

# SOIL AQUIFER TREATMENT TO REMOVE PRIORITY ORGANIC POLLUTANTS IN THE LLOBREGAT RIVER AREA



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### Introduction

The Llobregat River is the main source of water supply in this area. This river together with its aquifer has suffered from several damages which had contributed to endanger a suitable ecological and hydrological status; among them, pollution is a serious problem to deal with. In the last decades, the presence of organic pollutants in this river has been demonstrated [1,2]. Some of them are persistent to biological degradation and have shown to survive wastewater treatments almost unaltered and therefore they get surface waters where in some cases become recalcitrant pollutants. In order to mitigate the effect and presence of these compounds, