assessment of chloride concentration at observation points upstream injection well

The same effect can be seen in the horizontal (Left and Right) control points (see Figure 8).

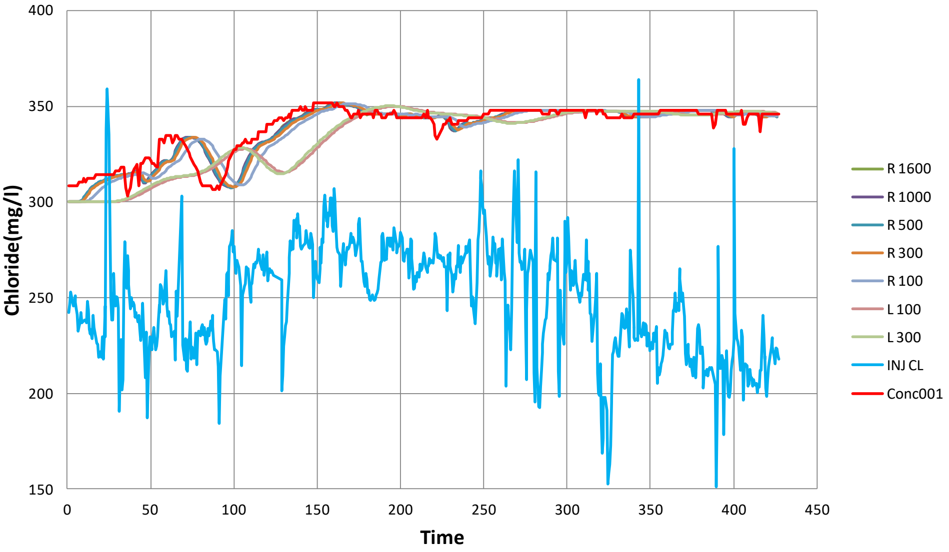


Figure 8: Assessment of chloride concentration at longitudinal observation points with respect to injection well

3.6.3. Residence time

As it has been observed in section 3.6.2, the water mineralization in the control points near the injection well decrease due to the influence of injection, and when injection stops the concentration tend to reach the native groundwater concentration. The residence time, which is referred to the time that injected water remains in piezometers, is exactly the time that, the concentration of a conservative tracer (in this case, chloride) take to reach the aquifer background value. Therefore, some periods after different injection stops have been considered to calculate it.

As it was shown in Figure 6, changes in water quality follow the same pattern in all downstream control piezometers. The closest control point to the injection well has been chosen due to its higher influence from injected water. Figure 9 shows one of the analysed periods. A zoom is done to better observe the effect of the injection stop. The residence time observed in this period was equal to 3 days. Others periods have been studied, in which similar residence times were obtained.

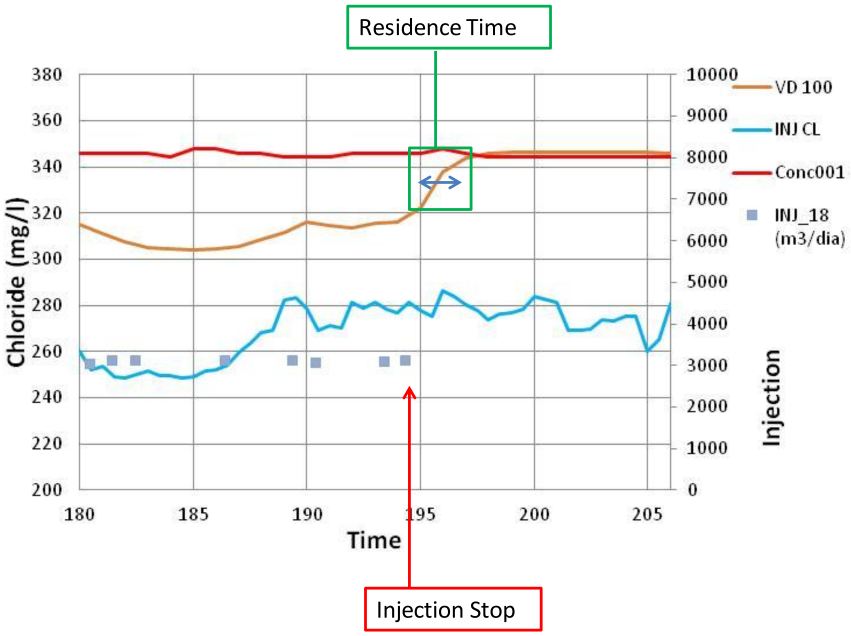


Figure 9: Residence time estimation based on closest downstream observation points (VD 100) to the injection well (P18)

4. Regional model simulation

4.1 Main characteristics

Four scenarios were planned to be simulated into the existing regional groundwater model (please see deliverable D22.4.C) named as VISUAL TRANSIN (Galarza *et al.,* 1995). The first one consisted in recharging 50 L/s at P18 injection well. The second one simulated the ASR system in current operational scheme (wells capable of injecting water in Sant Joan Despi and Cornella area), with injected water volumes of 5, 10 and 15 hm^3/year. For further details, the main results of these two scenarios can be found in the above-mentioned deliverable. The third scenario would consist in injecting water in Sant Joan Despi study area and recover it in the Cornella wellfield zone (Figure 10). The last one is referred to the water injection at 3 kilometres north from the study area, specifically at the proposed "*Injection Wells System*". These last two scenarios, representing an *Aquifer Storage, Transfer and Recovery* approach (ASTR), would imply the construction of new water infrastructure. From these two scenarios, the case 4 has been finally modelled, given its highest flexibility in terms of simulating different sub-scenarios.

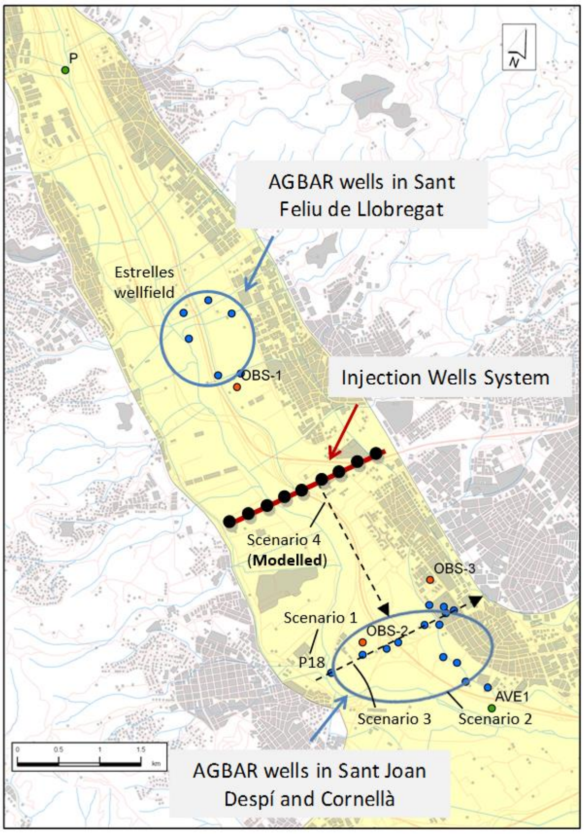


Figure 10: Location of ASR and ASTR systems along with the extraction and monitoring points

A reference scenario has been used in order to better compare the results obtained from the former ones. This scenario assumes an annual average extraction of about 50 hm^3, disaggregated into three zones: Sant Joan Despi and Cornella area (20 hm^3), Lower Llobregat Valley (10 hm^3) upstream from the study area, and other extraction zones out of the scope of the project (20 hm^3).

The simulation of the scenario 4 required the theoretical location of a new injection wells system. This system would be between the water facilities of Aigües de Barcelona in Sant Joan Despi and Cornella, and the facilities of Sant Feliu de Llobregat (Figure 10). This injection system is made of 9 wells, each one associated with one mesh node. The distance between them is 150 – 200 meters. Moreover, the simulated injection was equally distributed among the wells. The initial recharged and extracted water was 120 hm^3/year, the latter one concentrated in Sant Joan Despi and Cornella area (Table 3). It was simulated an additional sub-scenario in which water extraction was divided into Sant Joan Despi and Cornella area (≈70 hm^3) and Sant Feliu de Llobregat (≈50 hm^3).

4.2 Results of the simulations

A simplified water balance is shown in Table 3. All natural recharge components was jointly treated, such as rainfall percolation, runoff infiltration, and so on, and water extraction was divided into some areas. It is important to note that natural recharge decreases as the artificial recharge increases, because there are some terms from water balance that depends on the total infiltrated volume. As a response of the augmentation of groundwater resources through ASTR sub-scenarios (P 120 and P 70/50), they present higher piezometric levels in relation to the reference case (see Figure 11). Two piezometers have been chosen to visualise their evolution, one of them at the upper part of Lower Llobregat Valley (piezometer P), and the other one downstream Sant Joan Despi and Cornella area (piezometer AVE-1 in Figure 10). It can be seen a significant increase of water levels (≈20 m) in the upper part of the study area (piezometer P, P 120 sub-scenario). That is the reason for which a new simulation is proposed, with a more balanced water extraction scheme (P 70/50 sub-scenario).

Table 3: Summary results on water balance at Lower Llobregat alluvial aquifer under three modelled scenarios

Water balance (hm^3/year)	Reference scenario	Simulation_120	Simulation 70/50
Natural recharge	52.9	43.4	41.7
Artificial recharge	0.0	119.4	119.4
Total recharge	52.9	162.8	161.1
Extraction SJD and Cornella	-19.7	-119.4	-69.7
Extraction Estrelles	-7.1	-7.1	-56.7
Other extractions	-27.2	-27.7	-28.9
Total extractions	-54.0	-154.2	-155.2
Sea connection	1.3	0.8	-0.2
Storage	0.1	9.3	5.6

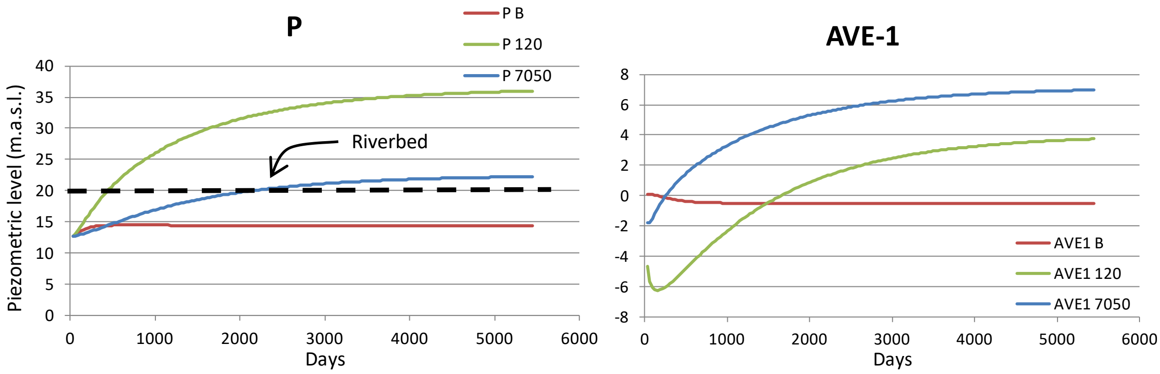


Figure 11: Evolution of piezometric levels in two piezometers located upstream (P) and downstream (AVE-1) from the injection zone. Note: m.a.s.l. = meters above sea level

The proposed water extraction allocation seems to impact on water levels in a more proportionate way, given they reach values of the same order of magnitude as the riverbed at Piezometer P (Figure 11). On the other hand, the increase of piezometric levels observed at piezometer AVE-1 is significant (they reach positive values). This increase is important to fight against the marine intrusion, in a context of climate change mitigation strategies.

4.3 Travel time of injected water

The origin of injected water is unknown at the moment, but probably it could come from Llobregat River. Therefore, the quality of recharge water will be different with respect to aquifer one and this must be taken into account in future studies. In this sense, the residence time of the injected water and the percentage of recovered water are two key variables to be considered.

In the same way as modelled scenarios 1 and 2 (ASR schemes), it has been applied a conservative solute transport model by using chloride as control variable. A theoretical concentration of 100 mg/L of chloride has been used to the injection water while native groundwater has no concentration. This sort of simulation allows to evaluate the percentage of recharged water. In Figure 12 is shown the percentage of mixture during the simulation period at three control piezometers (OBS-1, OBS-2, and OBS-3; see in Figure 10).

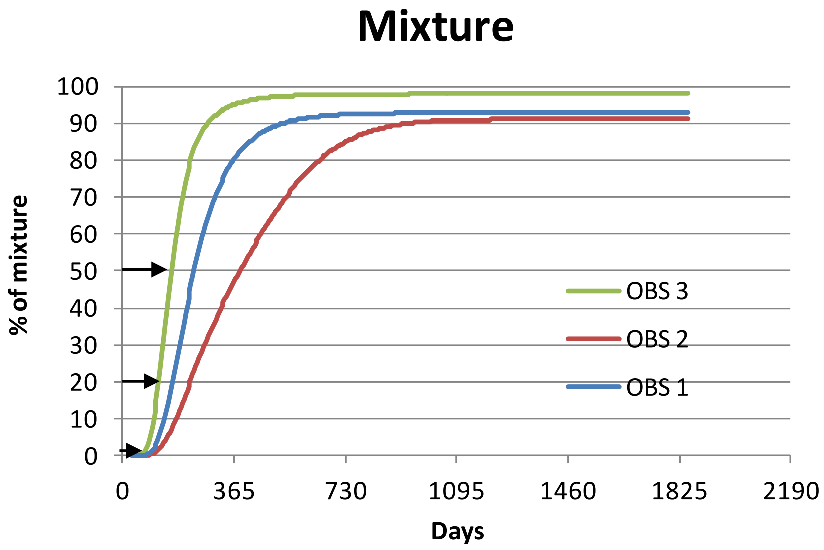


Figure 12: Evolution of mixture percentages at three control piezometers located upstream (OBS-1) and downstream (OBS-2, OBS-3) from the injection zone (see Figure 10)

The recharged water arrives faster and in a higher proportion at observation point 3 (OBS-3) with respect to the other control points. A mixture of 1, 20, and 50% of injected water arrives at OBS-3 in 45, 95 and 135 days, respectively. Without further information, this time could be enough for the aquifer to be capable of treating injected water, depending on the type of pollutants. This sort of analysis is out of the scope of the current chapter.

5. Conclusions

The demonstration phase data has been integrated in a local numerical model. The model has been then calibrated and validated. Therefore, the model has ready to implement future scenarios, regarding different regimes of water extraction and injection.

The calculated evolution of piezometric level is mostly influenced by the evolution of aquifer representative level, highly influenced by pumping regime. Thus the results about the water levels differences are not significant.

When the injection starts to work the chloride concentration of control piezometers decreases reaching the concentration of injected water. This effect it more noticeable in the observation points closer to the injection well. When injection system stops the chloride concentration showed an inverse trend, with values representing the native groundwater quality.

On the other hand, there is no influence of injected water both over the control points upstream the injection well and in horizontal direction. The residence time of injecting water at control piezometers is about 3 days, characteristic of the aquifer functioning close to the injection well.

Regarding regional model simulation, the obtained results correspond to a first approximation of the potential use of ASRT scenarios in Lower Llobregat alluvial aquifer. Based on the model, the aquifer has the sufficient storage capacity to regulate an infiltrated volume of 120 hm^3/year.

The observed piezometric increases suggest that water transfers from groundwater to Llobregat River could occur again, as in some control points it has been observed hydraulic heads very close to riverbed. Furthermore, in the water extraction scheme “70/50” it has been estimated a submarine groundwater discharge into the sea, which would be a positive result in terms of fighting against marine intrusion processes.

6. References

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Perez-Paricio, A. (1999). Experimental values from tracer test in well P13 (ARGW project publication)

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The research leading to these results has received funding from the European Union Seventh Framework Programme (FP7/2007-2013) under grant agreement no. 619039
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D35.1 (c) HYDRODYNAMIC AND HYDROGEOCHEMICAL IMPACT OF ASR USING PRE-POTABLE WATER IN BARCELONA

CETaqua, December 2017

The research leading to these results has received funding from the European Union Seventh Framework Programme (FP7/2007-2013) under grant agreement no. 619039

HYDRODYNAMIC AND HYDROGEOCHEMICAL IMPACT OF ASR USING PRE-POTABLE WATER IN BARCELONA

D35.1 (c): HYDRODYNAMIC AND HYDROGEOCHEMICAL IMPACT OF ASR USING PRE-POTABLE WATER IN BARCELONA

SUMMARY

An exhaustive study of the impact of sand-filtered water on the hydrodynamic and hydrogeochemical characteristics of the Lower Llobregat alluvial aquifer near Sant Joan Despi DWTP was carried out. Different types of compounds, such as physico-chemical, organic and microbiological were analysed under natural, potable injection and sand-filtered water conditions. A comparison was made between the measured values and the threshold limits and revealed that none of these compound were above Spanish legal recommendations for drinking water quality and good chemical groundwater status. By analysing recorded groundwater levels, electrical conductivity values and temperature data at nearby piezometers, it was confirmed the injection periods resulted in groundwater quality improvement and significant piezometric rises. The water quality improvement upon aquifer recharge was verified statistically by applying multivariate statistical techniques (PCA and Heatmap), reducing the dimensionality of dataset and extracting the most relevant information.

Regarding organic compounds (BTEX and emerging contaminants), the observed concentrations in the injection water were, in most cases, below both the limit of detection and the threshold established for drinking water. This allows to conclude that there is no risk of organic contamination under the injection conditions that took place during the demonstration phase. With respect to microbiology, the obtained results have demonstrated the presence of indicative microorganisms already in both sediment and groundwater samples prior to injecting pre-potable water. Injection of sand-filtered water resulted in a slight increase, which was however attenuated during aquifer passage. The results obtained from cleaning cycles (short but high-rate abstraction to clean the injection wells) indicated that after injecting sand-filtered water, a good-quality groundwater could be recovered from the vicinity of the ASR-well. These cleaning cycles have also shown that there is no significant clogging processes at control piezometers.

DELIVERABLE NUMBER	**WORK PACKAGE**
D35.1 (c)	WP35
LEAD BENEFICIARY	**DELIVERABLE AUTHOR(S)**
CETaqua	Marta Hernández (CETaqua) Manuel Argamasilla Ruiz (CETaqua)
QUALITY ASSURANCE	
AB (Aigües de Barcelona) KWR (Watercycle Research Institute)	Jordi Martín Koen Zuurbier
PLANNED DELIVERY DATE	**ACTUAL DELIVERY DATE**
31/12/2017 (M48)	19/01/2018
DISSEMINATION LEVEL	PU = Public

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5.1 Objectives

6.1 Objectives

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List of Acronyms and Abbreviations

ACA	Catalan Water Agency (regional public entity)
ASPC	Public Health Agency of Catalonia
ASR	Aquifer Storage and Recovery
CUADLL	Association of Users of The Llobregat Aquifer (non-profit organisation)
DWTP	Drinking Water treatment Plant
Pz-1	Piezometer number 1 drilled in SJD
Pz-2	Piezometer number 2 drilled in SJD
Pz-3	Piezometer number 3 already existing in SJD
SJD	Sant Joan Despí facility of Drinking Water Treatment Plant (Barcelona)
EOCs	Emerging Organic Contaminants
MAR	Managed Aquifer Recharge
SFW	Sand-filtered water

Executive summary

This deliverable analyses the impact of injecting sand-filtered water in hydrodynamic and hydrogeochemical functioning of Lower Llobregat alluvial aquifer (monitoring network at SJD DWTP). Different studies were carried out during the demonstration phase:

- The analysis of time series concerning piezometric heads, electrical conductivity and temperature at control piezometers. The obtained results allowed us to conclude the groundwater improvement, mainly referred to chemical status, with a significant decreasing trend in electrical conductivity values.
- A multivariate statistical analysis applied to all hydrogeochemical database was applied. This analysis has permitted to summarise all hydrogeochemical, organic and microbiological information which it has indicated the overall improvement of groundwater quality due to sand-filtered water injection. In addition, it marked the risky variables to take into account in future MAR projects, such as indicator microorganisms and chlorates. The results of this study clearly demonstrate the usefulness of multivariate statistical analysis as (PCA) in the ASR process investigation.
- The organic compounds characterization (BTEX and EOCs) in groundwater during injection phase revealed that none of the measured compound was above threshold values established by drinking water law.
- An exhaustive microbiological analysis, including environmental and indicator microorganisms, ATP (Adenosine Tri-Phosphate) determination, and virus and stygofauna characterization, allowed to jointly determine the impact of injecting sand-filtered water in a multi-approach way.
- The development of several cleaning cycles after different injection periods permitted to estimate the pumping schedule to obtained good-quality groundwater (≈ 1 hour of pumping for turbidity and heavy metals). It was not detected a risk regarding heavy metals mobilisation due to REDOX changes and clogging processes.

1. Introduction

Managed Aquifer Recharge (MAR) is a promising adaptation measure to reduce vulnerability to climate change and hydrological variability. MAR can play an important role as a measure to control over-abstraction and to restore the groundwater balance. It can be used to recharge aquifers subject to declining yields, to control saltwater intrusion or to prevent land subsidence. MAR may also be applied to sustain or improve the functioning of ecosystems and the quality of groundwater. However, in order to carry out a sustainable MAR in the short, medium and long-term, it is strictly necessary to evaluate the impact of such recharge on the hydrodynamic and hydrogeochemical aquifer functioning.

MAR is not always a remedy for solving water problems in all areas. Aquifer conditions must be suitable and (excess) source water must be present. In addition, the impact of injected water into the aquifer must be checked. In this sense, the potential of injected water to be applied in MAR applications must be preliminarily assessed as well as its impact in groundwater quality during and after the injection, as it has been done in DESSIN project.

2. Time series analysis (data-loggers)

2.1 Objectives

This section refers to the analysis of the time series registered at control piezometers during the injection of sand-filtered water, in which were measured piezometric levels, electrical conductivities and temperature during the injection period with water filtered by sand. The main goal of this section is to determine the impact of such injection in the hydrodynamic and physico-chemical response of the aquifer by using high-resolution time series.

2.2 Hydrodynamic response

In order to assess the hydrodynamic responses of Lower Llobregat alluvial aquifer to the managed aquifer recharge, it has been analysed the temporal evolution of water levels registered at one of the control piezometers (Pz-1, situated close to G piezometer in Figure 1) near well injection point named P-18. This evolution has been divided into six periods (A, B, C, D, F and G) based on the detection of different increasing and decreasing trends. At the study area is obvious that not all water level changes are caused by deep water injection, so it is necessary to identify the main factors controlling water table fluctuations.

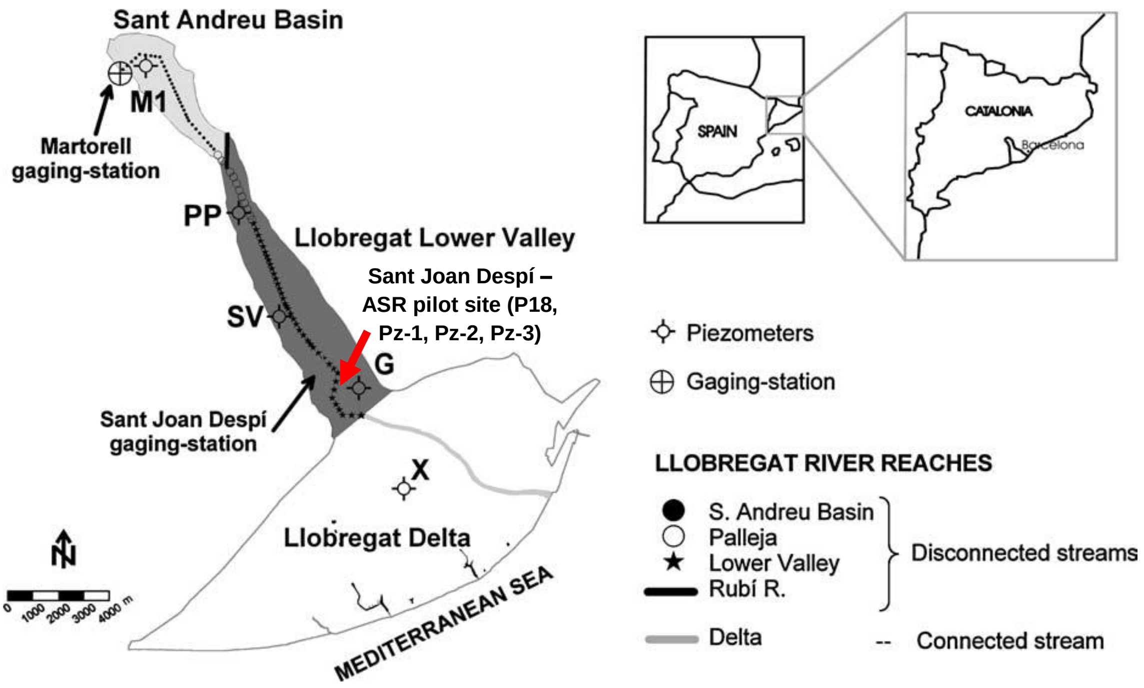

Figure 1: Map of the Lower Llobregat Aquifer units, Catalonia, Spain (modified from Vázquez-Suñé et al., 2009)

Other causes of water table fluctuation, apart from ASR operation, are due to: natural recharge from infiltrating rainfall and surface water, ocean tides; earth tides; barometric pressure changes; increases in gas pressure in the unsaturated zone (*Lisse* effect); pumping; and lateral flow (Crosbie *et al.,* 2005). These effects need to be avoided, minimized or removed from the water level signal to better interpret the hydrodynamic responses as a result of injected sand filtered water (SFW).

The effect of ocean tides is not significant due to control piezometers are all several kilometres inland. Moreover, unconfined aquifers are generally assumed to be insensitive to changes in barometric pressure (Freeze and Cherry, 1979). In relation to "false" water level rises, infiltrating rainfall or surface water can trap air in the unsaturated zone and cause the *Lisse* effect. As the infiltration moves through the soil profile, the air pressure is increased and the water table rises to compensate for the increase in pressure in the unsaturated zone (Heliotis and DeWitt, 1987). This is not recharge, as the infiltrating water has not yet reached the water table. In Figure 2 it is shown an illustrative example of this effect. The *Lisse* effect can be analysed by calculating partial cross correlations. If water table levels are affected by *Lisse* effect the partial cross correlations can reach negative values. Regarding the study site, the *Lisse* effect is not likely to be significant, due to it only occurs in areas with <1 - 1.3 m between the surface and the water table (Weeks, 2002). At the study area, the mean depth to water table ranges between 9 and 12 meters below ground. Therefore, data series of rainfall, Llobregat River streamflow and water extracted at P-18 well were taken into account to correctly interpret the hydrodynamic responses of the aquifer to managed aquifer recharge.

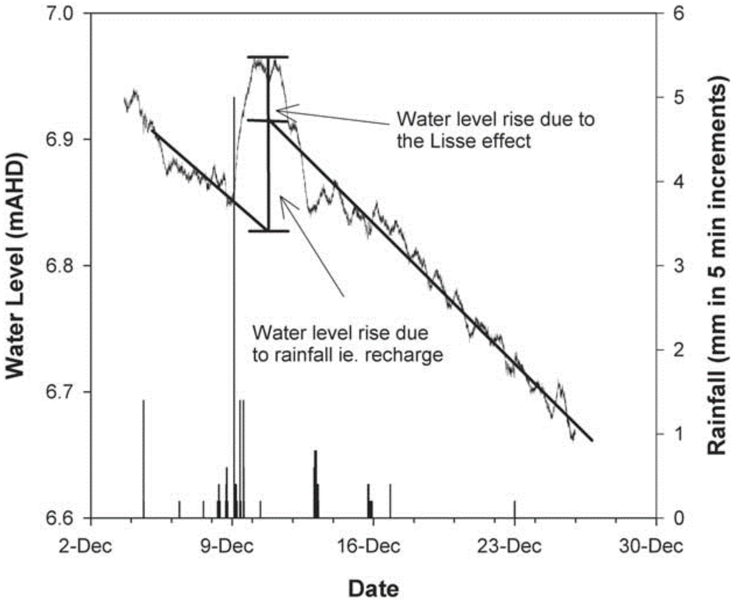

Figure 2: Water level signal at a well showing the Lisse effect. Taken from Crosbie et al. (2005)

With respect to meteorological and hydrological contexts, the evolutions of rainfall and Llobregat River streamflow throughout the monitoring period are shown in Figure 3. It can be observed two main periods, corresponding to increasing and decreasing rainfall trends, the former one starting at December 2014. The Llobregat River streamflow shows a significant correlation to rainfall data series, as can be seen from absolute and cumulative deviation values. During the water year in which ASR operation was active (2015/2016), the accumulated rainfall was 251.8 mm, with a maximum daily precipitation of 44.3 mm (02/11/2015). Given the average annual rainfall in Barcelona metropolitan area (628 mm/year), the period under study can be considered representative of dry or very dry conditions. In this sense, the average streamflow during the ASR operation was 7 m^3/s, 53% below the historical value at Sant Joan Despí gaging station (15 m^3/s).

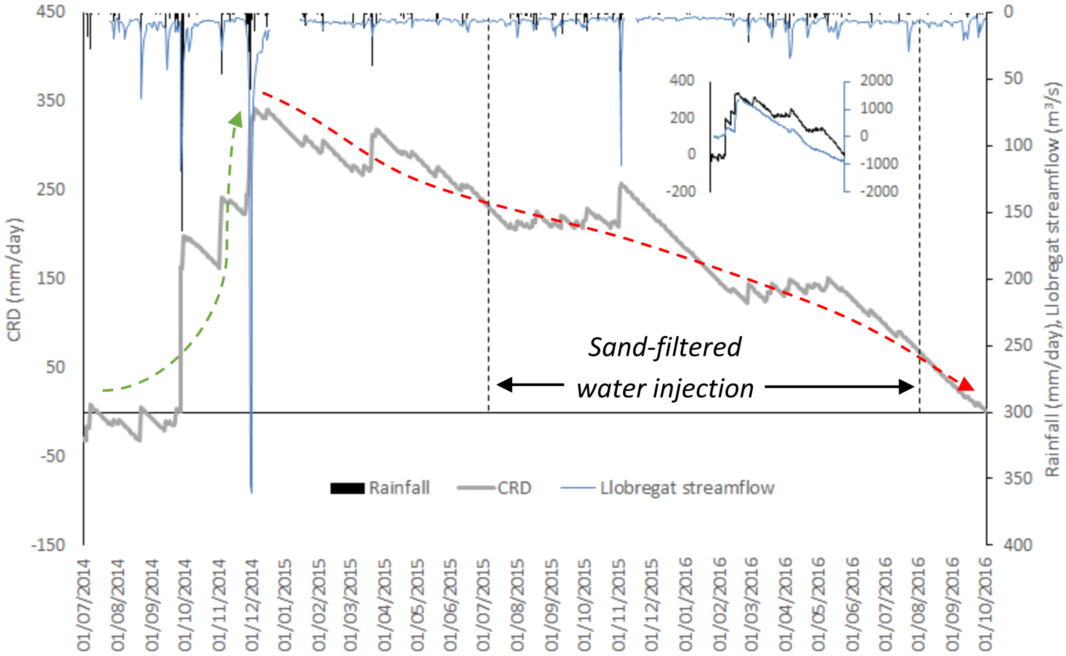

Figure 3: Temporal evolution of daily rainfall, cumulative rainfall deviation (CRD) and Llobregat River streamflow corresponding to monitoring period. Note: dashed lines are referred to the extent of the ASR operation period. The small graph at the upper right corner of the figure corresponds to the comparison between CRD of rainfall (black line) and Llobregat streamflow (blue line)

The third variable impacting the water table evolution is referred to the water withdrawal at drinking water well P-18. This effect can be clearly seen in Figure 4, in which the evolution of hydraulic heads measured at piezometers Pz-1 are shown, with instantaneous dropping water levels just after pumping water. For the analysis of the hydrodynamic responses to ASR operation it has been used the data from piezometer Pz-1, due to the similarity of water levels registered at the remaining control points (piezometers Pz-2 and Pz-3). The starting date for water table fluctuations analysis was October 2014, in order to discard the first records registered by the data-logger and obtain more feasible data.

During the first period (A) it was observed an increasing trend of water levels, with decreases associated with sporadic pumping operations (see Figure 4). In such a period, it was registered the higher amount of rainfall, with a total and average values of 235.5 mm and 2.3 mm/day, respectively, giving rise to a peak streamflow of 361 m^3/s. Therefore, it would be a period largely influenced by hydro-meteorological factors.

Period B was characterized by the maximum decrease in piezometric heads, with values dropping from 2.7 to -1.6 m.a.s.l., mainly due to intensive pumping during the month of March (97,383 m^3) along with the low registered rainfall values (49.3 mm). In the next period (C), water tables reached values similar to that of period A, sporadically interrupted by two main pumping events, with a mean instantaneous flow of 212 L/s. The accumulated rainfall from 14/03/2015 to 28/03/2015 was 67.4 mm, with a maximum daily value of 40 mm (21/03/2015). Such an intense rainfall events may be the responsible of important increase of water levels (Taylor *et al.,* 2013; Thomas *et al.,* 2016), like the one observed in period C.

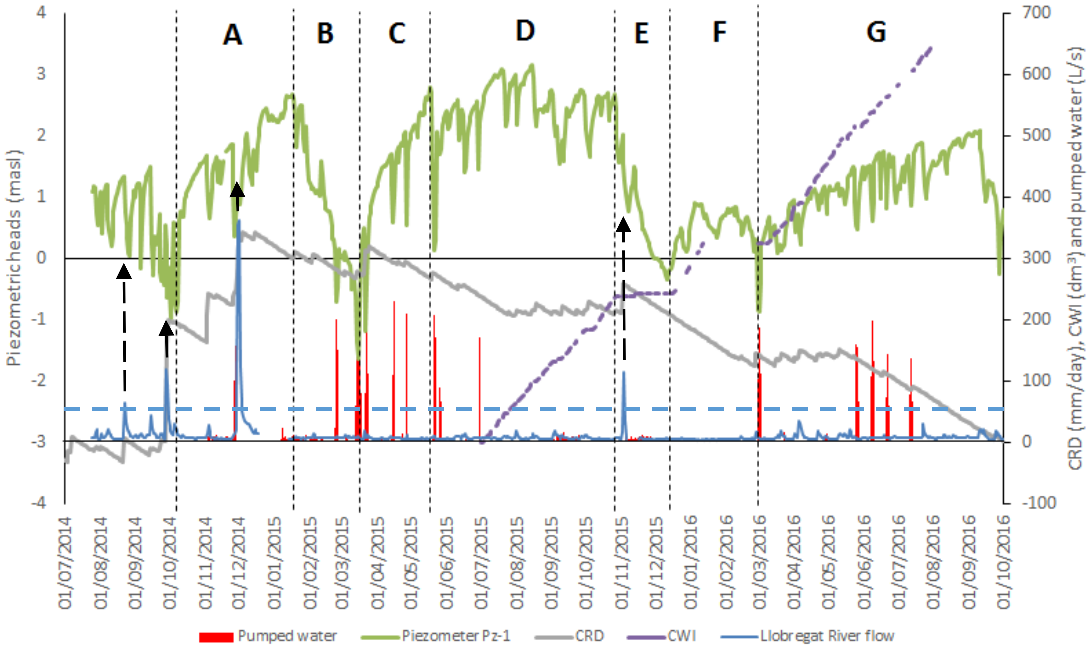

Figure 4: Evolution of daily piezometric heads, cumulative rainfall deviation (CRD), cumulative water injection (CWI), and pumped water and Llobregat River streamflow corresponding to monitoring period. Note: black dashed lines are referred to the different periods identified based on piezometric trends. Blue dashed lines corresponds to the value of 50 m^3/s, chosen by Vázquez-Suñé et al. (2009) as "minimum flood value" for significant piezometric head response

The evolution of piezometric heads during period D shows a no significant trend with rapid decreases related to stops in ASR operation, due to no pumping was performed since the start of the managed aquifer recharge. The direct correlation between piezometric heads and cumulative water injection was even more obvious in period E, in which the total injected water was practically zero and the water table reached a value of -0.3 m.a.s.l. This decrease was temporally interrupted by two recharge events associated with infiltrating rainfall and Llobregat River water, respectively (see Figure 4).

In period F, the decreasing trend observed in groundwater levels was inverted due to the start of ASR operation. The water levels were lower than those observed in period D, due both to the cumulative water injection (82,226 m^3) only represented 13% of total injected water and the unexpected lack of rainfall in winter months. In the latest period, the positive impact of deep water injection is markedly noticeable, with a continuous increase of water levels during summer, even when the monthly average pumped water was equal to 36,426 m^3. This situation is due to the amount of injected water, with a value of 318,373 m^3, representing 50% of total accumulated volume. The fact that the observed water levels were lower than those observed in period D could be related to several causes. On the one hand, the hydrodynamic state of the aquifer was different, given the dry conditions taking place before injecting water throughout period G. On the other hand, pumping was performed since the start of the managed aquifer recharge (concentrated in May, June and July), so it would be expected that water table to reach lower values. This hypothesis would discard the existence of significant bio-clogging processes and subsequent head losses at control piezometer (Pz-1) that could have been explained the observed differences in groundwater levels between periods D and G.

2.3 Hydrogeochemical and physico-chemical response

For the hydrogeochemical characterization of the response to sand-filtered water injection, data from piezometer Pz-1 has been used. Electrical conductivity and temperature were registered at 15-minute intervals. As with the piezometric heads, original values were grouped to a daily time scale in order to ease their interpretation and to allow their comparison with the rest of variables.

With respect to temperature data (Figure 5.1), its evolution perfectly marked the timing of sand-filtered water recharge, highly linked to river water temperature. When recharge water was injected into the aquifer during summer months (periods D and mostly G), groundwater temperature reached values up to 28 ºC, similar to those found in Llobregat River water. The circle symbols in Figure 5.1 highlight this thermal similarity. It may be observed a decreasing or increasing temperature trend when sand-filtered water injection was stopped, depending on whether the recharge water temperature was above or below groundwater background temperature (≈ 17 ºC).

Regarding electrical conductivity (E.C.) evolution (Figure 5.2), there is, in general, a decreasing trend until the period E, accentuated by the start of deep water injection since July 2015. This type of trend can be also detect at the start of period G. The periods in which most of sand-filtered water was injected (D and G) are characterized by higher E.C. variability with respect to non-injection periods, due to water injection was not continuous. In this sense, the injection of SFW provoked instantaneous decreases of E.C. values, given the lower ones registered in Llobregat River water

(Figure 5.2). Immediately after the stop of ASR operation, the E.C. reached values close to those found in native groundwater.

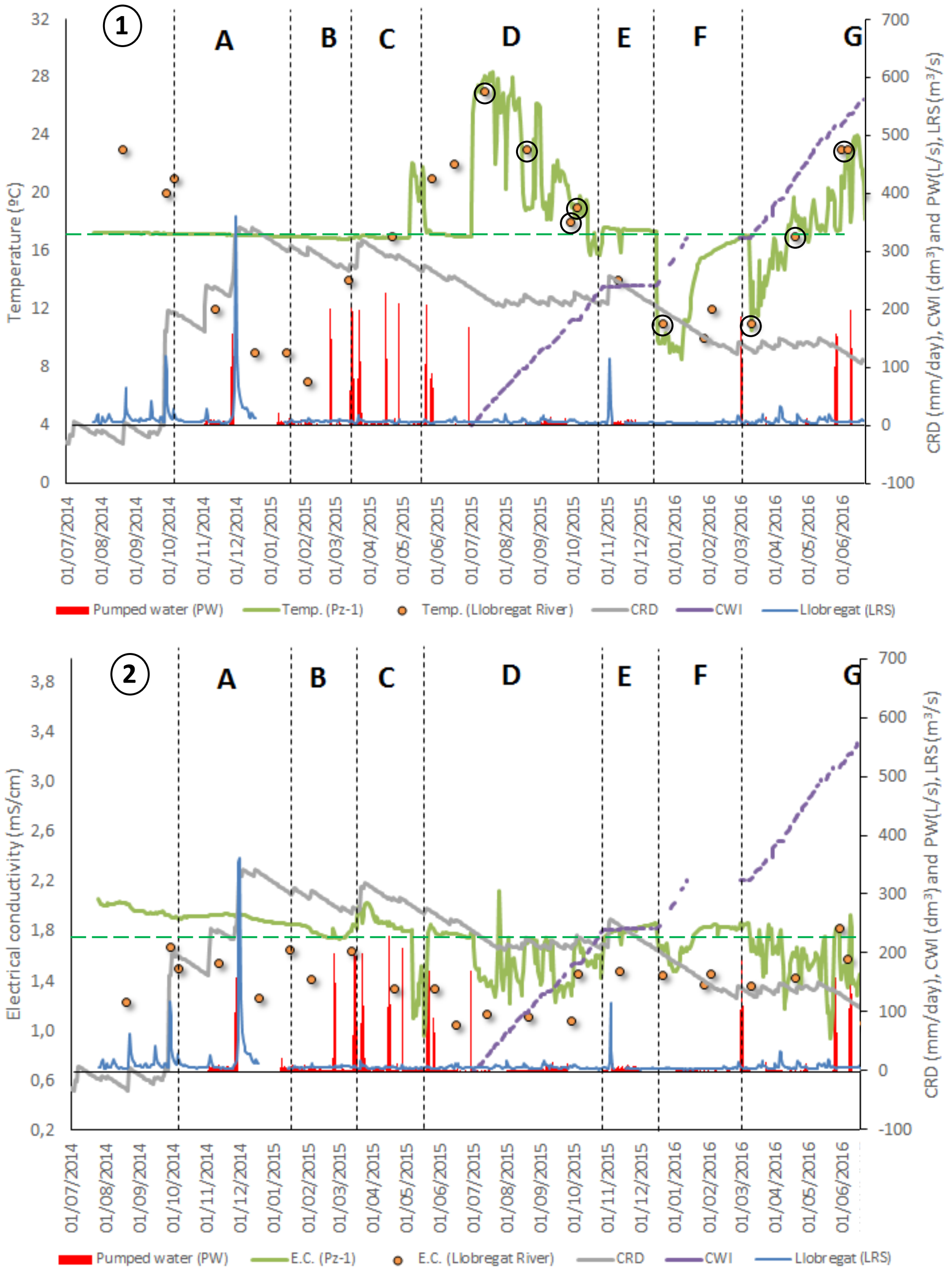

Figure 5: Evolution of daily temperature (1) and electrical conductivity (2) at piezometer Pz-1 along with the cumulative rainfall deviation (CRD), cumulative water injection (CWI) and pumped water at P-18 well, and Llobregat River streamflow (LRS). Note: black dashed lines are referred to the different periods identified based on piezometric trends. Green dashed line represent the groundwater temperature background value

In order to determine the impact of SFW injection into the aquifer, temperature has been used as natural tracer. Temperature appears to be a useful tracer in aquifers characterized by rapid flow. Moreover, it can be accurately measured at high resolution, which allows frequent determination of residence time (Martin and Dean, 1999). An example of this is shown in Figure 6. Two different periods have been chosen for that purpose, avoiding dates with intensive rainfall and/or pumping, which could alter the natural response of the aquifer. In the first period, between 12/01/2016 and 05/03/2016, the temperature changed from 11.1 to 17.1 ºC, respectively, with an estimated SFW residence time of 54 days.

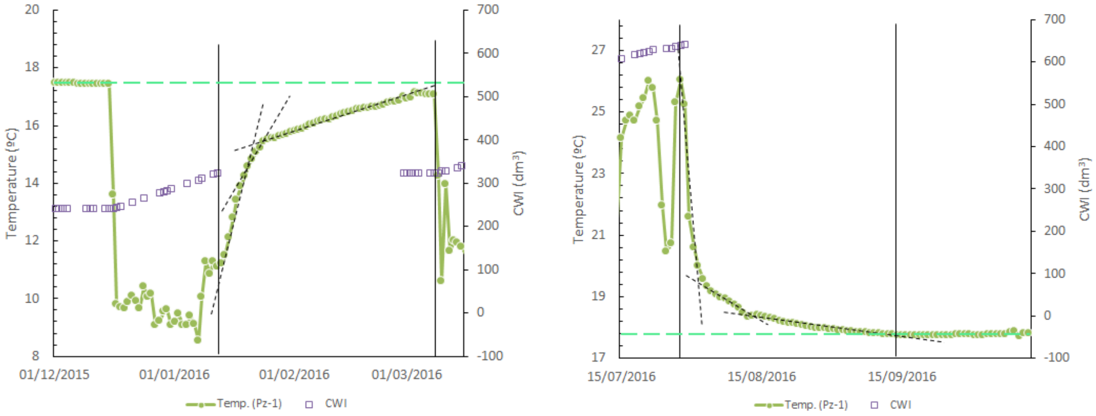

Figure 6: Estimation of sand-filtered water (SFW) residence time on Lower Llobregat alluvial aquifer by analysing recovery temperature curves at piezometer Pz-1. Note: CWI = cumulative water injection

The recovery temperature time obtained in the second period was very similar, with a value of 50 days. In that case, the temperature varied from 26 to 17.7 ºC, between 28/07/2016 and 15/09/2016. The total injected water just before the analysed periods was 323,503 and 318,373 m^3 (641,876 m^3 – 323,503 m^3). Therefore, the results derived from the two recovery temperature curves could be considered comparable among them and representative of the aquifer functioning.

