



# Arsenic and Boron Hydrogeochemical behaviour during Managed Aquifer Recharge Operations.

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# ABSTRACT

The Cornia Valley aquifer system (Tuscany, Italy) is the main source for irrigation, industrial purposes, and for potable water supply for the zone and the Elba island. Sixty years of its overexploitation caused a remarkable potentiometric drawdown accompanied with a wide seawater intrusion and a severe degradation of the quality of the groundwater. (Rossetto et al., 2018; 2019)

In the early 2000s, extensive research regarding anomalous high concentrations of Boron in the Cornia Valley was carried out. These studies studied the hydrochemistry of the area, determining also anomalous high concentrations of Arsenic (Pennisi et al., 2009). In addition, one of the biggest schemes treating Arsenic for drinking water started operating with other two plants for Boron (Comune di Suvereto, 2013). Furthermore, in 2015 the LIFE REWAT project was started in order to set a strategy to recover and improve the availability of water in the area through a series of technical and social interventions (Rossetto et al., 2018).

Within LIFE REWAT, Managed Aquifer Recharge (MAR) was identified as a solution to counterbalance the stressed hydrologic system. Thus, a pilot MAR scheme infiltrating harvested rainwater from the Cornia River was implemented. It is provided by a hi-tech high-frequency automated and remotely controlled system for operating the plant and monitoring water quantity and quality. This system is supported by the data gathered from different sensors installed in the area, recording into a database. Additionally, discrete groundwater sampling takes place monthly. (Rossetto et al., 2018; 2019)

The database contains recordings from two consecutive hydrological years. The first year measurements and samplings were done under natural recharge conditions, while during the second year the MAR scheme was under operation. This initial data provides insights on concentration variations of Boron and Arsenic after one-year operation of the MAR scheme. However, the main processes involved still need to be understood. Therefore, long-term and short-term dedicated field experiments are designed to analyse the induced variations. This work presents a model based hydrogeochemical approach for the behaviour analysis of these elements under MAR operations to determine the transiency of these concentration changes.



# INTRODUCTION

The Cornia Valley aquifer system (Tuscany, Italy) is the main source for irrigation, industrial purposes, and for potable water supply for the zone and the Elba island. Sixty years of its overexploitation caused a remarkable potentiometric drawdown accompanied with a wide seawater intrusion and a severe degradation of the quality of the groundwater. (Rossetto et al., 2018; 2019)

