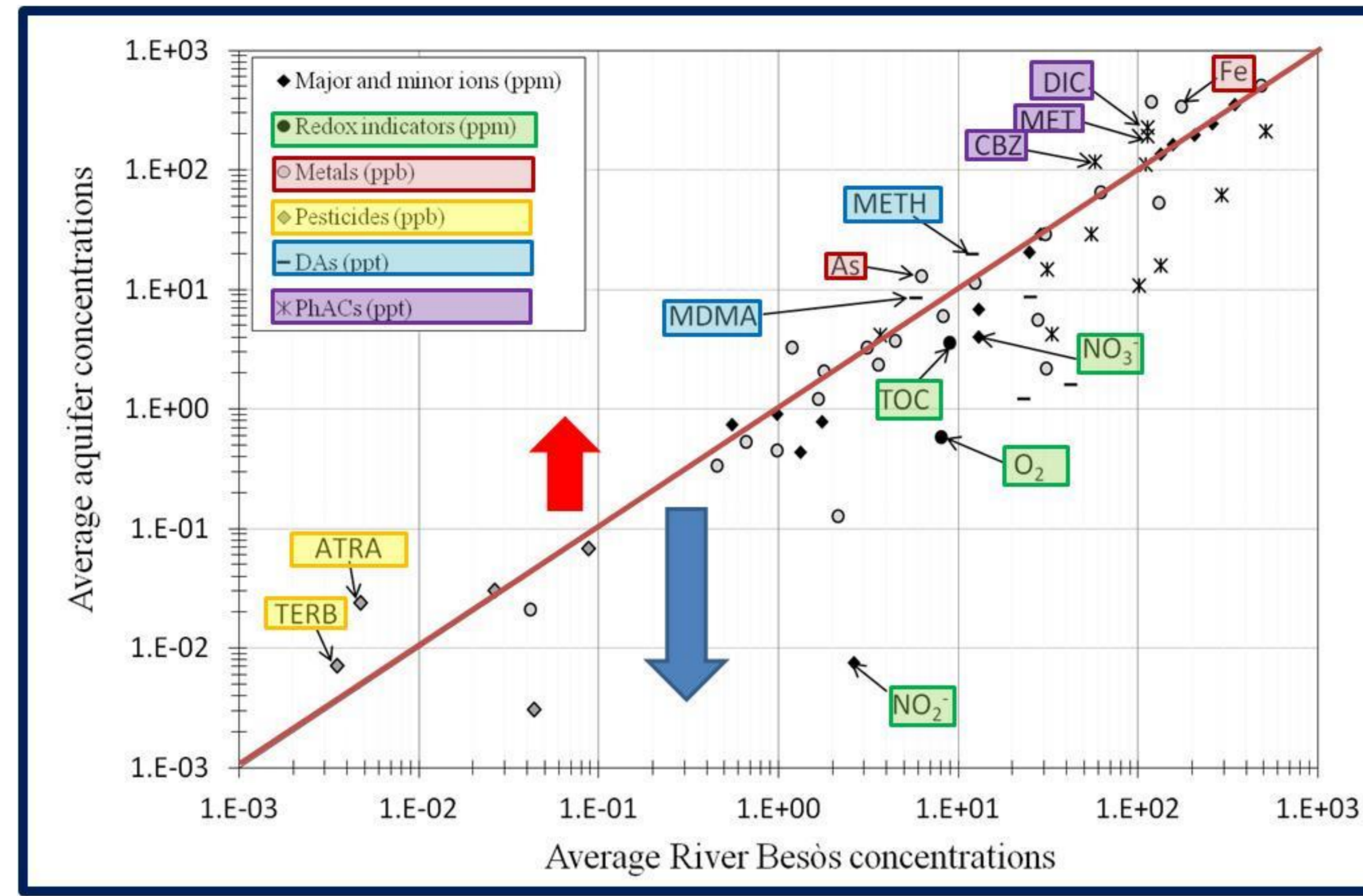


## 1. INTRODUCTION & OBJECTIVES

This work is motivated by a sound understanding of the chemical processes that affect the organic pollutants in an urban aquifer. Urban aquifers may suffer pollution from different recharge sources such as leakage from sewer and septic systems, seepage from rivers, seawater intrusion, and losses from water supply network. As a result, a wide range of organic pollutants are found in urban aquifers (Fig. 1). Since these pollutants reach groundwater environment, their occurrence depends on simultaneous transport and biogeochemical processes. However, the quantification of these processes is not an easy task. The **objective** of this work is to propose an approach to quantify the chemical processes that occurs when river water infiltrates an aquifer.