3. Multivariate statistical analysis

3.1 Objectives

Hydrochemical data are commonly used to evaluate the effectiveness of ASR operation in its function for improving water quality. A detailed characterization of the hydrogeochemical processes taking place into the aquifer is out of the scope of this chapter and will be carried out in future studies. Preliminary results have been already obtained in deliverable D22.4 (a) regarding aquifer hydrogeochemistry prior to artificial recharge. In this sense, the main objective of this section is referred to the application of a multivariate statistical analysis in order to synthesize all the information provided by the different variables, such as physico-chemical, microbiological, and so on, to provide a global view of the impact of recharging sand-filtered water into Lower Llobregat alluvial aquifer.

3.2 Methodology

Multivariate statistical analysis is recommended (almost mandatory) in cases of multiple data series and variables, in order to avoid redundant information and to reduce dimensionality of the data set, commonly used in environmental studies (Mendiguchía *et al.,* 2004; Han *et al.,* 2006; Rahman *et al.,* 2014). It has been applied two techniques (PCA and Heatmap) by using the software ClustVis (Metsalu and Vilo, 2015), a web tool for visualization clustering of multivariate data applying Principal Component Analysis and Heatmap. Before performing these two statistical techniques Log-transformation and standardization were applied to chemical parameters to ensure that each variable is, respectively, normally distributed and equally weighted. In order to check whether the sample is big enough it has been used the Kaiser-Meyer-Olkin measure of sampling adequacy (KMO-test).

PCA is an unbiased method which indicate associations between samples and/or variables (Kaufman, 1990; Jolliffe, 2002). It is a statistical technique that is used to analyse the interrelationships among a large number of variables and to explain these variables in terms of a smaller number of variables, called principal components, with a minimum loss of information. After the application of PCA, a varimax rotation was conducted, allowing the ‘‘cleaning up’’ of the PCs by increasing the participation of the variables with a higher contribution, and by simultaneously reducing that of the variables with a lower contribution.

Heat maps represent two-dimensional tables of numbers as shades of colors. This is a popular plotting technique in biology, used to depict gene expression and other multivariate data. The dense and intuitive display makes heat maps well-suited for presentation of high-throughput data.

Hundreds of rows and columns can be displayed on a screen. Heat maps rely fundamentally on color encoding and on meaningful reordering of the rows and columns.

Hierarchical clustering is one technique for reordering matrices that creates several display challenges. First, because there are 2n–1 possible arrangements for n rows or columns related by a cluster tree, a static heat map is only one of many possible outcomes (Metsalu and Vilo, 2015). Second, clustering creates useful relationship information captured in the cluster tree typically displayed on the sides of the matrix. Heat maps in which both rows and columns are clustered create blocks of similarly colored cells that are easy to spot, this is the case for the evaluation of the impact of sand-filtered water and potable water in groundwater at SJD demo site.

3.3 Results and discussions

3.3.1 Kaiser-Meyer-Olkin test

The sample is adequate if the value of KMO is greater than 0.5. KMO takes values between 0 and 1. A value near 0 indicates that the correlations are widespread and so are not clustering among a few variables, indicating a problem for factor analysis. On the contrary, a value near 1 indicates a good fit for PCA (Kaiser, 1974).

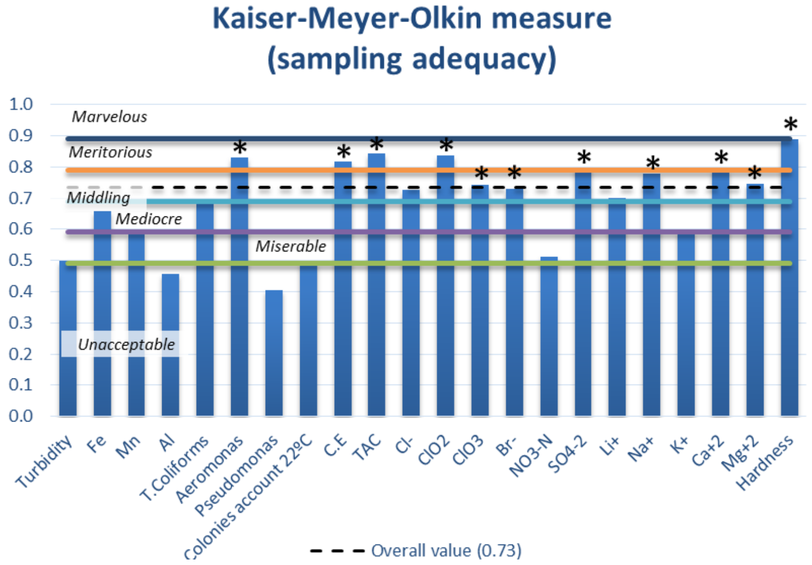

Figure 7: Kaiser-Meyer-Olkin measure of sampling adequacy for PCA

The overall obtained value was 0.73, which validates the use of the current dataset to carry out multivariate statistical techniques, such as PCA and Heatmap. The lower values were referred to turbidity and heavy metals, with all their values below overall result. The variables above the average value were Aeromonas, electrical conductivity, alkalinity, chlorites, chlorates, bromide, sodium, calcium, magnesium and hardness.

3.3.2 Principal Component Analysis

A PCA was used to determine the major hydrochemical processes that control the groundwater quality variations during ASR operations (see Figure 8). Principal component analysis (PCA) was applied on chemical and microbiological data of 49 groundwater samples, after applying several filters (samples with all selected variables and a charge balance error below 5%). It has allowed the reduction of the 22 variables to four significant PCs (factors F) that explain nearly 80% of the total variance. The first two factors explain 57% of total model variance. The first one could be called "aquifer salinization" and groups the variables characterizing native groundwater. The opposite relationship between major ions and microbiological and disinfection-by products parameters indicates that SFW injection impacts positively by reducing groundwater mineralization but, at the same time, tends to increase the concentrations of variables not naturally present into the aquifer, such as ClO_2^- and ClO_3^-. The application of additional water treatments to obtain potable water before injection (ultrafiltration, GAC, reverse osmosis) resulted in lower values of Br^-, Cl^- and K^+ in groundwater (PI code) in comparison to SFW-influenced water samples (see Figure 8).

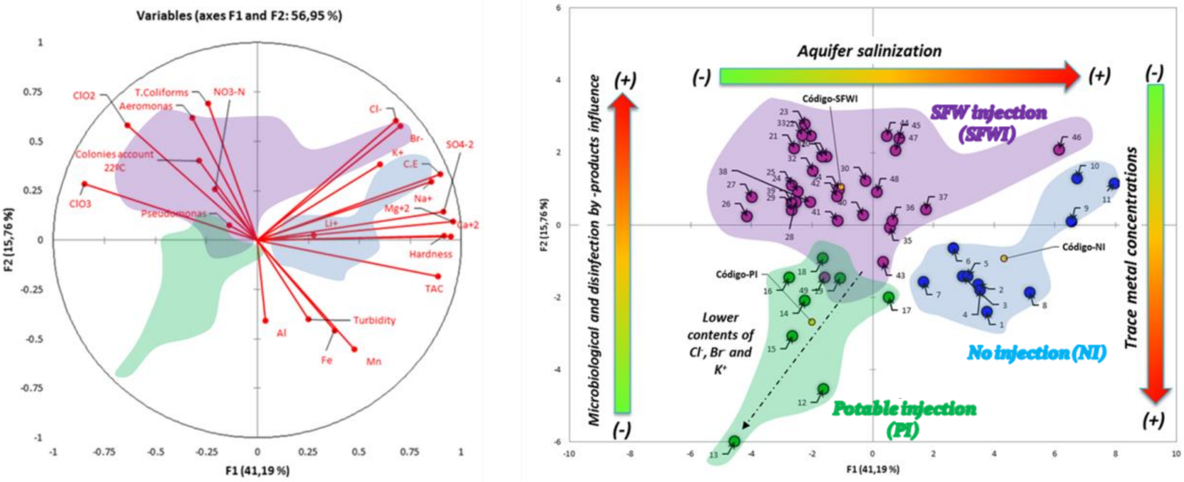

Figure 8: Plots of the two first principal component loadings concerning variables (A) and observations (B)

3.3.2 Heatmap technique

It has been implemented a Heatmap technique to complement the results derived from PCA. It can be clearly seen the effects of recharging water into groundwater quality, especially at the piezometers closer to the injection well (see Pz-1, Pz-2 in Figure 9). These groundwater samples show greener colours for variables characterising sand filtered-water (bottom cluster), both microbiological (colonies account, Pseudomonas, Aeromonas and total coliforms) and chlorine disinfection by-products (ClO_2, ClO_3). The higher NO_3-N contents in SFW also impacts on water quality, with more changes with respect to native groundwater at Pz-1 and Pz-2. ClO_2 and ClO_3 can be used as tracers of injecting water into the aquifer, due to their low degradation rates along the groundwater flow paths. The utilisation of microbiological parameters for that purpose is not fully recommended as their concentrations may be reduced into the aquifer due to natural attenuation processes. This attenuation process could explain the lowest values found at Pz-1 with respect to Pz-2 and Pz-3.

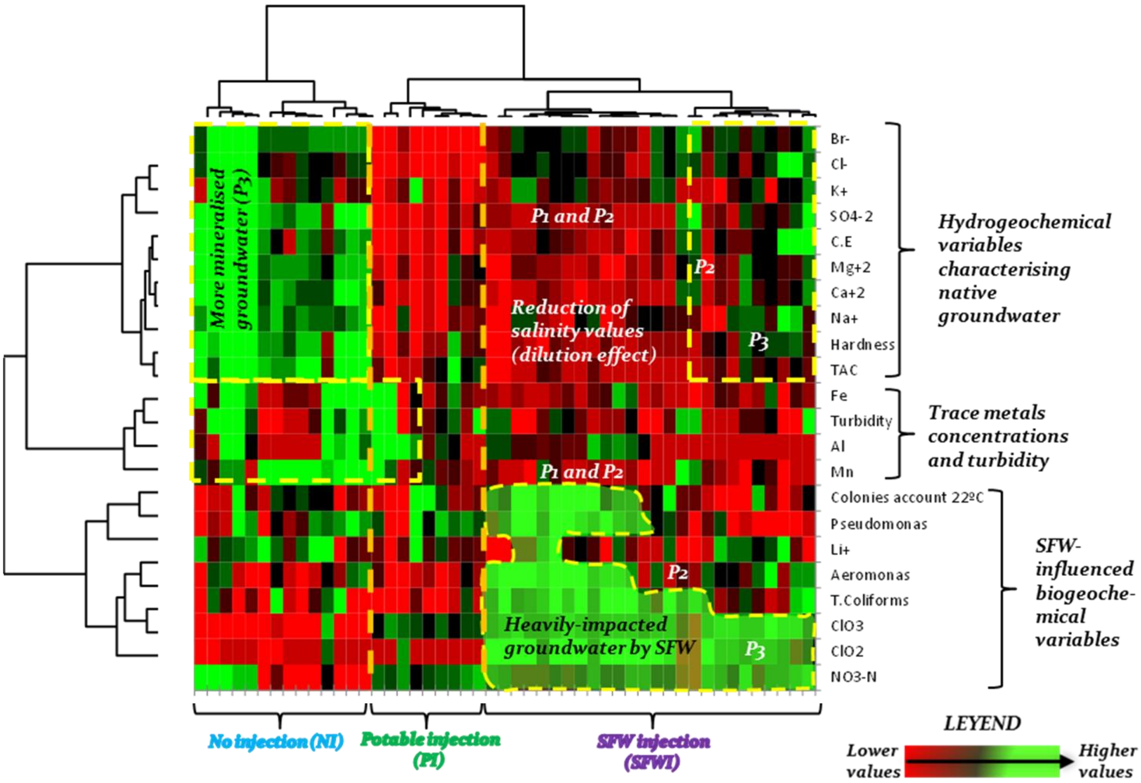

Figure 9: Heatmap of the variables used to discriminate between the different hydrodynamic conditions (no injection, potable injection and sand-filtered water injection)

Regarding hydrogeochemical variables conditioning background aquifer quality (top cluster in Figure 9), it may be concluded that the injection of pre-potable water has a positive impact in groundwater, with an overall reduction of the variables responsible for aquifer salinization. This reduction is less evident at Pz-3, due to not only to its higher distance from the injection well but the more mineralised initial water (Figure 9). There are not significant differences in Br^-, Cl^- and K^+ contents between groundwater and SFW. It can be easily explained for the similar concentrations found in both SFW and groundwater prior to water injection. This similarity does not occur in potable injection-affected groundwater samples due to the efforts carried out to treat the Llobregat River water (conventional treatment plus ultrafiltration, GAC and reverse osmosis). This additional treatment would explain the lower values (redder colours) obtained in most of groundwater sampled during potable water injection period (Figure 9), even though disinfection by-products (ClO_3) were still detected.

It has been identified an intermediate cluster characterised for two subgroups, made up of groundwater samples with higher turbidity and trace-metals values, constituted by water sampled during non-injection period (native groundwater), and another one concerning most of groundwater affected by potable and sand-filtered water injection. The statistical significance of Fe, Mn, and Al concentrations in non-injection groundwater group is limited, due to its high variability, as it was pointed out in Figure 7. In this sense, the range for these metals varied from 690-20 µg/L, 180-4 µg/L and 386-12.5 µg/L, respectively. These variables show a strong correlation with turbidity values (same trend detected along the different types of water), which could indicate a particulate origin. This fact has been subject of a more detailed study in section 6. The interest in determining the hydrogeochemical behaviour of these trace metals lies with the additional input of aluminium salts applied to the coagulation/flocculation treatment prior to water injection. Due to the existing ratio between total water injected and average natural recharge (0.6/53 ≈ 1%), the most feasible explanation would be related to dilution processes.

Therefore, the Heatmap highlighted the generalized improvement on water quality after SFW injection and the need to efficiently monitor SFW-influenced variables.

4. Analysis of organic pollutants

4.1 Objectives

The purpose of this section is to present the results referred to organic priority substances and emerging (non-regulated) pollutants to assess the impact of injected water into the aquifer. Although initially the project proposal did not include a review of these compounds, it was detected at the beginning of the project the need to quantify and evaluate their impact in groundwater geochemistry.

The document also contextualizes the results with bibliographic data and references in other parts of the Lower Llobregat and Delta aquifer system, where these compounds were analysed and quantified.

4.2 Methodology

The selection of compounds was based on a bibliographic study of historical data of Llobregat River and groundwater in the Lower Valley and Delta. It also were included the criteria of the Catalan Water Agency (ACA) and the Public Health Agency of Catalonia (ASPC) in order to validate a list of organic compounds, as complete as possible, representative of what might be found in sand-filtered water recharging the aquifer. The criteria that were considered were:

- Criterion 1: DMA priority list of compounds and new candidates. We did a review of the existing literature in the Llobregat study area (surface and groundwater) in order to see which of them might be the most important to be included (see Annex A).

- Criterion 2: Analytical capacity of the Laboratory of Aigües de Barcelona. This criterion is referred to the compounds found at some time in the Llobregat River and that can be potentially treated by sand filters. The Laboratory of Aigües de Barcelona specializes in the detection and quantification of organic compounds (regulated and unregulated) in natural waters and their removal through the treatment process (information available in Aigües de Barcelona).

- Criterion 3: Relevant parameters for ACA and ASPC.

Criterion 1: Review of organic compounds at Lower Llobregat study area

Annex A contains a list of 48 priority substances list and suggested to comply with the Water Framework Directive and the results of several research studies and published articles. No information was published of about 50% of the compounds. As regards as the substances reported in scientific articles, 10 of them have always results below the detection limits of the laboratories, and the remaining 15 have been able to be quantified from the references relative to surface water, groundwater and drinking water.

Criterion 2: Aigües de Barcelona

Given the analytical capacities for organic and inorganic determination in the Laboratory of Aigües de Barcelona, it has been identified a number of families of compounds to be determined. These families are in line with the project, as Aigües de Barcelona has specialized in the compounds with the greatest impact on the Llobregat River, which could be problematic in the future for exploitation. The proposal included:

- BTEX compounds and chlorinated solvents (9 substances)
- Pesticides regulated in drinking water (34 substances)
- Metals regulated in drinking water (18 substances)
- Metals non-regulated in drinking water (16 substances)
- Pesticides non-regulated in drinking water (6 substances)

Moreover, some compounds were discarded for their detection and quantification for not being on the river water, such as phthalate, which is contained in many plastics material sampling:

- Polycyclic aromatic hydrocarbons (17 substances)
- Persistent organic pollutants - PCBs and PBDEs - (15 substances)
- Hormones: Estradiol (E2) and Ethinylestradiol (EE2) (2 substances)
- Phthalate (Di(2-etilhexilftalat) (DEHP)) (1 substance)

The complete list of selected substances can be found in Appendix 2 of this document.

Taking advantage of the analytical capacity of the laboratory, a complete campaign (08/01/2015) was made by analysing all these substances (selected and discarded) to know the initial status of the selected quality control points before starting the project:

- Sand-filtered water
- Groundwater: Well - 18 (injection point)
- Groundwater: Wells 10, 13 and 21 (external monitoring network)

The results of this campaign can be found in Annex B of this document. In groundwater, low concentrations of metals was detected (Barium < 50 µg/L and Lithium < 30 mg/L) and phthalate (450 ng/L), which might be a false positive due to pipe material or sampling procedures.

Criterion 3: Additional compounds proposed by ASPC

Once the results of the screening campaign that included 122 substances was presented, the expertise of the Public Health Agency of Catalonia (ASPC) and the Catalan Water Agency (ACA) was considered, determining the need to expand the list of trace compounds with the following substances: acetaminophen, cotinine, and erythromycin codeine.

Final selection of organic compounds

Finally, the list of compounds to be monitored on a frequent basis was set, corresponding to major ions, microbiology variables, field parameters, etc. The frequency was half of the campaign to give routine monitoring throughout the project and adjust the estimated budget for water analytics (the schedule may be consulted in Annex C of the document).

Table 1: Selected priority organic compounds and indicators

Group	Compound	Detection limit (LOD)
BTEX compounds and chlorinated solvents	**Benzene**	0.5 µg/L
	Toluene	0.5 µg/L
	Ethylbenzene	0.5 µg/L
	m+p-Xylene	0.5 µg/L
	o-Xylene	0.5 µg/L
	Trichloroethene (tri)	0.5 µg/L
	Tetrachloroethene (tetra)	0.5 µg/L
	1-2 Dichloroethane	0.5 µg/L
	1.1.1-Trichloroethene	0.5 µg/L
Pesticides (SBE - CG/EM)	**Simazine**	0.015 µg/L
	Terbuthylazine	0.015 µg/L
	Diclofenac	10 ng/L
	Estradiol	10 ng/L
	Isoproturon	10 ng/L
	Diuron	10 ng/L

Emergent persistent organic pollutants	**Nonylphenol**	10 ng/L
	Octylphenol	10 ng/L
	Acetaminophen	10 ng/L
	Cotinine	10 ng/L
	Codeine	5 ng/L
	Erythromycin	10 ng/L

4.3 Results and discussions

It has been performed three complete campaigns, beginning 8 January 2015 (see Annex B). The remaining campaigns are planned for April 2016 and January 2017, coinciding with the last part of the project and in the same month that the first water sampling, so data are comparable seasonally. Thus, it is expected to have results from these campaigns on the dates listed in Table 2:

Table 2: Dates and conditions for complete water sampling (Screening)

Date	Conditions	Control points	Status
January 2015	Prior to injection	SFW, P10, P13, P18, P21	Done (see results in Annex B)
April 2016 - June 2016	During the injection (control points P18)	SFW, Pz-1, Pz-2, Pz-3, P18 (cleaning cycles each 15 minutes and 1 day)	Done SFW; Pz1; Pz2; Pz3 11/04/2016
2018	Prior to new SFW injection	SFW, P10, P13, P18, P21, Pz-1, Pz-2, Pz-3	Pending of water concession

4.3.1 BTEX compounds and chlorinated solvents

The Table 3 corresponds to a summary of the results obtained in each campaign and sampling points where benzene, toluene, ethylbenzene, and xylene were detected. As for the 1-2 Dichloroethane, trichloroethene, and tetrachloroethene, these compounds have been detected in some groundwater samples because of the historical contamination with chlorinated solvents. The concentrations have been above detection limits and present variable spatial distribution (see specific maps of trichloroethene and tetrachloroethene of Figures 10 and 11 of this document, with trichloroethene values of around 25 mg/L at Estrella well). The most remarkable conclusion about BTEX compounds and chlorinated solvents is that none of the 9 analysed substances have been detected in the sand-filtered water, so it may be supposed that the recharge water is producing a dilution of compounds that are naturally present in groundwater.

Table 3: Summary results of BTEX and chlorinated solvents

Note: (n=x) indicates the number of determinations made for that substance in those conditions. For PZ1, Pz2 and Pz3 and external network control points P10, P13 and P21 samples were taken at three points on all campaigns

	SFW (injection)	Pz-1 / Pz-2 /Pz-3 Native groundwater	Pz-1 / Pz-2 /Pz-3 during potable water injection	Pz-1 / Pz-2 /Pz-3 during SFW injection	External network (P10/P13/P21)
Benzene	<LOD (n=8)	<LOD (n=1)	<LOD (n=2)	<LOD (n=8)	<LOD (n=7)
Toluene	<LOD (n=8)	<LOD (n=1)	<LOD (n=2)	<LOD (n=8)	<LOD (n=7)
Ethylbenzene	<LOD (n=8)	<LOD (n=1)	<LOD (n=2)	<LOD (n=8)	<LOD (n=7)
m+p-Xylene	<LOD (n=8)	<LOD (n=1)	<LOD (n=2)	<LOD (n=8)	<LOD (n=7)
o-Xylene	<LOD (n=8)	<LOD (n=1)	<LOD (n=2)	<LOD (n=8)	<LOD (n=7)
1.1.1-Trichloroethene	<LOD (n=8)	<LOD (n=1)	<LOD (n=2)	<LOD (n=8)	<LOD (n=7)
1-2 Dichloroethane	<LOD (n=8)	<LOD (n=1)	<LOD (n=2)	<LOD (n=8)	see Table 6
Trichloroethene	<LOD (n=8)	see Table 4	see Table 4	see Table 4	see Table 4
Tetrachloroethene	<LOD (n=8)	see Table 5	see Table 5	see Table 5	see Table 5

Table 4: Summary results of trichloroethene results in all conditions and sampling points

Trichloroethene LOD = 0,5 µg/L	SFW	Pz-1	Pz-2	Pz-3	P13 (WELL)	P21 (WELL)	P10 (WELL)
NO INJECTION	< LOD	< LOD	< LOD	< LOD	5	< LOD	2.4
POTABLE INJECTION	< LOD	< LOD	< LOD	0.8	3	1.7	1.9
	< LOD	< LOD	< LOD	1.6	No sample	No sample	No sample
SFW INJECTION	< LOD	< LOD	< LOD	< LOD	3.9	1.5	1.5
	< LOD	0.5	< LOD	< LOD	4.3	1.5	1.6
	< LOD	< LOD	< LOD	< LOD	3.6	1.5	1.7
	< LOD	< LOD	< LOD	< LOD	3.5	1.3	No sample
	< LOD	< LOD	< LOD	0.7	3.7	1.5	No sample
	< LOD	< LOD	< LOD	1.1	4.4	1.3	No sample
	< LOD	< LOD	< LOD	0.74	4.2	< LOD	No sample
	< LOD	< LOD	< LOD	< LOD	No sample	No sample	No sample

Table 5: Summary results of tetrachloroethene results in all conditions and sampling points

Tetrachloroethene LOD = 0,5 µg/L	SFW	Pz-1	Pz-2	Pz-3	P13 (WELL)	P21 (WELL)	P10 (WELL)
NO INJECTION	< LOD	< LOD	< LOD	< LOD	< LOD	2.8	8.1
POTABLE INJECTION	< LOD	< LOD	< LOD	1.3	0.8	1.1	6.1
	< LOD	< LOD	< LOD	1.6	No sample	No sample	No sample
SFW INJECTION	< LOD	< LOD	< LOD	< LOD	0.8	1.7	4.9
	< LOD	6.6	0.81	0.5	0.8	1.8	6.3
	< LOD	< LOD	< LOD	< LOD	0.8	1.7	5.7
	< LOD	< LOD	< LOD	< LOD	0.5	1.6	No sample
	< LOD	< LOD	< LOD	0.8	0.7	1.9	No sample
	< LOD	< LOD	< LOD	< LOD	0.8	2.2	No sample
	< LOD	< LOD	< LOD	0.9	< LOD	2.1	No sample
	< LOD	< LOD	< LOD	< LOD	No sample	No sample	No sample

Table 6: Summary results of 1-2 Dichloroethane results in all conditions and sampling points

1-2 Dichloroethane LOD = 0,5 µg/L	SFW	Pz-1	Pz-2	Pz-3	P13 (WELL)	P21 (WELL)	P10 (WELL)
NO INJECTION	< LOD	< LOD	< LOD	< LOD	2	2.8	< LOD
POTABLE INJECTION	< LOD	< LOD	< LOD	< LOD	1.6	1.1	< LOD
	< LOD	< LOD	< LOD	< LOD	No sample	No sample	No sample
SFW INJECTION	< LOD	< LOD	< LOD	< LOD	1.7	1.7	< LOD
	< LOD	< LOD	< LOD	< LOD	1.7	1.8	< LOD
	< LOD	< LOD	< LOD	< LOD	1.6	1.7	< LOD
	< LOD	< LOD	< LOD	< LOD	0.9	1.6	No sample
	< LOD	< LOD	< LOD	< LOD	1	1.9	No sample
	< LOD	< LOD	< LOD	< LOD	1.3	2.2	No sample
	< LOD	< LOD	< LOD	< LOD	1.4	2.1	No sample
	< LOD	< LOD	< LOD	< LOD	No sample	No sample	No sample

4.3.2 Emerging organic contaminants

The Table 7 shows the summarized results for drugs and pesticides. Codeine and pentachlorophenol were not detected in any campaign or condition throughout the project. The positive results of other substances are presented in the following tables, in which can be seen what compounds are below the detection limit of the laboratory. Only 5 out of 12 substances were promptly detected in some campaign on sand-filtered water: erythromycin, cotinine, acetaminophen, diuron and isoproturon. Regarding these five compounds, it has been made a thorough analysis in order to contextualize concentrations found in other studies on groundwater and Llobregat River.

Table 7: Summary results of drugs and pesticides compounds

Note: (n=x) indicates the number of determinations made for that substance in those conditions. For Pz-1, Pz-2 and Pz-3 and external network control points P10, P13 and P21 samples were taken at three points on all campaigns

	SFW (injection)	Pz-1 / Pz-2 /Pz-3 Native groundwater	Pz-1 / Pz-2 /Pz-3 during potable water injection	Pz-1 / Pz-2 /Pz-3 during SFW injection	External network (P10/P13/P21)
Codeine	<LOD (n=8)	<LOD (n=1)	<LOD (n=2)	<LOD (n=8)	<LOD (n=7)
Erythromycin	see Table 17	<LOD (n=1)	<LOD (n=2)	see Table 17	see Table 17
Pentachlorophenol	<LOD (n=8)	<LOD (n=1)	<LOD (n=2)	<LOD (n=8)	<LOD (n=7)
Simazine	<LOD (n=8)	<LOD (n=1)	<LOD (n=2)	<LOD (n=8)	see Table 8
Terbuthylazine	<LOD (n=8)	<LOD (n=1)	<LOD (n=2)	<LOD (n=8)	see Table 9
Octylphenol	<LOD (n=8)	see Table 10	see Table 10	see Table 10	<LOD (n=7)
Nonylphenol	<LOD (n=8)	see Table 11	see Table 11	see Table 11	see Table 11
Diclofenac	<LOD (n=8)	see Table 12	see Table 12	see Table 12	<LOD (n=7)
Cotinine	see Table 13	<LOD (n=1)	see Table 13	see Table 13	<LOD (n=7)
Acetaminophen	see Table 14	<LOD (n=1)	see Table 14	see Table 14	<LOD (n=7)
Diuron	see Table 15	see Table 15	see Table 15	see Table 15	see Table 15
Isoproturon	see Table 16	<LOD (n=1)	<LOD (n=2)	see Table 16	<LOD (n=7)

Table 8: Summary results of simazine results in all conditions and sampling points

Simazine LOD = 5 ng/L	SFW	Pz-1	Pz-2	Pz-3	P13 (WELL)	P21 (WELL)	P10 (WELL)
NO INJECTION	< LOD	< LOD	< LOD	< LOD	6	2,8	< LOD
POTABLE INJECTION	< LOD	< LOD	< LOD	< LOD	< LOD	1,1	< LOD
	< LOD	< LOD	< LOD	< LOD	No sample	No sample	No sample
SFW INJECTION	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	No sample
	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	No sample
	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	No sample
	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	No sample
	< LOD	< LOD	< LOD	< LOD	< LOD	6	No sample

Table 9: Summary results of terbuthylazine results in all conditions and sampling points

Terbuthylazine LOD = 5 ng/L	SFW	Pz-1	Pz-2	Pz-3	P13 (WELL)	P21 (WELL)	P10 (WELL)
NO INJECTION	< LOD	< LOD	< LOD	< LOD	6	< LOD	< LOD
POTABLE INJECTION	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
	< LOD	< LOD	< LOD	< LOD	No sample	No sample	No sample
SFW INJECTION	< LOD	< LOD	< LOD	< LOD	6	6	No sample
	< LOD	< LOD	< LOD	< LOD	6	6	No sample
	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	No sample
	< LOD	< LOD	< LOD	< LOD	No sample	No sample	No sample
	< LOD	< LOD	< LOD	< LOD	5	< LOD	No sample
	< LOD	< LOD	< LOD	< LOD	< LOD	5	< LOD
	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD

Table 10: Summary results of octylphenol results in all conditions and sampling points

Octylphenol LOD = 25 ng/L	SFW	Pz-1	Pz-2	Pz-3	P13 (WELL)	P21 (WELL)	P10 (WELL)
NO INJECTION	< LOD	32	25	< LOD	< LOD	< LOD	< LOD
POTABLE INJECTION	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
	< LOD	< LOD	< LOD	< LOD	No sample	No sample	No sample
SFW INJECTION	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	No sample
	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	No sample
	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	No sample
	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	No sample
	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
	< LOD	< LOD	< LOD	< LOD	No sample	No sample	No sample

Table 11: Summary results of nonylphenol results in all conditions and sampling points

Nonylphenol LOD = 100 ng/L	SFW	Pz-1	Pz-2	Pz-3	P13 (WELL)	P21 (WELL)	P10 (WELL)
NO INJECTION	< LOD	450	440	< LOD	< LOD	< LOD	< LOD
POTABLE INJECTION	< LOD	No sample	< LOD	< LOD	< LOD	< LOD	< LOD
	< LOD	120	< LOD	< LOD	No sample	No sample	No sample
SFW INJECTION	< LOD	< LOD	110	< LOD	< LOD	350	No sample
	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	No sample
	< LOD	< LOD	150	< LOD	200	< LOD	No sample
	< LOD	< LOD	< LOD	< LOD	No sample	No sample	No sample
	< LOD	< LOD	360	< LOD	No sample	No sample	No sample
	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD

Table 12: Summary results of diclofenac results in all conditions and sampling points

Diclofenac LOD = 5 ng/L	SFW	Pz-1	Pz-2	Pz-3	P13 (WELL)	P21 (WELL)	P10 (WELL)
NO INJECTION	< LOD	63	48	< LOD	< LOD	< LOD	< LOD
POTABLE INJECTION	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
	< LOD	< LOD	10	< LOD	No sample	No sample	No sample
SFW INJECTION	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	No sample
	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	No sample
	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	No sample
	< LOD	< LOD	< LOD	< LOD	No sample	No sample	No sample
	< LOD	< LOD	31	< LOD	No sample	No sample	No sample
	< LOD	< LOD	18	< LOD	< LOD	< LOD	< LOD
	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD

Table 13: Summary results of cotinine results in all conditions and sampling points

Cotinine LOD = 10 ng/L	SFW	Pz-1	Pz-2	Pz-3	P13 (WELL)	P21 (WELL)	P10 (WELL)
NO INJECTION	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
POTABLE INJECTION	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD

	< LOD	< LOD	42	< LOD	No sample	No sample	No sample
SFW INJECTION	26	26	31	25	< LOD	< LOD	No sample
	25	29	31	25	< LOD	< LOD	No sample
	26	26	21	22	< LOD	< LOD	No sample
	32	32	35	48	No sample	No sample	No sample
	48	60	10	< LOD	No sample	No sample	No sample
	58	43	< LOD	< LOD	< LOD	< LOD	< LOD
	33	27	19	11	< LOD	< LOD	< LOD
	46	41	32	20	< LOD	< LOD	< LOD

Table 14: Summary results of acetaminophen results in all conditions and sampling points

Acetaminophen LOD = 10 ng/L	SFW	Pz-1	Pz-2	Pz-3	P13 (WELL)	P21 (WELL)	P10 (WELL)
NO INJECTION	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
POTABLE INJECTION	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
	< LOD	< LOD	< LOD	< LOD	No sample	No sample	No sample
SFW INJECTION	11	< LOD	< LOD	< LOD	< LOD	< LOD	No sample
	13	12	10	< LOD	< LOD	< LOD	No sample
	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	No sample
	17	< LOD	< LOD	< LOD	No sample	No sample	No sample
	17	< LOD	< LOD	< LOD	No sample	No sample	No sample
	37	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD

Table 15: Summary results of diuron results in all conditions and sampling points

Diuron LOD = 5 ng/L	SFW	Pz-1	Pz-2	Pz-3	P13 (WELL)	P21 (WELL)	P10 (WELL)
NO INJECTION	< LOD	11	13	< LOD	8	< LOD	12
POTABLE INJECTION	< LOD	< LOD	8	7	8	12	< LOD
	< LOD	< LOD	6	< LOD	No sample	No sample	No sample
SFW INJECTION	12	11	12	11	11	15	No sample
	9	9	9	12	6	15	No sample
	7	7	13	8	6	14	No sample
	9	10	13	21	No sample	No sample	No sample
	12	14	14	< LOD	No sample	No sample	No sample
	11	11	17	14	7	13	< LOD
	17	14	15	12	21	12	< LOD
	12	18	21	26	No sample	No sample	No sample

Table 16: Summary results of isoproturon results in all conditions and sampling points

Isoproturon LOD = 5 ng/L	SFW	Pz-1	Pz-2	Pz-3	P13 (WELL)	P21 (WELL)	P10 (WELL)
NO INJECTION	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
POTABLE INJECTION	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
	< LOD	< LOD	< LOD	< LOD	No sample	No sample	No sample
SFW INJECTION	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	No sample
	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	No sample
	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	No sample
	9	< LOD	< LOD	< LOD	No sample	No sample	No sample
	8	9	< LOD	< LOD	No sample	No sample	No sample
	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
	< LOD	< LOD	< LOD	< LOD	No sample	No sample	No sample

Table 17: Summary results of erythromycin results in all conditions and sampling points

Erythromycin LOD = 10 ng/L	SFW	Pz-1	Pz-2	Pz-3	P13 (WELL)	P21 (WELL)	P10 (WELL)
WITHOUT INJECTION	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
INJECTION (DRINKING)	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
	< LOD	< LOD	< LOD	< LOD	No sample	No sample	No sample
INJECTION (SFW)	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	No sample
	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	No sample
	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	No sample
	< LOD	< LOD	< LOD	< LOD	< LOD	No sample	No sample
	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
	31	< LOD	< LOD	37	21	16	< LOD
	< LOD	< LOD	11	< LOD	< LOD	< LOD	13

4.4 Trichloroethene and Tetrachloroethene: positive impact of SFW deep injection (concentration maps)

The following figures show the average concentrations detected in groundwater control points and the Llobregat River, in order to demonstrate the presence of these chlorinated solvents in concentrations above 10 mg/L in some parts of the aquifer. In this case, if the recharge water from sand filters was effective, there would be a dilution effect of anthropogenic concentrations of these compounds. In fact, in the area of Sant Vicent dels Horts, highly affected by chlorinated solvent contamination, was detected an improvement during continuous recharge episodes at infiltration ponds.

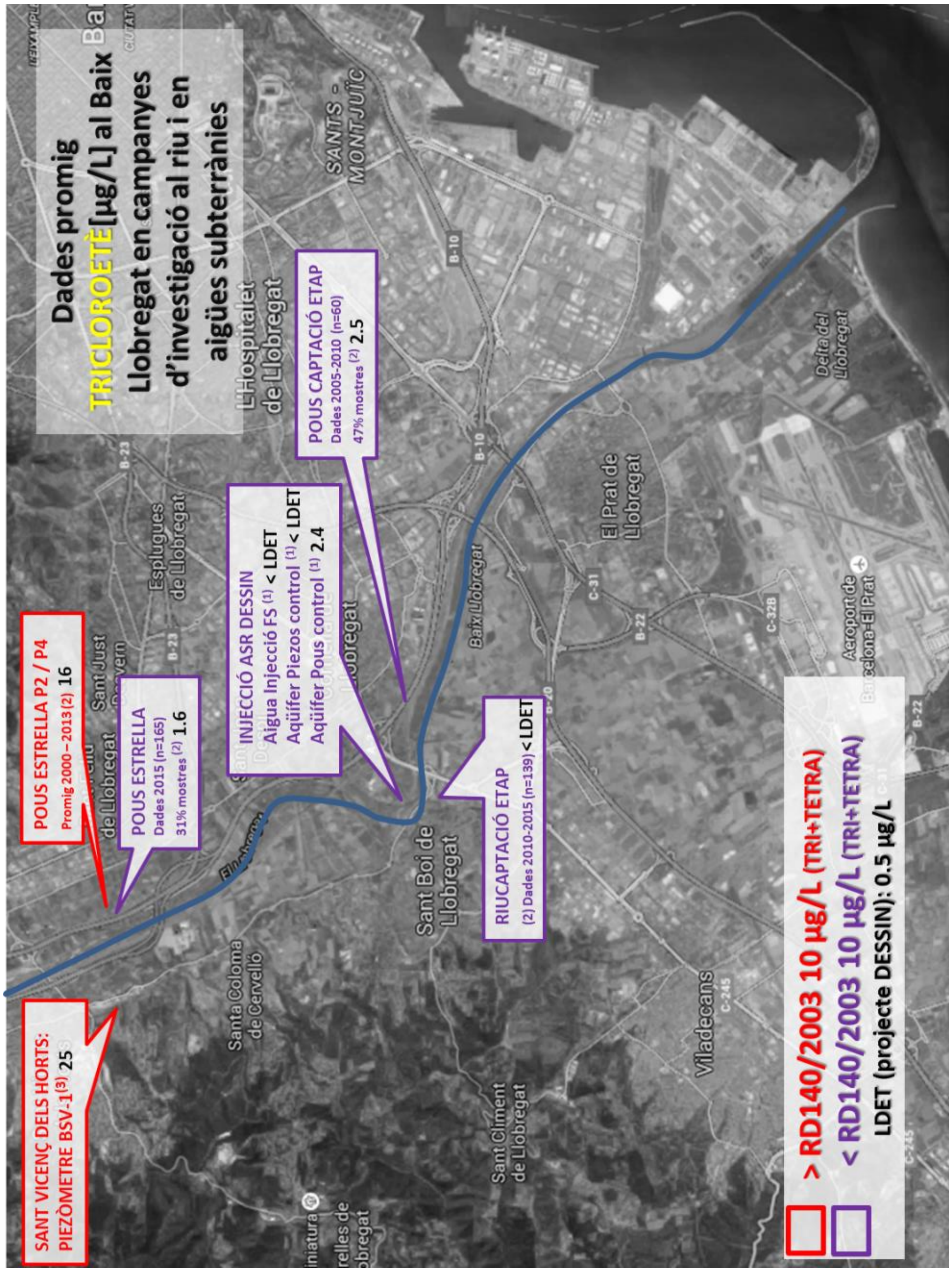

Figure 10: Trichloroethene concentration map in groundwater and surface water. Note: (1) information from DESSIN project (unpublished); (2) Aigües de Barcelona database and (3) ENSAT EU project

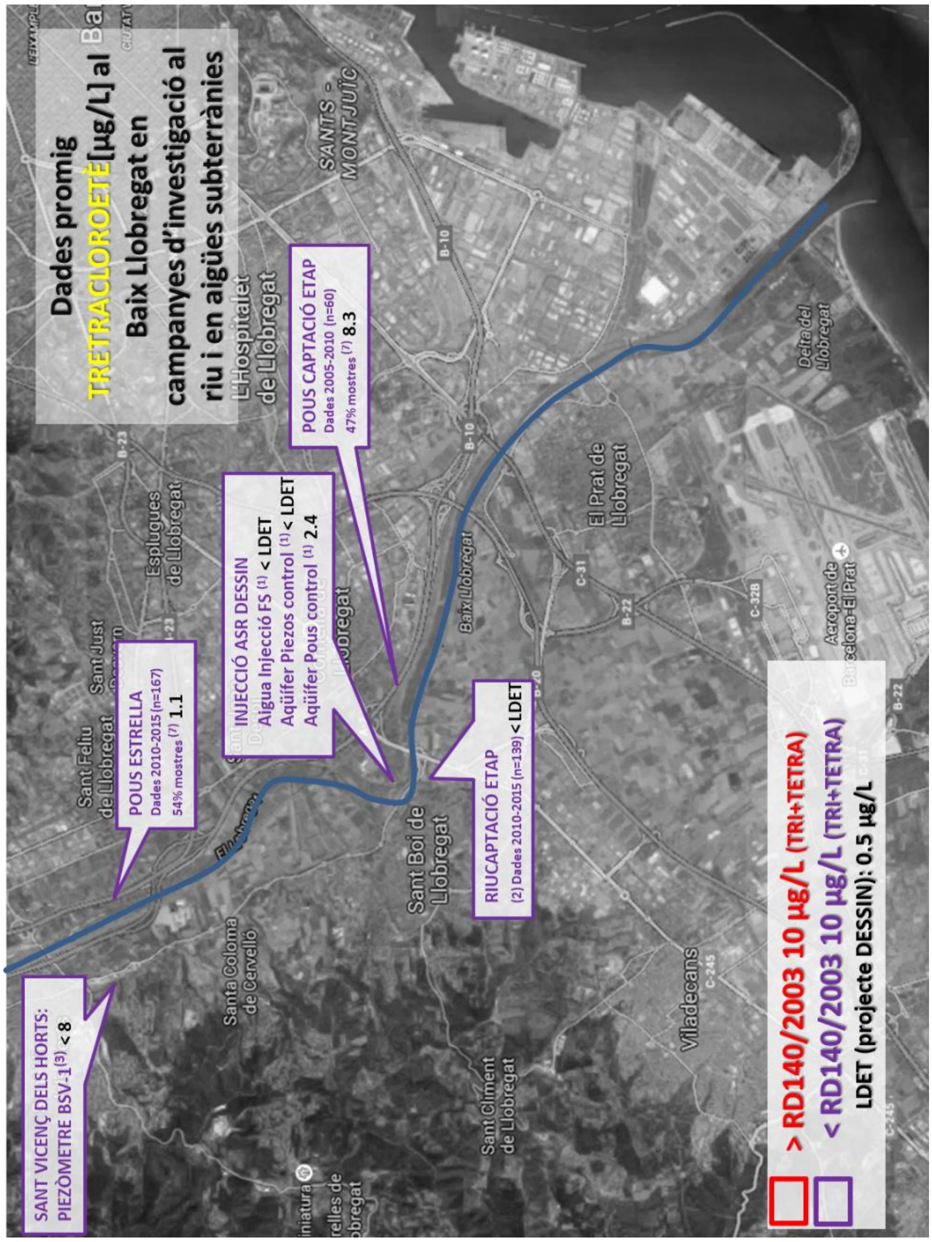

Figure 11: Tetrachloroethene concentration map in groundwater and surface water. Note: (1) information from DESSIN project (unpublished); (2) Aigües de Barcelona database and (3) ENSAT EU project

The tetrachloroethene and trichloroethene were no detected in sand-filtered water. The concentrations measured at external network control points (wells P10, P13 and P21) correspond to the historical contamination (background values) of BTEX and chlorinated solvents in groundwater. The values of trichloroethene are higher than those detected of tetrachloroethene, and in some cases, such as well named "Estrella" and Sant Vicenc dels Horts zone, the threshold of 10 mg/L for drinking water (RD 140/2003) was exceeded. The fact that these compounds are not present in detectable concentrations in SFW would explain their dilution in the aquifer sectors of Cornellà and Sant Joan Despí.

4.5 Emerging organic contaminants: reference values at Lower Llobregat study area (concentration maps)

This section will focus on the results of the compounds that present concentrations above the detection limit from the laboratory of Aigües de Barcelona (AB), which were: cotinine, acetaminophen, diuron, isoproturon and erythromycin. The first two compounds are not regulated, while diuron and isoproturon have reference values in EU legislation (EQS, Environmental Quality Standards, listed in Annex A of priority substances in the Water Framework Directive). The Table 18 shows the average values measured in sand-filtered water (SFW), where it is assumed that the concentrations below the detection limit are equal to ½ the set threshold.

Table 18: Comparative analysis between SFW and EQS standards

Compound	Average value in SFW [ng/L]	Detection limit AB [ng/L]	EQS [ng/L]
Cotinine	36.7	5	Not included
Acetaminophen	13.7	5	Not included
Diuron	11.1	10	200
Isoproturon	31.4	10	200
Erythromycin	23.8	10	Not included

Given the number of references about diuron values found in previous studies in the area of Lower Llobregat, the results obtained in previous research projects and scientific articles have been represented graphically in order to give an overview of the presence of this compound in groundwater. Although there are no reference values for this substance in groundwater, it has taken the threshold of 200 ng/L referred to surface waters.

All data reported in river water and infiltrated water through MAR systems are below 50 ng/L, substantially lower than the current maximum value established in surface waters (200 ng/L). However, it has been represented the concentration of diuron at the output of the tertiary treatment in Baix Llobregat WWTP, with an average value of 218.7 ng/L. This value corresponds to treatment system installed in the plant, consisting of coagulation - flocculation, laminar clarification and advanced processes of filtration and UV disinfection. It is noted that the additional plant built in relation to seawater intrusion barrier (SIB) and equipped with ultrafiltration (50% of the volume) and reverse osmosis (50% of the volume) promote the elimination of additional diuron. The final concentration prior to injection wells in SIB has been quantified at 24.7 ng/L (see Figure 12). The Diuron concentrations in Sant Joan Despí ASR system are even lower, with values of about 10 ng/L in both recharge well and water quality control points.

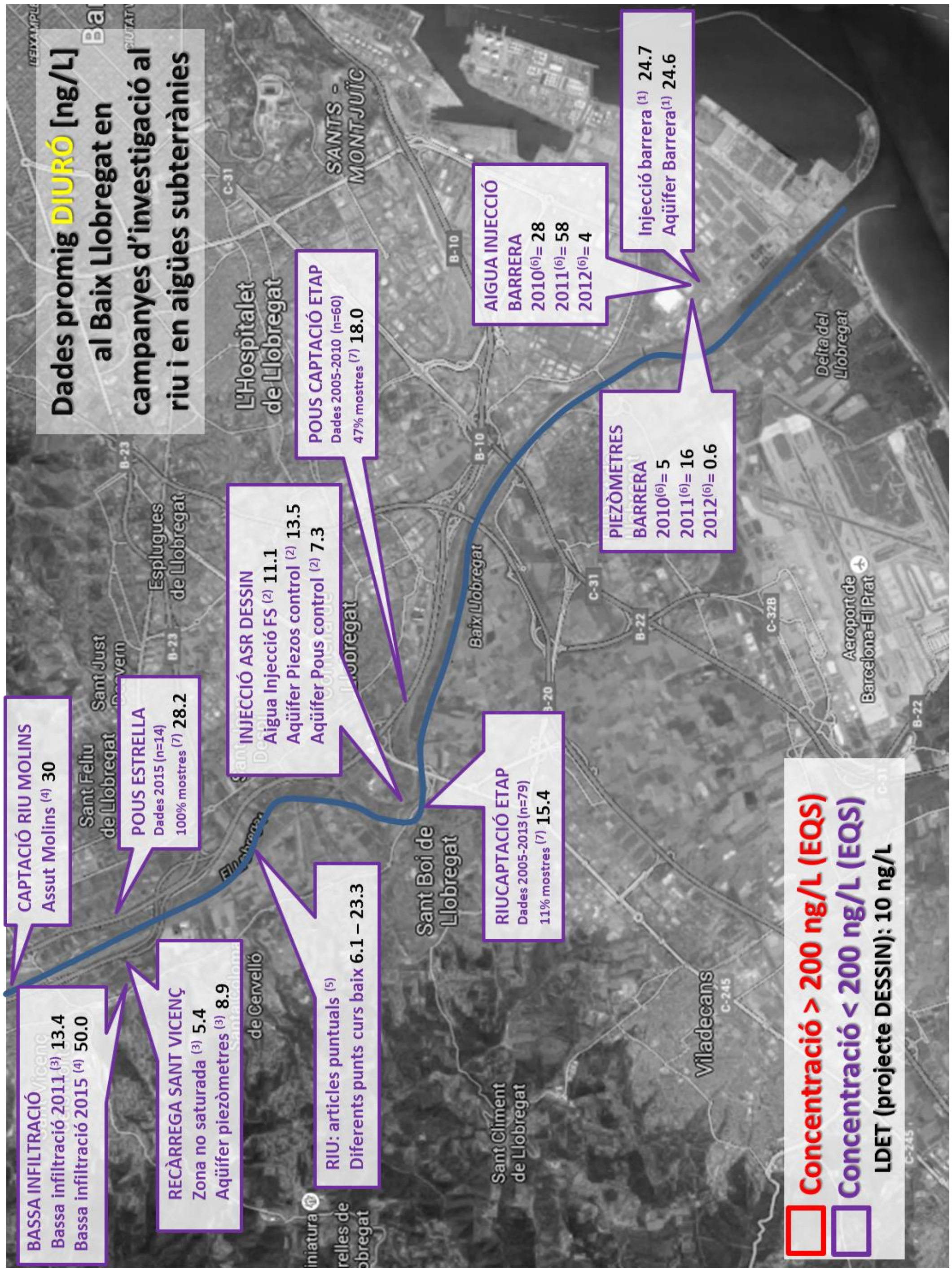

Figure 12: Diuron concentration map in groundwater and surface water. Note: (1) Teijón et al. (2010); (2) information from DESSIN project (unpublished); (3) ENSAT EU project; (4) DEMEAU EU project; (5) Masiá et al. (2015); (6) Cabeza et al. (2012); (7) Aigües de Barcelona database

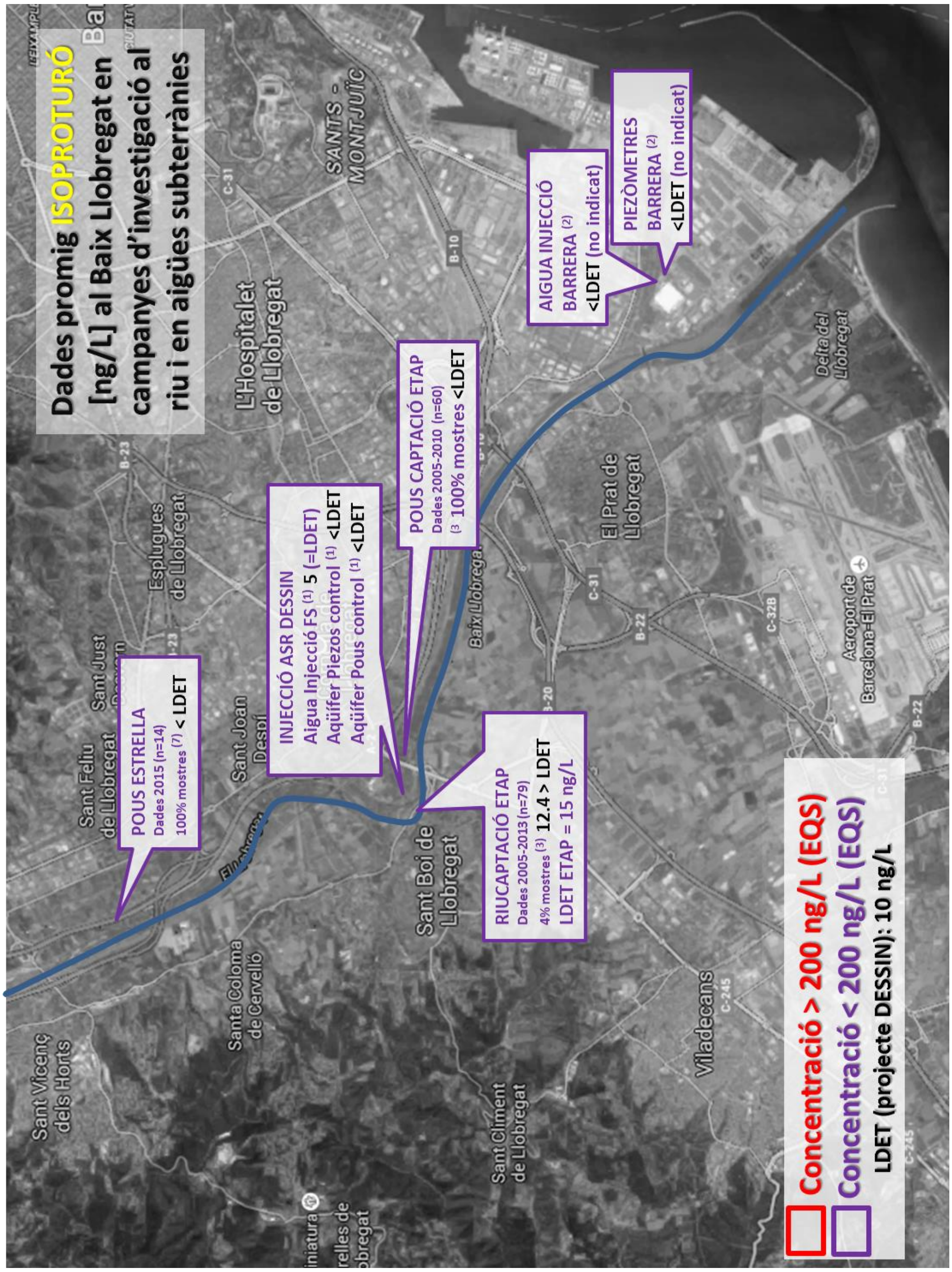

Figure 13: Isoproturon concentration map in groundwater and surface water. Note: (1) information from DESSIN project (unpublished); (2) Cabeza et al. (2012)

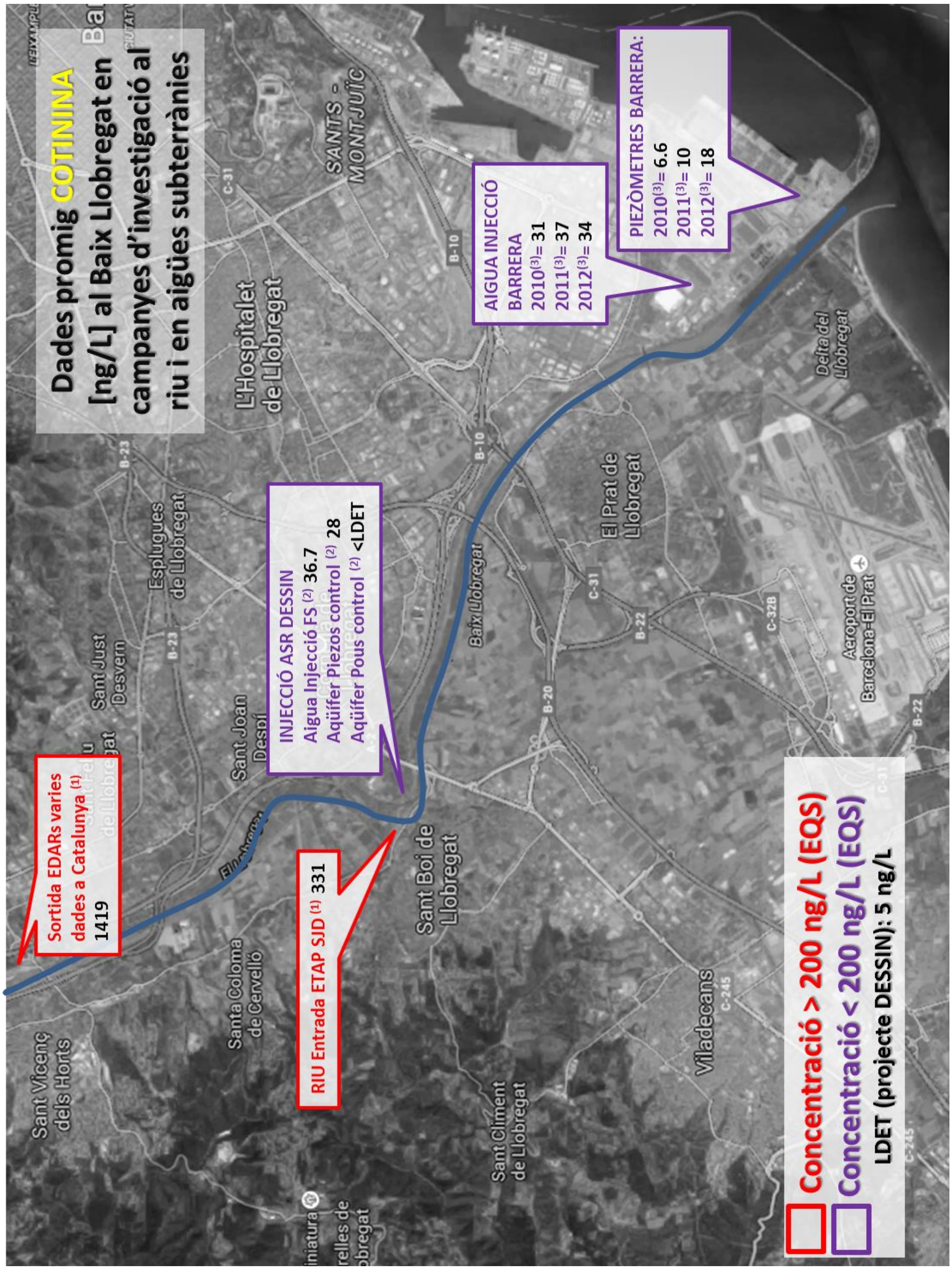

Figure 14: Cotinine concentration map in groundwater and surface water. Note: (1) information from HE0607 R+i Alliance project; (2) information from DESSIN project (unpublished); (3) Cabeza et al. (2012)

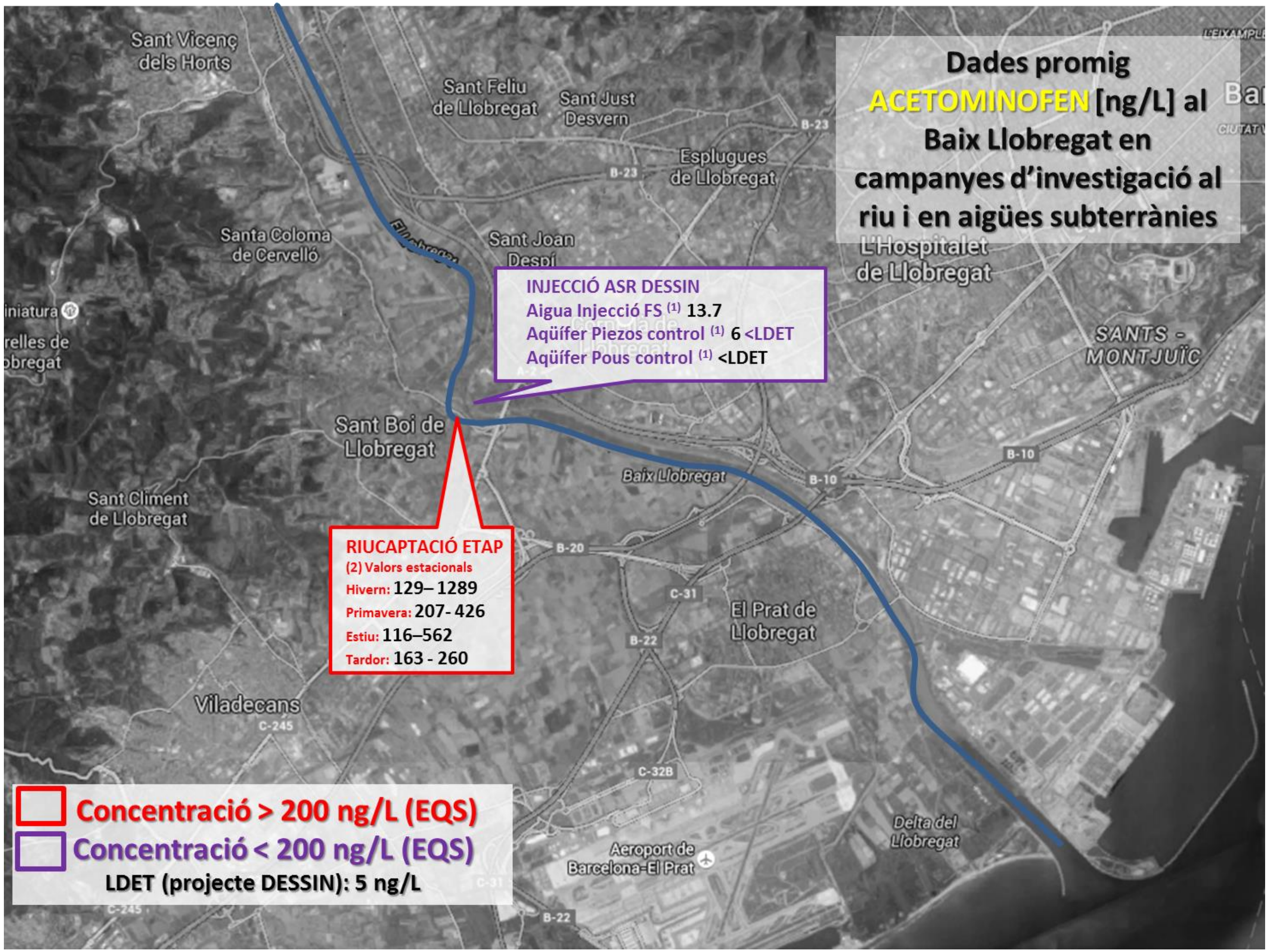

Figure 15: Acetaminophen concentration map in groundwater and surface water. Note: (1) information from DESSIN project (unpublished)

Figure 16: Erythromycin concentration map in groundwater and surface water. Note: (1) information from DESSIN project (unpublished); (2) Boleda et al. (2011); (3) Boleda et al. (2013)

None of the 5 substances in SFW exceeds this limit and its average values are substantially lower: 11 ng/L of Diuron, <10 ng/L of isoproturon, 37 ng/L of cotinine, 14 ng/L of acetaminophen and <10 ng/L of erythromycin. It is considered that these concentrations are very low and close to the detection limit of the laboratory, between 5 and 10 ng/L, depending on the compound.

In all consulted publications in relation to Llobregat River, the concentrations of acetaminophen and cotinine are greater than 200 ng/L (red boxes in concentration maps).

4.6 What are the toxicity bioassays?

There are a plenty of potentially anthropogenic pollutants that may be released to natural waters. They are present in very low concentrations (ng/L or mg/L) in waste water treatment effluents and drugs (human and animal farm), pesticides (herbicides, fungicides, and biocides), personal hygiene products, industrial waste and chemicals additives of different types. In recent decades, there is a debate on the impact of these substances on ecosystems, including the effect on biota and humans. Moreover, there has been progress in analytical techniques to identify and quantify these compounds (mostly organic), resulting in increasing equipped commercial laboratories.

Given the wide range of substances existing in aquatic environments, it is impossible to detect and quantify all of them. In addition, the cumulative effects of inhibition or synergies in the mixture of compounds may not be assessed by the individual quantification of each substance. For the scientific community, operators and managers of water quality, it is desirable to measure total toxicity in order to assess the overall impact on living organisms.

The toxicity bioassays appeared to respond to pollution thresholds set out in the annexes of the Water Framework Directive (WFD), specifically established in the "Environmental Quality Standards (EQS)". Some of them have been standardized and are accepted at national, European and international level. The bioassays are biological tools to quantify the effect (positive or negative) of a compound or a mixture of compounds in living organisms or in their components.

Toxicity can be evaluated in the laboratory by using living organisms and determining the threshold above which these organisms begins to present effects. Therefore, toxicity bioassays provide integrated information about environmental samples (water, sediment, soil). These tests can be used in living organisms, such as fish, invertebrates, plants and algae, bacteria, cells, cellular organisms, biochemical reactions, DNA or RNA.

Moreover, there is a great variety of indicators to estimate the degree of toxicity in organisms: mortality of individuals, growth inhibition, and inhibition of metabolic reactions such as photosynthesis, fluorescence, changes in reproductive rates or viability of new individuals, among others.

There are two main areas of application of toxicity tests:

- To determine the concentration at which a compound is toxic for an organism in order to set thresholds in water bodies.
- To know the integrated toxicity of a water sample without determining each compound separately.

The second application would be a revolution in the detection and quantification of compounds at analytical level, as it could reduce the number of compounds to be determined in water samples, with the concept of integrated toxicity assays.

4.7 Diuron as a reference compound in bioassays

There is a concept named “toxic equivalency” in order to evaluate the toxicity of a sample of unknown composition. The idea is to estimate the degree of toxicity of a sample in units of equivalent concentration of diuron. Therefore, it is possible to assimilate the responses of organisms due to known concentrations of diuron.

An example of application corresponds to the bioassays of the algae *Pseudokirchneriella subcapitata* (see Figure 17). The tests measured the inhibition of photosynthesis in individuals in contact with the “field” water sample, and the obtained reaction is compared with the same degree of response observed from a known concentration of diuron. There are other compounds such as atrazine or isoproturon that may also be used in inhibition experiments to determine the effects of compounds in water.

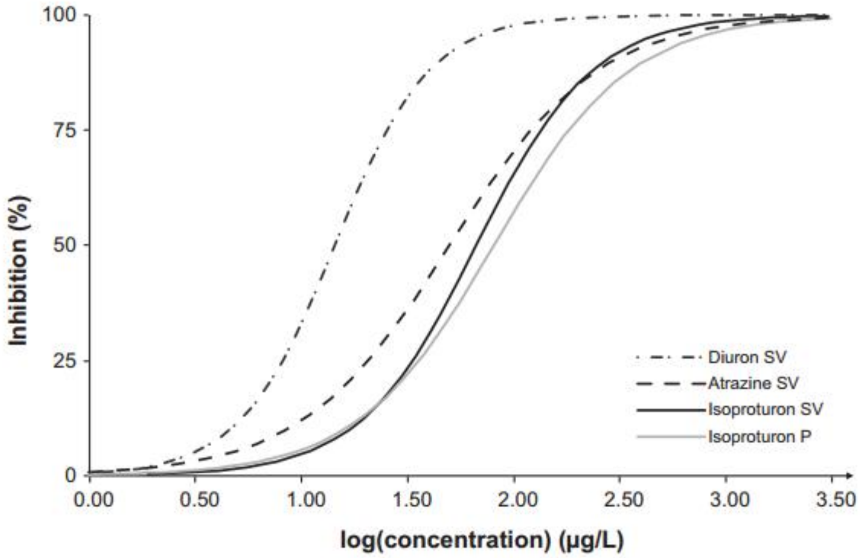

Figure 17: Dose-response curve for different types of algae and photosynthesis inhibitors (Copin and Chèvre, 2015). Note: dashed line: diuron, S. vacuolatus. Black dashed line: atrazine, S. vacuolatus. Continuous black line: isoproturon, S. vacuolatus. Continuous gray line: Isoproturon, P. subcapitata

4.7 Application to bioassays in Llobregat MAR experiences

This section gathered the works carried out in collaboration with the project DEMEAU (Eawag Center in Switzerland). At national level, there is trend for lowering the EQS thresholds for priority substances. Specifically, for diuron, there is a proposal to diminish the initial value from 200 ng/L to 20 ng/L.

In this context, the Eawag research group are working on designing and demonstrating the feasibility of bioassays to fulfil the requirements of environmental directives in natural waters. The bioassays are positioning as an applicable tool to detect the toxicity of water in an integrated way in complex mixtures of compounds in several concentrations. They are based on detecting changes in the activity of living organisms sensitive to these compounds, and biological mechanisms such as fluorescence, growth inhibition or mortality of individuals.

Regarding this collaboration, different bioassays were performed to the water coming from San Vicente dels Horts system (SVH). Figure 18 represents the results for 8 samples corresponding to the infiltration ponds. Vertical axis refers to the inhibition of photosynthesis of algae for each of the eight water samples, expressed as DEQ (diuron equivalent concentration). The samples of Figure 18.A were taken in high-flow conditions in July 2014 (Inf 1 and Inf 2 correspond to duplicate samples of infiltrated water, while other points are piezometers located at San Vicente dels Horts recharge system). The samples that were taken in May (Figure 18.B) are representative of mixed infiltration conditions (infiltration channels).

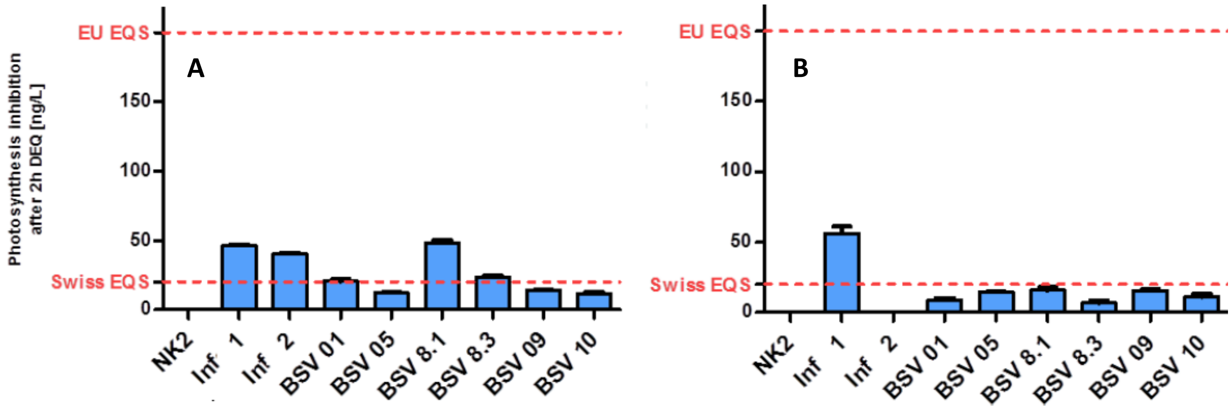

Figure 18: Inhibition of photosynthesis (after 2 hours of exposure) in SVH samples. Note: Left: Project DEMEAU first campaign - July 2014; Right: Project DEMEAU second campaign - March 2015. Results of diuron equivalent concentration are expressed in ng/L. NK refers to the negative control (HPLC water) that was analysed in the same conditions as the other samples. Red horizontal lines indicate the boundaries of the DMA (EU EQS) and the proposed regulations (Swiss EQS)

Finally, it can be seen that samples from San Vicente dels Horts present levels of toxicity in recharge water and piezometers below the EQS recommendation of 200 ng/L (diuron value). These results might be easily extrapolated to the ASR system with pre-potable water, given the similarity in concentrations and proximity at basin scale.

5. Microbiology, virus and stygofauna

5.1 Objectives

The objective of this section was to give an overview on how the recharge with pre-potable water (sand-filtered) can alter the microbiological composition of groundwater. On the other hand, it has been evaluated the potential use of microbiological parameters as artificial tracers of injected water plume and the capacity of the aquifer to retain and inactivate bacteriological contamination.

5.2 Methodology

5.2.1 Selection of measurable parameters

The selection of microbiological parameters to be included in groundwater sampling campaigns, the following criteria were taken into account:

- Criterion 1: RD140/2003 is the Spanish law that regulates the quality of drinking water. Specifically, the parameters related to bacteriological contamination are E. Coli, Enterococci, Clostridium Perfringens, coliform bacteria and bacterial counts at 22ºC. Except for the latter one, having a drinking threshold below 100 UFC (at DWTP output), the rest of the parameters need to be equal of 0 CFU/100 ml.

- Criterion 2: given the existing interactions between groundwater and surface water, it is considered that there are environmental microorganisms that can be naturally present into the aquifer. In this sense, the group of Aeromonas and Pseudomonas have been considered. Aeromonas is a genus of Gram-negative, facultative anaerobic, rod-shaped bacteria that morphologically resemble members of the family Enterobacteriaceae (Colwell *et al.,* 1986). Pseudomonas is another genus of bacilli that is also present in natural waters.

- Criterion 3: the analytical capacity of the Collblanc Laboratory (Aigües de Barcelona) was taken into account, in order to finally select the list of measurable microbiological parameters.

In Table 19 a list of the microbiological parameters selected in the project according to the criteria previously discussed is shown:

Table 19: Selection of microbiological parameters and their analytical method

Family	Parameter	Analytical method	Units
Indicator microorganisms	**Total Coliforms**	KIT COLILERT	MPN/100 mL
	E. Coli	KIT COLILERT	MPN/100 mL
	Clostridium Perfringens	Approved method AB MA/M-31	UFC/100 mL
	Bacterial counts at 22ºC	Approved method AB MA/M-07	UFC/ mL
Environmental microorganisms	**Aeromonas**	Method AB MA/M-11	UFC/100 mL
	Pseudomonas	Method AB MA/M-12	UFC/100 mL

5.2.2 Water sampling methodology

The water samples from control piezometers were pumped with a WATERRA device connected to a DERLIN (Polyoxymethylene) valve screwed to a semi-rigid PEDH tube (high density polyethylene), located at 5 meters below the water table. Prior to sampling, at least one full volume of each piezometer was recovered, with 10 minutes of continuous pumping and a flow rate between 5 and 7 L/min. The samples for microbiological analysis were taken in 250 ml bottles from Aigües de Barcelona Laboratory, and refrigerated at 4ºC until they were received at the laboratory. The different water components were measured in less than 24 hours from sampling. The analytical method applied by Aigües de Barcelona are shown in Table 19.

Figure 19: Water sampling procedure at SJD control piezometers

5.2.3 Sediment extraction procedure (sonication)

To evaluate the presence of environmental and indicator microorganisms in natural environment, groundwater-saturated porous sediment was sampled during the drilling work at one of the control piezometer (Pz-1). A representative mass of sediment was obtained at 25 and 40 meters, below the water table. A mass of sample was weighed (20 gr/100 mL) and it was put in contact with distilled water for sonication, a method widely used for the mobilization of microorganisms from the solid to the aqueous phase (Lunau *et al.,* 2005; Amalfitano and Fazi, 2008; Ugolini *et al.,* 2014). After sonication, the microbiological parameters listed in Table 19 were determined. Figure 21 illustrates the sample sampling and treatment procedure. The samples were analysed twice, hence, the final values correspond to the average of the two measures. The units of microbiological parameters analysed correspond to those measured in water samples.

Figure 20: Sediment samples and sterile sample bottles used during field works

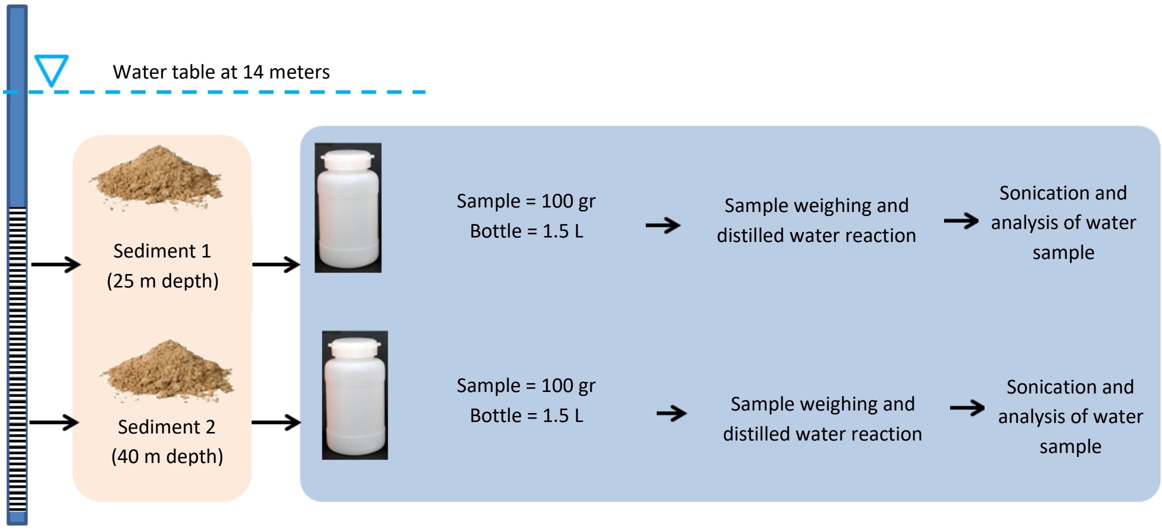

Figure 21: Sampling and treatment procedure for sediment sonication

It is important to keep in mind that the results derived from the microbiological analysis of sediments highly depends on the methodology used (Lehman, 2007), so the obtained conclusions should be taken as a first approximation to the sediment microbiology of the Lower Llobregat alluvial aquifer.

5.2.4 Luminiscent determination of ATP

During the demonstrative phase of the DESSIN project, Aigües de Barcelona Laboratory developed an ATP (Adenosine triphosphate) determination essay and some samples of the project were used to better understand the feasibility of this technique in studying the microbiological impact of managed aquifer recharge projects. The quantitation of ATP can be used for a variety of different purposes. Because ATP is the "coin" for energy transfer for almost all living organisms yet rapidly degrades in the absence of viable organisms, its existence can be used to identify the presence of viable organisms.

The first step for ATP determination involves the activation of the protein by ATP to produce a reactive mixed anhydride intermediate. In the second step, the active intermediate reacts with oxygen to create a transient dioxetane, which quickly breaks down to the oxidized product oxyluciferin and carbon dioxide along with a burst of light. When ATP is the limiting component, the intensity of light is proportional to the concentration of ATP. Thus the measurement of the light intensity using a luminometer permits the quantitation of ATP:

$$\text{ATP} + \text{O}_2 + \text{luciferin} \xrightarrow{\textit{luciferasa}} \text{AMP} + \text{PPi} + \text{oxyluciferin} + \text{light}$$

5.2.5 Virus characterization

Human adenovirus (HAdV) from human faecal sources is present in surface water and groundwater, but its transport in groundwater has not yet been widely studied (Stevenson *et al.,* 2015). Prevalent in urban stormwater runoff (Sidhu *et al.,* 2012), HAdV was also detected in a large river and its watershed (Corsi *et al.,* 2014; Rusiñol *et al.,* 2015) and has been found in groundwater (Futch *et al.,* 2010), possibly leaking into the subsurface from sewage pipes (Bradbury *et al.,* 2013). Because of its resistance to treatment such as chlorination and ultraviolet disinfection (Calgua *et al.,* 2014; Rodriguez *et al.,* 2008) and its persistence in sewage and treated water with a very long survival time, HAdV is a conservative pathogenic microorganism.

In order to detect the presence of these viruses in groundwater samples, each selected sampling point (sand-filtered water and Pz-1) were analysed twice. The presence of human adenoviruses has been carried out by using PCR (Polymerase Chain Reaction). The analysis was aimed to analyse the presence of human faecal contamination in the collected samples taking into account human adenoviruses as indicators. In this sense, samples of 10 L of water were gathered and sent to the Water and Food Contaminants Laboratory of the UB, where they were processed by using the organic flocculation method. After an extraction of viral nucleic acids (QIAmp® Viral RNA kit (QIAgen, Inc.)), the detection was performed by nested PCR (first sampling on October - November 2015) and quantitative PCR (second sampling on March of 2016). As a positive control of the analytical process, the bacteriophage MS2 was added to each one of the samples.

Figure 22: Pictures of the first virus sampling campaign (October – November 2015)

5.2.6 Stygofauna characterization

The methodology followed for the realization of this study is based on:

- Water and stygofauna sampling procedures in the existing groundwater monitoring network for the evaluation of the potential effects of artificial recharge in the alluvial aquifer. In particular, a field campaign was conducted between October and November of 2015, where a total of 9 points were sampled. During the sampling, the main physicochemical parameters (pH, electrical conductivity (CE), dissolved oxygen, Eh and temperature) were measured every 25 litres of pumped water. In addition, water samples was taken at the beginning and at the end of each sampling (at 25 and 300 L) for later analysis.
- The 300 litres of pumped water were filtered with a 50 µm sieve, and separated into two samples, the first from the extraction of 0-100 L and the second, from the filtration of the volume extracted from 100 to 300 L.

- Processing and identification of the stygofauna existing in the study area, by using a Motic SMX-168 magnifier (up to 50x) and a Motic BA410 microscope (in this study have been used up to 200x).

5.3 Results and discussions

This section shows the obtained results classified as a function of the hydrodynamic situation of the aquifer: (1) Natural conditions without artificial recharge (Green bars); (2) Potable water injection (blue bars); and (3) sand-filtered water injection (brown bars). It has been represented with a brown circle those value above the determination limit (e.g., > 10,000). The grey column of all figures is referred to the average concentration of microbiological components in Llobregat river water throughout 2014 (raw water, N = 51).

In order to give an idea about the natural abundance of microorganisms in groundwater ecosystems, the study of Griebler and Lueders (2009) has been taken as a reference. The total number of bacteria found in these ecosystems may vary by several orders of magnitude between 10^2 and 10^6 cells/cm^3 of groundwater and between 10^4 and 10^8 cells/cm^3 of sediment, due to sediment surfaces are geochemically more diverse and offer more ecological niches than groundwater (Bouwer and McCarty, 1984). The microorganisms analysed in the DESSIN project correspond mainly to bacteria (Table 20).

Table 20: Bacterial abundance in different subsurface habitats. Modified from Griebler and Lueders (2009)

Groups	Habitat	Contamination	Abundance (cells/cm^3)	Reference
Bacteria	Water from karst and cave system	No	10^2-10^5	Gounot (1994); Farnleitner *et al.* (2005)
	Sediment from cave waters	No	10^4-10^8	Gounot (1994); Rusterholtz and Mallory (1994)
	Water from granite and basalt systems	No	10^2-10^5	Stevens and McKinley (1995); Pedersen (1997)
	Groundwater	No	10^3-10^6	Ghiorse and Wilson (1998); Madsen and Ghiorse (1993); Pedersen (2000); Griebler (2001)
		Yes	10^3-10^7	
	Groundwater-saturated porous sediment	No	10^5-10^8	
		Yes	Up to 10^{10}	
	Vadose zone sediment	No	10^4-10^8	Brockman *et al.* (1992); Kieft *et al.* (1993)

The microbiology of groundwater samples collected from wells is subject to artefacts related to numerous sources associated with well construction and sampling. Artefact sources may include well diameter, well casing material, and age of the well, pump type and construction, purging duration, flow velocity, and casing/borehole colonization (Hirsch and Rades-Rohkohl, 1988). In this type of studies the ideal solution is referred to a combined approach, as used in DESSIN project, sampling both groundwater and cores samples, in order to take into account an overall vision of the aquifer microbiology.

5.3.1 Environmental microorganisms

Regarding Aeromonas and Pseudomonas, as they are environmental microorganisms, they are present in all conditions (Figure 23 and Figure 24). It is necessary to emphasize the significant change in the order of magnitude of environmental microorganisms found in the river with respect to the rest of sampled water. The values characterising Llobregat River are about 10^6 CFU/100 mL for Aeromonas and 10^5 CFU/100 mL for Pseudomonas, whereas in sand-filtered water most of concentrations ranged between 10^2 and 10^4 CFU/100 mL, respectively, giving rise to a noticeable reduction in environmental microorganisms. In the case of Aeromonas, during sand-filtered water injection the concentrations were clearly above the natural conditions values (one order of magnitude). These environmental microorganisms are not pathogenic in most cases (only *Aeromonas hydrophila*, *Aeromonas caviae*, *Aeromonas veronii* and *Pseudomonas aeruginosa* may pose certain health risk), and they could promote the degradations of organic and inorganic compounds present in water environments (Shah, 2014; Rana *et al., 2015*).

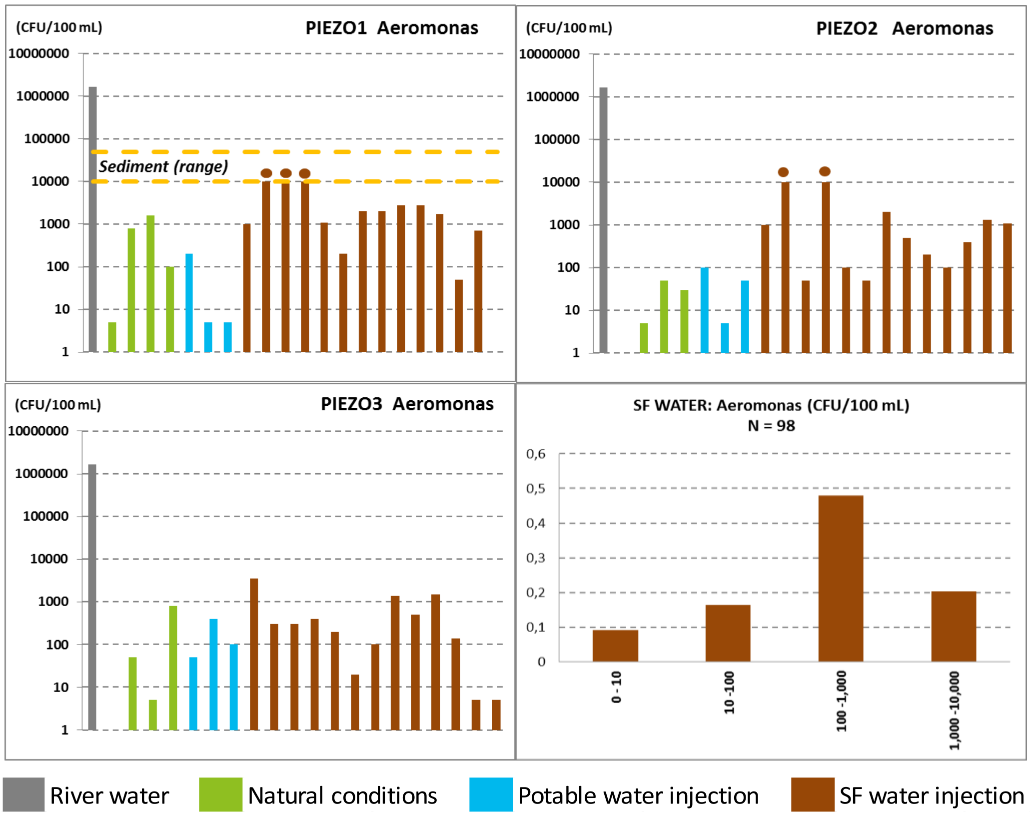

Figure 23: Results of Aeromonas depending on different recharge conditions and histogram for the values of sand-filtered water

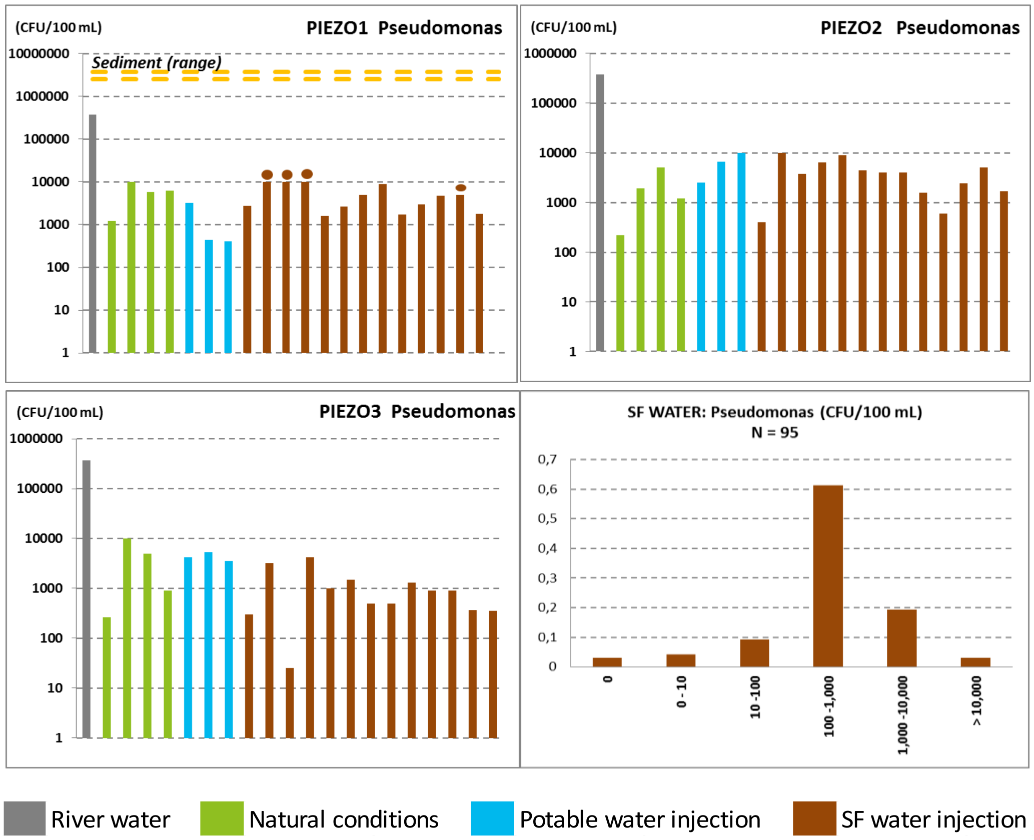

Figure 24: Results of Pseudomonas depending on different recharge conditions and histogram for the values of sand-filtered water

It is interesting to mention that concentrations of Aeromonas and Pseudomonas in the sampled sediments are higher (Figure 23 and Figure 24) than those obtained in groundwater during any of the recharge conditions (natural conditions, potable water injection and sand-filtered water injection). This trend is coherent with that observed in Table 20, where the total abundance of bacteria in water-saturated sediment (groundwater-saturated porous sediment) is, on average, 2 orders of magnitude higher than in groundwater. It should be noted that the Pseudomonas values in the sediment samples are clearly above the average concentration observed in Llobregat river water. The reasons that could explain this circumstance would require more in-depth investigations that are out of the project's scope.

5.3.2 Indicator microorganisms

Total Coliforms

The concentrations in Llobregat river water are between 10^5 and 10^6 MPN/100 mL, which is significantly reduced by applying conventional treatment, reaching values mainly from 10^1 to 10^3 MPN/100 mL (Figure 25). In natural conditions, total coliforms were present in native groundwater and they were also found in sediments analysed by sonication. During potable water injection, total coliforms reached values between 5^{-1} and 10^2 MPN/100 mL. In the phase of sand-filtered water injection, it can be seen a reduction of total coliforms as groundwater moves from the injection well to the control piezometers (from Pz-1, Pz-2 and Pz-3). If this comparative analysis is extended to external control points (P10 and P13) a complete elimination of bacteriological risk is checked (Figure 26).

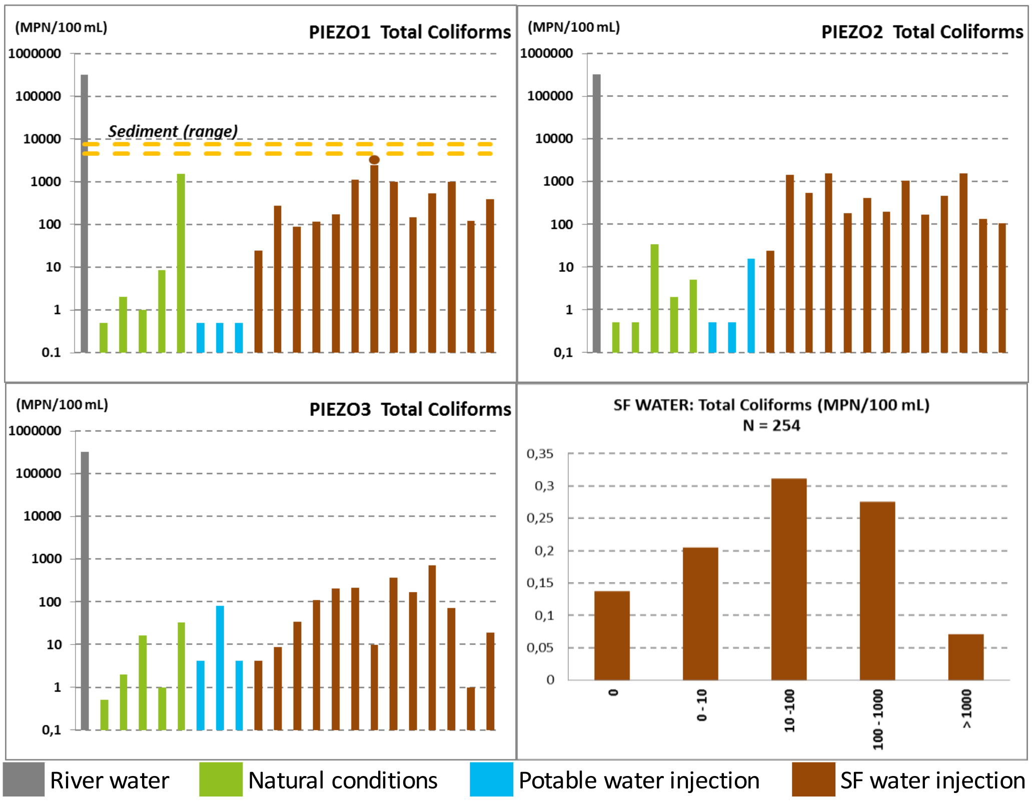

Figure 25: Results of Total Coliforms depending on different recharge conditions and histogram for the values of sand-filtered water

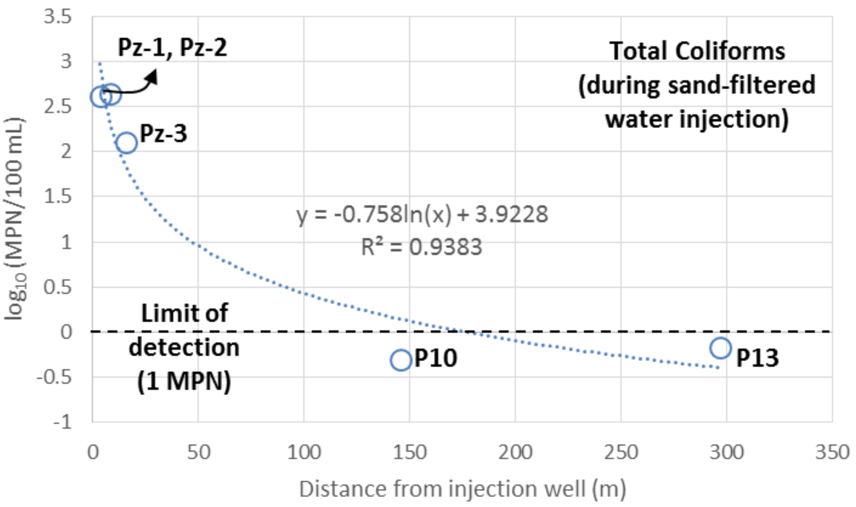

Figure 26: Total coliforms attenuation as groundwater moves from injection well to observation points

In section 6.3.4 it has been demonstrated that sand-filtered water plume arrived in P10 and P13, due to the presence of chlorates (only present in pre-potable water) above detection limit (40 µg/L). The reasons that would explain the arrival of these disinfection-by products and, at the same time, the elimination of those characterising bacteriological contamination are diverse and could not be explained through dilution alone, given the proximity of the observation points with respect to injection well (less than 300 meters). Reductions might be the result of bacteria retention and inactivation, natural attenuation processes observed in groundwater (Page *et al.,* 2015). The presence in the aquifer of interbedded clayey and silty layers could be partially limiting the groundwater flow, fostering natural attenuation capacity.

Bacterial counts at 22ºC

In Figure 27, it can be observed that average concentration in Llobregat river water ranges between 10^5 - 10^6 CFU/mL. Regarding sand-filtered water, it is observed that 50% of the samples are in the range of 10^3 - 10^4 CFU/mL. At piezometers Pz-1 and Pz-2, the concentrations are higher than those observed in piezometer Pz-3, coinciding with the Total Coliforms trend (Figure 25). It is remarkable that bacterial counts at 22ºC are also present in natural conditions, during potable water injection and analysed sediments.

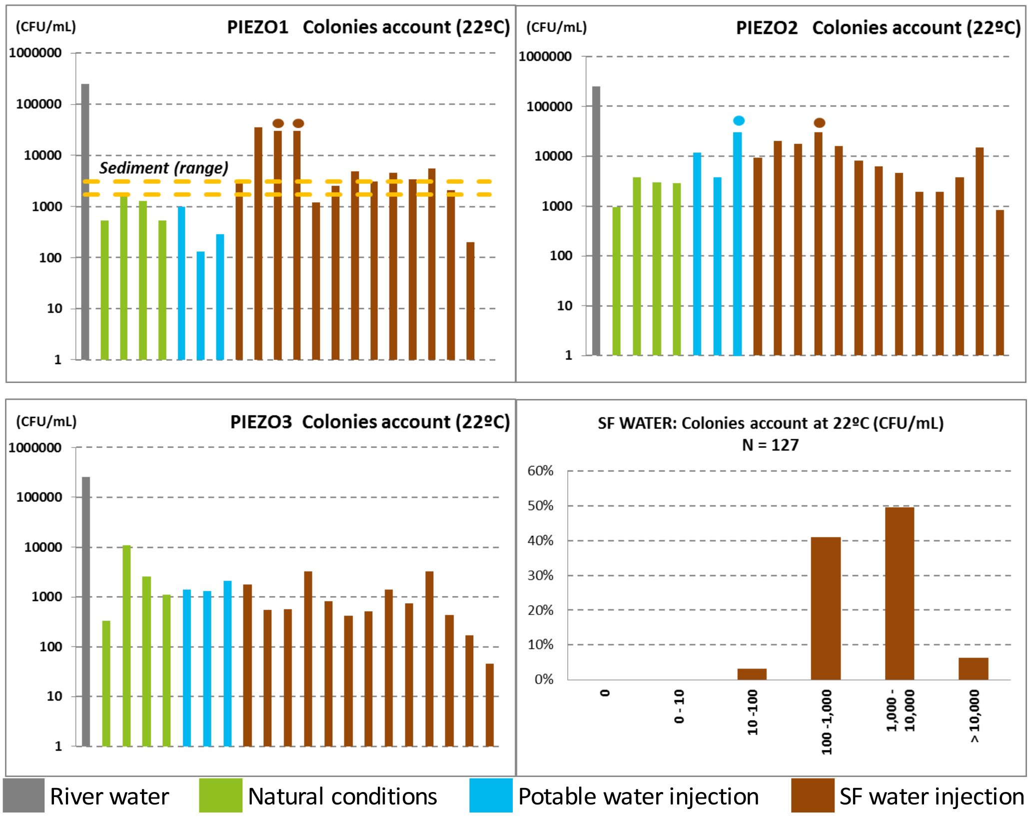

Figure 27: Results of bacterial counts at 22ºC depending on different recharge conditions and histogram for the values of sand-filtered water

Escherichia Coli (E. Coli)

During sand-filterd water injection E. Coli steadily decreases below detection limit (1 MPN/1000 mL) as groundwater moves from the injection point, being the piezometer Pz-1 the control point with a highest number of positive values (MPN > 1). These results point out the existence of a significant degradation of E. coli along the groundwater flow path. In addition, the concentration observed in Llobregat river water with respect to sand-filtered water shows the highest decrease of all studied indicator microorganisms, from 10^4-10^5 to 10^0-10^2 MPN/100 mL, respectively (see Figure 28). The results obtained are coherent with the concentrations observed in different aquifers globally (Lucena *et al.,* 2006). Regarding the sediment microbiology, it is worth noting the presence of E. Coli in the samples analyzed. This result could be related to the interactions between river water and groundwater. In this sense, E. Coli may have reached the aquifer in an episode of high-flow conditions in the river, recharging the aquifer with a water enriched in E.Coli, common in alluvial formations (Cox *et al.,* 2005).

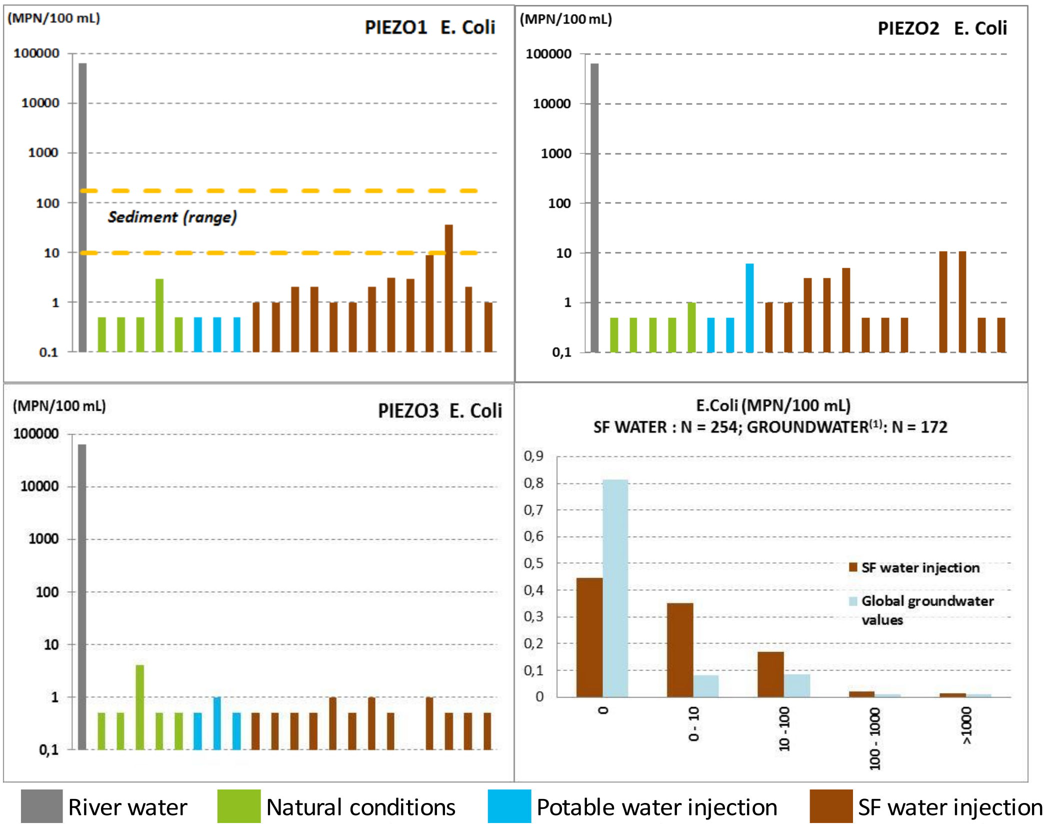

Figure 28: Results of E. Coli depending on different recharge conditions and histogram for the values of sand-filtered water and global groundwater (Lucena et al., 2006)

E. coli and total coliforms seem to be the best indicators of faecal contamination. The results obtained from both variables are coherent and stable enough to serve as indicators. There are several studies that have evaluated the survival rate of E. Coli in artificial recharge systems. Banning *et al.* (2005) determined that E. Coli's concentration was drastically reduced in non-sterilized ambients compared to sterilized ones. The RECLAIM WATER European project (http://cordis.europa.eu/result/rcn/46853_en.html) reached a similar conclusion in a study conducted in Adelaide (Australia), where it was found an E. Coli's reduction rate in unfiltered and filtered water (filter of 0.2 µm) of $-10\ \log{*}\mathrm{day}^{-1}$ and $-5\ \log{*}\mathrm{day}^{-1}$, respectively (Tandoi *et al.,* 2012). In Table 21 a summary is presented concerning reduction rates (T_{90}) in various MAR projects.

Table 21: Minimum reduction rate (T_{90}) of *E. Coli* in several MAR systems

Parameter	Days	Reference	Comments
T_{90}[1]	3	NRMMC-EPHC-NHMRC, (2009)	In-situ conditions in Australian aquifers, aerobic and anaerobic conditions at 20ºC
T_{90}	0.1	Tandoi *et al.* (2012)	Essays in diffusion chamber at Adelaide (Australia)
T_{90}	1	Gordon and Toze (2003)	Aerobic conditions. Study focused on the reduction rates of several pathogens. Same results obtained at 18ºC and 25 ºC.
T_{90}	3	Toze *et al.* (2002)	Aerobic conditions. Specific simulation study of artificial recharge system (22ºC)
T_{90}	1	Toze and Hanna (2002)	Aerobic conditions. Specific simulation study of artificial recharge system (22ºC)

Clostridium Perfringens

This indicator microorganism has been found below the detection limit in most of the hydrodynamic conditions (see Figure 29). The grey bar correspond to the average concentration in Llobregat River, ranging between 10^4 and 10^5 CFU/100 mL. The positive values in piezometer Pz-3 during the potable water injection could be an analytical error, given injecting sand-filtered water C. Perfringens was not detected. Abundance of microbial groups can vary between boreholes of the same aquifer as well as with depth, depending on physico-chemical conditions (Kölbel-Boelke and Nehrkorn, 1992). The results obtained in Lower Llobregat alluvial aquifer are consistent with those observed in global groundwater study (Lucena *et al.,* 2006), in which most of the aquifers (≈75%) presented negative values.

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[1] T_{90} = The time taken for 90% die-off

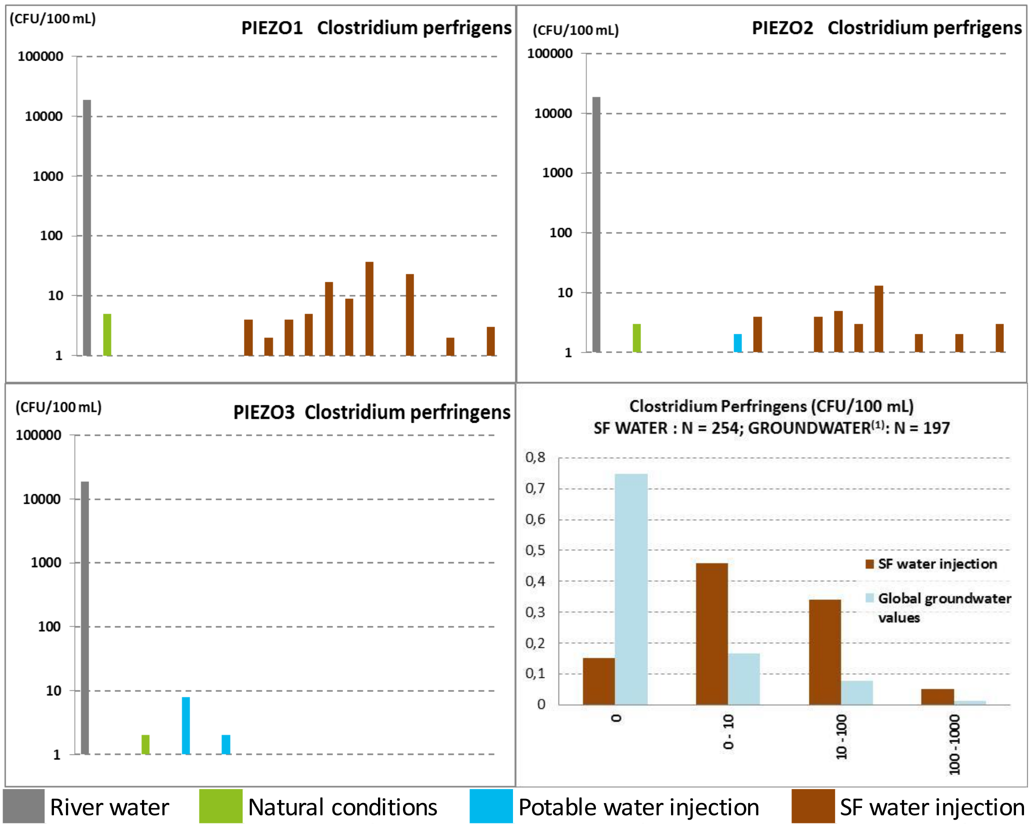

Figure 29: Results of Clostridium Perfringens depending on different recharge conditions and histogram for the values of sand-filtered water and global groundwater (Lucena et al., 2006)

5.3.3 ATP results and correlation analysis

The use of ATP is well-established in drinking water-related research and is used as a relievable method to estimate microbial activity (Hammes *et al.,* 2010). This method is fast, low-cost and easy to perform, thus is an ideal tool for monitoring purposes.

In Table 22 it can be seen the values of ATP found in the different phases of the recharge, as well as in the initial stages (river intake) and final (drinking water distribution) of the SJD DWTP. The samples corresponding to sand-filtered water are referred to routine sampling of the DWTP and those measured during DESSIN project. The most relevant data is the difference between the values of ATP in the river water (2544 pg/ml) and at the output of DWTP (33 pg/ml). Control piezometers (Pz-1, Pz-2 and Pz-3) show values slightly higher than those observed in sand-filtered water, even lower in the case of piezometer Pz-3 (Figure 30), which is coherent with the obtained results in previous section. It could mean that pre-potable water has limited impact in altering the microbial activity in the surrounding of the injection well. Even so, it would be necessary in-depth studies in order to conclude in a more robust way.

Table 22: Average ATP values during the different phases of artificial recharge and drinking water treatment

Type of sample	n	ATP [pg/ml]	Logarithm of ATP [pg/ml]
Raw water (Llobregat river)	17	2544	3,41
SFW (SJD DWTP)	9	149	2,17
SFW (DESSIN project)	12	124	2,09
Pz-1	15	227	2,36
Pz-2	15	288	2,46
Pz-3	15	101	2,00
Final phase of SJD DWTP	11	33	1,52

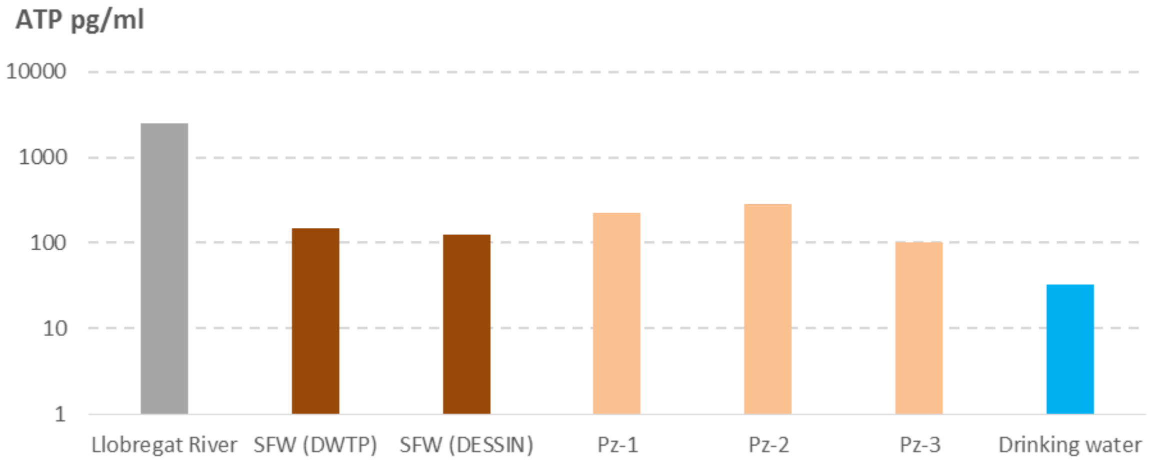

Figure 30: Average ATP values during the different phases of ASR operation and drinking water treatment

In a complementary way, the ATP data were compared to the other microbiological parameters to carry out a regression analysis. The objective was to see if the concentration of ATP can complement the information provided by microbiological parameters, both environmental and indicator. If so, it would be a faster control indicator of bacteriological contamination, and would allow a more exhaustive control of DWTP treatment processes.

Figure 31 represents the correlation matrix between the analysed variables. It is clear that three parameters are significantly correlated with the concentration of ATP, such as, Colonies at 22ºC, Aeromonas and Pseudomonas. These microbiological parameters are just referred to the more generic group, representing more families of microorganisms.

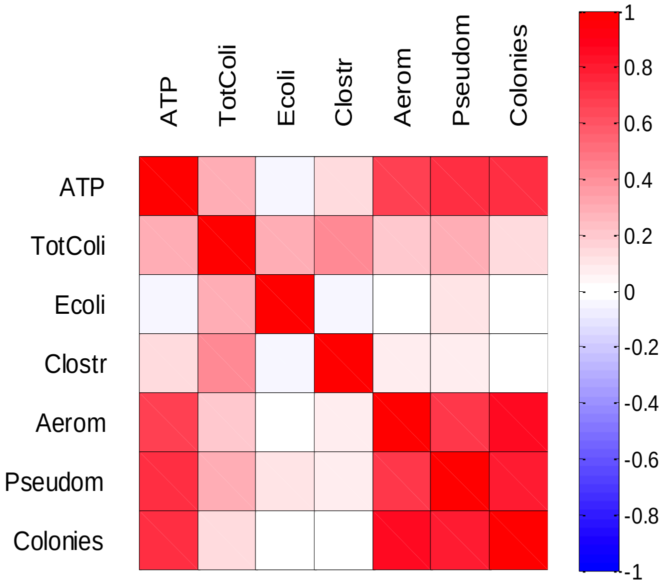

Figure 31: Correlation matrix between ATP and microbiological parameters (Pearson coefficient)

5.3.4 Human adenoviruses (HAdV)

Adenoviruses are common causes of respiratory illness, but most infections are not severe. They are very resistant to drinking water treatment processes and stable in the environment. These viruses can be detected in almost 100% of domestic effluents and those related to wastewater treatment plant with secondary biological phase, showing they are good faecal contamination indicators.

A study in Barcelona, tested samples of effluent from Sant Joan Despí DWTP next to the Llobregat River found a 2 $\log_{10}$ removal (two orders of magnitude decrease) of HAdV compared with the raw influent water; however, low concentrations of HAdV were still detected, whereas faecal bacterial indicators were no longer detected (Albinana-Gimenez *et al.,* 2006). These data have been used to complement the results obtained in DESSIN project.

Water samples corresponding to the first campaign (October - November 2015) were negative for human adenoviruses (Table 23). If there were adenoviruses in the samples, they were present in concentrations below limit of detection (low concentration). Because water sampling took place during high turbidity conditions (Figure 22), it is likely that the concentration of adenoviruses was lower than expected due to adsorption processes in particulate material. Given this situation, a new sampling campaign was carried out in March 2016 (Table 24).

Table 23: First adenovirus sampling campaign (October – November 2015)

Data	Sampling point	Expected conditions	Volume	Human adenovirus (genome copies/L)
26/10/2015	Piezometer Pz-1	ASR influence	10 L	< LOD
26/10/2015	Piezometer Pz-2	ASR influence	10 L	< LOD
17/11/2015	PIEZOMETER BSV-8.1	Infiltration ponds – no recharge	10 L	< LOD
17/11/2015	PIEZOMETER BSV-8.3	Infiltration ponds – no recharge	10 L	< LOD
17/11/2015	PIEZOMETER BSV-10	Infiltration ponds – no recharge	10 L	< LOD
28/10/2016	PIEZOMETER SC-15	Natural conditions	10 L	< LOD
26/10/2015	PIEZOMETER SC-35	Natural conditions	10 L	< LOD
28/10/2016	PIEZOMETER ESCAR4	Scarification influence	10 L	< LOD
28/10/2016	PIEZOMETER ESCAR8	Scarification influence	10 L	< LOD

Table 24: Second adenovirus sampling campaign (March 2016). Note: (1) Data from Albinana-Gimenez et al. (2006)

Data	Sampling point	Expected conditions	Volume	Human adenovirus (genome copies/L)
21/03/2016	Sand-filtered water	Higher presence of HAdV	4 x 10 L	3170
21/03/2016	Sand-filtered water	Higher presence of HAdV	4 x 10 L	682
21/03/2016	Sand-filtered water	Higher presence of HAdV	4 x 10 L	511
21/03/2016	Sand-filtered water	Higher presence of HAdV	4 x 30 L	1350
21/03/2016	Piezometer Pz-1	Lower presence of HAdV	4 x 10 L	2290
21/03/2016	Piezometer Pz-1	Lower presence of HAdV	4 x 10 L	97,7
21/03/2016	Piezometer Pz-1	Lower presence of HAdV	4 x 10 L	378
21/03/2016	Piezometer Pz-1	Lower presence of HAdV	4 x 10 L	514
11/2004 – 05/2006 (1)	Llobregat River water	-	200 – 300 L	400
11/2004 – 05/2006 (1)	Ter River water	-	95 – 105 L	290
11/2004 – 05/2006 (1)	Urban sewage	-	50 mL	14,000,000
11/2004 – 05/2006 (1)	GAC-filtered Llobregat River Water (DWTP)	-	900 – 1100 L	4.5

The second campaign showed results above the limit of detection and it reveals that the concentration of human adenovirus in sand-filtered water was higher, on average, compared to piezometer Pz-1, with 1428 gc/L and 819 gc/L, respectively. However, the high variability of the data would recommend to treat these results as a preliminary approach in absence of more precise information.

5.3.5 Stygofauna characterization

In the case of groundwater and, in particular, aquatic ecosystems, the set of indicators to determine their ecological quality is still not extended, because these ecosystems have been traditionally out of the scope of biological studies. However, the structure of groundwater aquatic communities can provide information on the quality and impacts of these types of ecosystems. In this sense, the study of macro-invertebrates in the rivers has allowed us to evaluate the ecological quality of surface water, and we will use the study of stygofauna (animals surviving in groundwater ecosystems) to evaluate which actions, both natural and anthropogenic, can affect the quality of their ecosystem.

The location of the different piezometers sampled is shown in Figure 32, and they are representative of distinct aquifer hydrological conditions:

- Control points not affected by aquifer storage and recovery experience (piezometers of Santa Coloma de Cervello – SC15 and SC35 - and those located in the zone of river scarification – SR4 and SR8);

- Control points affected by artificial recharge at infiltration ponds of Sant Vicenç dels Horts (BSV8.1, BSV8.3 and BSV10). At the date of the water sampling campaign they were stopped;

- Control points affected by the pre-potable water injection taking place in Sant Joan Despi DWTP (piezometers Pz-1 and Pz-2).

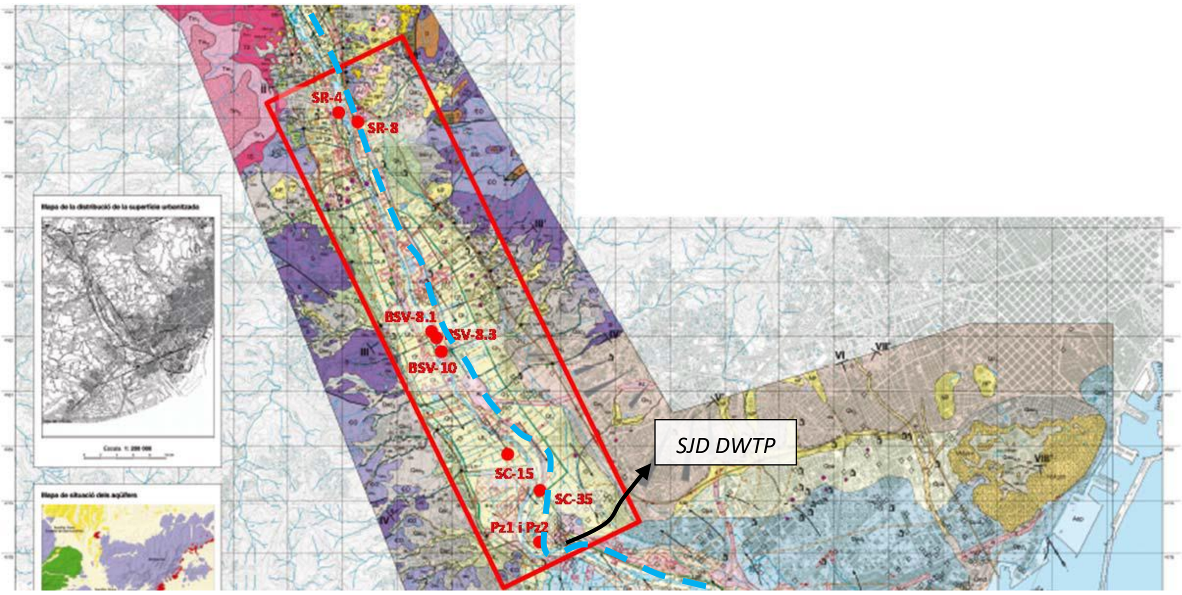

Figure 32: Situation map of the control points monitored during the stygofauna sampling campaign. Modified from (ICC, 2006). Legend can be viewed on www.icc.cat

The control points monitored in the study area have the following characteristics (Table 25).

Table 25: Main characteristics of the selected control piezometers. Notes: WL = water level

Hydrological condition	Control point	Depth (m)	Well screen (m)	WL (m)	UTM-X	UTM-Y
ASR	Pz-1 Pz-2	50 50	30-50 30-50	10.49 10.31	420404 420406	4578072 4578074
Infiltration pond	BSV8.1 BSV8.3 BSV10	16 10 22.5	13-15 7-9 6-20	6.9 6.9 9.04	418568 418568 418568	4581984 4581984 4581984
Natural conditions	SC15 SC35 SR4 SR8	38.2 30 11 16	4-38 16-24 - -	10.5 10.3 7.04 9.76	419908 420563 417020 417142	4579925 4579567 4586339 4585913

The specific objective of this sub-chapter is to analyse the stygofauna of the Lower Llobregat alluvial aquifer to evaluate the potential effects of the ASR system carried out in Sant Joan Despi DWTP. In addition, we have considered of special interest the following secondary goals:

- The characterization of the stygofauna existing in the study area, as it has never been described.

- The evaluation of the possible changes in the community of organisms due to the different hydrological situations previously identified. Particularly, the assessment of the differences between the three above-mentioned groups of piezometers and wells.

The results derived from the analysis of stygofauna samples are shown in Tables 26 and 27. In the first one, the organisms identified in the first 100 L of sampled water are shown, while in Table 27, the total number of organisms identified throughout the sampling is referred to the total filtered water (300 L).

Table 26: Stygofauna identified in the first 100 litres of sampled water

Stygofauna	ASR		Natural conditions				Infiltration ponds		
	Pz1	Pz2	SC-15	SC-35	SR-4	SR-8	BSV-10	BSV-8.1	BSV-8.3
Copepods									
Cyclopods	35	20	4	0	153	3	149	13	121
Harpacticods	0	0	0	23	9	2	122	7	11
Amphipods	0	0	0	0	6	0	52	37	51
Syncarides	0	0	9	0	0	0	7	9	7
Isopods	0	0	0	0	10	1	6	3	2
Ostracods	0	0	0	0	0	1	4	9	9
Hydracarina	0	0	0	3	0	0	0	0	0
Oligochaetes	10	8	8	0	156	8	19	53	90
Others	13	2	6	4	6	6	57	13	80
Nº of taxa	2	2	3	2	5	5	7	7	7
Abundance	49	20	24	24	180	16	355	66	280

Table 27: Stygofauna identified in all filtered water sample (300 litres)

Stygofauna	ASR		Natural conditions				Infiltration ponds		
	Pz1	Pz2	SC-15	SC-35	SR-4	SR-8	BSV-10	BSV-8.1	BSV-8.3
Copepods									
Cyclopods	62	26	4	2	245	14	179	22	296
Harpacticods	0	0	0	31	37	4	231	9	38
Amphipods	0	0	0	0	14	1	58	58	88
Syncarides	0	0	17	0	0	0	15	9	17
Isopods	0	0	0	0	16	1	9	4	6
Ostracods	0	0	0	0	0	1	4	9	16
Hydracarina	0	0	0	3	0	0	0	0	0
Oligochaetes	37	12	27	1	271	21	35	126	379
Others	15	7	11	6	8	7	30	17	66
Nº of taxa	2	2	3	4	5	6	7	7	7
Abundance	99	38	48	37	583	42	531	237	840

The organisms identified in the different piezometers are mainly crustaceans (copepods, amphipods, syncarides, isopods and ostracods), but also arachnids (hydracarina) and different types of oligochaetes (Figure 33 and Table 26 and Table 27). Some of these organisms are considered stigophiles, performing most of their life cycle in groundwater, as would be the case of most crustaceans. There are also others micro-organisms, which can be considered as stigoxenes, representing those who just develop part of the life cycle in groundwater or are accidentally found. This second group would be made of copepods, ostracodes, hydracarina and oligochaetes, whose degree of dependence on groundwater may be uncertain.

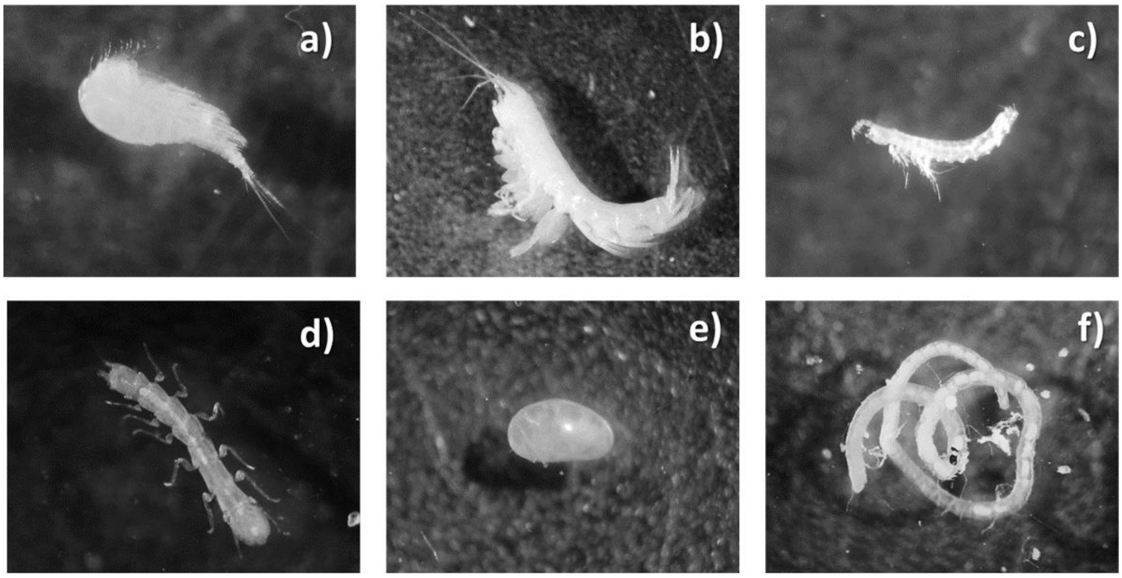

Figure 33: Some of the microorganisms detected in sampled groundwater for stygofauna characterization. Note: a) = copepods; b) = amphipods; c) = syncarides; d) = isopods; e) = ostracods; f) = oligochaetes

The control piezometers that present a greater diversity of taxa are those located in the infiltration ponds (BSV8.1, BSV8.3 and BSV10), where 7 out of 8 taxa considered in this analysis have been identified. Secondly, it has been found the piezometers characterising natural conditions (without artificial recharge) - SR-4, SR-8, SC-15 and SC-35, with a number of taxa between 3 and 6. Finally, the points near the pre-potable injection well (Pz-1 and Pz-2) are those with the lowest biodiversity, presenting only two different taxa (Table 26 and Table 27). It is important to note that the likelihood of capturing invertebrates depends upon the velocity induced by pumping, highly correlated with the aquifer type (Sorensen *et al.,* 2013).

Regarding the type of organisms, the most abundant are the copepods, mainly the cyclopods, and also the oligoquets, which are found in most of the sampled points (Table 26 and Table 27). There is another group of copepods, the harpacticods, only found in the piezometers without anthropic influence (SC-15, SC-35, SR-4 and SR-8) and those drilled at the infiltration ponds (BSV8.1, BSV8.3 and BSV10). The presence of amphipods, sincarides and ostracods is more limited, given they are all found in piezometers at infiltration ponds, and also in the control points characterising natural conditions, although their distribution is more heterogeneous.

In Figure 34, the micro-organisms have been classified into two groups, those indicative of the entrance of organic matter (Korbel and Hose, 2011) and, therefore, of recharge processes (cyclopods, ostracods and oligoquets), both natural and managed, and on the other hand, indicator organisms whose presence is characteristic of a good ecological status of groundwater ecosystems (Gibert *at al.,* 2009), such as harpacticods, amphipods, syncarides and isopods.

In the case of the piezometers Pz-1 and Pz-2 (ASR operation), the organisms mainly found are stigoxenes, due to it has been identified just a group of copepods (cyclopods), and oligoquets, also indicator organisms of the entrance of organic matter into the aquifer (Figure 34). In this sense, the influence of ASR operation is clearly detected.

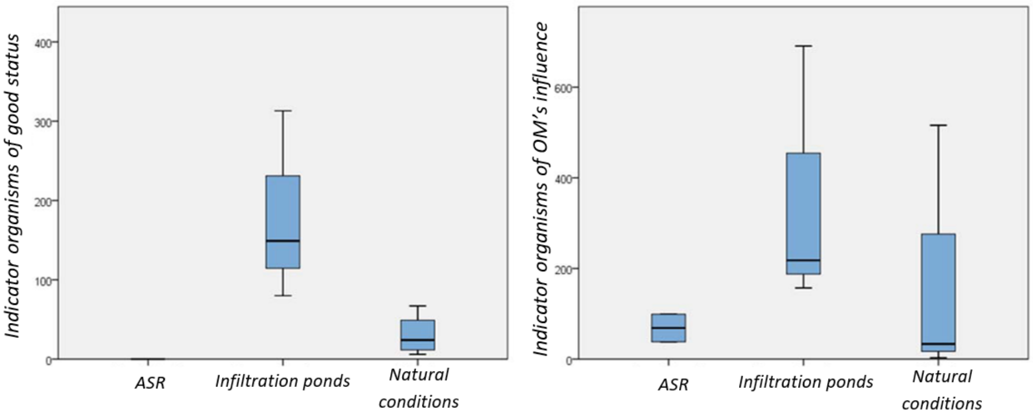

Figure 34: Comparison of the different hydrodynamic situations in the study area, in relation to the presence of indicator microorganisms of good ecological status (total number of harpacticods, amphipods, syncarides and isopods), and organic matter (OM) influence (total number of cyclopods, ostracods and oligochaetes)

6. Cleaning cycles at injection well P18

6.1 Objectives

The objectives of this section are to identify the optimum operating regime for the wells to be recharged with pre-potable (sand-filtered) water and to verify if the dynamic regime permits the recovery of native groundwater. To this end, it has been carried out an analysis of pumped well water (P-18 in Sant Joan Despí DWTP) after several recharge periods with variable volumes of water injected.

It has been set out two phases with different specific objectives:

- **Injection + Cleaning + Injection:** forced regime in order to evidence head losses at P-18 from the analysis of water table fluctuations.

- **Injection + Cleaning + Pumping:** usual operative regime with the aim of assessing the changes in water quality during the extraction period.

6.2 Methodology

Seven cleanings cycles (codes from 1 to 7) and an initial pumping (code 0) at P-18 were carried out, as indicated in Table 28. In the Annex D may be consulted the complete schedule of injection, extraction and shutdown phases from February 2016 until July 2016.

Table 28 : Schedule of cleaning cycles

Code	Date	Condition	Previous injected water [m^3]
# 0	29/02/2016	P18 – no influenced by injection or pumping during 2 consecutive months	0
# 1	23/03/2016	Injection + cleaning + injection	32,583
# 2	15/04/2016	Injection + cleaning + injection	59,030
# 3	03/05/2016	Injection + cleaning + injection	49,965
# 4	24/05/2016	Injection + cleaning + pumping	49,995
# 5	07/06/2016	Injection + cleaning + pumping	21,349
# 6	20/06/2016	Injection + cleaning + pumping	25,699
# 7	11/07/2016	Injection + cleaning + pumping	42,176

All cleanings were manually done by notifying the orders to the Sant Joan Despí DWTP. The field work methodology consisted in the following steps:

1. Stop of water injection and data protocol (see Annex D).

2. Preparation of water sampling devices:

- Multi-parameter data-logger connected to the flow cell
- Sample bottles for turbidity
- Sample bottles for complete determination in laboratory

3. Initial cleaning and water sampling (see Annex D)

4. Pumping with a duration of 15 minutes. The water resulting from the extraction was released to a drainage

5. Water sampling (complete determination) after 15 minutes of pumping

6. Pumping with a duration of 45 minutes. The water resulting from the extraction was released to the plant (valve change)

7. Water sampling from #0 to #3: Stop of cleaning

8. Water sampling from #4 to #7: pumping with a duration of 2-3 days and water sampling at the end of the period

9. Start of water injection

Table 29: List of analysed compounds

Inorganic compounds			Organic compounds	Microbiological parameters
Aluminium	Copper	Nitrates	Acetaminophen	Clostridium perfringens
Ammonium	Chromium	Nitrites	Codeine	Colony counts at 22 °
Antimony	Tin	Palladium	Cotinine	Total Coliforms
Silver	Strontium	Lead	Diclofenac	E. Coli
Arsenic	Iron	Potasium	Diuron	**Field data / PEM**
Barium	Phosphorus	Rubidium	Eythromycin	TOC
Beryllium	Gallium	Selenium	Isoproturon	Turbidity
Bismuth	Indium	Silicon	Nonylphenol	Suspended solids
Boron	Lanthanum	Sodium	Octylphenol	pH
Cadmium	Lithium	Thallium	Pentachlorophenol	Electrical conductivity
Calcium	Magnesium	Titanium	Simazine	Eh redox potential

Chlorates	Manganese	Vanadium	Terbuthylazine	Hardness
Chlorites	Molybdenum	Wolfram		
Cobalt	Nickel	Zinc		

6.3 Results and discussions

6.3.1 Turbidity

Turbidity was measured as an indicator of the relative amount of suspended solids present in groundwater that could contribute solid-bound analytes to dissolved phase concentrations. While turbidity is readily accepted as a relative measure of the suspended solids content of a water sample, the degree to which suspended solids affect light scatter is dependent upon the type of material suspended (Tease and Dowling, 2012).

Turbidity is important because it affects the selection and efficiency of treatment processes, particularly the efficiency of disinfection with chlorine since it exerts a chlorine demand and protects microorganisms and may also stimulate the growth of bacteria. In all processes in which disinfection is used, the turbidity must always be low—preferably below 1 NTU. It is recommended that, for water to be disinfected, the turbidity should be consistently less than 5 NTU and ideally have a median value of less than 1 NTU (WHO, 1997).

Similar values were not reached in groundwater until 1 hour of pumping (see Figure 35), always below the threshold of 10 NTU. This time is similar than the calculated by Ivahnenko *et al.* (2001) in the unconfined sand and gravel Kirkwood-Cohansey aquifer system (New Jersey, EEUU), with a value of 90 minutes. Turbidity varied by an order of a magnitude (or more) during the first 10 to 15 minutes of well purging. Turbidity was initially high, increased quickly in the first two to three minutes of pumping until a peak value was reached, then decreased, quickly at first, then gradually until a nearly steady state value was achieved (NTU ≈ 10). A large decrease in turbidity during well purging is typical of shallow wells (Gibs *et al.,* 2000).