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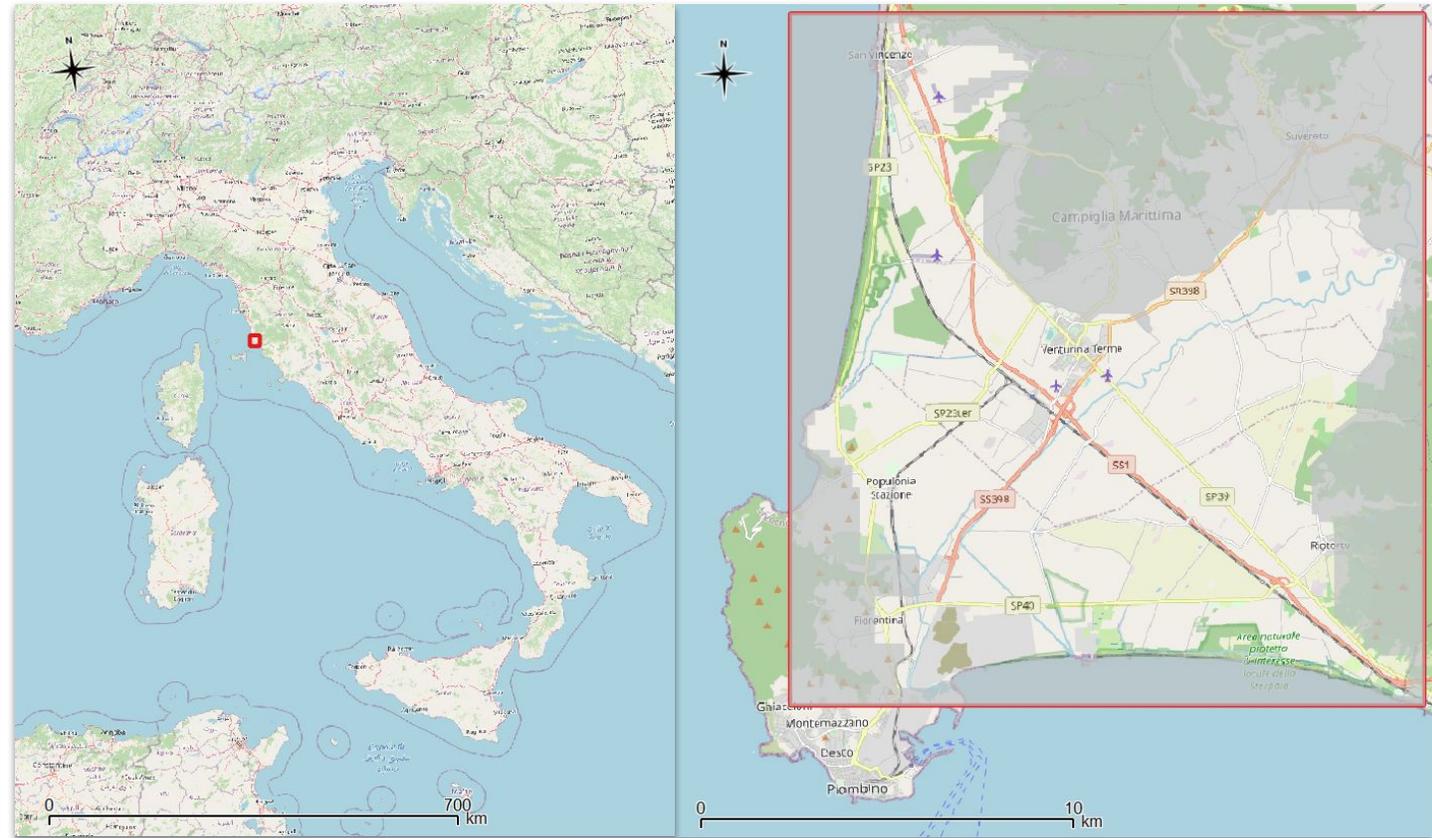


Figure 1 - Study Area (QGIS, 2020; OpenStreetMap, 2020)



# MATERIALS AND METHODS

## MANAGED AQUIFER RECHARGE SCHEME

Within LIFE REWAT, Managed Aquifer Recharge (MAR) was identified as a solution to counterbalance the stressed hydrologic system. Thus, a pilot MAR scheme infiltrating harvested rainwater from the Cornia River was implemented (**Figure 2**). It is provided by a hi-tech high-frequency automated and remotely controlled system for operating the plant and monitoring water quantity and quality. This system is supported by the data gathered from different sensors installed in the area, recording into a database. Additionally, discrete groundwater sampling takes place monthly. (Rossetto et al., 2018; 2019)

## SAMPLING CAMPAIGNS

A total of 25 sampling campaigns of surface water and groundwater were carried between April 2016 and November 2019. The beginning of MAR operations started on December 4<sup>th</sup>, 2018. The groundwater samples were collected from monitoring wells constituted of piezometers and production wells used by the local farmers and the water service agency (**Figure 3**). The samples from the piezometers were done with a submersible pump after purging them three times their volume. While the sampling from the production wells were done using the installed pumps until the parameters measured with a multiparametric probe stabilized (i.e. EC, pH, temperature, DO, and ORP). The samples were carried in 100 ml polyethylene bottles previously rinsed three times with the sampled water. The samples to be analyzed for Arsenic were acidified with 1 ml of HNO<sub>3</sub>, and all the samples were conserved at 4°C until their analysis. Field parameters (i.e. EC, pH, temperature, DO, and ORP) were also measured *in-situ* with a multiparametric probe.

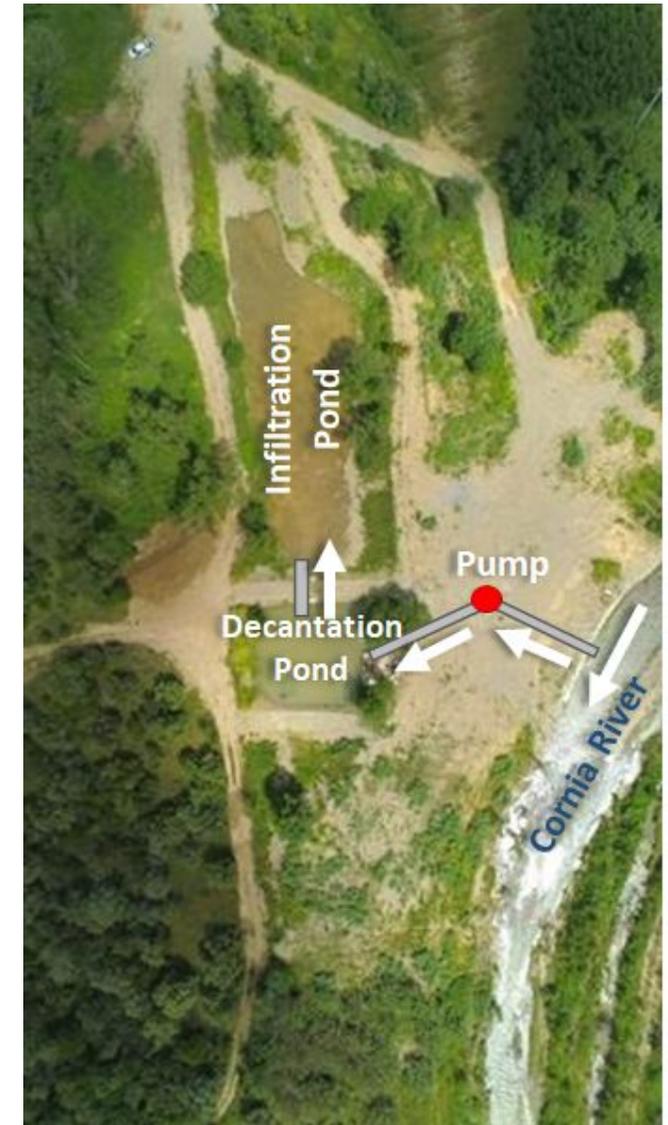


Figure 2 - LIFE REWAT Infiltration Basin - MAR Scheme





# RESULTS AND DISCUSSION

The database contains recordings from two consecutive hydrological years. The first year measurements and samplings were done under natural recharge conditions, while during the second year the MAR scheme was under operation. This initial data provides insights on concentration variations of Boron and Arsenic after one-year operation of the MAR scheme. **Figure 4** to **Figure 8** show the results obtained from the sampling campaigns before the MAR operations and after the first MAR operation on the 4<sup>th</sup> of December of 2018. **Figure 6** and **Figure 7** show the variation of Arsenic and Boron Concentration in both periods. As a reference of the background concentration, the concentrations of the piezometer REW\_5 is shown, which is located upstream of the recharge area related to the groundwater flow, together with the concentrations of the river in the intake point. On the other hand, the piezometer REW\_10 is located in the center of the Infiltration Pond, while the other monitoring wells are distributed along the aquifer.

The tables below show the total data used for this initial and simple statistical analysis. The values below the Limit of Quantification (<LoQ) were considered equal to the Limit of Quantification (LoQ), but they will be treated as censored data in the proposed methodology.