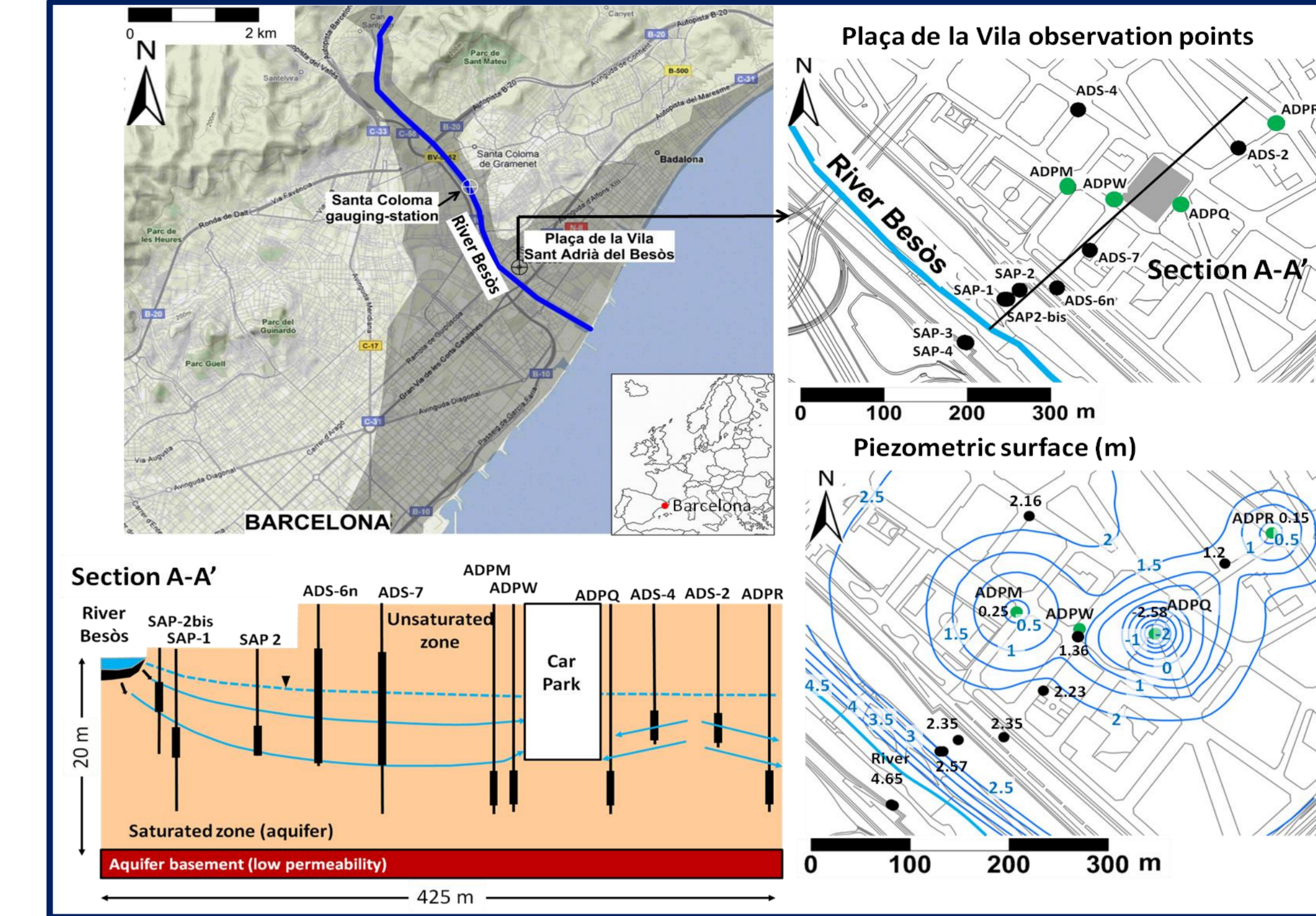
**Figure 1.** Average concentrations in the River Besòs and in the aquifer for major and minor ion, metals, redox indicators, pesticides, drugs of abuse (DAs, Jurado et al., 2012) and pharmaceutical active compounds (PhACs, López-Serna et al., 2013).

## 2. METHODOLOGY

The methodology consists of the following steps:

- ✓ identification of the recharge sources and selection of the species to be used
- ✓ identification of the chemical processes
- ✓ evaluation of mixing ratios including the chemical processes.