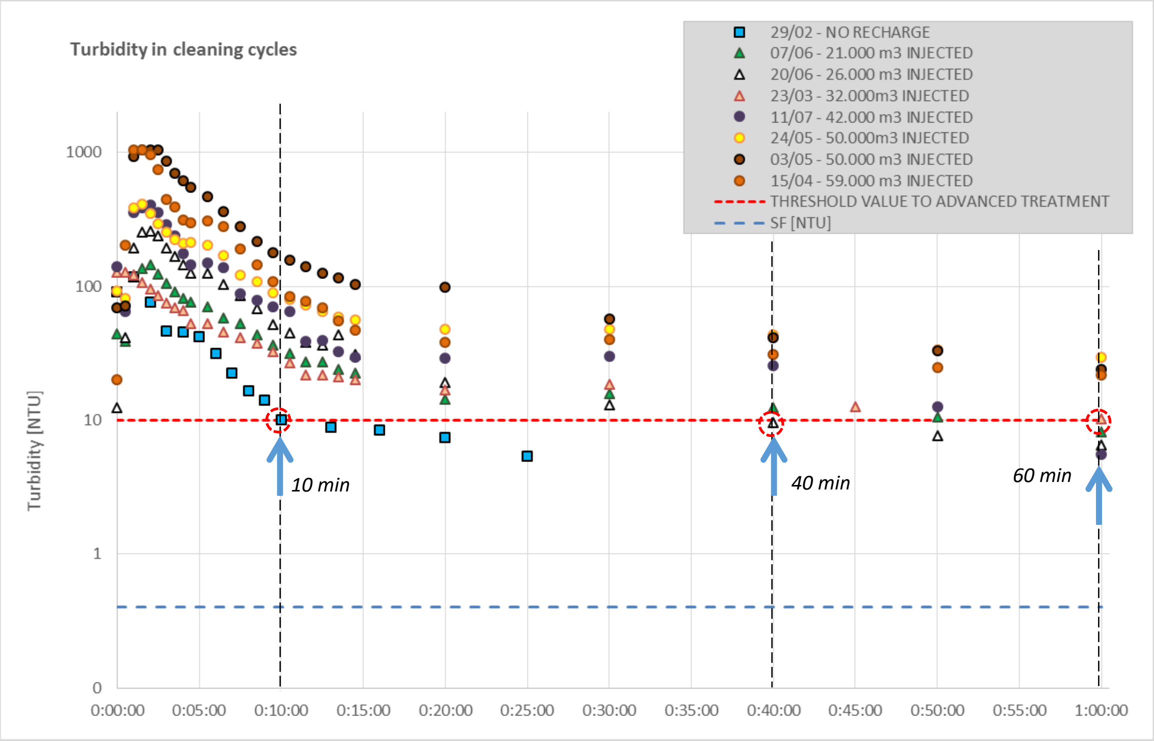

Figure 35: Turbidity during the first hour of cleaning at P18 well. Notes: three different conditions are distinguished in this figure, squares: initial cleaning after an inactive period of recharge and pumping; triangles: cleanings performed after injecting water from 21,000 to 36,000 m3; circles: cleanings performed after injecting water from 42,000 to 59,000 m3

As the steady state was approached, the minute-to-minute variability in turbidity decreased to less than ± 10%. It can be seen that the greater the volume of injected water the greater the time required to reach the threshold value of 10 NTU, reference value to advanced treatment. The changes in turbidity might be caused by particulates artificially mobilized from the well screen or surrounding aquifer matrix in response to the sudden changes in flow shear and water back siphoning from the discharge line into the well.

In Figure 36, it has been represented the evolution of the turbidity registered during the different cleaning cycles performed during DESSIN project along with the historical data from Azcón and Dolz (1978). The maximum turbidity values (of about 1000 NTU) are similar for both experiments, although historical values below 10 NTU are found much before than those relative to DESSIN project (5-10 minutes), even though the volume of injected water was higher (69,000 m^3). These differences could be explain for the hydrodynamic states of the aquifer prior to water injection (high or low flow periods) and the existence of variable extraction rates during cleaning cycles (Tease and Downling, 2012). It may also be related to differential accuracy and precision of turbidity measurements in each research project.

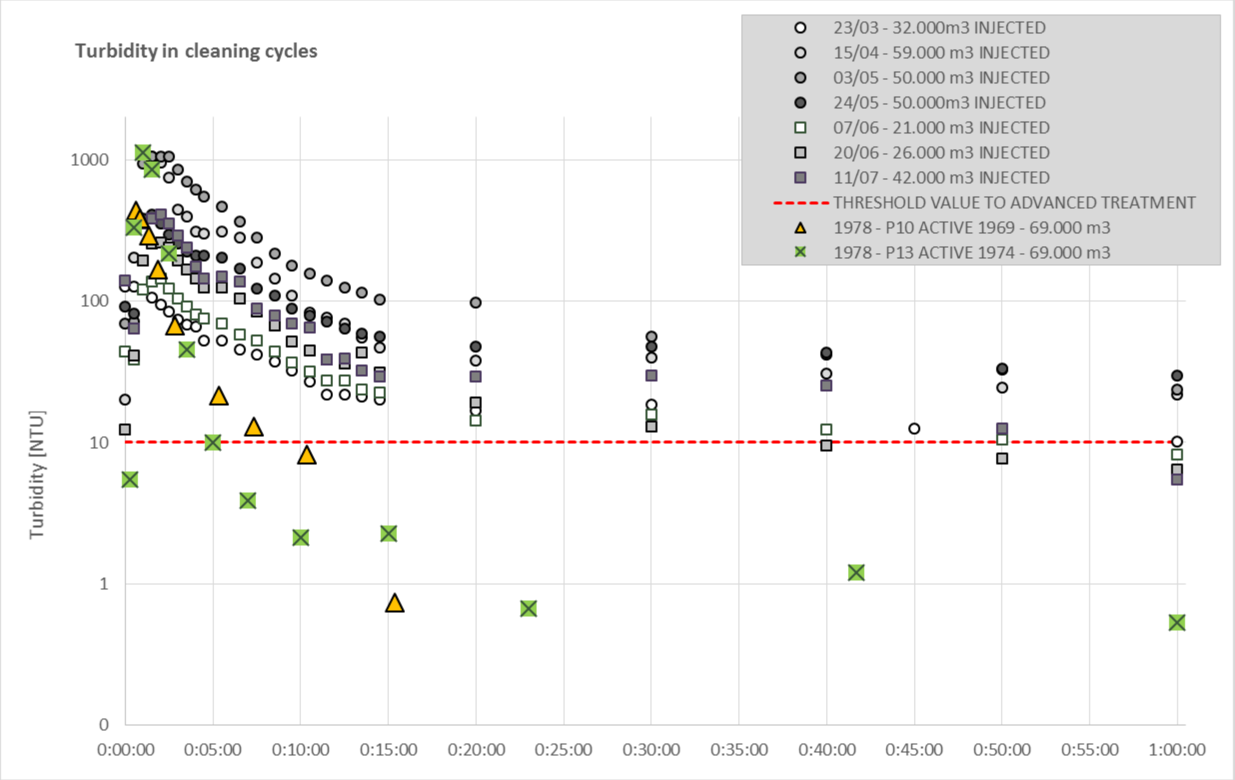

Figure 36: Turbidity during the first hour of cleaning and comparative analysis with historical data (1978). Note: two different conditions are distinguished in this figure, grey scale: cleaning cycles relative to DESSIN project; orange and green: historical data from Azcón and Dolz (1978)

6.3.2 Analysis of the aluminium, iron and manganese behaviour during cleaning cycles

Metals in surface water and groundwater exist in the form of particulate metals and dissolved metals. Any artificially introduced variability in the particulate load entrained in groundwater will thus result in a variation in the concentration of aluminium - Al, iron - Fe and manganese - Mn (Gibs *et al.,* 2000). Similar time-dependent curves as the observed for turbidity were identified for Al, Fe and Mn, but with much more variable values depending on the cleaning cycle. The highest values of Al, Fe and Mn correspond to July 2016 (11/07/2016), with a volume of injected water of 42,000 m^3 (Figures 37, 38 and 39). Of all the performed cleaning processes, the lesser variation was observed when the injected water was equal to 21.000 m^3 (07/06/2016), without a significant peak value in comparison to steady state concentration, reached after 1 hour of pumping.

The needed time to reach the maximum values found in sand-filtered water was 1 hour, except for manganese, with characteristic values of sand-filtered water after 10 minutes of pumping (Figure 39). This time (1 hour) coincides with the observed one in turbidity graphs (Figures 35 and 36) to fall below the threshold of 10 NTU. This physico-chemical behaviour is coherent with the scientifically proven relationship between turbidity and metal concentrations, in both particulate and dissolved fractions (Yao et *al.,* 2016; Gibs *et al.,* 2000). It could indicate that the occurrence of the three metals in sampled water might be directly related to suspended solids. This hypothesis will be validated with regression analysis.

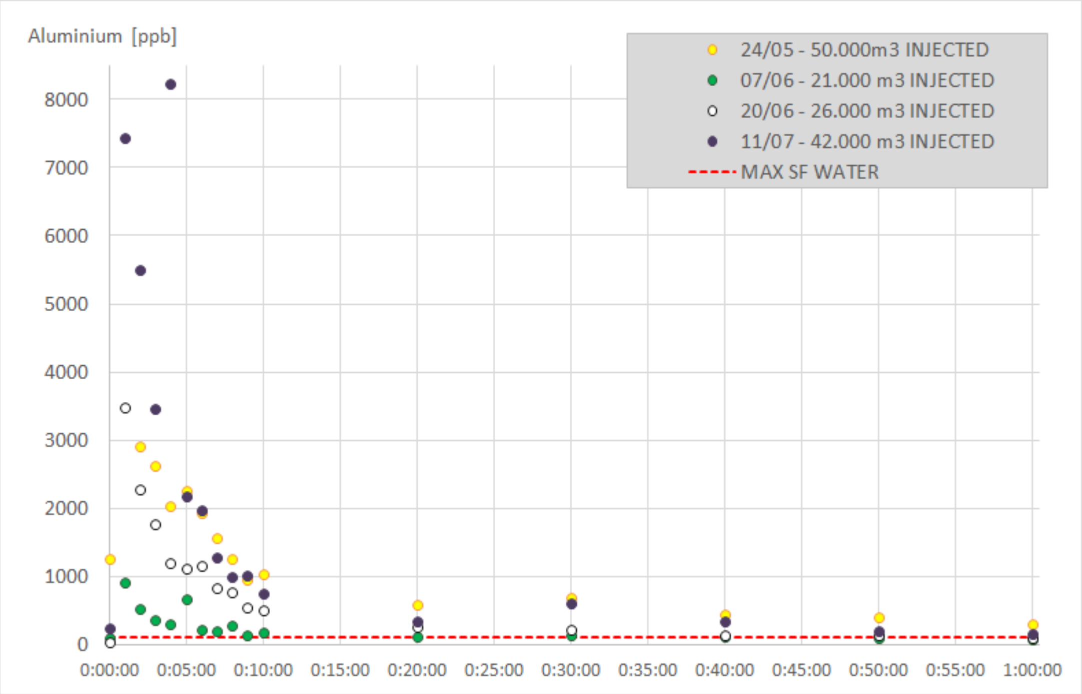

Figure 37: Aluminium values during the first hour of pump cleaning at P18 well. Note: SF = sand-filtered water. Note: ppb = µg/L

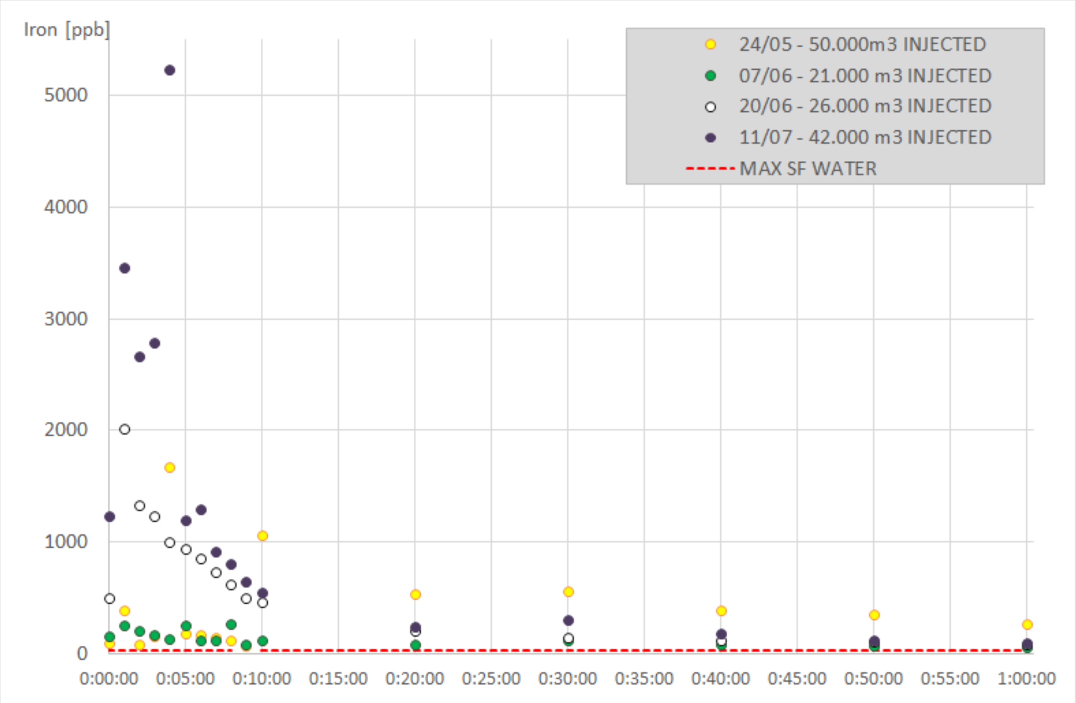

Figure 38: Iron values during the first hour of pump cleaning at P18 well. Note: SF = sand-filtered water

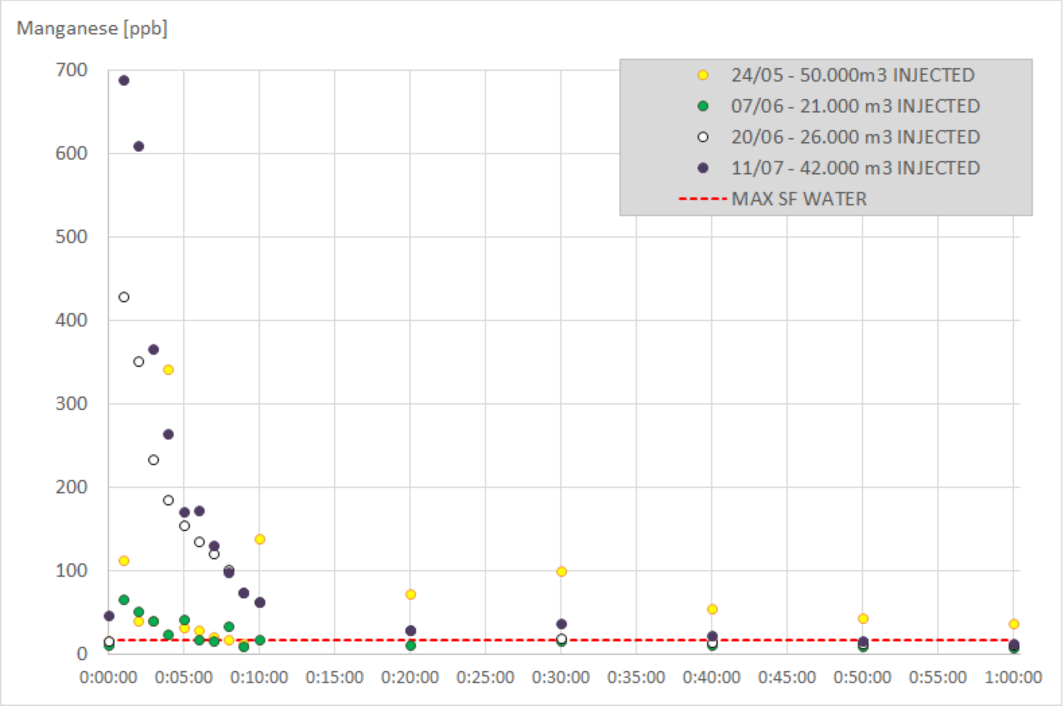

Figure 39: Manganese values during the first hour of pump cleaning at P18 well. Note: SF = sand-filtered water

The correlation between turbidity and the three metals analysed has been studied through the adjustment of data to power-law functions. With respect to aluminium, it is observed a good correlation in any of the cleaning cycle, with coefficients of determination (R^2) above 0.7, similar to those reached with all data (Figure 40). The higher value of R^2 corresponds to the experiment performed in May 2016 (R^2 = 0.93). The same behaviour is observed for iron and manganese; with better goodness-of-fit in June and July (Figures 41 and 42). At this respect, it could be possible to approximate these metal concentrations by using the proposed power-law functions, depending on turbidity values.

The estimation and prediction process of metals' concentration has indicated that exploring the relationship between metals and turbidity values might be one effective technique to facilitate better long-term monitoring with high temporal density, due to the availability and economic feasibility of turbidity data-loggers. However, this methodology should be subject to calibration with field measurements, in order to correct the differences between the observed and estimated values.

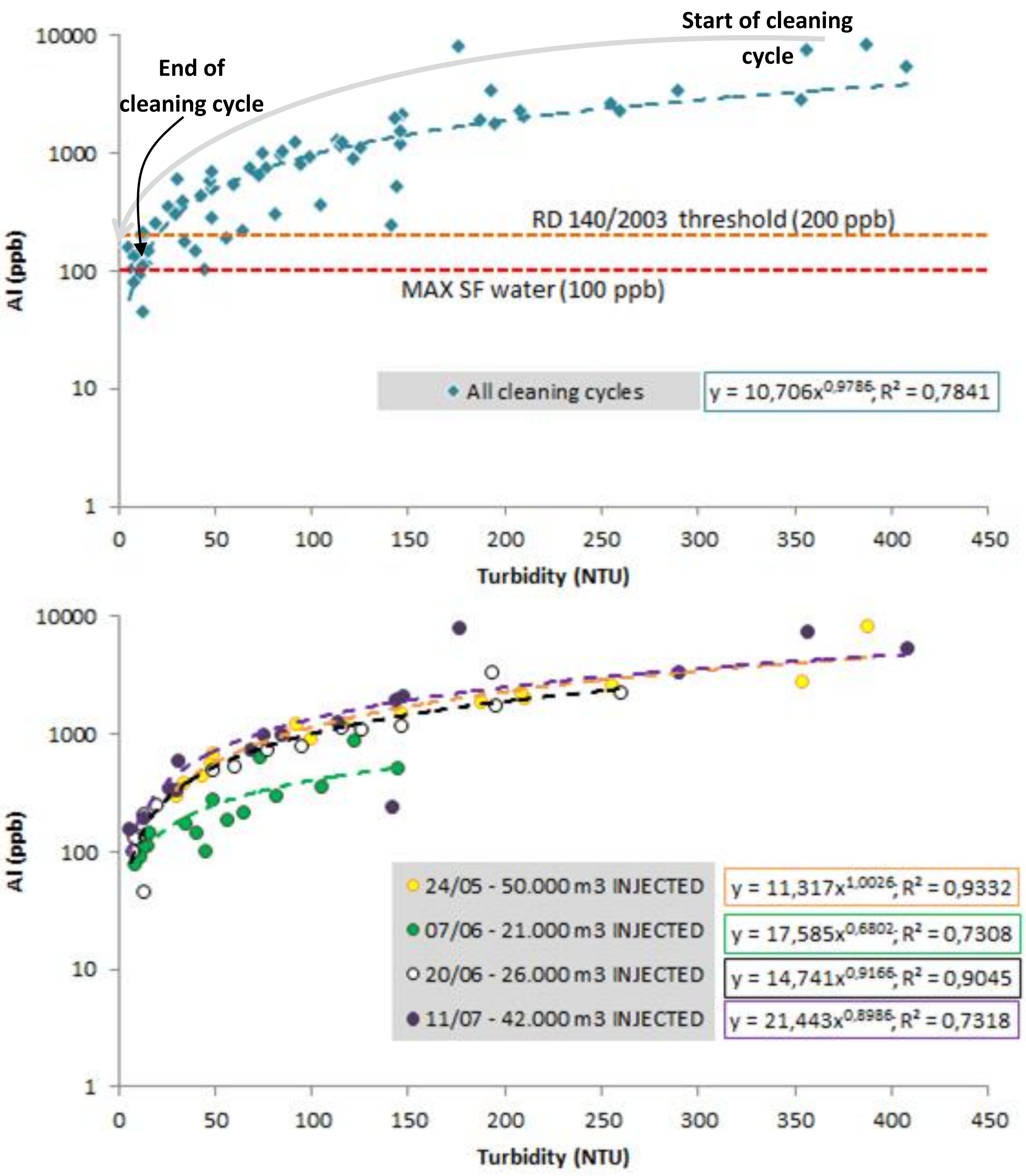

Figure 40: Correlation analysis between turbidity (NTU) and aluminium (ppb) values during the first hour of pump cleaning at P18 well

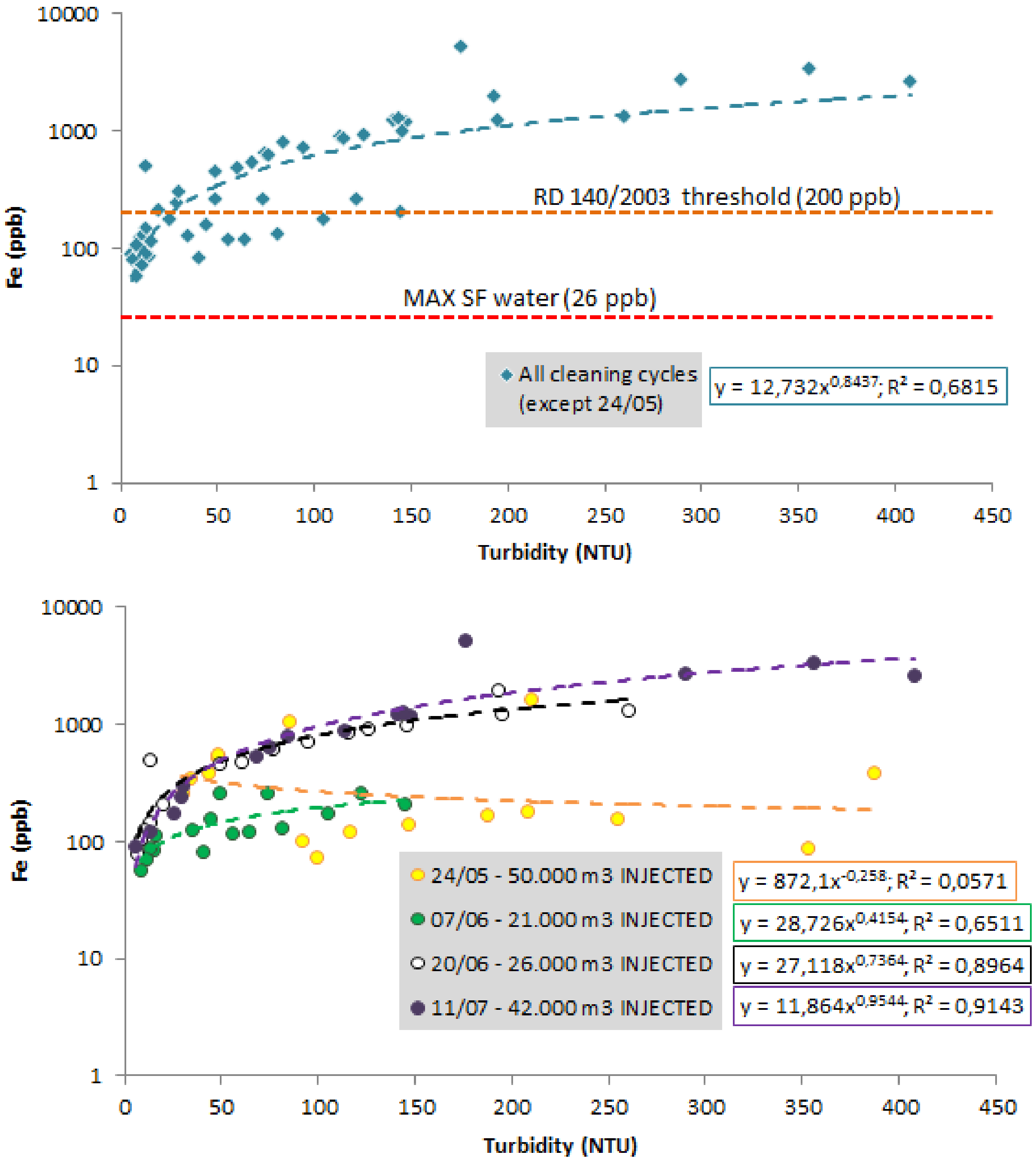

Figure 41: Correlation analysis between turbidity (NTU) and iron (ppb) values during the first hour of pump cleaning at P18 well

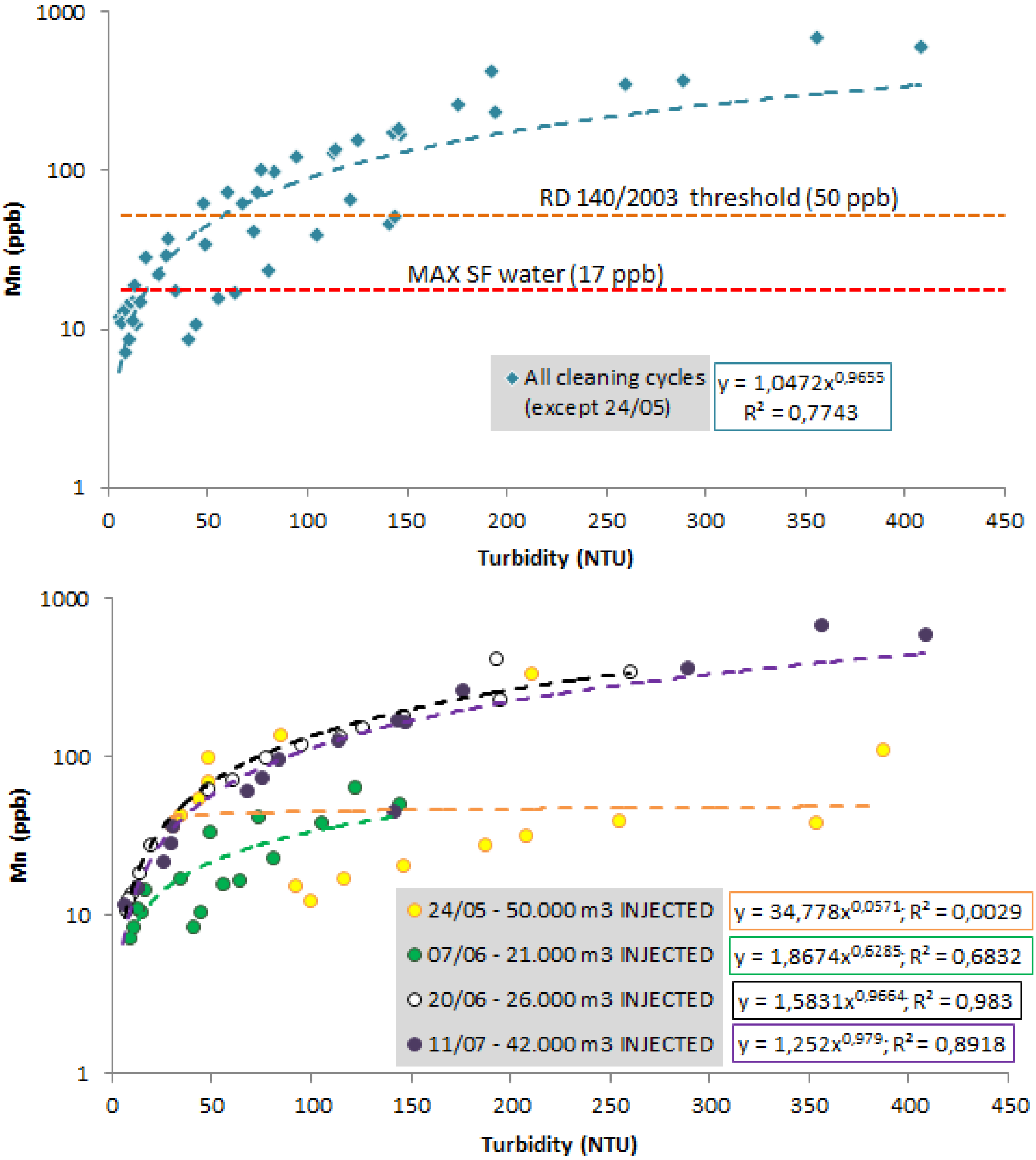

Figure 42: Correlation analysis between turbidity (NTU) and manganese (ppb) values during the first hour of pump cleaning at P18 well

6.3.3 Influence of sand-filtered water on redox potentials

With respect to the study of the electrochemical stability of iron and manganese, it has used several Pourbaix diagrams in order to evaluate the potential mobilisation of trace metals by mixing processes between recharge water and native groundwater.

As the pH drops below 5, hydroxide minerals, most commonly iron and aluminium hydroxides, become partly unstable and start to dissolve (Søgaard and Madsen, 2013). This is not the case for sand-filtered water and native groundwater, with pH values than range between 6.9 and 7.9 (see Tables 30 and 31). The evolution of pH during all cleaning cycles present the same trend, decreasing quickly at first, then gradually until a nearly steady state value of 7, confirming that dissolution of hydroxide minerals (mobilization) does not seem to represent a source for iron and aluminium concentrations.

With respect to redox potential, it has been used the values from sand-filtered water, and groundwater not-influenced and influenced by recharge (Tables 30 and 31). In groundwater systems the Eh is generally less oxidizing than in surface water systems because of the lack of a source of molecular oxygen below the water table and the presence of reducing solids in the aquifer (Deutsch, 1997). It has to be noted that there is too much difference between the average redox potentials of Pz-1 (Eh = 25 mV) and Pz-2 (Eh = -165.4 mV), especially when the distance among them is about 5 meters. In that context, it has performed a comparative analysis with data from ACA groundwater monitoring network, focused on a longitudinal profiles of redox potential (Figure 43), in order to consider a more representative “native” value characterising the aquifer geochemistry. The regional value calculated from the control points was about 300 mV, more coherent with the mean dissolved oxygen concentration observed at well P18 and piezometers Pz-1, Pz-2 and Pz-3 (Figure 44), with average values of 5.9, 4.6, 3.5 and 3.4, respectively. These values are typical of oxic environments (Schilling and Jacobson, 2015). It is observed a decreasing trend on dissolved oxygen concentration as water moves through the aquifer (from Pz-1 to Pz-3), indicating that the positive impact of injecting water in the aquifer decreases with distance.

Table 30: Redox and pH values for sand-filtered water

Date	Redox (Eh) [mV]	Date	pH (Laboratory)	Date	pH (Laboratory)
28/12/2015	176	06/07/2015	7,1	04/08/2015	7,8
29/12/2015	237	07/07/2015	7,2	14/09/2015	7,5
30/12/2015	229	13/07/2015	7,3	21/09/2015	7,1
31/12/2015	225	14/07/2015	7,4	28/09/2015	7,4
04/01/2016	209	21/07/2015	7,3	21/03/2016	6,9
07/01/2016	207	22/07/2015	7,3	11/04/2016	7,2
08/01/2016	241	27/07/2015	7,2	02/05/2016	7,1
11/01/2016	200	28/07/2015	7,3	03/06/2016	7,2
		03/08/2015	7,9	15/06/2016	7,3
				06/07/2016	7,2

The redox potentials obtained at piezometer Pz-2 are typical of strong reducing environments (Naudet *et al.,* 2004), such as deep wells (but not always), areas where groundwater flow is slow, and/or where water flows through organic matter rich soils. Eh values below 100 mV (relatively reducing groundwater) have been reported in aquifers beneath and down-gradient of bogs/swamps, landfills, and leaky underground storage tanks containing organic compounds (Deutsch, 1997), circumstances that do not occur in the study area. For that reason, it has used the average values obtained from Catalan Water Agency's database, specifically the redox potentials of the nearest groundwater control points to Sant Joan Despí DWTP (circle in Figure 43).

Table 31: Redox y pH values at Pz-1 and Pz-2 piezometers (prior to water injection)

Date	Pz-1 - (Eh) [mV]	Pz-2 - (Eh) [mV]	Pz-1 - pH (Laboratory)	Pz-2 - pH (Laboratory)
13/04/2015	-57	-211	6,8	6,9
20/04/2015	121	-177	6,7	7
27/04/2015	12	-285	7,7	7,3
05/05/2015	18	-235		
30/06/2015	30	82	7,4	7,4

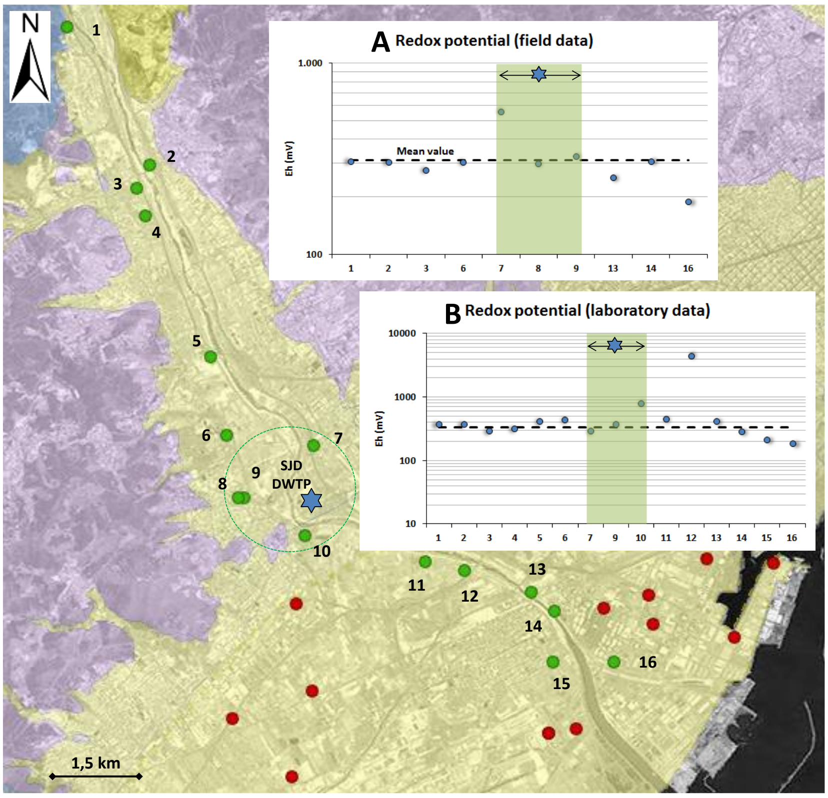

Figure 43: Longitudinal profiles of redox potential (Eh) in lower valley aquifer and deep delta aquifer, relative to average values during the periods (A) June-2014/July-2016 and (B) May-2007/Dec-2010. Note: SJD DWTP = Sant Joan Despí Drinking Water Treatment Plant

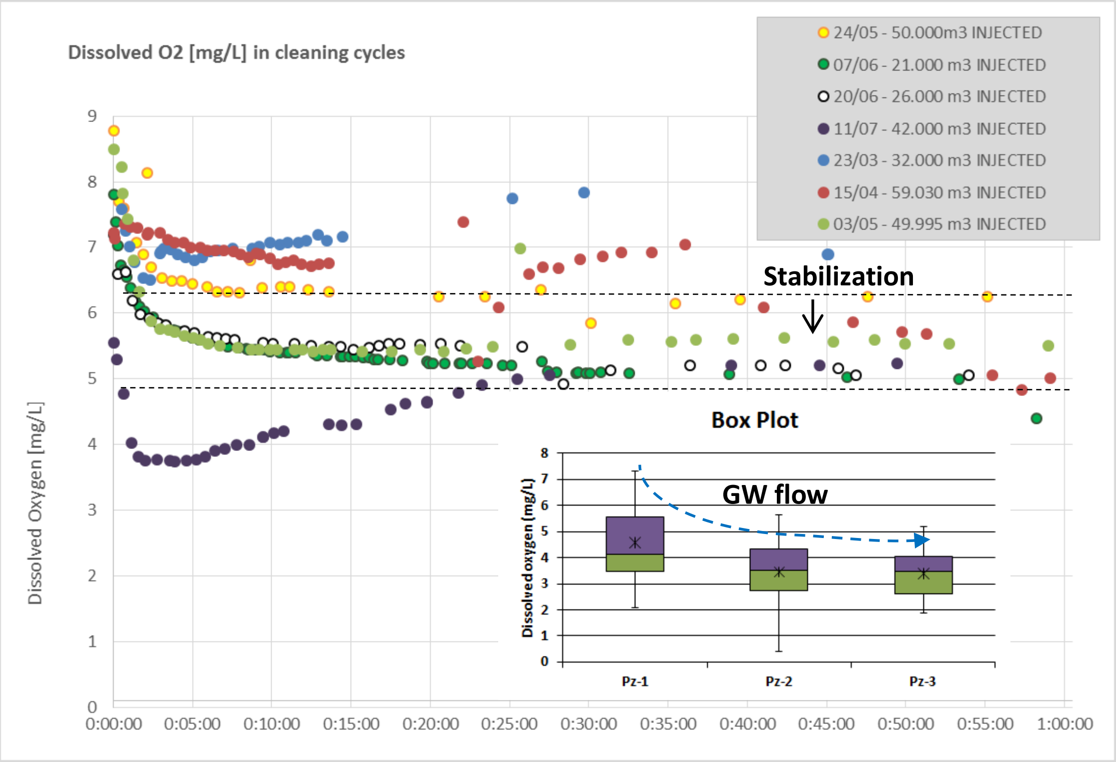

Figure 44: Dissolved oxygen values during the first hour of pump cleaning at P18 well. Note: the box plot is referred to groundwater sampled at piezometers Pz-1, Pz-2 and Pz-3 during sand-filtered water injection (from July-2015 to July-2016)

A pH-*E*h diagrams for iron and manganese are shown in Figure 45. Within the pH range typical of groundwater, Fe(OH)$_3$(s) is thermodynamically stable at moderate to high *E*h values. If man's activities disturb the pH-Eh regime, a zone that initially has a strong capability for trace-metal adsorption may lose this capability, or the reverse situation may occur. The most common sources of iron and manganese in groundwater are naturally occurring, for example from weathering of iron and manganese bearing minerals and rocks. Industrial effluent, acid-mine drainage, sewage and landfill leachate may also contribute iron and manganese to local groundwater. Some of these activities have been identified in the study area (ACA, 2005), such as industrial and sewage effluents. The mobilisation of iron and manganese is favoured by anoxic conditions, and that is not the case for the study area (Figures 44 and 45).

In sand filtration phase, solid precipitates are filtrated from raw water (Llobregat River water), and it is here when the largest part of the oxidation reactions takes place (Søgaard and Madsen, 2013). The oxidation of ferrous to ferric ions results in iron precipitating from the water as ferrihydrite -Fe- because of its low solubility. The position of the sand-filtered water samples in pH-Eh diagram indicates an oxic environment, with pH and Eh values ranging between 6.9 - 7.9 and 176 - 241 mV, respectively. The variability in groundwater samples taken at P18 during cleaning cycles is significantly lesser than the former ones, with lower values of Eh (Figure 45). The average regional groundwater value (Eh) is higher than the rest of water samples (300 mV). This value is of the same order of magnitude that the one observed in several types of aquifers (Chen and Liu, 2003; Edmunds *et al.,* 1984; Smedley and Edmunds, 2002).

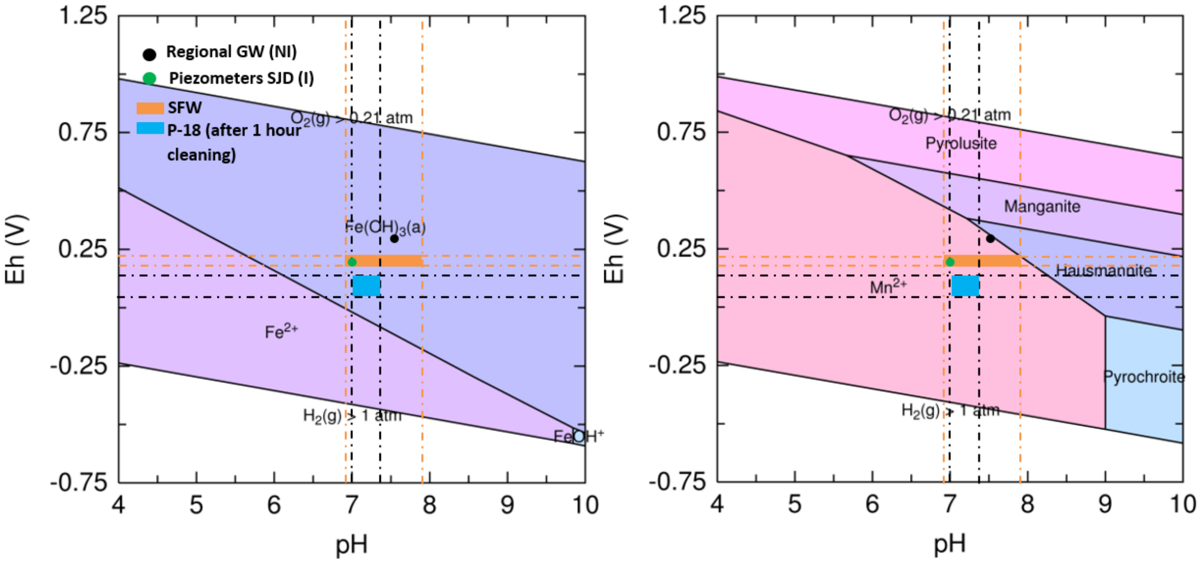

Figure 45: Pourbaix diagrams for iron and manganese as a function of Eh and pH. Note: SFW = sand-filtered water, NI = not influenced by SFW injection, I = influenced by SFW injection. Local GW is referred to Catalan Water Agency's database

Regarding redox processes governing groundwater geochemistry, it can be conclude that there is no a significant risk of mobilisation of heavy metals, in particular of iron and manganese, due to the injection into the aquifer of oxidant sand-filtered water coming from Llobregat River. Nonetheless, the high temporal variability of recharge water quality recommends making a continuous monitoring of pH and Eh values during the ASR operation.

6.3.4 Chlorites and chlorates

Chlorite ($NaClO_2$) and chlorate ($NaClO_3$) are disinfection by-products resulting from the use of chlorine dioxide (ClO_2) as a disinfectant and for odour/taste control in water. ClO_2 rapidly decomposes into $NaClO_2$, $NaClO_3$ and Cl^- ions in treated water, $NaClO_2$ being the predominant species. This reaction is favoured by alkaline conditions (WHO, 2005). $NaClO_2$ ions will be mobile in soils and may leach into groundwater; however, oxidation–reduction reactions may reduce the concentration of $NaClO_2$ ions capable of leaching into groundwater (ATSDR, 2004). Due to the fact that artificial recharge at SDJ DWTP corresponds to a deep injection well, there is no possibility of reducing $NaClO_2$ and $NaClO_3$ concentrations as water moves through vadose zone, more geochemically reactive than the saturated zone.

The total dosage of ClO_2 could be an indicator of the potential upper-bound concentrations of

$NaClO_3$ and $NaClO_2$ (WHO, 2016). Gates *et al.* (2009) suggest that $NaClO_2$ levels can generally range from 30% to 70% of the ClO_2 dose and that $NaClO_3$ levels are generally less than that, at about <20% of the dose. In US water treatment plants using ClO_2, the median $NaClO_3$ concentration was 129 µg/L, the 90th percentile concentration was 264 µg/L and the maximum concentration was 691 µg/L (USEPA, 2006). In a more recent study (Alfredo *et al.,* 2015), the median and maximum values were 200 and 880 µg/L, respectively (Figure 46). The values obtained during the cleaning cycles performed at P18 well are shown in Figure 47. It can be observed a clear reduction of $NaClO_2$ and $NaClO_3$ as the time left after taking the water sample was higher (bars with diagonal lines), reaching values between 100 and 140 µg/L (Figure 47). The maximum concentration of $NaClO_2$ and $NaClO_3$ was 240 and 400 µg/L, respectively. The World Health Organization (WHO) provisional guideline for $NaClO_3$ is 700 µg/L, although its application is highly variable depending on the country legislation. For instance, the standards set by Canada (1,000 µg/L) and New Zealand (800 µg/L) are higher than WHO's proposal of 700 µg/L, and those of Japan (600 µg/L) and the Dominican Republic (200 µg/L) are lower (Alfredo *et al.,* 2015). These authors recommend a health reference level (HRL) of 210 µg/L, taking into account a reference dose of 0.03 mg/kg/d, a 70-kg adult consuming 2 L/d of water and a default relative source contribution of 20% (fraction of the reference dose received from drinking water). The maximum value of $NaClO_3$ is within the upper-bound observed in 88 US water treatment plants using chlorine dioxide as a disinfectant and coincides with the average concentration measured in sand-filtered water at SDJ DWTP (Figure 46).