Arsenic (LoQ = 1 [microg/l])				
Sampling Point	Total Data pre-Mar Operation	<LoQ pre-MAR Operation	Total Data MAR Operation	<LoQ MAR Operation
Cornia River	3	1	9	3
REW_5	16	4	9	3
REW_10	3	1	9	3
REW_6	14	1	9	1
REW_11	3	2	9	4
REW_14	1	0	9	1
REW_17	1	0	8	1
REW_23	1	0	8	0
REW_141	15	2	9	0
REW_142	14	0	8	0

Boron (LoQ = 0.05 [mg/l])				
Sampling Point	Total Data pre-Mar Operation	<LoQ pre-MAR Operation	Total Data MAR Operation	<LoQ MAR Operation
Cornia River	3	0	9	0
REW_5	16	0	9	0
REW_10	3	0	9	0
REW_6	14	0	9	0
REW_11	3	0	9	0
REW_14	1	0	9	0
REW_17	1	0	8	0
REW_23	1	0	8	0
REW_141	15	0	9	0
REW_142	14	0	8	0



# RESULTS AND DISCUSSION

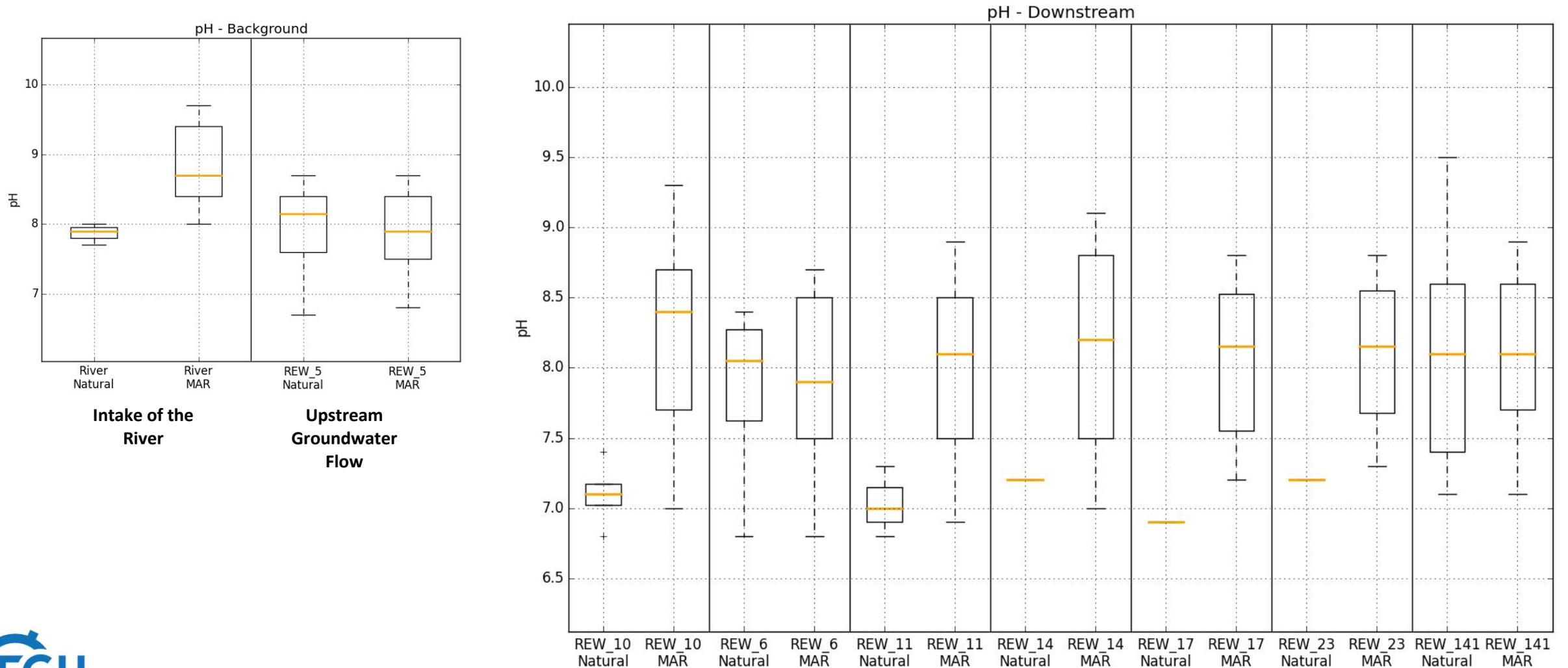


Figure 4 - pH variation with the implementation of the MAR Scheme



# RESULTS AND DISCUSSION

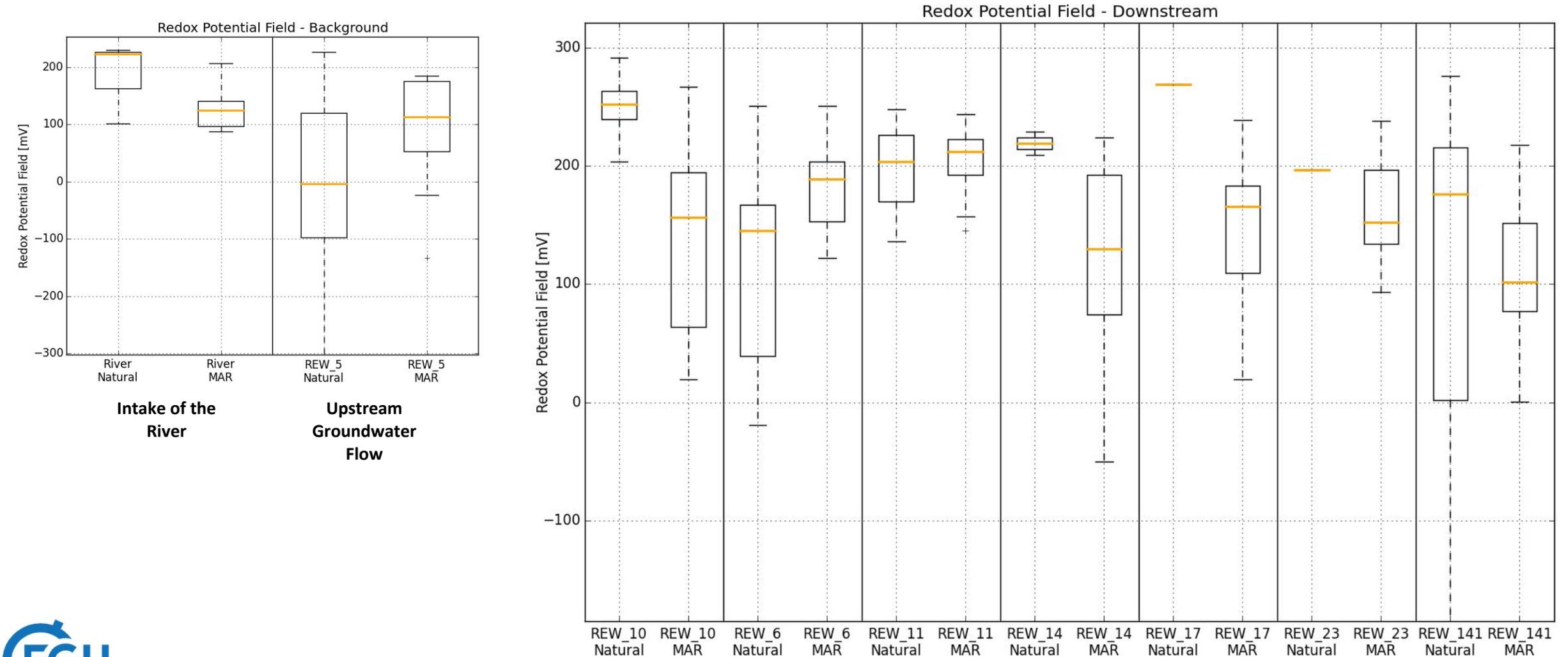


Figure 5 - Redox Potential Field variation with the implementation of the MAR Scheme