This methodology has been applied in the Besòs River Delta aquifers (NE Barcelona, Spain, Fig. 2) using the MIX Code (Carrera et al., 2004)

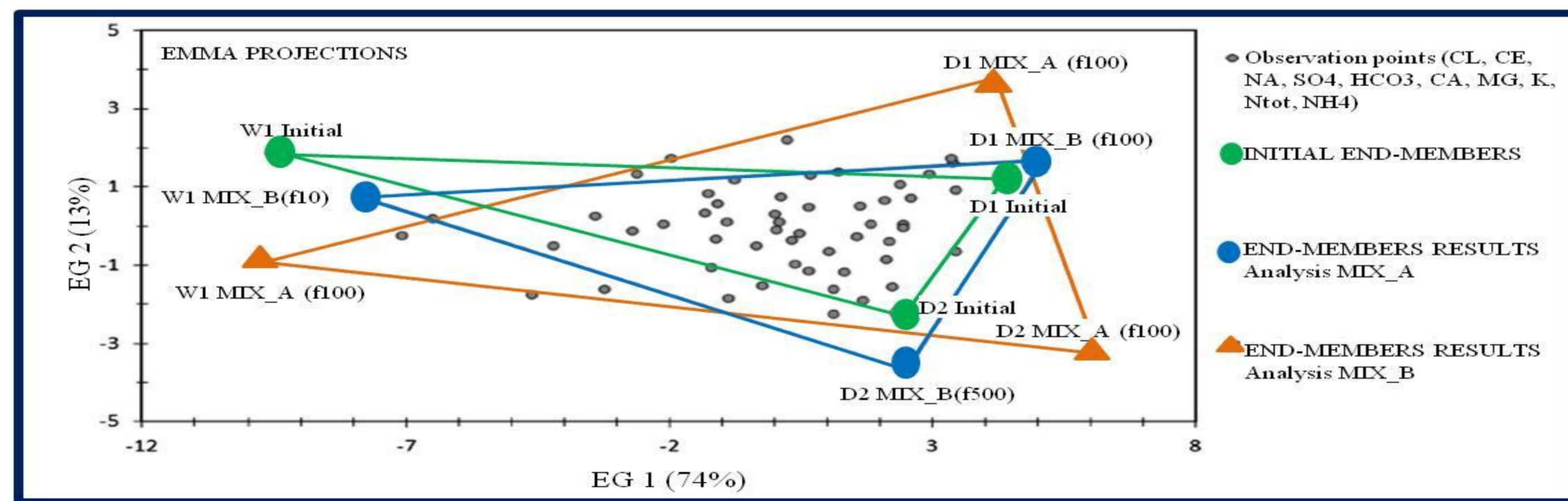


**Figure 2.** Location of the study area and schematic description of the hydrogeological conceptual model. The screen depths of the pumping wells and the piezometers are also indicated.