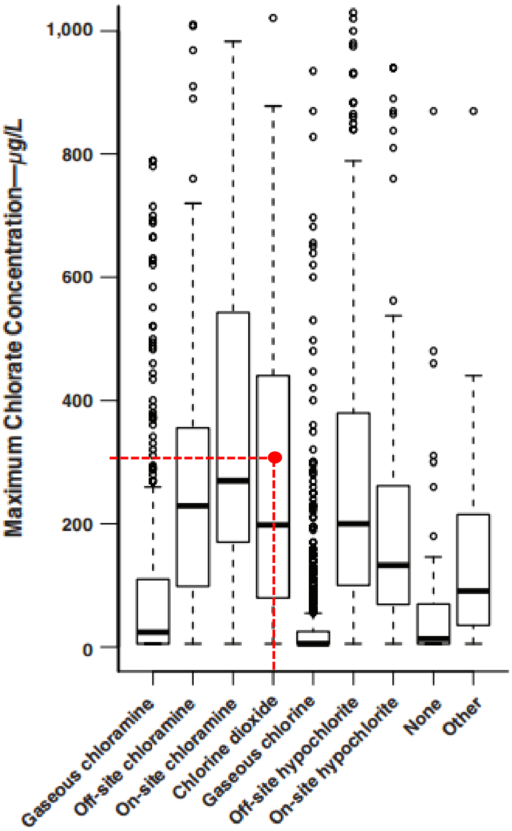

Figure 46: Maximum chlorate ($NaClO_3$) concentrations at different US utilities analysed by disinfection type. Source: Alfredo et al. (2015). Note: red dot corresponds to maximum value measured in sand-filtered water

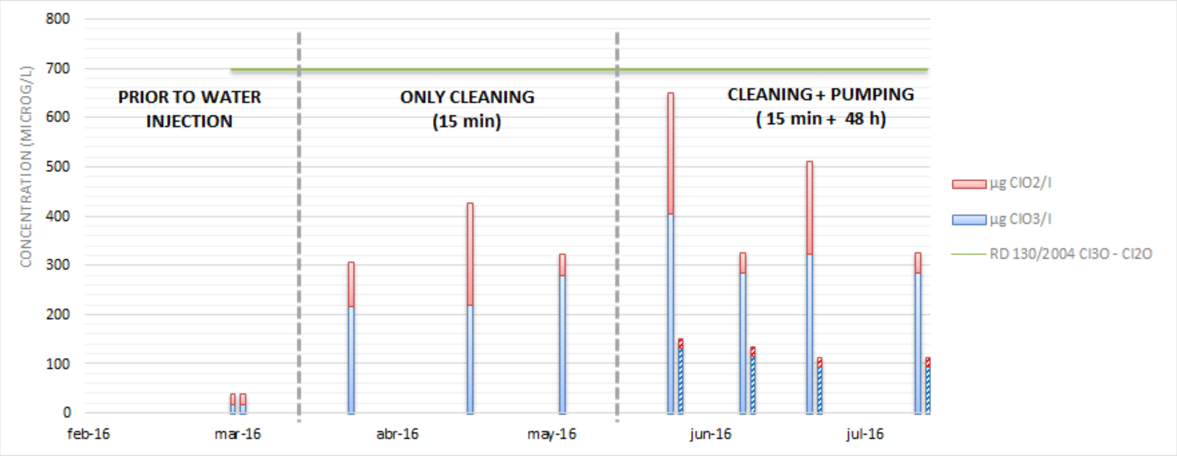

Figure 47: Chlorites and chlorites analysed in P18 well after pumping for 15 minutes and 48 hours (bars with diagonal lines). Note: bars with diagonal lines correspond to 48 h – pumping phase

With respect to sand-filtered water, the maximum concentrations of $NaClO_2$ and $NaClO_3$ during the water injection were 726 and 327 µg/L, higher than the values observed at P18 well (Figure 47), especially after pumping for 2 days. It would be related to a dilution effect of sand-filtered water within the aquifer.

Regarding water technologies focused on reducing these compounds, anion exchange and reverse osmosis are possible options for the removal of $NaClO_3$ (Alfredo *et al.,* 2015). Concentrations of $NaClO_2$ can be reduced using ferrous iron, sulphur reducing agents or activated carbon and may particularly be needed when ClO_2 is used as a pre-oxidant. The key to deal with a potential chlorate contamination event is to prevent or minimize the compound's formation. In the study area and based on the US nationwide assessment, it might be addressed by changing the type of disinfectant, from chlorine dioxide to gaseous chloramine or *on-site* hypochlorite. Another possibility would be to analyse the total amount of ClO_2 currently applied to the treatment system, in order to assess whether its dosage could be reduced or not, and, in turn, the potential formation of $NaClO_2$ and $NaClO_3$. In any case, these changes should incorporate a local cost-benefit analysis.

With respect to spatial extent of recharged water it can be inferred from Figure 48. Values are ordered from distance to the Llobregat River. The lesser concentration of chlorates in the second injection period (2016) in comparison with the first one is related to the existence of pumping throughout the latter period, that might be induced a groundwater flow to injection well (P18), reducing the amount of SFW arriving at control piezometers. In addition, this period includes rainy months (from March to May), with precipitation events provoking dilution processes. Moreover, it has not been observed chlorate accumulation at the end of the recharge experience. The higher concentrations measured at Pz-3 could be due to a lower renovation of its water column, given it is an old piezometer and the well screen may be more clogged with respect to Pz-1 and Pz-2, drilled during DESSIN project.

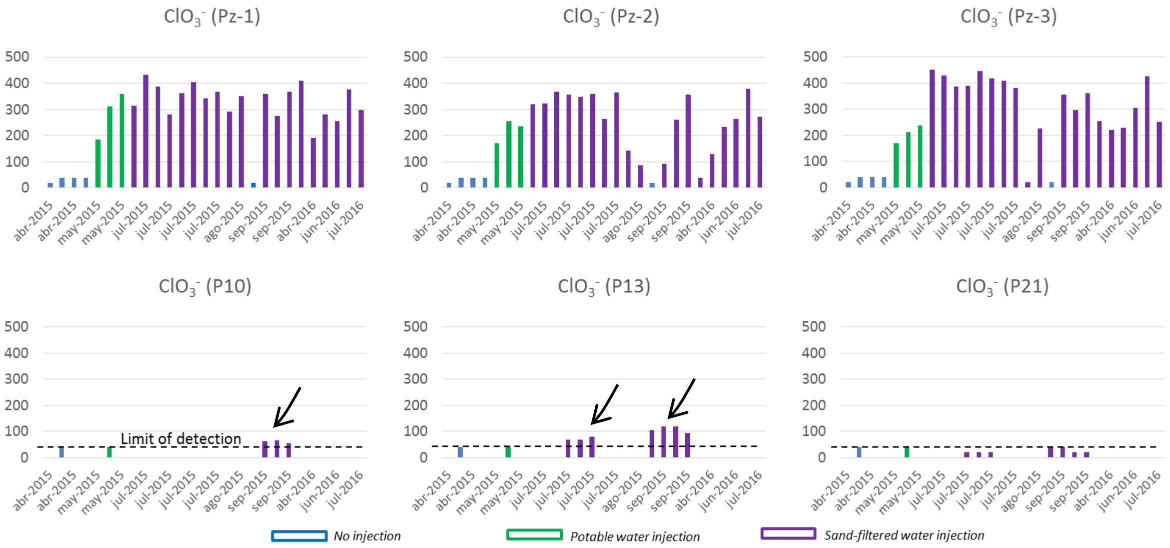

Figure 48: Chlorates (ClO_3^-) concentrations in monitoring network during ASR operation. Notes: units = µg/L; the arrows indicate the arrival of the injected SFW

6.3.5 Emerging organic contaminants

During cleaning cycles, water samples were taken to measure the selected organic compounds (see Table 29). The average concentrations for each compound are shown in Figure 49, taking the half of the detection limit for the calculation of samples below the corresponding threshold. The value of 200 ng/L has been taken as reference, as it is included within the Environmental Quality Standards and Water Framework Directive (diuron and other similar compounds). It is observed that all compounds, except Nonylphenol, are below 200 ng/L, in both “15 minutes” and “2 days” water sampling procedures. Moreover, the values obtained after pumping for 2 days are, in general, below the concentrations observed in sand-filtered water and water sampled 15 minutes since the beginning of the cleaning procedure.

Of all the emerging organic contaminants analysed, there is one that deserves particular focus. This is the case of Nonylphenol, which reaches high values in some campaigns (maximum value of 710 ng/L after pumping for 15 minutes). It could be taken into account in designing the operational regime of ASR system. The proposal of EOCs to be included in ASR operation at real scale is presented in D35.1 (d).

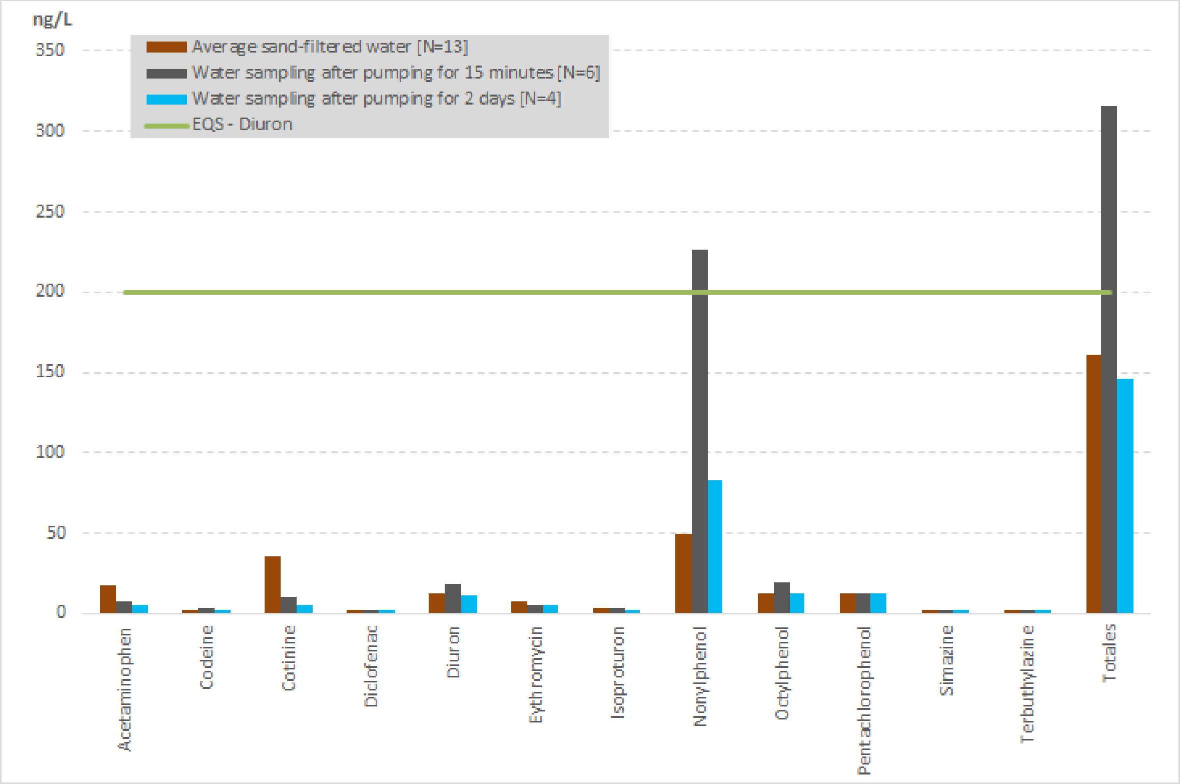

Figure 49: Concentrations of organic and emerging pollutants during injection and cleaning cycles at P18 well

6.3.6 Head losses and clogging processes

It has been carried out a groundwater level monitoring at P18 well and piezometers Pz-1, Pz-2, and Pz-3 during several recharge events. At the end of the first 2 hours after injecting sand-filtered water, the water level rise was recorded. Unfortunately, the P18 well data-logging system failed during the last part of the cleaning procedures.

It may be observed rapid piezometric rises (300 - 500 mm) at P18 well, with a progressive increase from the first recharge event to the latter ones (Figure 50), corresponding to the period when water injection was discontinuous (first injection phase). Once a cleaning cycle is completed (pumping at 220 L/s), the instantaneous rise at P18 well is reduced up to 250 mm, and this decreasing trend is found until the fourth cleaning cycle. Due to the lack of data it is not possible to come to an accurate conclusion that allow explaining the evolution of water table rises, which could be influenced by external variables (rainfall and/or pumping). The magnitude of piezometric rises at piezometers Pz-1, Pz-2, and Pz-3 is lower than the observed at P18 well, ranging between 100 and 200 mm. The evolution of mean and maximum water level rises throughout the different injection/cleaning phases is shown in Figure 51. It has been detected a slightly decreasing trend along the monitoring period, more evident from maximum values (Figure 51.a). Based on the available information, it has not been possible to evidence significant head losses associated with clogging processes. It would be necessary a long-term groundwater level monitoring in response to specific recharge events in order to corroborate the obtained results.

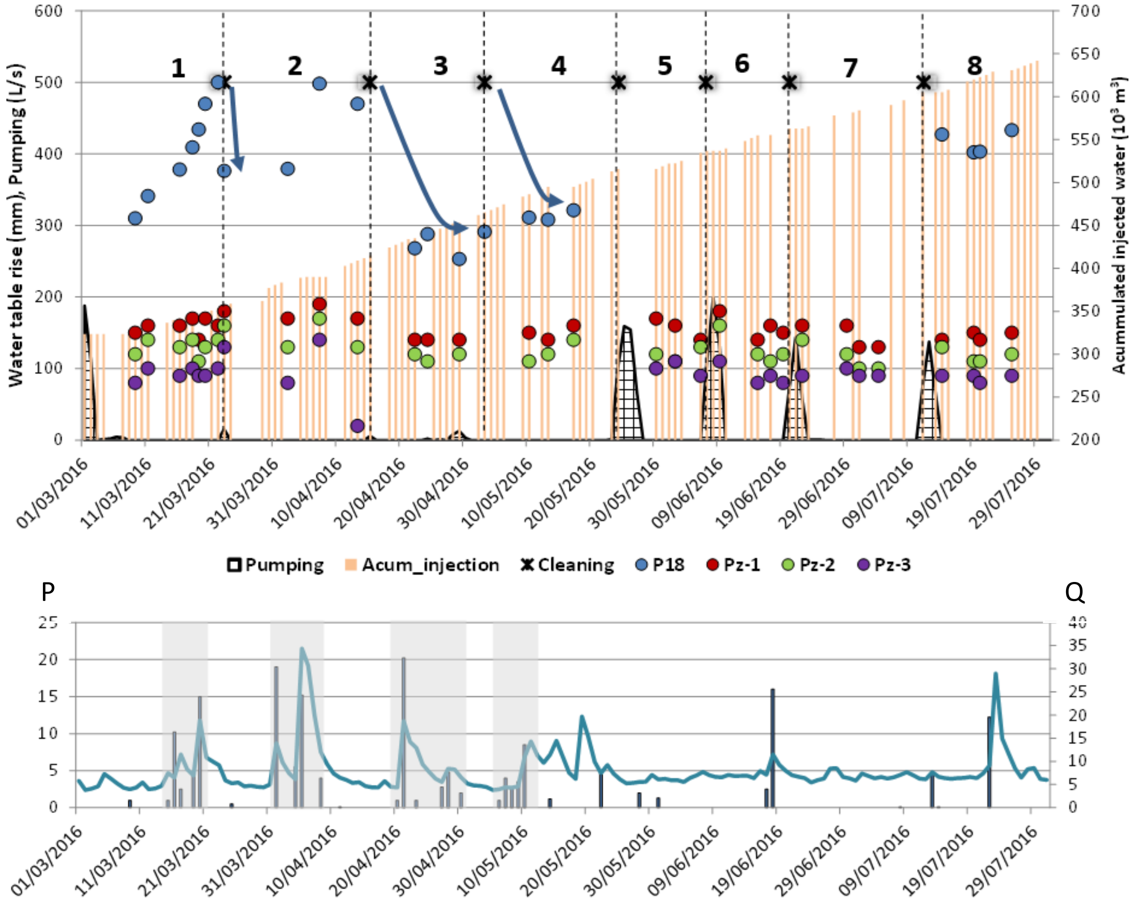

Figure 50: Maximum water table rise during the first 2 hours after water injection in relation to different explanatory variables. Note: grey areas represent several rainfall events that could have influenced in the observed piezometric rises; P = daily precipitation (mm); Q = daily Llobregat River streamflow (m^3/s)

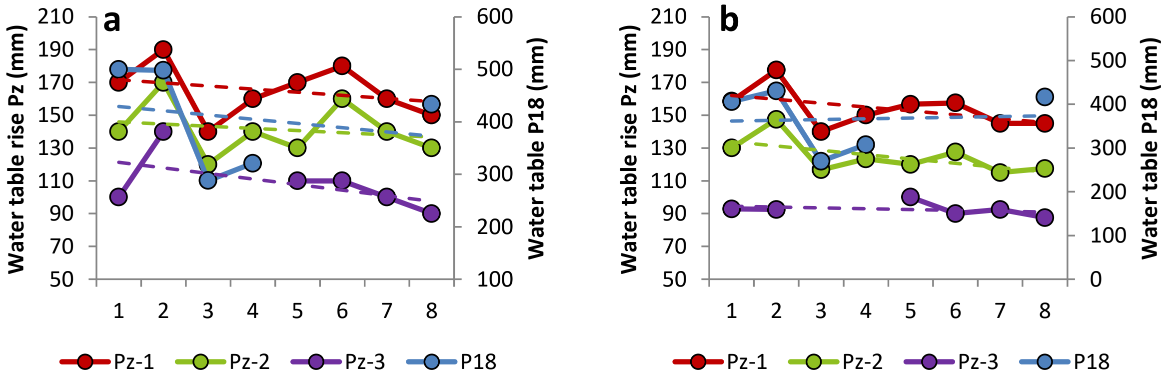

Figure 51: Maximum (a) and mean (b) water table rises during the first 2 hours of each recharge events. Note: dashed lines correspond to linear trends. Pz = piezometer

7. Conclusions

The analysis of the time series registered in the control piezometers near injection well has permitted to determine the impact of such injection in the hydrodynamic and physico-chemical response of the aquifer by using high-resolution data series, highlighting the overall improvement largely in terms of reducing groundwater salinization.

The application of multivariate statistical techniques have shown the improvement of groundwater quality due to the injection of sand-filtered water, similar to that obtained by injecting potable water. It may be concluded that the injection of pre-potable water has a positive impact in groundwater, with an overall reduction of the variables responsible for aquifer salinization. This analysis has allowed to identify the risky variables to take into account in future MAR projects, such as indicator microorganisms and chlorates.

With respect to organic compounds study, it has been demonstrated that ASR operation with sand-filtered water fosters dilution processes of industrial compounds such as chlorinated solvents, as may be observed in concentration maps of Lower Llobregat. Only 5 out of 12 selected EOCs were above the detection limit in one or several water sampling campaigns, as well as in groundwater sampled at several piezometers and wells. Therefore, slight contamination took place in few samples and with associated values very close to the detection limit of the analytical method.

Regarding microbiological analysis, it has been observed a decreasing trend in microbial abundance as a function of distance from injection well, as groundwater moves through the aquifer along the flow path. To demonstrate and characterize this decrease, it would be necessary to carry out specific tests with more controlled residence times, since it seems to be the main attenuation factor in consulted references. The determination of ATP could be a potential real-time parameter for detecting microbial ingress in drinking water contaminated with wastewater or surface water. The high variability of the obtained results concerning human adenoviruses would recommend to treat these results as a preliminary approach in absence of more precise information. With respect to stygofauna characterization, the proximity of piezometers Pz-1 and Pz-2 to the pre-potable water injection well (≈ 5 - 10 m) could explain the lower number of taxa detected. The realization of a new sampling campaign would allow to check the obtained results and evaluate more adequately the effects of different injection regimen in stygofauna communities.

The implementation of different cleaning cycles allowed to identify the optimum operating regime for the wells to be recharged with pre-potable (sand-filtered) water taking into account key variables, such as turbidity and heavy metals, changes in redox potential, disinfection-by products and potential head losses due to clogging.

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ANNEX A: Incidence of priority substances in surface waters and groundwater at Lower Llobregat

Reported in scientific papers: concentration in Llobregat River and/or aquifer > LOD
Reported in scientific papers: concentration in Llobregat River and/or aquifer < LOD
Not reported / Not studied compounds

#	Name of priority substance(iii)	Type of substance	Mean concentration found in literature	Reference
1	Alachlor	Herbicide (currently forbidden compound)	not measured sampling campaigns SJD (2009-2010) *"in Ebro River alachlor surpassed its maximum allowable concentration (700 ng/L) and in only two out of 104 water samples."*	Köck-Schulmeyer, 2012
			WWTP Secondary effluent El Prat: NOT DETECTED WWTP Tertiary effluent el Prat: NOT DETECTED Llobregat aquifer: NOT DETECTED	Teijon, 2010
2	Anthracene	polycyclic aromatic hydrocarbon (PAH)	WWTP Secondary effluent El Prat: NOT DETECTED WWTP Tertiary effluent el Prat: NOT DETECTED Llobregat aquifer: NOT DETECTED	Teijon, 2010
3	Atrazine	Pesticide	2,7 / 1,5 / 1,7 ng/L 3 sampling campaigns SJD (2009-2010)	Köck-Schulmeyer, 2012
			0,65 ng/L Llobregat River basin 2010 14% positive samples	Masiá, 2015
			0,73 ng/L Llobregat River basin 2011 14% positive samples	Masiá, 2015
			6,7 ng/L influent WWTP El Prat 6,7 ng/L effluent WWTP El Prat Llobregat aquifer: NOT DETECTED	Teijon, 2010
4	Benzene	polycyclic aromatic hydrocarbon (PAH)	Analysed in the Llobregat aquifer: Benzo(a)pyrene Benzo(b)Fluoranthene Benzo(ghi)perylene Benzo(k)fluoranthene Concetrations: 0,8 - 2,5 ng/L	Teijon, 2010
5	Brominated diphenylether Pentabromodiphenylether (congener numbers 28, 47, 99, 100, 153 and 154)	Flame retardant		
6	Cadmium and its compounds	Heavy metal	Sant Joan Despí treatment plant: Sand Filter effluent < 1 µg/L (detection limit) in all the samples analysed	Aigües de Barcelona results

#	Name of priority substance(iii)	Type of substance	Mean concentration found in literature	Reference
			WWTP Secondary effluent El Prat: 5 mg/L WWTP Tertiary effluent el Prat: 5 mg/L Llobregat aquifer: 0,45 mg/L	Teijon, 2010
7	Chloroalkanes, C10-13 iv	Hydrocarbon		
8	Chlorfenvinphos	Pesticide	0,39 ng/L Llobregat River basin 2010 14% positive samples	Masiá, 2015
			0,1 ng/L Llobregat River basin 2011 7% positive samples	Masiá, 2015
			2,3 ng/L Llobregat aquifer 4,8% positive samples	Teijon, 2010
9	Chlorpyrifos (1)	Pesticide	3,95 ng/L Llobregat River basin 2010 100% positive samples	Masiá, 2015
			5,31 ng/L Llobregat River basin 2011 100% positive samples	Masiá, 2015
	(Chlorpyrifos-ethyl) (2)		4,98 ng/L Llobregat aquifer 85% positive samples	Teijon, 2010
10	1,2-Dichloroethane	Plaguicide		
11	Dichloromethane	Dissolvent		
12	Di(2-ethylhexyl)phthalate (DEHP)	Plasticizers		
13	Diuron	Pesticide (Herbicide)	20,3 / 10,7 / 5,8 ng/L 3 sampling campaigns SJD (2009-2010)	Köck-Schulmeyer, 2012
			6,06 ng/L Llobregat River basin 2010 86% positive samples	Masiá, 2015
			23,29 ng/L Llobregat River basin 2011 21% positive samples	Masiá, 2015
			24,6 ng/L Llobregat aquifer 26% positive samples	Teijon, 2010
			WWTP Secondary effluent El Prat: 324 ng/L WWTP Tertiary effluent el Prat: 218 ng/L	Teijon, 2011
14	Endosulfan	Insecticide	Alpha-Endosulfan / Beta-Endosulfan were not detected in the Llobregat aquifer	Teijon, 2010
15	Fluoranthene	polycyclic aromatic hydrocarbon (PAH)	WWTP Secondary effluent El Prat: NOT DETECTED WWTP Tertiary effluent el Prat: NOT DETECTED Llobregat aquifer: 1,17 ng/L	Teijon, 2010
16	Hexachlorobenzene	Fungicide	2,04 ng/L Secondary effluent WWTP El Prat 2,04 ng/L Tetiary effluent WWTP El Prat 1,62 ng/L Llobregat aquifer	Teijon, 2010
17	Hexachlorobutadiene	Dissolvent	WWTP Secondary effluent El Prat: NOT DETECTED WWTP Tertiary effluent El Prat: NOT DETECTED Llobregat aquifer: 6,56 ng/L	Teijon, 2010

#	Name of priority substance(iii)	Type of substance	Mean concentration found in literature	Reference
18	α-HCH Hexachlorocyclohexane	Pesticide	WWTP Secondary effluent el Prat: 0,2 ng/L WWTP Tertiary effluent el Prat: 0,2ng/L Llobregat aquifer: 6,56 ng/L	Teijon, 2010
	β-HCH Hexachlorocyclohexane		WWTP Secondary effluent el Prat: 1,57 ng/L WWTP Tertiary effluent el Prat: 1,78 ng/L Llobregat aquifer: 1,24 ng/L	Teijon, 2010
	δ-HCH Hexachlorocyclohexane		WWTP Secondary effluent el Prat: 3,54 ng/L WWTP Tertiary effluent el Prat:3,46 ng/L Llobregat aquifer: 0,99 ng/L	Teijon, 2010
19	Isoproturon	Pesticide	2,8 / 13,7 / 3,0 ng/L 3 sampling campaigns SJD (2009-2010)	Köck-Schulmeyer, 2012
			WWTP Secondary effluent El Prat: NOT DETECTED WWTP Tertiary effluent el Prat: NOT DETECTED Llobregat aquifer: NOT DETECTED	Teijon, 2010
			1,48 ng/L Llobregat River basin 2010 57% positive samples	Masiá, 2015
			1,65 ng/L Llobregat River basin 2011 57% positive samples	Masiá, 2015
20	Lead and its compounds	Heavy metal	Sant Joan Despí treatment plant: Sand Filter effluent < 5 µg/L (detection limit) in all the samples analysed	Aigües de Barcelona results
			WWTP Secondary effluent el Prat: 5,21 mg/L WWTP Tertiary effluent el Prat: 6,06 mg/L Llobregat aquifer: 2,58 mg/L	Teijon, 2010
21	Mercury and its compounds	Heavy metal	WWTP Secondary effluent el Prat: 0,37 mg/L WWTP Tertiary effluent el Prat: 0,37 mg/L Llobregat aquifer: NOT DETECTED	Teijon, 2010
22	Naphthalene	polycyclic aromatic hydrocarbon (PAH)	WWTP Secondary effluent el Prat: NOT DETECTED WWTP Tertiary effluent el Prat: NOT DETECTED Llobregat aquifer: NOT DETECTED	Teijon, 2010
23	Nickel and its compounds	Heavy metal	Sant Joan Despí treatment plant: Sand Filter effluent < 5 µg/L (detection limit) in all the samples analysed except punctual values (maximum 2013 = 16µg/L)	Aigües de Barcelona results
			WWTP Secondary effluent el Prat: 47,5 mg/L WWTP Tertiary effluent el Prat: 46,5 mg/L Llobregat aquifer: 12,1 mg/L	Teijon, 2010
			12 µg/L and 5 µg/L in punctual samples in DEMEAU project (AB Laboratory) in the infiltration ponds	CETaqua results (DEMEAU)
24	Nonylphenols	Detergent		
	(4-nonylphenol)			
25	Octylphenols	Detergent		

#	Name of priority substance(iii)	Type of substance	Mean concentration found in literature	Reference
26	Pentachlorobenzene	PAH	WWTP Secondary effluent el Prat: NOT DETECTED WWTP Tertiary effluent el Prat: NOT DETECTED Llobregat aquifer: 0,49 ng/L	Teijon, 2010
27	Pentachlorophenol	Pesticide		
28	Polyaromatic hydrocarbons	PAH		
	(Benzo(a)pyrene)		WWTP Secondary effluent el Prat: NOT DETECTED WWTP Tertiary effluent el Prat: NOT DETECTED Llobregat aquifer: 0,83 ng/L	Teijon, 2010
	(Benzo(b)fluoranthene)		WWTP Secondary effluent el Prat: NOT DETECTED WWTP Tertiary effluent el Prat: NOT DETECTED Llobregat aquifer: 2,5 ng/L	Teijon, 2010
	(Benzo(g,h,i)perylene)		WWTP Secondary effluent el Prat: NOT DETECTED WWTP Tertiary effluent el Prat: NOT DETECTED Llobregat aquifer: 0,41 ng/L	Teijon, 2010
	(Benzo(k)Fluoranthene)		WWTP Secondary effluent el Prat: NOT DETECTED WWTP Tertiary effluent el Prat: NOT DETECTED Llobregat aquifer: 0,9 ng/L	Teijon, 2010
	(Indeno(1,2,3-cd)pyrene)		WWTP Secondary effluent el Prat: NOT DETECTED WWTP Tertiary effluent el Prat: NOT DETECTED Llobregat aquifer: NOT DETECTED	Teijon, 2010
29	Simazine	Pesticide	2,4 / 2,2 / 13,3 ng/L 3 sampling campaings SJD (2009-2010)	Köck-Schulmeyer, 2012
			1,94 ng/L Llobregat River basin 2010 78% positive samples	Masiá, 2015
			8,03 ng/L Llobregat River basin 2011 57% postive samples	Masiá, 2015
			16,3 ng/L Secondary effluent WWTP El Prat 19,5 ng/L Tertiary effluent WWTP El Prat 3 ng/L Llobregat aquifer (2% positive samples in groundwater)	Teijon, 2010
30	Tributyltin compounds	Biocide		
	(Tributyltin-cation)			
31	Trichlorobenzenes (TCB)	Herbicide	WWTP Secondary effluent el Prat: NOT DETECTED WWTP Tertiary effluent el Prat: NOT DETECTED Llobregat aquifer:0,48-1,63ng/L	Teijon, 2010 (1,3,5 TCB; 1,2,3 TCB; 1,2,4 TCB)
32	Trichloromethane (chloroform)	Dissolvent		
33	Trifluralin	pre-emergence herbicide	WWTP Secondary effluent el Prat: NOT DETECTED WWTP Tertiary effluent el Prat: NOT DETECTED 1,03 ng/L Llobregat aquifer (14% positive samples in groundwater)	Teijon, 2010
34	Dicolfol	Biocide		

#	Name of priority substance(iii)	Type of substance	Mean concentration found in literature	Reference
35	Perfluorooctane sulfonic acid and its derivatives	Metabolizante		
36	Quinoxyfen	Funguicide		
37	Dioxins and dioxin-like compounds	PCV		
38	Aclonifen	Herbicide		
39	Bifenox	Herbicide		
40	Cybutryne	Pesticide		
41	Cypermethrin	Insecticide		
42	Dichlorvos	Insecticide		
43	Hexabromocyclododecanes (HBCDD)	Flame retardant		
44	Heptachlor and heptachlor epoxide	Insecticide		
45	Terbutryn	Pesticide	0,69 ng/L Llobregat River basin 2010 7% positive samples	Masiá, 2015
			3,71 ng/L Llobregat River basin 2011 28% positive samples	Masiá, 2015
46	alpha-ethinylestradiol			
47	beta-estradiol			
48	Diclofenac	Pharmaceutical: Phenylacetic acid (Anti-inflammatory)	Not detected at SJD catchment	Kuster & Jordi Martín, 2008
			WWTP Secondary effluent el Prat: 1867,7 ng/L WWTP Tertiary effluent el Prat: 406,5 ng/L Llobregat aquifer 256 ng/L	Teijon, 2010
			Llobregat River basin: 2,2 µg/L	Ginebreda, 2010

ANNEX B: Water sampling results - Initial screening

Compounds selected for routine monitoring

Compounds selected for quarterly monitoring (3 campaigns / project)

Discarded compounds

Name	Unit	Sand Filtered	P18	P13	P10	P21
Mercury (Hg)	µg/L	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05
BTEX and Chlorinated solvents						
Benzene	µg/L	<0.5	<0.5	<0.5	<0.5	<0.5
Toluene	µg/L	<1	<1	<1	<1	<1
Ethylbenzene	µg/L	<1	<1	<1	<1	<1
m+p-Xylene	µg/L	<1	<1	<1	<1	<1
o-Xylene	µg/L	<1	<1	<1	<1	<1
Trichloroethene (tri)	µg/L	<0.5	4.1	2.5	1.5	2
Tetrachloroethene (tetra)	µg/L	<0.5	4.3	1.8	5.9	0.92
1-2 Dichloroethane	µg/L	<0.5	<0.5	1	<0.5	1.3
1,1,1 Trichloroethane	µg/L	<1	<1	<1	<1	<1
Tri + Tetra	µg/L	<1	8.4	4.3	7.4	2.9
PAH (Polycyclic Aromatic Hidrocarbons)						
~~Nafthalene~~	µg/L	<0.025	<0.025	<0.025	<0.025	<0.025
~~Acenafthilene~~	µg/L	<0.025	<0.025	<0.025	<0.025	<0.025
~~Acenaftthene~~	µg/L	<0.025	<0.025	<0.025	<0.025	<0.025
~~Fluorene~~	µg/L	<0.015	<0.015	<0.015	<0.015	<0.015
~~Fenanthrene~~	µg/L	<0.015	<0.015	<0.015	<0.015	<0.015
~~Anthracene~~	µg/L	<0.015	<0.015	<0.015	<0.015	<0.015
~~Fluoranthene~~	µg/L	<0.015	<0.015	<0.015	<0.015	<0.015
~~Pirene~~	µg/L	<0.015	<0.015	<0.015	<0.015	<0.015
~~Benzo(a)anthracene~~	µg/L	<0.015	<0.015	<0.015	<0.015	<0.015
~~Crisene~~	µg/L	<0.015	<0.015	<0.015	<0.015	<0.015
~~Benzo(b)fluoranthene~~	µg/L	<0.015	<0.015	<0.015	<0.015	<0.015
~~Benzo(k)fluoranthene~~	µg/L	<0.015	<0.015	<0.015	<0.015	<0.015
~~Indeno(1,2,3,c,d)pyrene~~	µg/L	<0.015	<0.015	<0.015	<0.015	<0.015
~~Dibenzo(a,h)anthracene~~	µg/L	<0.015	<0.015	<0.015	<0.015	<0.015
~~Benzo(g,h,i)perylene~~	µg/L	<0.015	<0.015	<0.015	<0.015	<0.015
~~Benzo(a)pyrene~~	µg/L	<0.005	<0.005	<0.005	<0.005	<0.005
~~Sum 4 PAH Directive 98/83/CE~~	µg/L	<0.06	<0.06	<0.06	<0.06	<0.06

Compounds selected for routine monitoring
Compounds selected for quarterly monitoring (3 campaigns / project)
Discarded compounds

Pesticides (SBE - CG/EM)						
Simazine	µg/L	<0.015	<0.015	<0.015	<0.015	<0.015
Atrazine	µg/L	<0.015	<0.015	<0.015	<0.015	<0.015
Propazine	µg/L	<0.015	<0.015	<0.015	<0.015	<0.015
Terbuthylazine	µg/L	<0.015	<0.015	<0.015	<0.015	<0.015
Ametrine	µg/L	<0.015	<0.015	<0.015	<0.015	<0.015
Prometrine	µg/L	<0.015	<0.015	<0.015	<0.015	<0.015
Terbutryn	µg/L	<0.015	<0.015	<0.015	<0.015	<0.015
Aldrin	µg/L	<0.015	<0.015	<0.015	<0.015	<0.015
Dieldrin	µg/L	<0.015	<0.015	<0.015	<0.015	<0.015
Heptachlor	µg/L	<0.015	<0.015	<0.015	<0.015	<0.015
Heptachlor-epoxide	µg/L	<0.015	<0.015	<0.015	<0.015	<0.015
Alfa-Endosulfan	µg/L	<0.015	<0.015	<0.015	<0.015	<0.015
Alfa-HCH	µg/L	<0.025	<0.025	<0.025	<0.025	<0.025
beta-endosulphane	µg/L	<0.015	<0.015	<0.015	<0.015	<0.015
Lindane	µg/L	<0.025	<0.025	<0.025	<0.025	<0.025
4-4'-DDE	µg/L	<0.015	<0.015	<0.015	<0.015	<0.015
4-4'-DDD	µg/L	<0.025	<0.025	<0.025	<0.025	<0.025
4-4'-DDT	µg/L	<0.025	<0.025	<0.025	<0.025	<0.025
Diclobenil	µg/L	<0.015	<0.015	<0.015	<0.015	<0.015
Molinate	µg/L	<0.025	<0.025	<0.025	<0.025	<0.025
Trifluraline	µg/L	<0.015	<0.015	<0.015	<0.015	<0.015
Diazinon	µg/L	<0.015	<0.015	<0.015	<0.015	<0.015
Alachlor	µg/L	<0.015	<0.015	<0.015	<0.015	<0.015
Primicarb	µg/L	<0.025	<0.025	<0.025	<0.025	<0.025
Propanil	µg/L	<0.015	<0.015	<0.015	<0.015	<0.015
Metil-Paration	µg/L	<0.025	<0.025	<0.025	<0.025	<0.025
Fenitrotion	µg/L	<0.015	<0.015	<0.015	<0.015	<0.015
Etofumesate	µg/L	<0.015	<0.015	<0.015	<0.015	<0.015
Tioberncarb	µg/L	<0.015	<0.015	<0.015	<0.015	<0.015
Paration	µg/L	<0.025	<0.025	<0.025	<0.025	<0.025
Metolachlor	µg/L	<0.015	<0.015	<0.015	<0.015	<0.015
Chlorpyrifos	µg/L	<0.015	<0.015	<0.015	<0.015	<0.015
Pendimetaline	µg/L	<0.025	<0.025	<0.025	<0.025	<0.025
Clorfenvinvos	µg/L	<0.025	<0.025	<0.025	<0.025	<0.025
Total Pesticides	µg/L	<0.025	<0.025	<0.025	<0.025	<0.025

Compounds selected for routine monitoring

Compounds selected for quarterly monitoring (3 campaigns / project)

Discarded compounds

Name	Symbol	Unit	Sand Filtered	P18	P13	P10	P21
Physico-Chemical parameters (not regulated) - Total Metals ICP							
Argent	Ag	µg/L	<3	<3	<3	<3	<3
Barium	Ba	µg/L	54	29	31	44	34
Berilium	Be	µg/L	<2	<2	<2	<2	<2
Cobalt	Co	µg/L	<2	<2	<2	<2	<2
Molybdenum	Mo	µg/L	<2	<2	<2	<2	<2
Zinc	Zn	µg/L	<100	<100	<100	<100	109
Vanadium	Va	µg/L	<2	<2	<2	<2	<2
Titanium	Ti	µg/L	<2	<2	<2	<2	<2
Lithium	Li	µg/L	24	23	18	24	20
Galium	Ga	µg/L	<5	<5	<5	<5	<5
Bismut	Bi	µg/L	<5	<5	<5	<5	<5
Indium	In	µg/L	<5	<5	<5	<5	<5
Phosporous	Pb	µg/L	<20	<20	<20	<20	<20
Wolframium	W	µg/L	<5	<5	7	<5	<5
Talium	Ta	µg/L	<5	<5	<2	<5	<5
Tin	Sn	µg/L	<5	<5	<2	<5	<5
Paladium	Pa	µg/L	<5	<5	<2	<5	<5
Rubidium	Ru	µg/L	<25	<25	<25	<25	<25
Lantanium	La	µg/L	<2	<2	<2	<2	<2
Organic emerging micropollutants							
~~PCB: CB 28~~		ng/L	<0.1	<0.1	<0.1	<0.1	<0.1
~~PCB: CB 52~~		ng/L	<0.1	<0.1	<0.1	<0.1	<0.1
~~PCB: CB 101~~		ng/L	<0.1	<0.1	<0.1	<0.1	<0.1
~~PCB: CB 118~~		ng/L	<0.1	<0.1	<0.1	<0.1	<0.1
~~PCB: CB 138~~		ng/L	<0.1	<0.1	<0.1	<0.1	<0.1
~~PCB: CB 153~~		ng/L	<0.1	<0.1	<0.1	<0.1	<0.1
~~PCB: CB 180~~		ng/L	<0.1	<0.1	<0.1	<0.1	<0.1
~~Total PCBs~~		ng/L	<5	<5	<5	<5	<5
~~BDE - 28~~		ng/L	<5	<5	<5	<5	<5
~~BDE - 47~~		ng/L	<5	<5	<5	<5	<5
~~BDE - 100~~		ng/L	<5	<5	<5	<5	<5
~~BDE - 99~~		ng/L	<5	<5	<5	<5	<5
~~BDE - 153~~		ng/L	<5	<5	<5	<5	<5
~~BDE - 154~~		ng/L	<5	<5	<5	<5	<5
~~BDE - 183~~		ng/L	<5	<5	<5	<5	<5

Compounds selected for routine monitoring

Compounds selected for quarterly monitoring (3 campaigns / project)

Discarded compounds

Organic emerging micropollutants							
Diclofenac		ng/L	<10	<10	<10	<10	<10
~~Estradiol~~	-	ng/L	<100	<100	<100	<100	<100
~~Esinil estradiol~~	-	ng/L	<100	<100	<100	<100	<100
Isoproturon		ng/L	<10	<10	<10	<10	<10
Diuron		ng/L	<10	<10	<10	<10	<10
Nonylphenol		ng/L	<100	<100	<100	<100	<100
Octylphenol		ng/L	<100	<100	<100	<100	<100
Pentachlorophenol		ng/L	<100	<100	<100	<100	<100
~~Di-2-ethilhexile-phtalate (DEHP)~~		ng/L	450	43	61	88	101
Total metals (ICP)							
Cadmium	Cd	µg/L	<1	<1	<1	<1	<1
Copper	Cu	µg/L	<10	<10	<10	21	<10
Chromium	Cr	µg/L	<5	<5	<5	<5	<5
Nickel	Ni	µg/L	<5	<5	<5	<5	<5
Lead	Pb	µg/L	<3	<3	<3	<3	<3
Arsenic	As	µg/L	<3	<3	<3	<3	<3
Selenium	Se	µg/L	<3	<3	<3	<3	<3
Antimomium	Sb	µg/L	<3	<3	<3	<3	<3
Boron	B	µg/L	136	225	194	193	224
Indicator metals (ICP / AES)							
Iron	Fe	µg/L	38	21	10	24	16
Manganese	Mn	µg/L	3.7	12	5.6	15	2
Aluminium	Al	µg/L	42	<25	<25	26	<25
Sodium	Na	mg/L	142	152	141	153	204
Strontium	Sr	mg/L	2.13	1.92	1.79	1.65	2.05
Potassium	K	mg/L	27	23	29	12	27
Calcium	Ca	mg/L	126	177	14	187	144
Magnesium	Mg	mg/L	41	49	40	54	50
Silicon	Si	mg/L	1.22	4.23	3.5	5.69	3.64

ANNEX C: Schedule for water analysis

Règim operació: SENSE INJECCIÓ & INJECCIÓ POTABLE
Objectiu: Avaluació de de les condicions naturals de l'aqüífer i impacte de l'aigua potable per a tenir un escenari comparatiu als punts de control.
Resultats: Coneixement de l'aqüífer i del nivell de contaminants inicial (orgànics, en especial BTEX, que no provenen de la recàrrega).