# RESULTS AND DISCUSSION

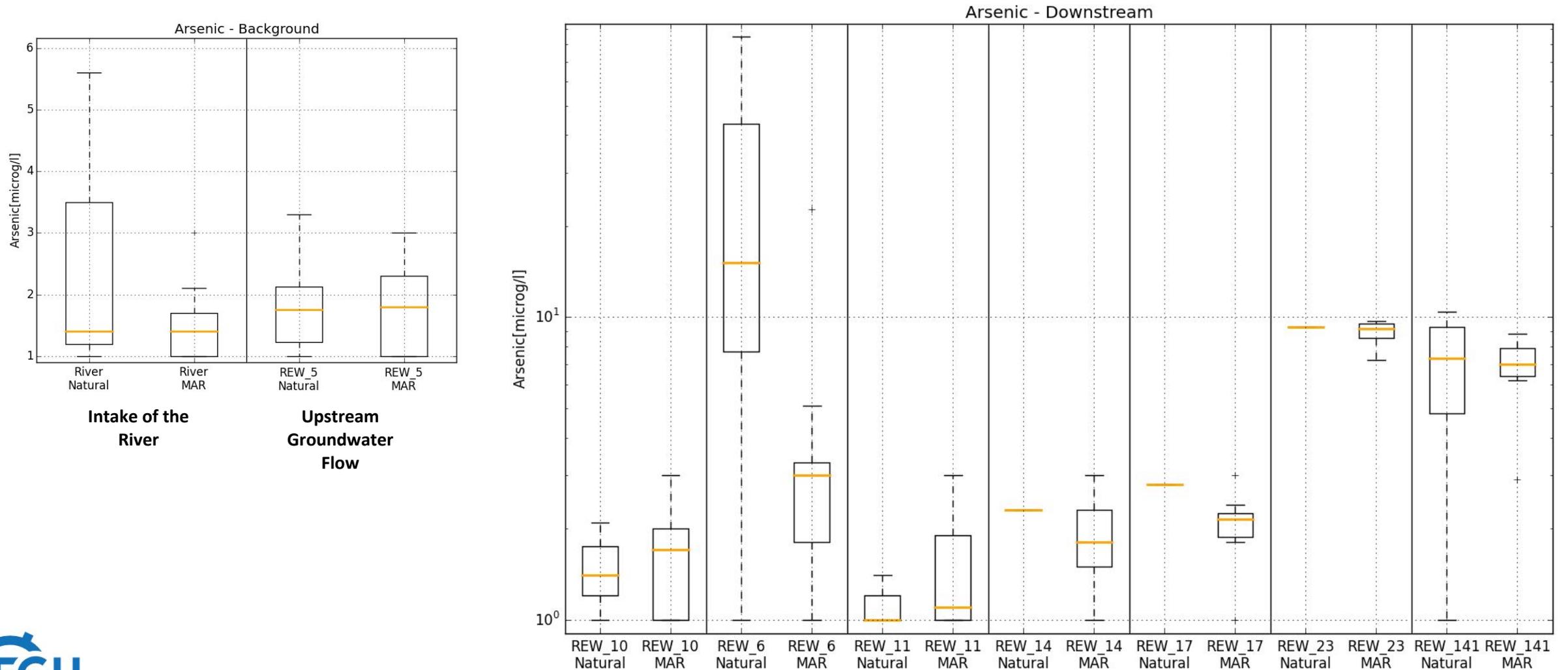


Figure 6 - Arsenic Concentration variation with the implementation of the MAR Scheme