## 3. RESULTS & DISCUSSION

### 3.1 Identification of the recharge sources and selection of the appropriate species

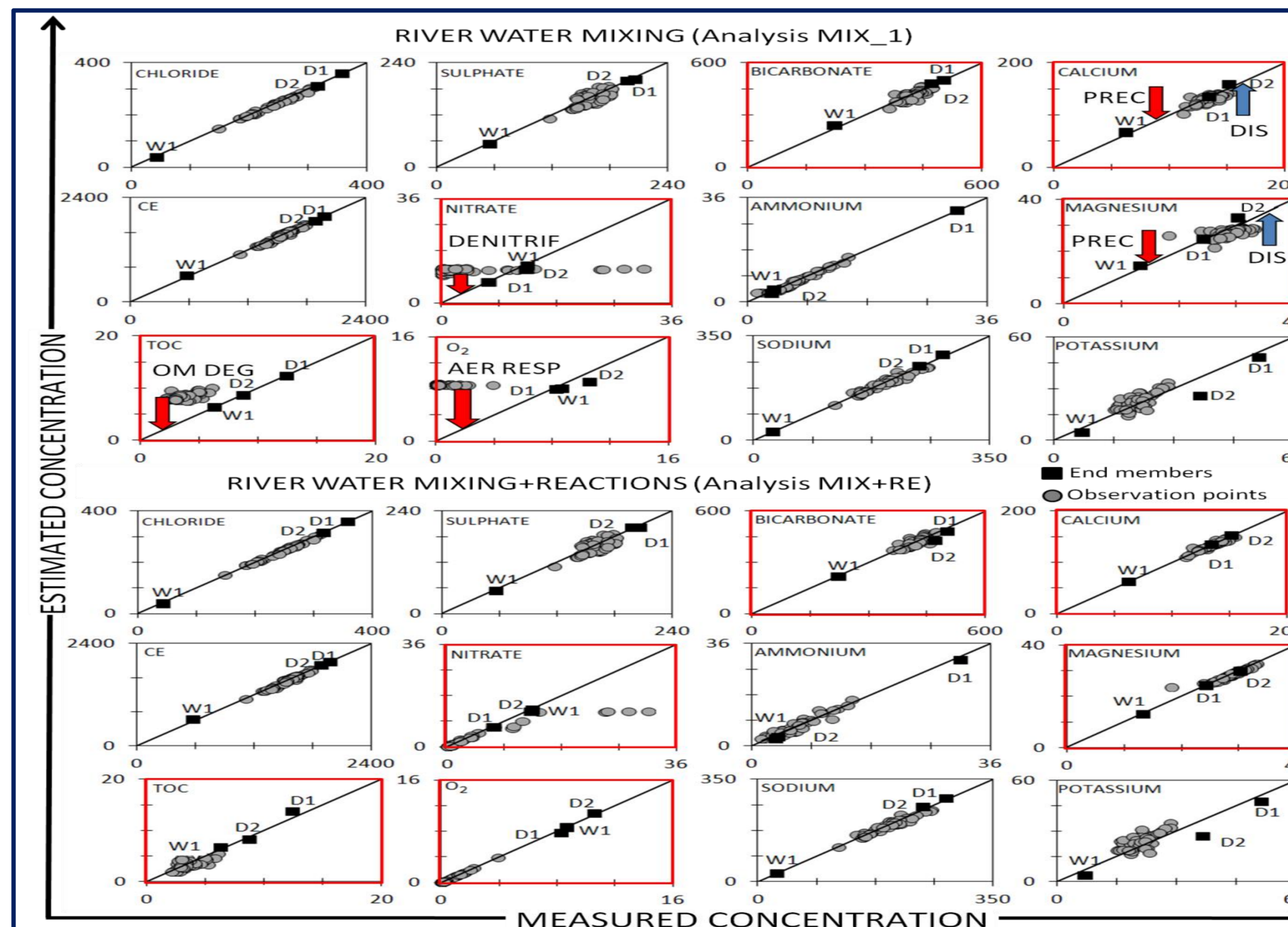
- ✓ An EMMA analysis was carried out to identify the minimum number of river end-members needed to account for the seasonal variability of the River Besòs (Tubau et al., 2014) (Fig. 3).
- ✓ Three river end-members were finally selected: Two from the dry season (D1 and D2) and one to the wet season (W1).
- ✓ The tracers selected were: Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, Na<sup>+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>, K<sup>+</sup>, HCO<sub>3</sub><sup>-</sup>, NO<sub>3</sub><sup>-</sup>, NH<sub>4</sub><sup>+</sup>, TOC and O<sub>2</sub>.



**Figure 3.** Projection of the eigenvectors 1 and 2. The difference between the analysis and MIX\_A and MIX\_B is the variances assigned to the tracers of the three end-members: W1, D1 and D2. (Modified from Tubau et al., 2014).