🟦	Sand Filtered water injection (36 L/s)
□	Potable Water injection (50 L/s)
🟫	Pumping (250 L/s)
■	ASR Stopped
X	Sampling campaigns

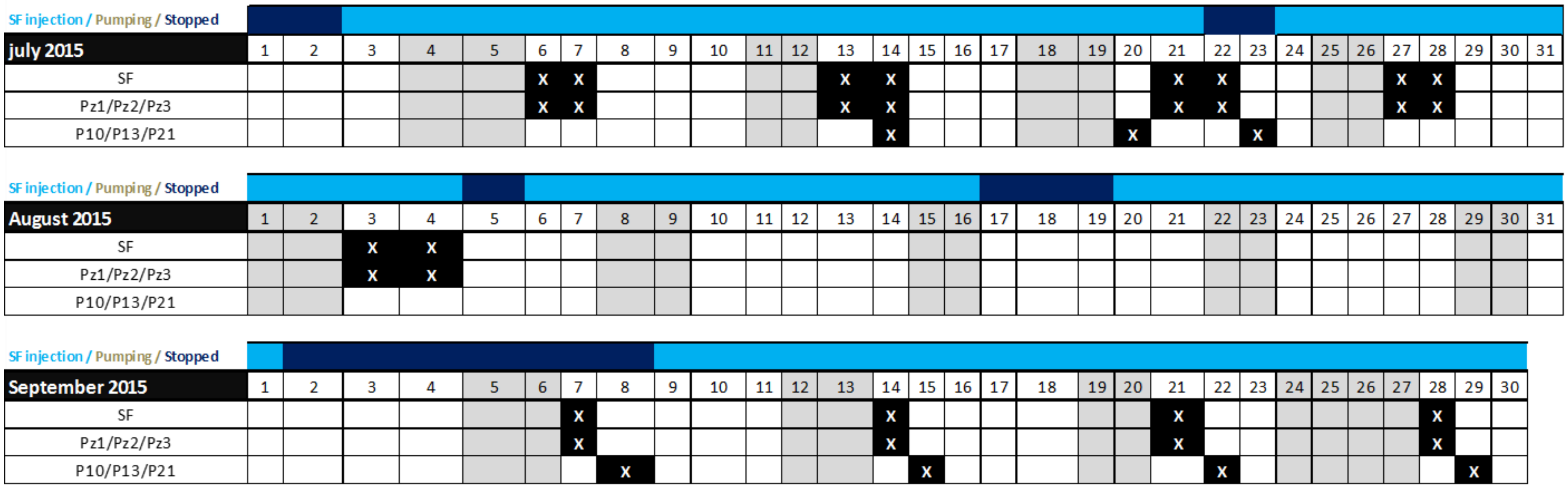
SF injection / Pumping / Stopped	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■
April 2015	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30
SF																														
Pz1/Pz2/Pz3													X							X							X			
P10/P13/P21																				X										

SF injection / Pumping / Stopped	■	■	■	■	■	■	■	□	□	□	□	□	■	□	□	□	□	□	□	■	■	■	■	■	■	■	■	■	■	■	■
may-15	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31
Drinking water												X						X													
Pz1/Pz2/Pz3												X																			
P10/P13/P21												X																			

SF injection / Pumping / Stopped	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■
june 2015	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30
SF																														
Pz1/Pz2/Pz3																														X
P10/P13/P21																														

🟦 Sand Filtered water injection (36 L/s)
▨ Pumping (250 L/s)
⬛ ASR Stopped
X Sampling campaigns

Règim operació: INJECCIÓ CONTINUADA
Objectiu: Avaluació químic de l' aigua filtrada per sorra en injecció continuada per tenir representativitat en estat estacionari.
Resultats: Avaluació de la degradabilitat de les subtàncies injectades (clorits, clorats, paràmetres orgànics) en les condicions més desfavorables d'operació. Identificació de canvis hidrogeoquímics a l'aqüifer (no detectats)



SF injection / Pumping / Stopped

july 2015	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31
SF						X	X						X	X							X	X					X	X			
Pz1/Pz2/Pz3						X	X						X	X							X	X					X	X			
P10/P13/P21														X						X			X								

SF injection / Pumping / Stopped

August 2015	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31
SF			X	X																											
Pz1/Pz2/Pz3			X	X																											
P10/P13/P21																															

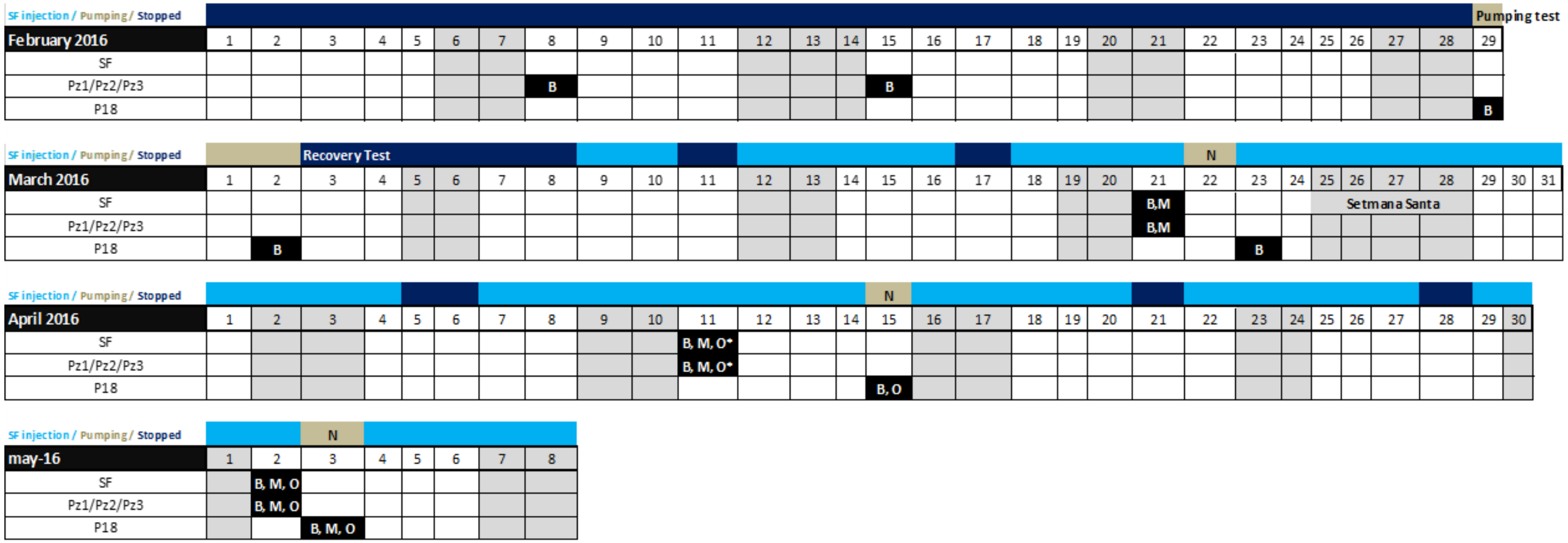
SF injection / Pumping / Stopped

September 2015	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30
SF							X							X							X							X		
Pz1/Pz2/Pz3							X							X							X							X		
P10/P13/P21								X							X							X							X	

ANNEX D: Schedule for cleaning cycles

- Sand Filtered water injection (36 L/s)
- Pumping (250 L/s) N = **Neteja**
- ASR Stopped
- Sampling (**B** = Basic; **M**=Micro; **O**=Organic)
- * Organic compounds complete

Operational Regime: INJECTION + CLEANING + INJECTION
Objective: Evaluation of the efectiveness of periodical cleanings in the "injectivity" recovery by anasysing changes ni the dynamic groundwater level in the well and quality of recovered water.
Results: Recommendations for cleaning operation. Validation of turbidity as control parameter.



SF injection / Pumping / Stopped																													Pumping test
February 2016	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29
SF																													
Pz1/Pz2/Pz3								B							B														
P18																													B

SF injection / Pumping / Stopped			Recovery Test																			N									
March 2016	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31
SF																					B,M				Setmana Santa						
Pz1/Pz2/Pz3																					B,M										
P18		B																					B								

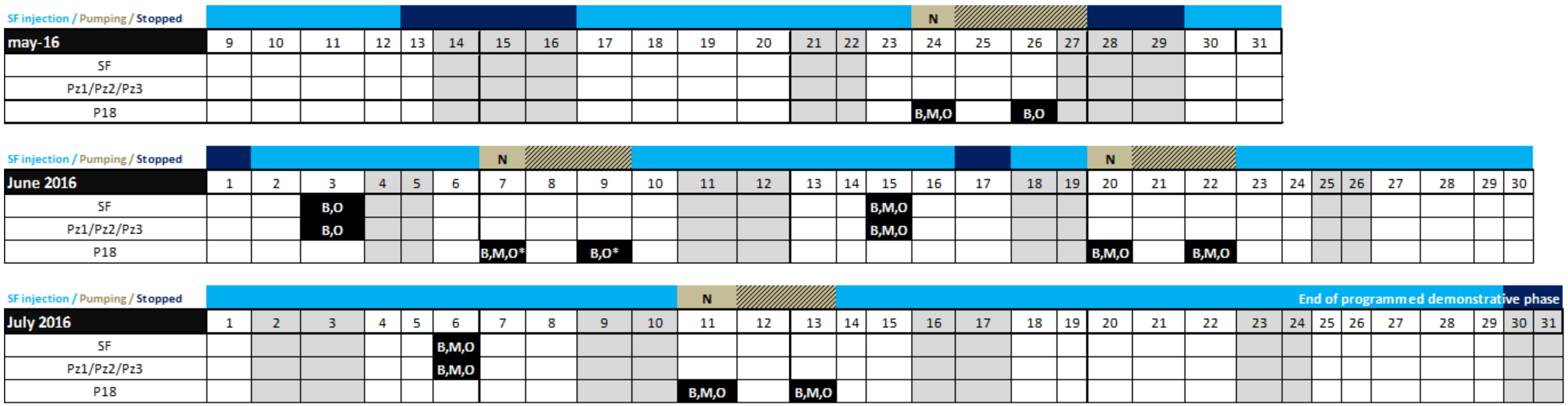
SF injection / Pumping / Stopped															N															
April 2016	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30
SF											B, M, O*																			
Pz1/Pz2/Pz3											B, M, O*																			
P18															B, O															

SF injection / Pumping / Stopped			N					
may-16	1	2	3	4	5	6	7	8
SF		B, M, O						
Pz1/Pz2/Pz3		B, M, O						
P18			B, M, O					

🟦 Sand Filtered water injection (36 L/s)
🟫 Pumping (250 L/s) **N = Neteja**
■ ASR Stopped
▨ native GW pumped

Sampling (**B** = Basic; **M**=Micro; **O**=Organic)
* Organic compounds complete

Operational Regime: INJECTION + CLEANING + PUMPING
Objective: Evaluation of the capacity of the well to recovery the quality of native groundwater. Verify if there are traces of sand filtered water after two days of continuous extration, corresponding to the volume injected.
Results: Assessment of the impact of injection-extraction dynamic regime (comparing the response with the continuous injection at the beginning of the project.



SF injection / Pumping / Stopped	🟦	🟦	🟦	🟦	■	■	■	■	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟫 N	▨	▨	▨	■	■	🟦	🟦
may-16	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31
SF																							
Pz1/Pz2/Pz3																							
P18																B,M,O		B,O					

SF injection / Pumping / Stopped	■	🟦	🟦	🟦	🟦	🟦	🟫 N	▨	▨	🟦	🟦	🟦	🟦	🟦	🟦	🟦	■	🟦	🟦	🟫 N	▨	▨	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦
June 2016	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30
SF			B,O												B,M,O															
Pz1/Pz2/Pz3			B,O												B,M,O															
P18							B,M,O*		B,O*											B,M,O		B,M,O								

SF injection / Pumping / Stopped	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟫 N	▨	▨	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	■	■
																									End of programmed demonstrative phase						
July 2016	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31
SF						B,M,O																									
Pz1/Pz2/Pz3						B,M,O																									
P18											B,M,O		B,M,O																		

The research leading to these results has received funding from the European Union Seventh Framework Programme (FP7/2007-2013) under grant agreement no. 619039

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D35.1 (d) GUIDELINES AND RECOMMENDATIONS FOR ASR IMPLEMENTATION USING PRE-POTABLE WATER

CETaqua, December 2017

The research leading to these results has received funding from the European Union Seventh Framework Programme (FP7/2007-2013) under grant agreement no. 619039

GUIDELINES AND RECOMMENDATIONS FOR ASR IMPLEMENTATION USING PRE-POTABLE WATER

D35.1(d): GUIDELINES AND RECOMMENDATIONS FOR ASR IMPLEMENTATION USING PRE-POTABLE WATER

SUMMARY

The most important aspects in managed aquifer recharge projects with pre-potable water were determined, with a focus on use for human consumption. An operational guide waas used for the evaluation of managed aquifer recharge projects, which included the main factors to be taken into account for its correct implementation. It is recommendable to perform several types of analysis, such as hydrogeological, technical, economic and legal, in order to assess the feasibility of the relevant project. In each case, it would be an "ad-hoc" assessment, mainly due to the existence of different types of aquifers, recharge water, and quality threshold values prior to water injection, set by the legislation of each Member State.

The need to generate a methodological approach that could serve as a starting point to responsibly inject pre-potable water into the aquifer was raised. Therefore, it was decided to apply the existing methodology for risk management in drinking water and wastewater treatment plants (Water Safety Plans) to the managed aquifer recharge projects. In the case of the recharge with pre-potable water into the Lower Llobregat alluvial aquifer, the main hazards were, among others, the increase of chlorites and chlorates concentrations and potential EOCs bio-accumulation. A series of Critical Control Points and threshold values for the different variables were defined based on current legislation.

The implementation of these risk management plans at European level, which could be named as "Managed Aquifer Recharge Safety Plans", will require specific studies, due to the different aquifer functioning depending on their nature, the variability of recharge water quality and the large differences observed in the legal thresholds values required in each Member State.

DELIVERABLE NUMBER	WORK PACKAGE
D35.1 (d)	WP35
LEAD BENEFICIARY	**DELIVERABLE AUTHOR(S)**
CETaqua	Manuel Argamasilla Ruiz (CETaqua) Pere Camprovin (CETaqua)
QUALITY ASSURANCE	
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PLANNED DELIVERY DATE	**ACTUAL DELIVERY DATE**
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List of Acronyms and Abbreviations

MAR-SP	Managed Aquifer Recharge Safety Plan
ACA	Catalan Water Agency (regional public entity)
ASPCAT	Catalan Public Health Administration (regional public entity)
AB	Aigües de Barcelona
ASR	Aquifer Storage and Recovery
CUADLL	Association of Users of The Llobregat Aquifer (non-profit organisation)
DWTP	Drinking Water treatment Plant
Pz-1	Piezometer number 1 drilled in SJD
Pz-2	Piezometer number 2 drilled in SJD
Pz-3	Piezometer number 3 already existing in SJD
SJD	Sant Joan Despi facility of Drinking Water Treatment Plant (Barcelona)
TVs	Threshold values
WFM	Water Framework Directive
GWD	Groundwater Directive
MS	Member State
RBD	River Basin District
RBMP	River Basin Management Plan
WSP	Water Safety Plan
HACCP	Analysis of Hazards and Critical Control Points
CCP	Critical Control Points
CL	Critical Limits
EOCs	Emerging Organic Contaminants
PhACs	Pharmaceutically Active Compounds

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Executive summary

The correct implementation of a managed aquifer recharge project implies taking into account several factors, such as technical, economic and legal, among others. In order to be able to assess how the risk is transferred through the different phases (potential users affected/benefited by the recharge, impacts on the groundwater quality, the need to implement corrective and preventive measures, etc.) the “Water Safety Plan” methodology has been applied to pre-potable water injection into Lower Llobregat alluvial aquifer.

With regard to the more generic analysis, the existence of large differences in the quality thresholds required to comply with the good chemical status of groundwater bodies in the EU Member States has been revealed. This fact has a clear impact on the effective implementation of managed aquifer recharge experiences, limited largely by the recharge water quality. In addition, at European level there are only groundwater quality standards for two variables, nitrates (50 mg/L) and pesticides (individual - 0.1 µg/L - and total - 0.5 µg/L -). This circumstance makes difficult, from the legal point of view, to extrapolate the results derived from the impact analysis in a specific aquifer.

The Catalan Water Agency (ACA) approved in 2017 the River Basin Management Plan of Internal Basins of Catalonia, which includes the indicators determining the good or bad chemical status for each of the groundwater bodies. The calculation of their threshold values has been too conservative, due to the lack of specific studies in the different aquifers. In this sense, most of the threshold values established in groundwater correspond to the limits required by Spanish drinking water law (RD 140/2003), which it is an overly restricted view given that these water resources are not only used for human consumption, and they would require lower quality standards (agriculture or industrial water users). In addition, in Llobregat demo site, the groundwater extracted from the aquifer is treated via advanced purification processes, such as ultrafiltration, ozonation, activated carbon filtration and reverse osmosis, prior to its distribution to the drinking supply network.

The application of Water Safety Plan methodology to pre-potable water injection into the Lower Llobregat alluvial aquifer, has allowed to establish the main hazards, their causes and possible preventive measures to be taken into account. In addition, by using the results from the hydrogeological modelling and the analysis of the current legislation, the Critical Control Points and the Critical Limits of the chemical status indicators have been obtained. Special attention has been given to the identification of potential emerging organic contaminants in both, recharge water and groundwater, for their inclusion in the Water Safety Plan, renamed as Managed Aquifer Recharge Safety Plan (MAR-SP).

The phases of the Managed Aquifer Recharge Safety Plan more linked to the operational control of the managed recharge (validation and verification of the plan, record of results, etc.) would be carried out in case of obtaining the administrative permission for injecting pre-potable water at real scale.

1. Introduction

The following subchapters are focused on the development of an operative guidelines to safe pre-potable water injection via managed aquifer recharge. The study presented here pretends to be a more detailed analysis, based on previous hydrogeochemical assessment, in order to turn from local scale demo site results to real scale MAR operation. In order to do this, it has been performed an exhaustive identification of key variables that must be taken into account in the proposed guideline, that could be named as Managed Aquifer Recharge Safety Plan (*MAR–SP*).

For many groundwater recharge projects the inherent risks to public health and the environment are low and this can be easily demonstrated. This alleviates the need for more rigorous evaluation. Generic criteria to pass simple assessment are:

1. the aquifer being recharged is not used as a drinking water supply
2. the scale of recharge is small, for example domestic-scale rainwater harvesting
3. the water being recharged is roof runoff or non-polluted runoff and contains no wastes
4. the area around the recharge zone is never waterlogged

Additional criteria, may be required by the regional authority to deal with local conditions. For example the regional authority may specify qualifying criteria for the design and construction of recharge systems, as it was accomplished at DESSIN framework project. In this sense, at the beginning of the project the list of measurable contaminants was jointly defined by water authority (ACA), public health administration (ASPCAT) and water operator (AB).

The viability assessment evaluates the apparent viability of a proposed recharge project using relevant existing data and information. This fact has been widely demonstrated during the operation of the Llobregat ASR site in the framework of DESSIN project. Generic questions to pass viability assessment are:

1. Is there a sufficient demand for water?
2. Is there an adequate source of water available for allocation to recharge?
3. Is there a suitable aquifer for storage and recovery of the required volume?
4. Is there sufficient space available for capture and treatment of the water?

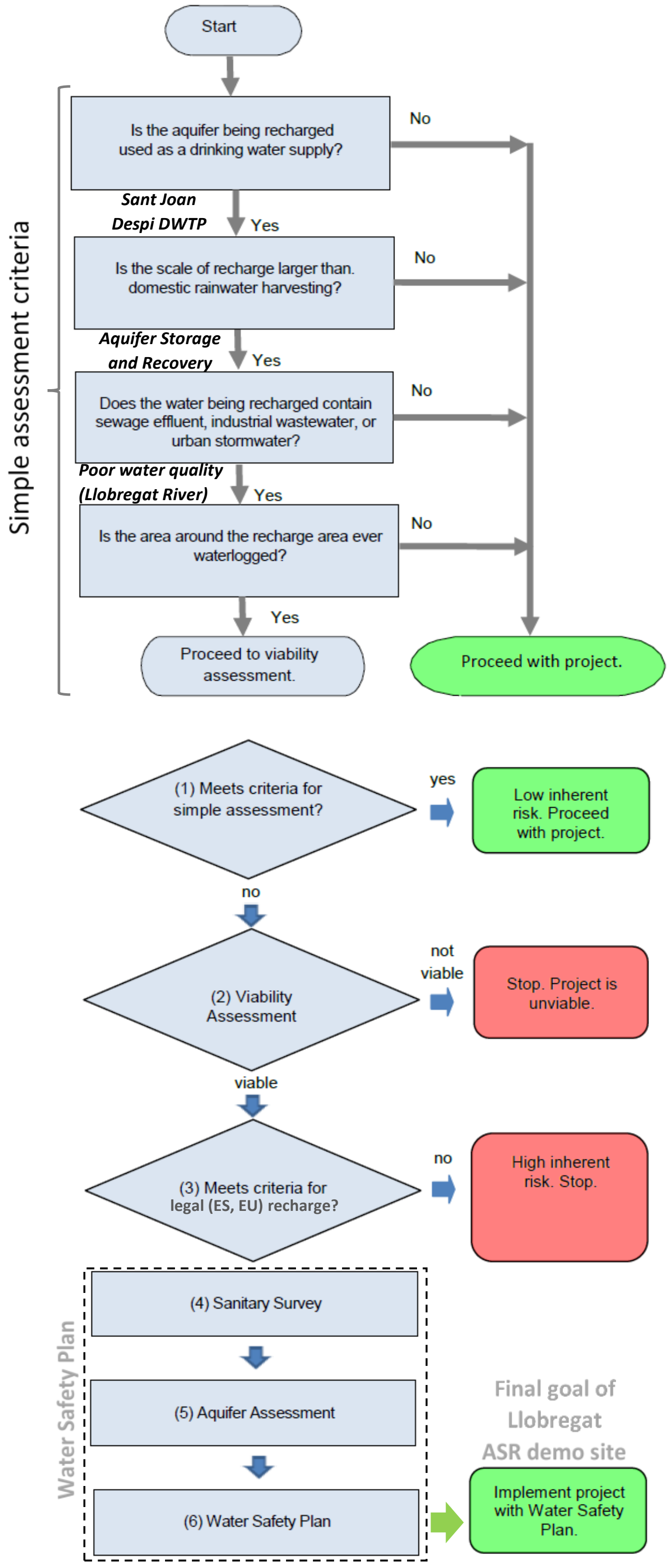


Figure 1: A diagram of the steps involved in applying a guideline for managed aquifer recharge including implementation of a water safety plan. Modified from Dillon et al. (2014)

2. Objectives

The objectives of the present deliverable are:

1. To developed risk-based guidelines and recommendations for managed aquifer recharge using pre-potable water

2. To apply these guidelines and recommendations in Llobregat demo site, identifying the main variables that must be taken into account to turn demonstrative phase into operative phase

3. Legal framework applied to groundwater

The establishment of legal criteria applied to both recharge water and aquifer water is one of the main challenges in developing a guideline for safe pre-potable water injection. The integration of managed aquifer recharge into a Water Safety Plan (WSF) should be able to assess the impact of such recharge on the status of the groundwater body. In this sense, the analysis would be more focused on aspects related to the chemical status, given that the quantitative one is expected to improve in any scenario. In the recent hydrological plan of the Catalan river basin district (ACA, 2017), the groundwater body *Vall Baixa i Delta del Llobregat* (code ES100MSBT39_001) is defined as poor chemical and quantitative status.

Currently, one of the main constraints is that there is no specific legislation for groundwater, setting the threshold values (TVs) for the different pollutants that need to be evaluated (see Figure 2). In the case of groundwater, the EU Groundwater Directive (2006/118/EC) – GWD – sets a threshold of 50 mg/L for nitrates and 0.1 µg/L for each individual pesticide (total pesticides: 0.5 µg/L), with no limits to be applied concerning most of emerging organic contaminants. This European normative was transposed into Spanish law via Royal Decree 1514/2009 of October 2, setting rules and regulations for protecting groundwater against pollution.

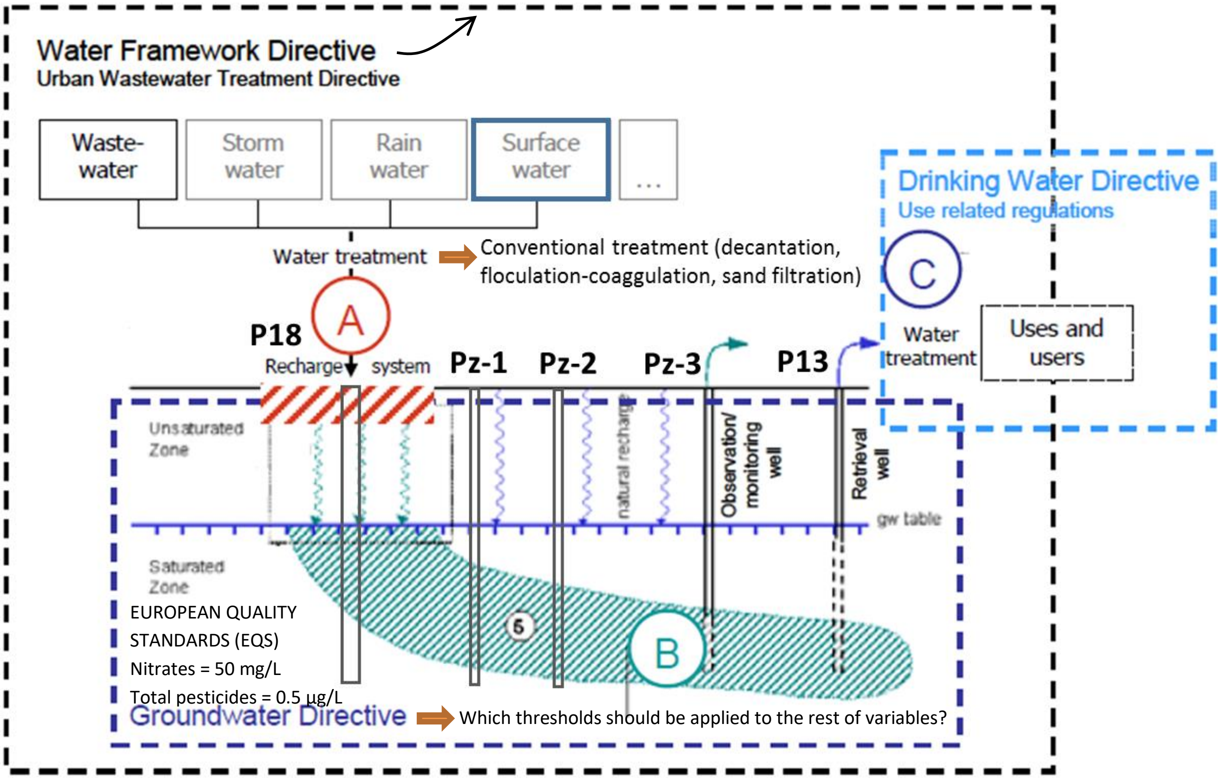
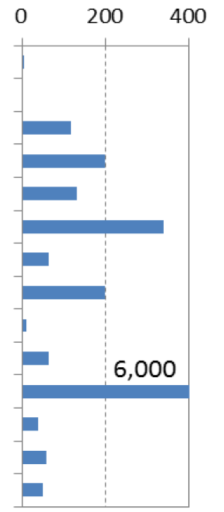


Figure 2: Legal framework governing managed aquifer recharge experiences in EU, focusing on Llobregat ASR demo site. Source: modified from

There is a great variability regarding threshold values provided by the Member States of the European Union (Table 1), with differences ranging from 5 (nitrates) to 6,000 x-times (Anthracene). Nitrates and total pesticides are covered by Annex I of the GWD giving common European quality standards for groundwater chemical status assessment. For the Annex II substances, TVs were most commonly established in Europe, among them ammonium, arsenic, cadmium, chloride and lead showed considerably high ranges of TVs between Member States but also within international RBDs. Copper, nickel and zinc are other naturally occurring substances not listed in Annex II GWD but were also reported by a considerable number of Member States. Anthracene, chloroform, toluene and xylene were the most frequently reported synthetic substances, all with considerably high variations of TVs, especially in the case of Anthracene (Table 1).

Table 1: Ranges of groundwater threshold values reported by European Member States (MS) and River Basin Districts (RBDs). Source: Scheidleder (2012)

Selected substance	**Reported from**		**Threshold values**		**Unit**	**TV Range (x-times)**
	MS	**RBDs**	**from**	**to**		
Nitrates*	5	30	10.68	50	mg/l	5
Total Pesticides*	1	7	0.375		µg/l	
Ammonium**	23	114	0.084^{+}	9.9	mg/l	118
Chloride**	25	126	24	4,750	mg/l	198
Arsenic**	22	116	5	653	µg/l	131
Cadmium**	20	114	0.08	27	µg/l	338
Lead**	22	116	5	320	µg/l	64
Copper	9	47	10.1	2,000	µg/l	198
Nickel	11	77	10	116	µg/l	12
Zinc	6	43	58	3,750	µg/l	65
Anthracene	3	28	0.01	60	µg/l	6,000
Chloroform	5	28	2.53	100	µg/l	40
Toluene	5	28	12	700	µg/l	58
Xylene	5	28	10	500	µg/l	50
Total	**25**	**133**				



* Annex I substance ** Annex II substance $^{+}$ reported for NH_4-N and recalculated to NH_4

In general, Member States based the establishment of TVs on the requirements of WFD and GWD and they also frequently reported having considered and applied the procedures laid down in the *CIS Guidance Document No. 182* which aims at supporting Member States in the establishment of groundwater threshold values and the assessment of groundwater status. However, the WFD and the GWD leave too much flexibility to the Member States in establishing TVs, and hence in assessing groundwater chemical status, as it may be observed in Table 1.

Regarding Llobregat demo site, the reported substances for Scheidleder (2012) coincide with those defined by Spanish administration (Annex II of RD 1514/2009), which also included sulphates, nitrites, phosphates, trichloroethylene, tetrachloroethylene and electrical conductivity, required by the Annex II of GWD (2006). In the hydrological plan of Catalan river basin district (ACA, 2017) have been estimated regional threshold values based on Spanish law and additional characterization for specific compounds. These estimates can be found in Annex VIII (environmental objectives) and may serve as a reference values to evaluate the suitability of pre-potable water as a source for aquifer storage and recovery (ASR), comparing the Catalan TVs with the values obtained during DESSIN project (Table 2). In this sense, none of the analysed variables in sand-filtered water (SFW) and groundwater control points (Pz-1, Pz-2, and Pz-3) during deep injection were above the threshold values set by Catalan Water Agency (ACA) and even for Spanish drinking water standards (RD 140/2003), with the exception of chloride in the case of control piezometers (CP).

Table 2: Groundwater threshold values conditioning the chemical status of "Vall Baixa i Delta del Llobregat" GWB along with different legal regulations and DESSIN results. Source: ACA (2017), GWD (2006), Scheidleder (2012), RD 140/2003 (Spanish drinking water law). Notes: CP (mean value from control piezometers), SFW (mean value from pre-potable water), LOD (limit of detection). Total pesticides* = Diuron + Isoproturon + Simazine

		Groundwater			Drinking water	DESSIN project		
Chemical status indicators	**Units**	**ACA (2017)**	**GWD (2006)**	**Scheidleder (2012)**	**RD 140/2003**	**GW**	**SFW**	**LOD**
As	µg/L	20	-	5 - 653	10	<LOD	<LOD	3
B	µg/L	1000	-	-	1000	128	139	30
Cd	µg/L	4	-	0.08 - 27	5	<LOD	<LOD	1
Cr	µg/L	30	-	-	50	<LOD	<LOD	5
Hg	µg/L	1	-	-	1	<LOD	<LOD	0.05
Pb	µg/L	18	-	5 - 320	10	2.7	1.9	3
EC (20ºC)	µs/cm	2300	-	-	2500	1513	1308	-
Cl	mg/L	480	-	24 - 4750	250	252	235	10
NO_3	mg/L	50	50	10 - 50	50	7.3	7.2	0.5/1
NH_4	mg/L	0.5	-	0.1 - 10	0.5	0.1	<LOD	0.08
SO_4	mg/L	300	-	-	250	139	125	5
Tetrachloroethylene	µg/L	5	-		$\Sigma < 10$	0.5	<LOD	0.5
Trichloroethylene	µg/L	5	-			0.3	<LOD	0.5
Pesticide	µg/L	0.1	0.1	-		-	-	-
Total pesticides*	µg/L	0.5	0.5	0.375		0.0196	0.0175	0.005

In Table 2 it can be clearly seen how the thresholds established by ACA to determine the chemical status of the "*Vall Baixa i Delta del Llobregat*" GWB are very close to those values characterising Spanish drinking water law. It can be concluded that groundwater are treated as if they were practically potable water, being a quite restrictive approach. The two only variables where the Catalan TVs are significantly higher in groundwater with respect to drinking water standards correspond to Cl^- and SO_4^{2-}, with values of 480 and 300 mg/L, respectively, significantly higher than those obtained in groundwater during deep pre-potable water injection.

4. Managed Aquifer Recharge Safety Plan

Once it has been demonstrated that sand-filtered water meets the legal criteria for its use in Llobregat ASR demo site, it is necessary to get through the steps defined in Figure 1 to effectively include the aquifer storage and recovery scheme in the existing Water Safety Plan (WSP) at SJD DWTP (see Figure 3). In fact, the last section (3) could be considered as the legal requirements of the WSP.

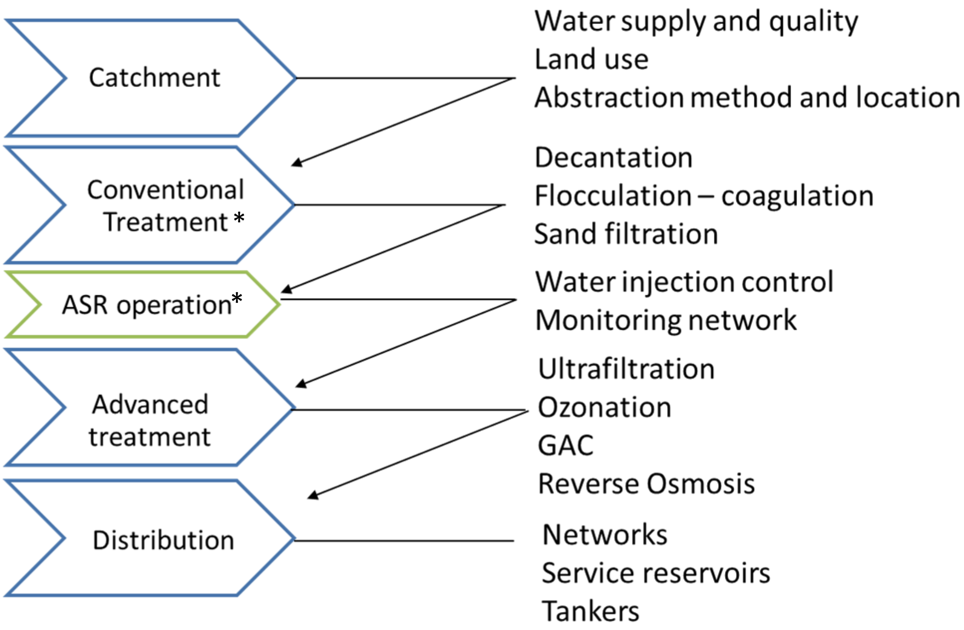


Figure 3: Operative inclusion of ASR scheme in the functioning of the SJD DWTP. Notes: * = key phases

The risk assessment carried out by WSP is based on the *HACCP* methodology (Analysis of Hazards and Critical Control Points), in order to systematically identify the hazards that would affect the water system, the control measures that would correspond to each of these hazards, and their monitoring programme. The main steps to carry out a WSP are:

1. Identify hazards and preventive measures
2. Identify Critical Control Points (CCP)
3. Establish Critical Limits (CL)
4. Establish a monitoring programme for the CCP
5. Establish corrective actions
6. Validation and verification of the WSP
7. Register of result, observations and corrective measures

This type of methodological approach has been applied to different managed aquifer recharge projects (Swierc *et al.,* 2005; Page *et al.,* 2008; Dillon *et al.,* 2014; Ji and Lee, 2016) covering different facilities (RBF, ASR, ASTR, etc.), but, in general, it has not been extensively used. In the following sections the preliminary study carried out in Llobregat ASR demo site will be described.

4.1 Identify hazards and preventive measures

The main hazards that have been identified in the injection phase of sand filtered water into the aquifer are strongly determined by the Llobregat River quality, which presents numerous wastewater and industrial discharges from the middle part of its basin to the water intake pipe used to transport raw water to DWTP. In addition, its Mediterranean regime adds more uncertainty on the temporal evolution of the main quality parameters to take into account in the Water Safety Plan, highly influenced by more frequent and intense drought and flood events due to climate change. In Figure 4 it is shown one of the main identified hazards, related to contamination episodes linked to heavy rainfall and, consequently, to mobilization of contaminated materials and combined sewer overflows discharges.

Figure 4: Simplified scheme of an episode of surface water contamination during high-flow conditions in Llobregat River

The riskiness of injecting heavily contaminated surface/sand-filtered water into the aquifer is partly limited by the current operating rule established in SJD DWTP. AB's Water Safety Plan has implemented a preventive measure to surface water intake pipe in order to control the pollution by unsaturated organic matter, analysing the turbidity via UV Absorbance (A254 nm) as a control parameter. This control parameter has an operational threshold of 20 Abs/100 cm (at 254 nm), above which the DWTP stops drawing off water from Llobregat River.

Besides the hazards related to pollution by organic compounds, it has been identified six hazards directly associated with the phase concerning deep water injection via ASR (Table 3). This assessment was based on the microbiological and hydrogeochemical analysis covered by the present deliverable. As it was said before, most of the hazards are conditioned by the quality of the injected water. The preventive measures to be set to meet a safe pre-potable water injection are related to systematic and real-time control both sand-filtered water and groundwater. The risk assessment for each of the identified hazards is a pending task.

Regarding bio-clogging hazard, after evaluation of a pilot scale work, it is suggested to use SFW as injection water because it is demonstrated that although clogging can occur, it is expected that it will not negatively affect the correct operation of the ASR Llobregat system. Future research at the Llobregat site focusing on SFW injection in a fully-operative ASR well will allow us to confirm these preliminary conclusions (Camprovin *et al.,* 2016).

Table 3: Hazards, causes and preventive measures identification in the phase of ASR operation. Notes: EOCs = emerging organic contaminants

Phase	Hazards	Causes	Preventive measures
ASR OPERATION	Increasing number of enteropathogenic bacteria	Presence in sand-filtered water	The presence of residual chlorine must be ensured in the final stage of chlorination
	Presence of viruses	Presence in sand-filtered water	The concentration of virus in sand-filtered water is systematically controlled
	Mobilization of heavy metals	Change in REDOX conditions	Real-time control of pH and redox potential (Eh) in sand-filtered water and groundwater monitoring network
	EOCs bio-accumulation	Presence in sand-filtered water	These compounds are found in sand-filtered water. It is planned to perform sampling campaigns in groundwater monitoring network to evaluate the impact of the possible bioaccumulation of EOCs in the short, medium and long term
	Chlorites and chlorates accumulation	Presence in sand-filtered water	Optimize the ClO_2 dosage as much as possible
	Nitrate contamination	Presence in sand-filtered water	The concentration of NO_3 is systematically controlled in sand-filtered water and groundwater monitoring network
	Bio-clogging in injection wells	High values of TOC and turbidity	Real-time control of TOC and turbidity in sand-filtered water

4.2 Identify Critical Control Points

It is important to note that a risk screening process was applied to the Llobregat demo site at the beginning of the project, searching for control points to effectively assessed the of ASR in groundwater quality. It was related to the choice of the points (control piezometers and existing wells) at which compliance with the GWD has been evaluated. Points of compliance (POC) were defined by WFD-CIS (2007) and can be applied to MAR facilities according to:

- POC 0: this POC is located at the base of the source in the unsaturated zone. It could therefore be situated just below the point/area of recharge (e.g. infiltration pond). The purpose of POC 0 is to assess if a pollutant input takes place, what the pollutants are, and whether the groundwater could be affected.

- POC 1: this POC is located at the point of input into the groundwater; for a direct input (e.g. well injection), POC 0 is the same as POC 1, but the function is different. At POC 1 the actual concentration in the groundwater itself is primarily taken into account, whereas at POC 0 one primarily looks at the properties of the source itself as explained above. Conceptually, POC 1 would correspond to control piezometers Pz-1, Pz-2 and Pz-3 (see Figure 5).

- POC 2: this POC is located hydraulically down gradient from the recharge area in between POC 1 and a receptor. The purpose of this compliance point is to provide an early warning that the receptor might be impacted. It is also used during the risk assessment process for predicting the potential impact of the input. POC 2 would refer to wells P10 and P13.

- POC 3: This POC is used to assess whether the desired groundwater quality is reached and to monitor the impact at the receptor. If a risk assessment shows that the pollutant will exceed the compliance value at this POC, then pollution is likely to occur as a result of the input. Measures/controls will need to be put in place to remove this impact, or the activity should not be permitted. For a more detailed control of injected water, wells P19 and P11 might be included as POC 3.

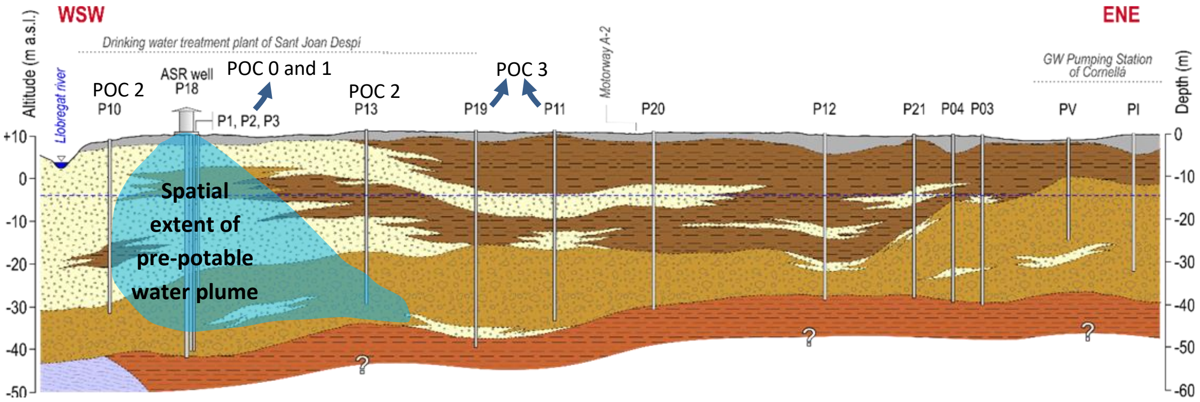


Figure 5: Components of MAR and possible points of compliance (POC). Notes: the extent of pre-potable water plume has been estimated by using chlorates as an artificial tracer during demonstration phase

In case of MAR schemes the receptor at risk can be defined by the groundwater beyond the attenuation zone at POC 3. The attenuation zone is the area surrounding the recharge area where groundwater quality changes takes place due to natural processes in the aquifer (e.g. straining, degradation, sorption, dissolution/precipitation, inactivation (die-off), decay or mixing). During MAR schemes such as deep well injection (Llobregat demo site) unsaturated conditions below the injection point are not always considered, and POC 0 and POC 1 cannot be clearly distinguished.

When managed aquifer recharge occurs nearby a public source of drinking water, it is necessary to take into account all the potential impact affecting other water users (Dillon *et al.,* 2014). This raises the need for good quantitative information on water quality impacts so that there is no deterioration in the safety of the water supplies. In this sense, during DESSIN project has been developed a groundwater flow model in order to know the extent of the injected pre-potable water. Different scenarios were numerically modelled (deliverable D22.4.C), injecting 5, 10 and 15 hm^3 per year, and the maximum distance reached by injected water was 3 km, corresponding to the last scenario (Figure 6). This extent, mainly downstream injection zone, is out of the water supply wells from El Prat de Llobregat, considering the maximum value of injected water during historic ASR operation and a period of simulation of 30 years. It is proposed to combine the regional water quality network (surrounding points to the injection zone), the Cornella's wellfield and other public water supply wells (e.g. Aigües del Prat) in order to give confidence on the effects of artificial recharge on groundwater levels and quality at regional level.

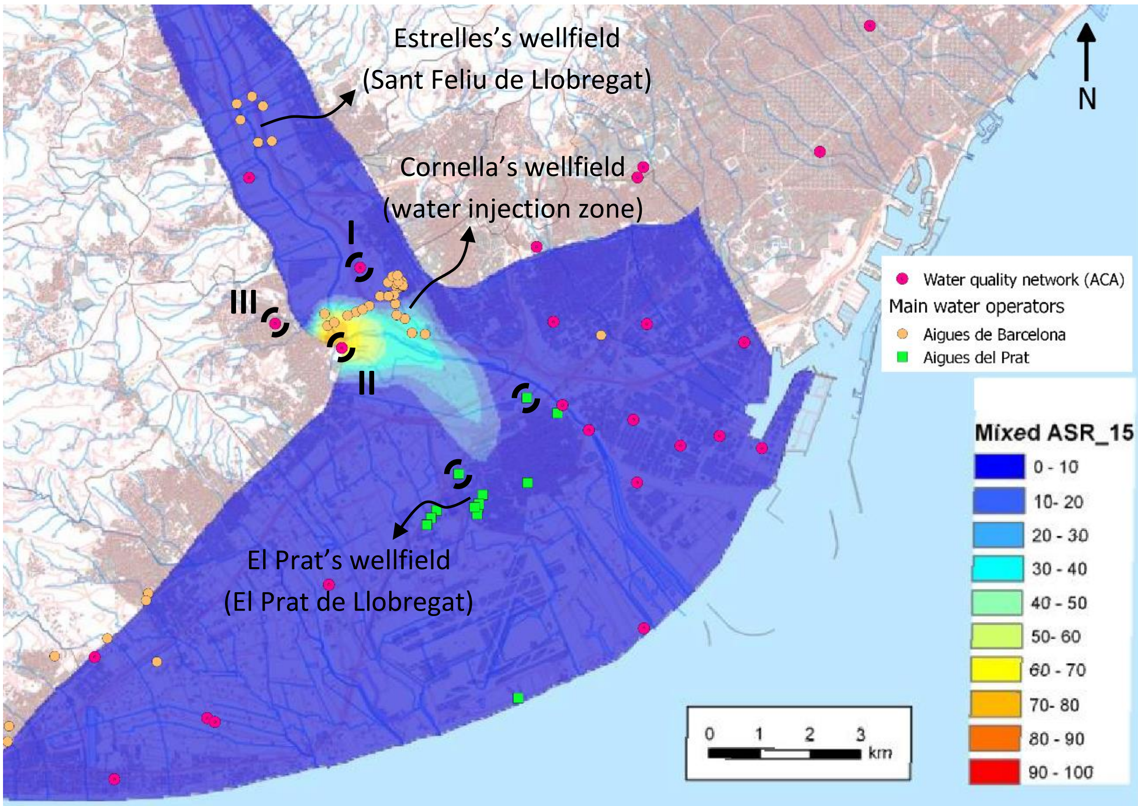


Figure 6: Proposal of an external groundwater monitoring network taking into account the arrival plume (% of mixture) in the full-scale phase (volume injected = 15 Mm^3/year). Notes: I = Pou Gallina Blanca 1; II = Pou 1 Estació Servei Oasis; III = Pou 1 Complex Benito Menni. Source: modified from deliverable D22.4.C. Notes: external monitoring points with dashed lines would be included in the list of CCP

Regarding recharge water, other important CCPs would be the water intake point at the Llobregat River supplying water to the DWTP and the water coming from the sand filters before deep injection. These points are already part of the Water Safety Plant regulating the functioning of SJD DWTP.