# RESULTS AND DISCUSSION

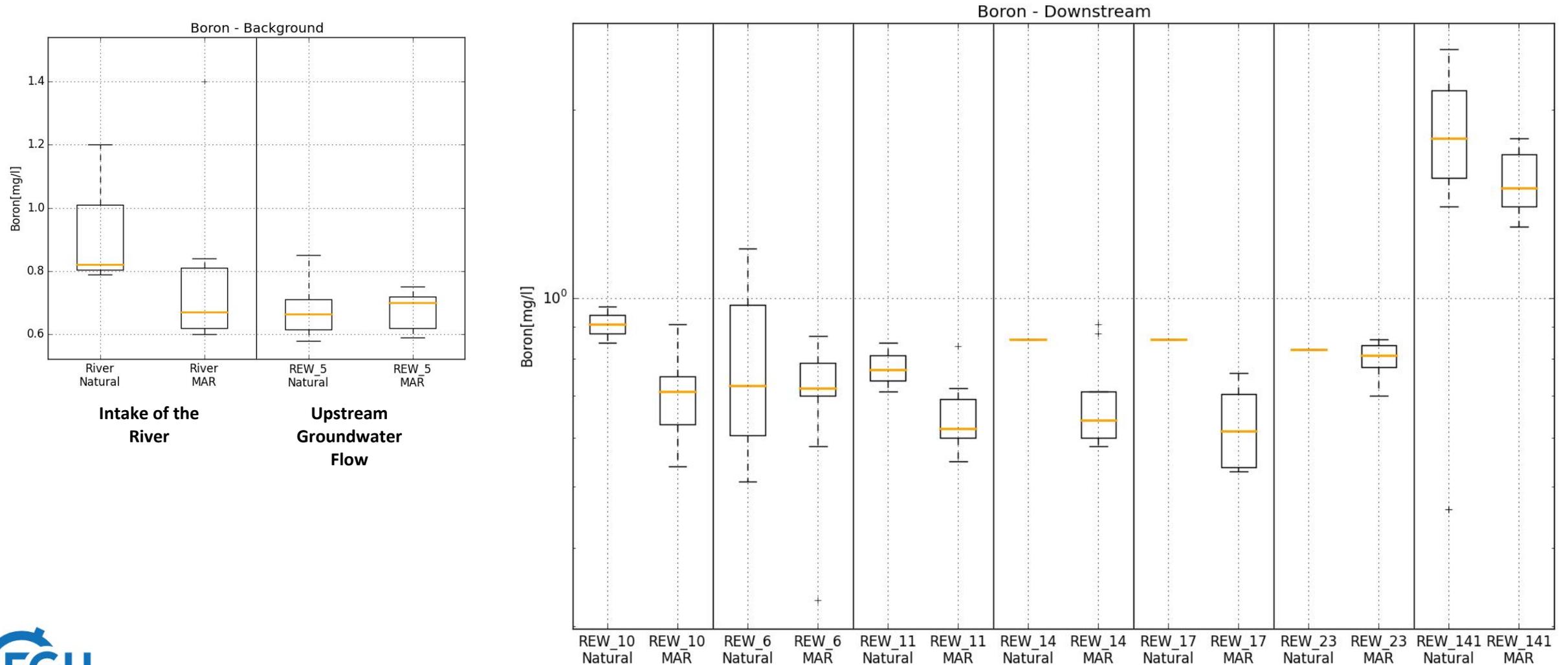


Figure 7 - Boron Concentration variation with the implementation of the MAR Scheme