Analysis	Initial concentrations							Initial values (Rr)							Applied standard deviation													
	MIX <sub>i</sub> & MIX <sub>RE</sub>							MIX+RE							MIX <sub>i</sub> & MIX <sub>RE</sub>							MIX+RE						
	EM1	W1	EM2	D1	EM3	D2		EM4:R1	EM5:R2	EM6:R3	EM7:R4		MIX_1	MIX_2	MIX+RE	MIX <sub>i</sub>	MIX+RE	MIX+RE	MIX_1	MIX_2	MIX+RE	MIX <sub>i</sub>	MIX+RE	MIX+RE				
Chloride	44	356	316	-	-	-	-	6100	6100	6100	6100	0.05-Rg	0.05-Rg	0.05-Rg	0.04-Ri	0.04-Ri	-	0.05-Rg	0.05-Rg	0.05-Rg	0.04-Ri	0.04-Ri	-					
Sulphate	53	206	199	-	-	-	-	-	-	-	-	0.11-Rg	0.11-Rg	0.11-Rg	0.04-Ri	0.04-Ri	-	0.11-Rg	0.11-Rg	0.11-Rg	0.04-Ri	0.04-Ri	-					
Bicarbonate	223	500	470	-	-	-	-	4000	-	-	-	0.15-Rg	0.15-Rg	0.1-Rg	0.07-Ri	0.07-Ri	0.025-Rr	0.15-Rg	0.15-Rg	0.1-Rg	0.07-Ri	0.07-Ri	0.025-Rr					
Calcium	62	134	151	-	-	-	-	-	-	-	-	0.16-Rg	0.16-Rg	0.1-Rg	0.07-Ri	0.07-Ri	-	0.16-Rg	0.16-Rg	0.1-Rg	0.07-Ri	0.07-Ri	-					
EC	586	1997	1891	-	-	-	-	-	-	-	-	0.06-Rg	0.06-Rg	0.06-Rg	0.04-Ri	0.04-Ri	-	0.06-Rg	0.06-Rg	0.06-Rg	0.04-Ri	0.04-Ri	-					
Nitrate	13.4	7.4	13.2	-	-	-	-4960	-	-	-	-	15-Rg	1-Rg	0.15-Rg	0.45-Ri	0.04-Ri	0.025-Rr	15-Rg	1-Rg	0.15-Rg	0.45-Ri	0.04-Ri	0.025-Rr					
Ammonium	4.1	31.5	3.6	-	-	-	-	-	-	-	-	0.3-Rg	0.3-Rg	0.2-Rg	0.25-Ri	0.05-Ri	-	0.3-Rg	0.3-Rg	0.2-Rg	0.25-Ri	0.05-Ri	-					
Magnesium	13.3	24.2	30	-	-	-	2430	-	-	-	-	0.3-Rg	0.3-Rg	0.15-Rg	0.1-Ri	0.07-Ri	0.025-Rr	0.3-Rg	0.3-Rg	0.15-Rg	0.1-Ri	0.07-Ri	0.025-Rr					
TOC	6.3	12.4	8.7	-	-	-	-1200	-	-	-	-	25-Rg	1-Rg	0.12-Rg	0.25-Ri	0.04-Ri	-	25-Rg	1-Rg	0.12-Rg	0.25-Ri	0.04-Ri	-					
Dissolved oxygen	8.7	8.3	10.6	-	-	-	-3200	-	-	-	-	50-Rg	1-Rg	0.15-Rg	0.25-Ri	0.04-Ri	0.025-Rr	50-Rg	1-Rg	0.15-Rg	0.25-Ri	0.04-Ri	0.025-Rr					
Sodium	29	281	247	-	-	-	-	-	-	-	-	0.07-Rg	0.07-Rg	0.07-Rg	0.05-Ri	0.05-Ri	-	0.07-Rg	0.07-Rg	0.07-Rg	0.05-Ri	0.05-Ri	-					
Potassium	7.2	51	37	-	-	-	-	-	-	-	-	0.6-Rg	0.6-Rg	0.5-Rg	0.17-Ri	0.1-Ri	-	0.6-Rg	0.6-Rg	0.5-Rg	0.17-Ri	0.1-Ri	-					

**Table 1.** River end-member initial concentrations and standard deviations assigned to the end-members and the observation points for the analyses MIX<sub>i</sub> (river water mixing, Analyses MIX<sub>1</sub> and MIX<sub>2</sub>) and MIX+RE (river water mixing and reactions). “Rg”: Average concentration at the groundwater observation points”, “Ri”: Average concentration at the river end-members”



**Figure 4.** Plots of measured versus estimated concentrations at the river end-members and observation points considering: river water mixing (analysis MIX<sub>1</sub>) and river water mixing plus the reactions (analysis MIX+RE). The concentrations are expressed in mg/L and the electrical conductivity in μS/cm. The abbreviations are: “PREC: Precipitation”, “DIS: Dissolution”, “OM DEG: Organic matter degradation”, “DENITRIF: Denitrification”, “AER RESP: Aerobic respiration”.

## 4. CONCLUSIONS

- A methodology that has proved to be useful not only to quantify mixing ratios but also chemical reactions is presented.
- This methodology was applied in the Besòs River Delta aquifers where some chemical processes occur when river water infiltrates the aquifer (redox processes and dissolution of carbonates).
- River water mixing was the most relevant process (99.2%). Generally, dry river end-members (71.5%) predominated over the wet one (27.7%). In contrast, chemical reactions accounted for less than 1 % of the composition at the observation points. However, their contribution to the better fit of the non-conservative species was significant.
- This methodology can be applied in any other aquifer in a rapid, simple and effective way.

## 5. References

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### 3.3 Evaluation of mixing ratios including the chemical processes (Analysis MIX+RE)

- ✓ Apart from the three River Besòs end-members, each reaction was included as a new end-member (Table 1, Fig 4).

$$X_{ij} = \sum_e \lambda_{ej} \hat{Y}_{ie} + R_{ij}$$

$$X_{ij} = \sum_e \lambda_{ej} \hat{Y}_{ie} + \sum_k \delta_{ik} r_{kj} = \text{Mixture of end-members} + \text{Reactions}$$