4.3 Establish Critical Limits (CL) and measurable variables

With regard to the critical limits and measurable variables, it is proposed to use the TVs established by the Catalan Water Agency (ACA, 2017) for the identified parameters in its hydrological plan (Table 2). Due to the increasing importance of emerging organic contaminants (EOCs), the inherent uncertainty about their potential effects in human health and the type recharge water (pre-potable water) it has carried out a screening of most abundant compounds existing in Llobregat River water and groundwater ACA database.

4.3.1 Review of EOCs occurrence in Spanish and European aquifers

Rivers are usually heavily polluted because of the effluents of WWTPs, industries and agriculture runoff. Understanding the interactions between groundwater and surface water is a key issue to assess the fate of EOCs in the aquifers, especially in heavily pumped aquifers, where rivers are the main source of groundwater recharge. This is certainly the case at the River Llobregat (Vàzquez-Suñé et al., 2007). There are some studies where the concentrations of some EOCs in the river (Llobregat and Besòs) can be compared with those of the aquifers (Quintana *et al.*, 2001; López-Roldán *et al.*, 2004; Rodriguez-Mozaz *et al.*, 2004; Kampioti *et al.*, 2005; Tubau *et al.*, 2010; Huerta-Fontela *et al.*, 2011; Jurado *et al.,* 2012a). In general, the concentrations in the surface waters were higher than in the aquifers accounting for a wide array of pesticides, PhACs, DAs and selected industrial compounds (see Figure 7). These should indicate natural attenuation capacity in the aquifer due to physical processes, such as sorption and dilution and biochemical processes. However, some compounds presented higher maximum concentration in the aquifer, such as the pesticides simazine, isoproturon, metolachlor, DEA, propanil, cyanazine, TBA and molinate, the industrial compounds NP, OP, NP2EC and DEHP and the DAs methadone (METH) and ecstasy (MDMA). From these compounds, simazine, isoproturon, NP and OP were measured during DESSIN project at several control points close to injection well P18. The concentration of EOCs monitored in such a project has been compared with the maximum values obtained in Spanish and European groundwater studies.

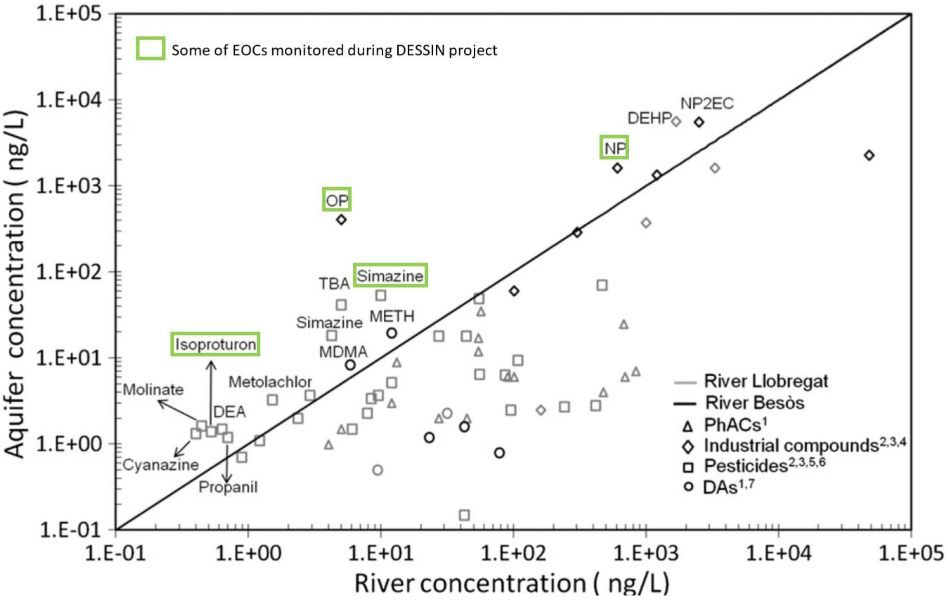


Figure 7: Measured concentrations of some EOCs in Llobregat (grey) and Besòs (black) rivers versus the concentrations reported in the aquifers of Barcelona. Note that aquifer concentrations are consistently much lower than surface waters for a wide array of compounds, suggesting the natural attenuation capacity of the aquifer. [1]Boleda et al. (2009), [2]López-Roldán et al. (2004), [3]Rodriguez-Mozaz et al. (2004), [4]Tubau et al. (2010), [5]Quintana et al. (2001), [6]Kampioti et al. (2005) and [7]Jurado et al. (2012a)

We decided to establish a comparison of the maximum concentrations detected and taking into account the most recent works performed in European countries. We used the study performed by Loos *et al.* (2010) to compare the maximum concentrations of EOCs because it is the unique representative work that has monitored polar organic pollutants in European groundwater. The maximum concentrations detected in the groundwater of Spain (Jurado *et al.,* 2012b), in DESSIN project and in the Pan-European survey for selected pesticides, PhACs, industrial compounds and life-style compounds are plotted in Figure 8.

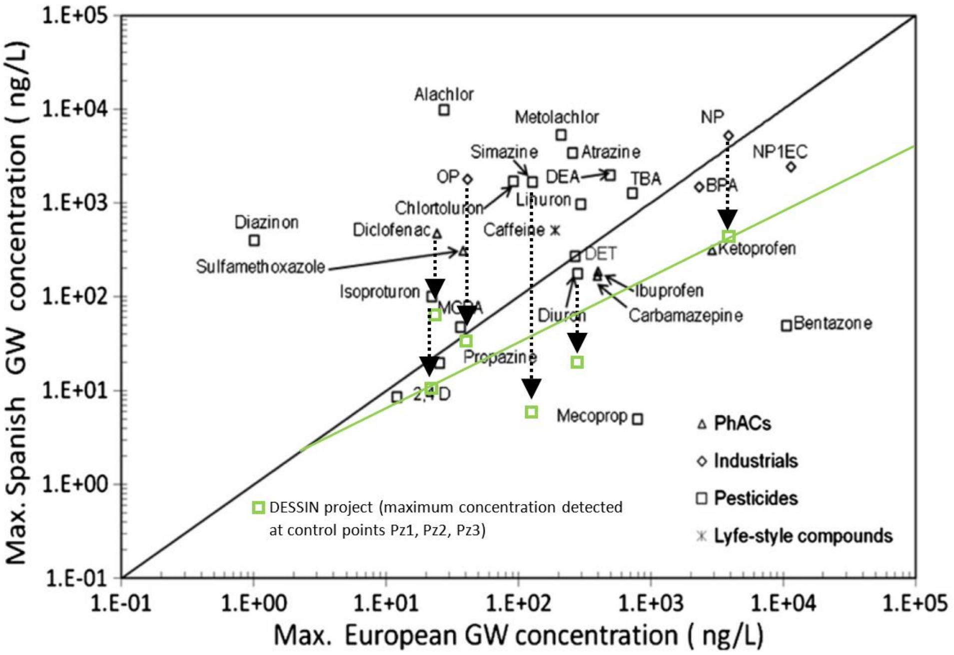


Figure 8: Maximum concentration of some EOCs in the groundwater (GW) of Spain and Lower Llobregat alluvial aquifer versus the maximum concentration reported in the study of Loos et al. (2010). The EOCs include PhACs, pesticides, industrial compounds and life-style compounds. Note: arrows represent the change in concentration between Spanish GW and DESSIN GW samples

In general, Spanish groundwater presents higher maximum concentrations than the Pan-European groundwater survey. The profile of groundwater contamination seems to be dominated by industrial compounds (the APEOs DPs NP and OP and BPA) because they show high maximum concentrations in Spain and the European countries' aquifers. Pesticides (mainly atrazine and its metabolite DEA, simazine and TBA and its transformation product desethylterbuthylazine (DET)) also contribute to groundwater contamination. With respect to DESSIN project, it can be seen that the maximum concentrations measured at control points during ASR operation are lower than the observed in Spain and European groundwater. It could be indicating that, at current operation scheme (average injection flow of 36 L/s), the infiltration of pre-potable water does not pose a significant risk of EOCs pollution.

4.3.2 Review of occurrence of EOCs in Llobregat River water and groundwater monitoring points (ACA database)

In order to identify those parameters that could be included in the MAR-SP, the ACA database concerning the Llobregat river station near the SJD ETAP and several groundwater control points nearby to the injection well were analysed. Regarding surface water, it has been identified five compounds with most of their measures above the limit of detection. These compounds can be seen in Table 4 along with the Spanish environmental quality standards (NCA), that regulate the fulfilment of the good chemical status for surface water bodies based on Water Framework Directive.

The temporal evolution of these variables is presented in Figure 9. Based on this evolution and the NCA thresholds, it has been proposed a warning system divided into four stages (normality, pre-alert, alert and emergency). The starting point to activate the warning system would correspond to a defined action limit of 10 ng/L, recommended in the EU project called KNAPPE (http://cordis.europa.eu/result/rcn/47745_en.html), below which it is assumed that the specific compound is unlikely to represent a risk for the environment.

Table 4: Spanish quality standards for the main emerging pollutants detected in Llobregat River water (2007 – 2017). Source: RD 817/2015; ACA database

Compound	Group	NCA-MA (ASC)	NCA-CMA (ASC)	GWD (2006)
Chlorpyrifos	Pesticide	30	100	100
Diazinon	Pesticide	-	-	
Metolachlor	Pesticide	-	-	
Terbutryne	Pesticide	65	340	
Terbuthylazine	Herbicide	-	-	
Notes:				
NCA	Spanish environmental Quality Standard (RD 817/2015)			
MA	Annual average (ng/L)			
CMA	Maximum Allowable Concentration (ng/L)			
ASC	Continental Surface Water (surface water)			

From the analysis of the organic compounds mostly detected in Llobregat River water, it has not been possible to identify any significant trend, with an overall time-constant behaviour throughout the studied period. It is recommended to perform more frequent chemical analysis of terbutryne and terbuthylazine, given their medians were found in the range characterising pre-alert phase, with values of about 20 ng/L (Figure 9). Due to the high variability observed in Chlorpyrifos concentrations (with several peaks above 100 ng/L) it should be included on the list of organic compounds most frequently analysed. In general, the highest emerging pollutants concentrations coincide in time for all studied variables. The correlation between the Llobregat River streamflow and the concentration of these pollutants has been evaluated by comparing the EOCs peak events with the associated Llobregat River discharge (Figure 10). The interest of this analysis relies on the fact that SJD DWTP closes the water intake pipe at Llobregat River during high-turbidity events. This analysis would be able to evaluate if this operating rule could impact somehow in minimising the risk of injecting high

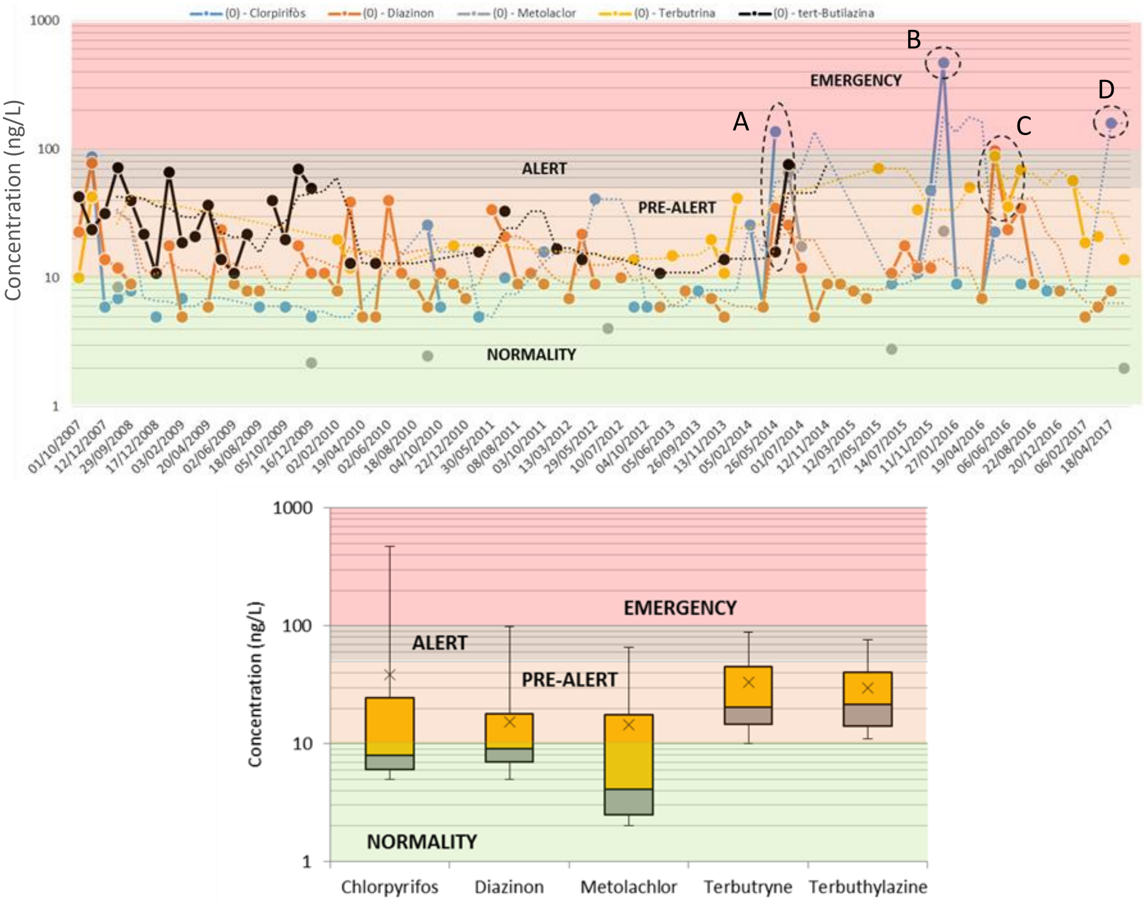
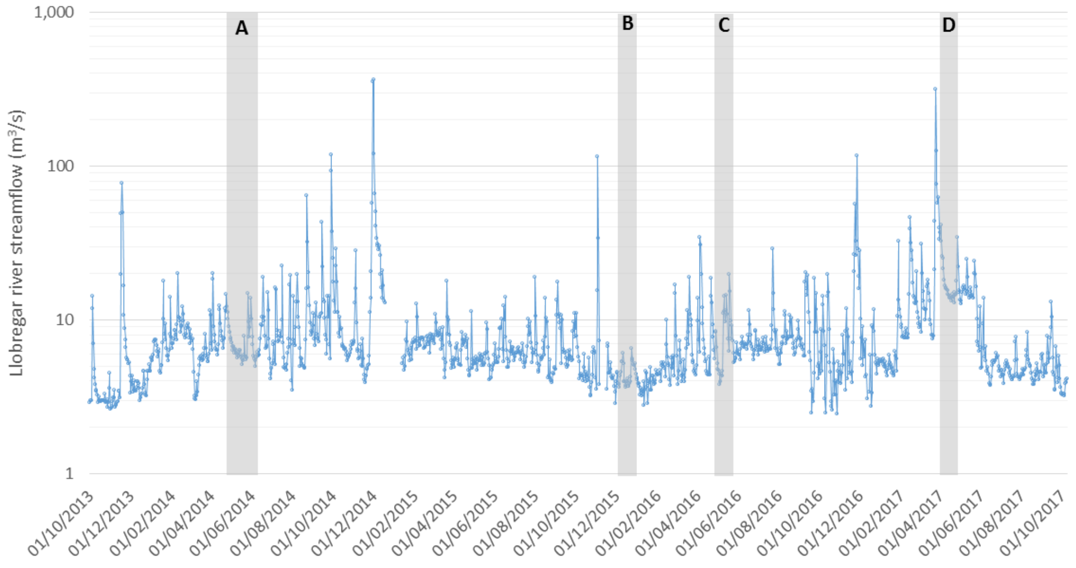


Figure 9: Temporal evolution and box-plots of the main emerging pollutants detected in Llobregat River gauging station, nearby SJD ETAP. Source: ACA database. Note: thin dashed lines are referred to 4 period moving average and thick dashed lines to EOCs peak events (A, B, C and D)



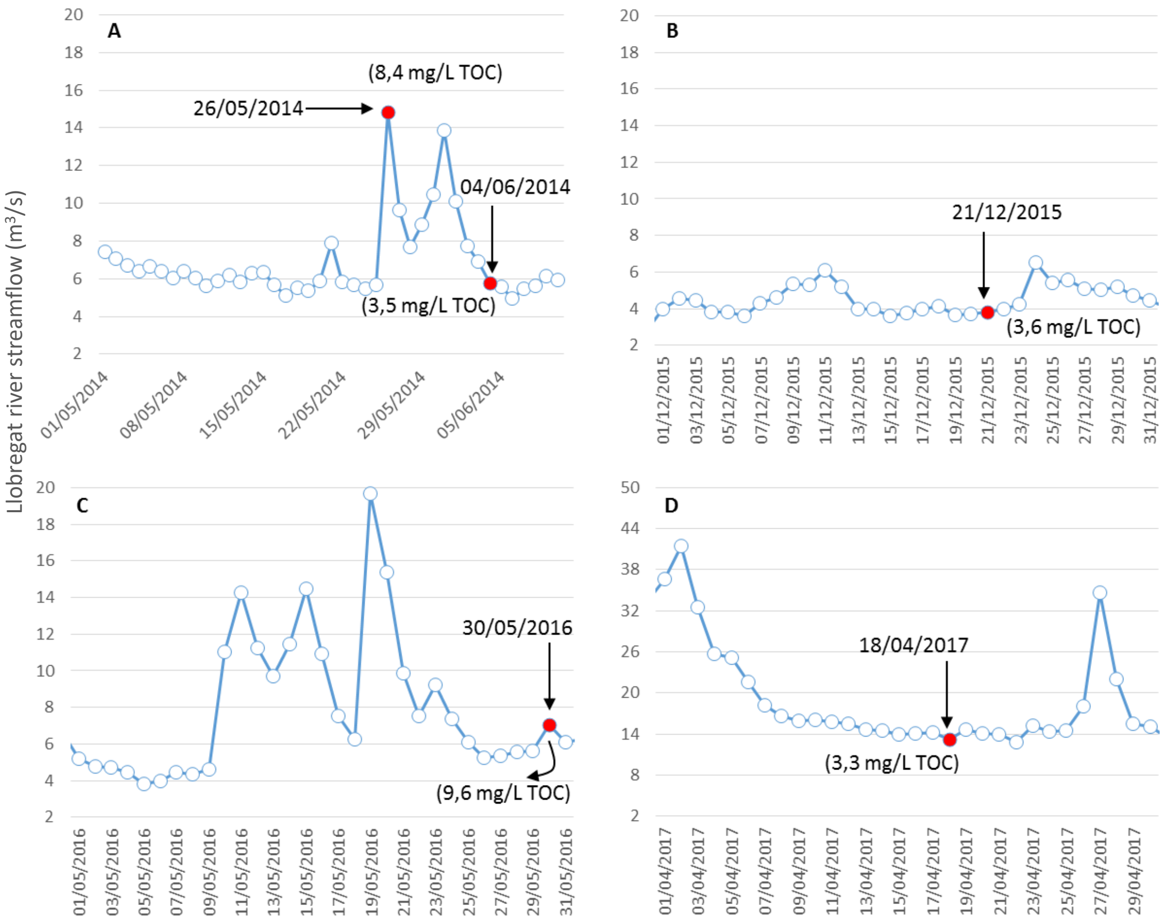


Figure 10: Temporal evolution of Llobregat River discharge (m^3/s) at SJD gauging station with sub-graphs indicating the sampling date in which the highest concentration of EOCs was measured (red circle). Notes: TOC = Total Organic Carbon. Source: ACA database

EOCs concentrations via aquifer storage and recovery infrastructure. In Figure 10 it can be observed that there is no clear relationship between highest EOCs concentrations and highest Llobregat River discharges, especially for Chlorpyrifos concentrations at events B and D (Figs. 9 and 10). The highest EOCs concentration during peak events A and C could be related with the dominant high-flow conditions in Llobregat River water, given the existence of recent runoff peaks few days before water sampling (Figure 10). This fact suggests that further research is needed to understand the behaviour of the EOCs during peak flows and their importance on risk assessment concerning ASR operation with pre-potable water.

Concerning groundwater monitoring points from ACA database, the main EOCs identified are completely different. They correspond to organic compounds and chlorinated solvents (Figure 11), related to past industrial activities that took place in the study area. These activities gave rise to a historical contamination at Lower Llobregat alluvial aquifer, as it was mentioned in the chapter concerning organic compounds evaluation during ASR operation. In this chapter was demonstrated that sand-filtered water did not contain organic halogen compounds in concentrations above limits of detection. In the same way as Llobregat River water, it has been gathered the Spanish quality standards for the variables identified to establish a preliminary threshold, as well as River Basin Management Plan chemical status indicators (ACA, 2017).

Table 5: Spanish quality standards for the main emerging pollutants detected in groundwater monitoring points (2007 – 2017). Source: RD 817/2015; ACA database

Compound	Group	NCA-MA (ASC)	ACA (2017)
1,1,2-Trichloroethane	Organic halogen compound	-	-
Bromoform	Brominated organic solvent	-	-
Methyl tert-butyl ether	Organic compound	-	-
Tetrachloroethylene	Organic halogen compound	10	5
Trichloroethylene	Organic halogen compound	10	5
Trichloromethane	Organic halogen compound	2.5	-
Notes:			
NCA	Spanish environmental Quality Standard (RD 817/2015)		
MA	Annual average (µg/L)		
ASC	Continental Surface Water (surface water)		

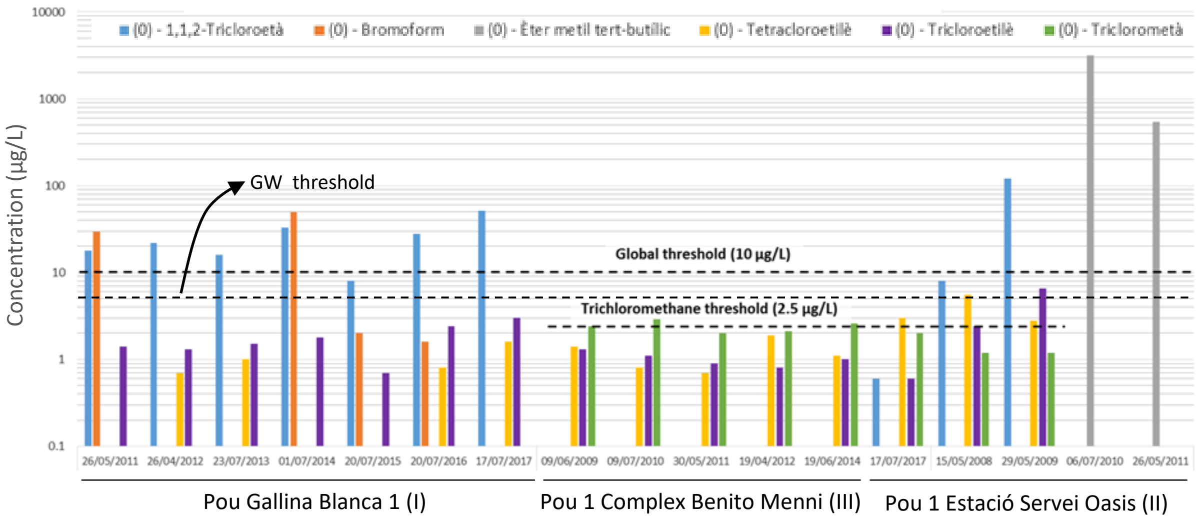


Figure 11: Temporal evolution of the main organic pollutants detected in groundwater monitoring points, nearby SJD ETAP. Source: ACA database

The groundwater monitoring point with a higher percentage of water samples above threshold limits corresponds to "*Pou Gallina Blanca 1"*, especially for the 1,1,2-Trichloroethane and Bromoform. The concentration of these compounds in surface water are significantly lower than the observed in groundwater, with values below limit of detection for the former (LOD = 2.5 µg/L) and an average value of 0.93 µg/L for the latter. The peak concentrations observed for Methyl tert-butyl ether (MTBE) at "*Pou Estació Servei Oasis*" well (3,140 and 539 µg/L) could be related to fuel leakage from the service station located nearby the control point. MTBE is a gasoline additive, used as an oxygenate to raise the octane number. Its use is controversial because of groundwater contamination and legislation favouring ethanol.

Therefore, the proposed organic chlorinated compounds to be included on the list of measured contaminants in pre-potable injected water are: 1,1,2 – Trichloroethane and Bromoform due to their higher concentration with respect to the rest of organic compounds, and tetrachloroethylene and trichloroethylene given the existence of groundwater-based legal limitations (see ACA values in Table 5). These variables are already included in the Water Safety Plan established by AB in SJD Drinking Water Treatment Plan, concerning groundwater extraction phase.

4.3.3 Review of occurrence of EOCs in Llobregat River water – basin scale studies

Banjact *et al.* (2015) performed an exhaustive analysis of 160 priority and emerging contaminants belonging to different families (pharmaceuticals and hormones, personal care compounds, pesticides, PFASs, illegal drugs, and industrial organic products) at Llobregat River basin. They also calculated in-stream removal of pollutants, expressed as the fraction of the total emission which is eliminated by the river for every compound. This elimination rate will be used to determine the constituents included on the list of sand-filtered water control EOCs, as well as their maximum river concentration. In this sense, the existent relationship between maximum concentration and river attenuation is shown in Figure 12 for each group of emerging pollutants.

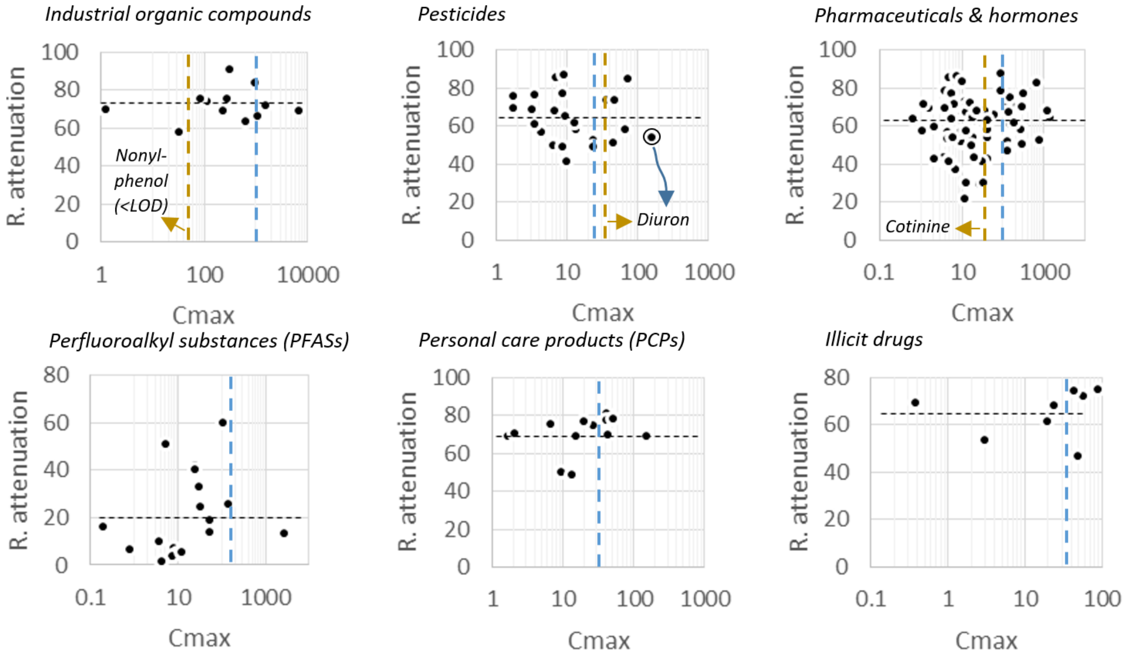


Figure 12: Relationship between maximum EOCs concentration (ng/L) and their associated mean river attenuation rates (%) for each group of pollutants at Llobregat River basin. Source: Banjac et al. (2015). Notes: black and blue dashed lines are referred to average river attenuation rate and maximum EOCs concentration, respectively; brown dashed line corresponds to sand-filtered water maximum EOCs concentration; LOD = limit of detection

Industrial organic compounds are still dominant (average value of 1,000 ng/L) over the other classes, being pharmaceuticals and PFASs about one order of magnitude less, and pesticides, PCPs and illicit drugs occupying the last positions. In-stream removal of pollutants may be seen as a 'detoxification' process provided by the aquatic environment, and in that sense it could be truly qualified as an ecosystem service related to water purification. Elimination of organic micropollutants in the river encompasses several biotic and abiotic processes such as biodegradation, sorption by sediments and suspended particulate material, photolysis, hydrolysis, volatilization, etc. (Banjac *et al.,* 2015).

The percentage of the original emissions that has been depleted by in-stream processes for the different compounds showed an average of 58%, although huge variability was apparent (see Figure 12). The rates of elimination were, on average, around 60 to 70% for all classes, except for PFASs, which were poorly eliminated ca. 20% on average and can be therefore considered as persistent (i.e., quasi conservative). Therefore, some of these compounds must be included on the list of sand-filtered water control EOCs. The sand-filtered water maximum EOCs concentrations for industrial organic compounds, pesticides and pharmaceutical products are within the range of the Llobregat River samples analysed by Banjac *et al.* (2015), with higher values in the case of Diuron, although the maximum concentration (33 ng/L) was below European drinking water threshold (100 ng/L).

In order to assess the order of magnitude of the emerging pollutants analysed during ASR operation at Llobregat demo site, it has been carried out a comparative study between the maximum concentrations measured by Banjac *et al.* (2015) at Llobregat River, the Spanish quality standards for surface water (RD 817/2015) and DESSIN EOCs results (Figure 13).

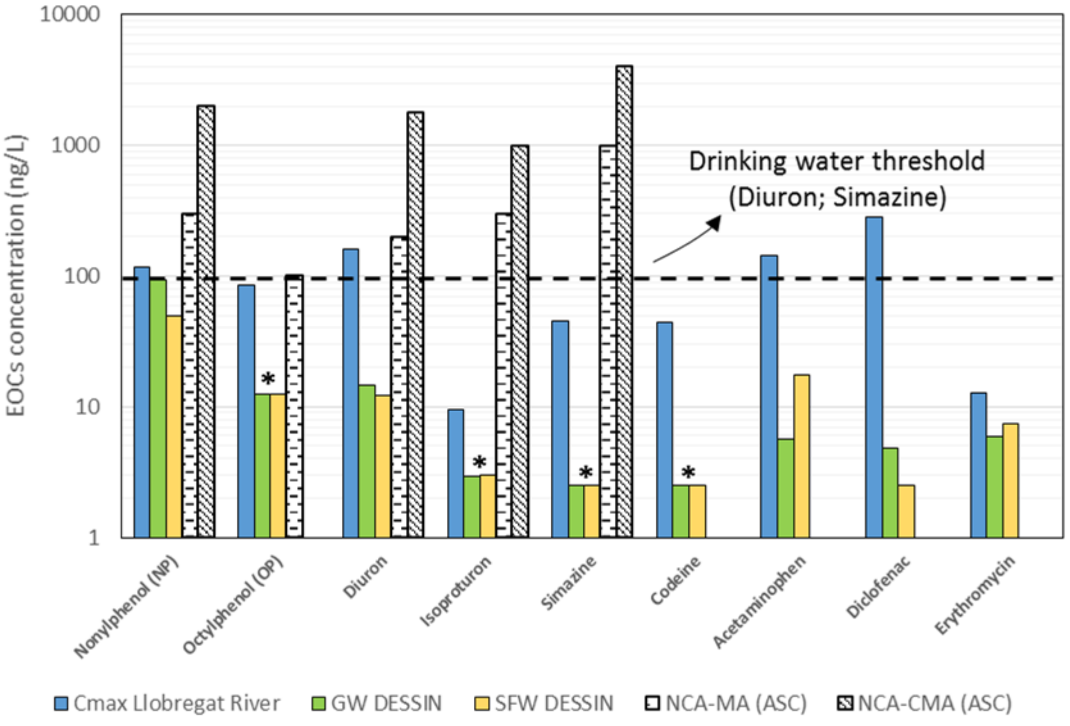


Figure 13: EOCs concentration (ng/L) corresponding to Banjac et al. (2015) study (blue bars), Spanish quality standards for surface water quality assessment (filled bars), and average DESSIN results for groundwater (GW) and sand-filtered water (SFW). Source: Banjac et al. (2015); RD 817/2015. Notes: asterisks are referred to compounds with all their values below limits of detection; significance for NCA values can be found in Table 4

It can be observed that for most of the analysed organic compounds, DESSIN results were found to be below the action limit of 10 ng/L, showing no significant risk of EOCs accumulation in groundwater at current injection boundary conditions. With respect to Llobregat River water, it shows concentrations significantly lower than those established in Spanish surface water quality legislation, with maximum allowable concentration (NCA-CMA) about one order of magnitude higher. The concentration of Nonylphenol for GW DESSIN is supposed to be due to contamination during the water sampling procedure, because this industrial organic compound was not detected in sand-filtered water (50 ng/L < LOD).

The selection of new EOCs to be included on the list of measured contaminants in pre-potable injected water has done following different aspects; such as the maximum concentration in Llobregat River water (C_{max}), the in-stream natural attenuation and the potential bioaccumulation concerning water solubility (S_w) and octanol – water partition coefficient (K_{ow}).

With respect to the maximum concentration and river attenuation rates, it has been used the results published in Banjac *et al.* (2015) in relation to Llobregat River water. The proposal of seven new EOCs has been mainly based on the maximum concentration measured in surface water, with concentrations one order of magnitude higher (≥ 1,000 ng/L) than those observed in DESSSIN-controlled organic compounds (Figure 14). The river attenuation rates are very similar among the different EOCs, except for L-PFOS (Perfluoroalkyl substance), so it is not a useful parameter to discriminate between organic micro-contaminants to be controlled in real-scale aquifer storage and recovery (ASR).

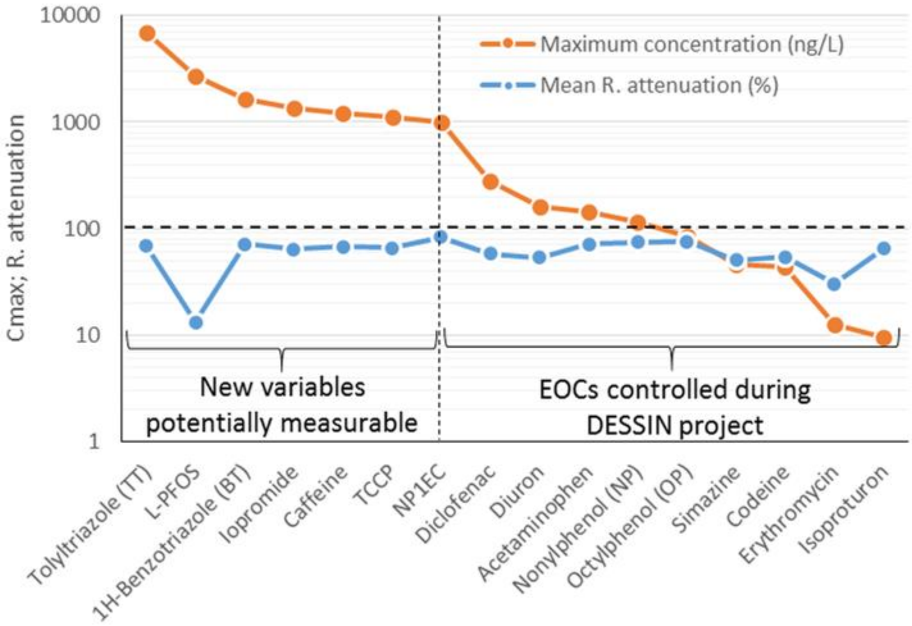


Figure 14: Emerging organic contaminants (EOCs) detected in Llobregat River water classified by its maximum concentration (ng/L) and river attenuation rate (%). Source: Banjac et al. (2015)

Regarding potential bio-accumulation (see Figure 15), it has been consulted the study developed by Jurado *et al.* (2012b) about the physic-chemical properties of EOCs. Among contaminants properties, the octanol-water partition coefficient (K_{ow}) and the water solubility (S_w) are valuable parameters. The octanol-water partition coefficient is usually expressed as log K_{ow}. It measures how hydrophilic (log $K_{ow} < 4$) or hydrophobic (log $K_{ow} > 4$) and EOC is. Hydrophobic EOCs tend to bioaccumulate and usually have a high adsorption capacity especially onto organic matter (Jurado *et al.,* 2012b). Conversely, EOCs with low log K_{ow} values tend to have high S_w and both lower bioaccumulation potential and soil/sediment adsorption coefficients (Silva *et al.,* 2012).

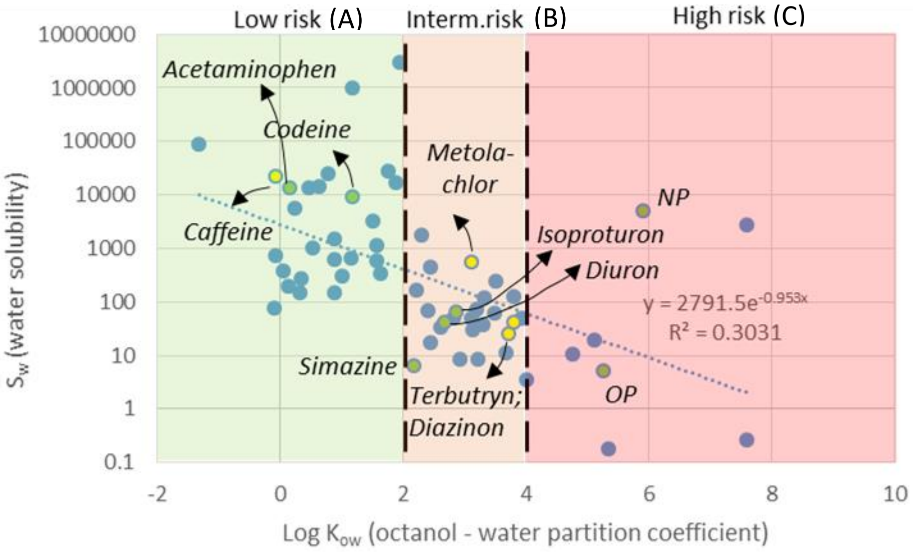


Figure 15: Assessment of potential risk of bio-accumulation of EOCs in groundwater from the analysis of water solubility (Sw) and octanol – water partition coefficient (Kow). Notes: green circles (EOCs controlled in DESSIN project); yellow circles (some of the new variables potentially measurable). Source: modified from Jurado et al. (2012a)

With regards to considered PhACs (A: acetaminophen, codeine and caffeine), are not expected to present hydrophobic behaviour (Log $K_{ow} > 4$ and low solubility). Pesticides would correspond to the group of compounds (B) with an intermediate risk of bio-accumulation ($2 \leq$ Log $K_{ow} \leq 4$ and moderate S_w). Industrial compounds (C: NP, OP) have moderately low S_w and high log K_{ow} values and hence can be considered moderately hydrophobic compounds (Figure 15).

With respect to long-term effects of EOCs in aquifer geochemistry, the concentration of EOCs in aquifers is affected by numerous processes, including concentration at the source, dilution, adsorption and degradation. Most studies are motivated by testing of pollution hypotheses. Therefore, they provide a biased picture of the actual state of groundwater bodies. In addition to the tendency to sorb onto both organic and inorganic solids, many EOCs are removed from water by transformation (Barbieri *et al.,* 2012) or degradation, especially if the water has undergone a broad range of redox states (Christensen *et al.,* 2001; Barbieri *et al.,* 2011). This, together the higher residence time of water in aquifers in comparison to surface waters, suggests that the most EOCs will tend to disappear (Jurado *et al.,* 2012b*).* The continuity of the ASR operation in the future will required the strict monitoring of EOCs focusing on their degradation rate along the groundwater flow path.

4.3.4 Proposal of EOCs included in MAR-SP

As a result of the analysis of the occurrence of EOCs, both at Llobregat river water and at some quality groundwater control points nearby injection well, as well as from overall studies at river basin scale, the following substances have been selected and could be included in the monitoring program of the MAR-SP.

Group of EOCs	Substance	DESSIN project	MAR-SP	Reason for I or E
PhACs	Codeine	●		1
PhACs	Erythromycin	●		1
PhACs	Diclofenac	●	●	2
PhACs	Acetaminophen	●	●	2
PhACs	Cotinine	●	●	2
PhACs	Iopromide		●	5
PhACs	Caffeine		●	5
Pesticide	Pentachlorophenol	●		1
Pesticide	Terbutilazine	●	●	3
Pesticide	Diuron	●	●	2
Pesticide	Isoproturon	●		1
Pesticide	Simazine	●		1
Pesticide	Diazinon		●	3
Pesticide	Chlorpyrifos		●	3
Pesticide	Terbutryn		●	3
Industrial compound	Octylphenol	●	●	4
Industrial compound	Nonylphenol	●	●	4
Industrial compound	Tolyltriazole		●	5
Industrial compound	TCCP		●	5
Industrial compound	NP1EC		●	5
Industrial compound	1H-Benzotriazole		●	5
Perfluoroalkyl substance	L-PFOS		●	5

Notes: I = inclusion; E = exclusion

No. Code	Brief description
1	All groundwater and recharge water samples < LOD, Cmax < 1000 ng/L and/or low bio-accumulation risk
2	Some groundwater and recharge water samples > LOD and Cmax > or ≈ 100 ng/L
3	EOC identified in most of the Llobregat River water samples analysed at SJD gauging station
4	Some groundwater samples > LOD and/or intermediate - high risk of bio-accumulation
5	EOCs with Cmax > 1 µg/L (basin scale studies)

Figure 16: List of EOCs to be included in the future MAR-SP

Regarding Critical Limits, the European recommended value of 100 ng/L should be applied in the absence of any further information, due to the existing uncertainty about the behaviour of EOCs in groundwater.

4.4 Establish a monitoring program for the CCP and other WSP phases

The establishment of the control program will depend in the first place on whether the defined critical control points are part of any monitoring network already exists. All the control points that have been identified during the preliminary development of the Managed Aquifer Recharge Safety Plan are included in control programs, whether private (water catchment network in Barcelona) or public (wells for supply to the Prat de Llobregat and for quality control at regional level).

Once private water operator (AB) renewed the concession from water public administration (ACA) to keep recharging the Lower Llobregat alluvial aquifer with pre-potable water, the rest of the phases of the WSP will be evaluated, such as validation and verification of the WSP or register of result, observations and corrective measures.

Regarding MAR-SP monitoring program, physico-chemical and microbiological parameters should be monthly measured, with more frequent analysis before, during and after pre-potable water injection. With respect to EOCs monitoring, it is not necessary to implement monthly sampling campaigns. In this sense, depending on the obtained results during ASR at operational scale, the sampling frequency may be increased, especially when some EOC continuously exceeds the action limit of 10 ng/L.

In order to carry out a gradual evaluation of the impact of injecting pre-potable water into the aquifer, an increasing annual recharge volume is proposed for five years (e.g., 1, 2.5, 5, 10 and 15 hm^3/ year). This would allow a more accurate assessment of all potential hazards identified during HACCP approach, especially those related to EOCs bio-accumulation.

5. Conclusions

The obtained results in the different chapters of this deliverable, focusing on the evaluation of the impact on aquifer quality due to the injection of pre-potable water (microbiological, physicochemical analysis, emerging contaminants, etc.) have allowed generating useful information for generating a methodological framework for safe managed aquifer recharge projects.

In order to satisfactorily implement a managed aquifer recharge facility, it is essential to carry out a exhaustive analysis of the applicable legislation, in order to verify that the recharge water quality fulfils all the established requirements. In this sense, it is not enough to solely deal with the European legislation, but it is necessary to collect more detailed information, which is usually contained in River Basin Management Plans. Each EU Member State has calculated its own threshold values, highly variable from one MS to another (up to 6000%). Therefore, it would be necessary to aim towards a homogenisation of such threshold values not only between EU Member States but between surface water and groundwater, given the unity of the hydrological cycle.

The risk management approach called "Water Safety Plan" based on HACCP can be applied to MAR projects with pre-potable water in a simple and transparent manner, taking into account all the factors involved in risk transfer among different water users. This tool has the ability to include these factors in a combined and integrated way, minimizing such risk. The preliminary analysis regarding deep pre-potable water injection into Lower Llobregat alluvial aquifer has allowed listing the main hazards affecting groundwater quality (increase of enteropathogenic bacteria, possible mobilization of heavy metals, etc.), as well as critical control points to effectively monitor the water injection and critical limits for chemical status indicators. In this type of studies, special analysis must be carried out in determining the emerging organic pollutants to be measured, given these substances are not adequately considered in legislation. Their control might include an assessment on the natural attenuation capacity of the aquifer to degrade such compounds.

The implementation of managed aquifer recharge experiences by using deep pre-potable water injection within other European regions would require its inclusion in a risk management plan (new or existing one), and the development of specific studies characterising the storage and self-purification capacity of the aquifer, the quality of the recharge water and the potential hazards conditioning the success of ASR operation, among others.

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