# RESULTS AND DISCUSSION

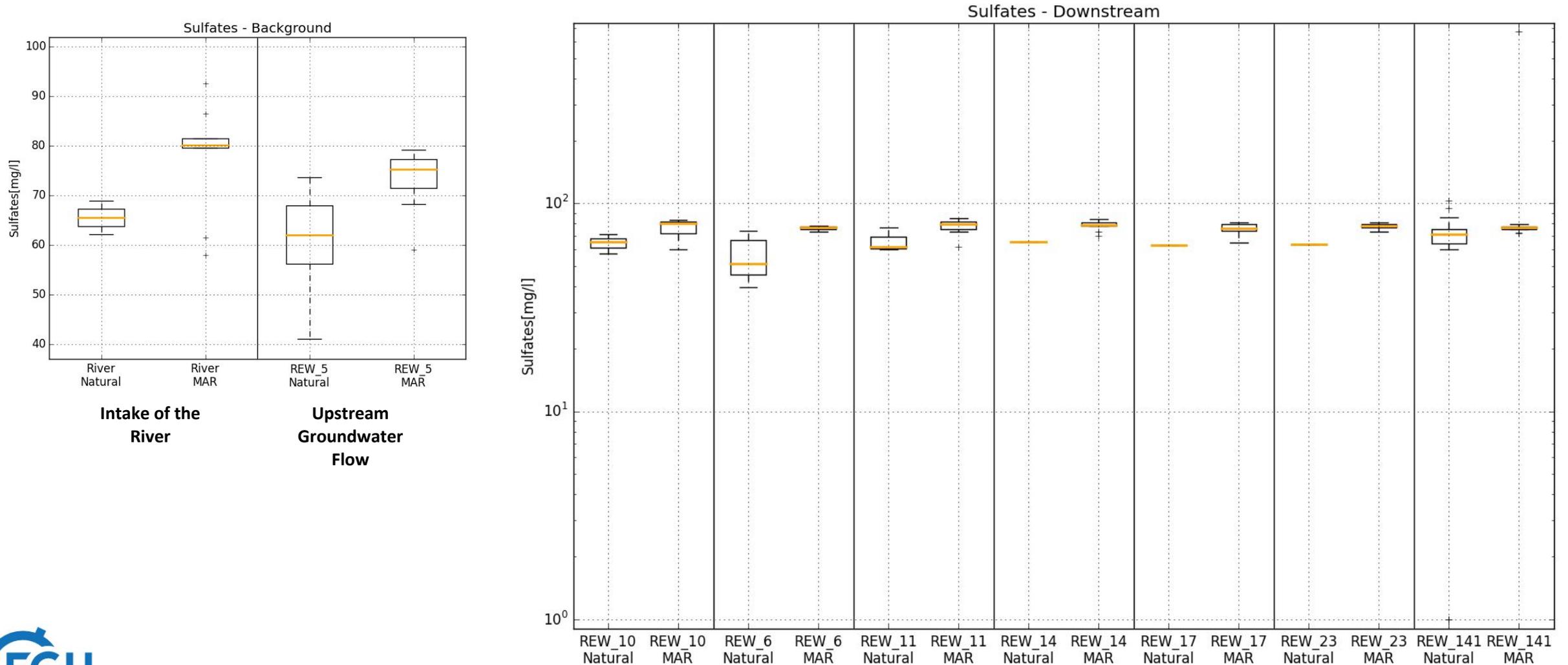


Figure 8 - Sulfates Concentration variation with the implementation of the MAR Scheme



# PROPOSED METHODOLOGY

However, the main processes involved still need to be understood. Therefore, long-term and short-term dedicated field experiments are designed to analyse the induced variations. This work presents a model based hydrogeochemical approach for the behaviour analysis of these elements under MAR operations to determine the transiency of these concentration changes.

The short-term dedicated field experiments will be designed to evaluate changes with high frequency. Field parameters measurements will be measured with a stepped frequency, starting with daily measurements and continuing with a bidaily frequency up to a weekly frequency. For the measurements, multiparametric probes measuring Head, Electrical Conductivity, pH, Temperature, Dissolved Oxygen, and Oxygen Reduction Potential will be used. The experiment will be focused in the piezometers located in the vicinity of the infiltration pond, and the measurements will be used to calibrate an existing local groundwater flow model.

The long-term experiment is aimed to quantify the chemical variations induced in the aquifer by the MAR Scheme and its extension. For this purpose, historical data and monthly sampling and field parameters measurements will be used, gathering measurements from April 2016 until April 2022. This data will be implemented in the calibrated groundwater flow model, and will be used coupled with a Reactive Transport Model. The reactive transport model will be used to understand the hydrogeochemical behaviour under Managed Aquifer Recharge operations.

The models will be developed using the open-source GIS based modelling platform FREEWAT (Rossetto et al., 2018b) implemented as a Plugin within the open-source GIS software QGis (QGis, 2020). A Reactive Transport Model will be integrated into the FREEWAT Software Platform, and will be applied to study the hydrogeochemical behaviour of Arsenic and Boron under MAR operations.



# ACKNOWLEDGEMENTS

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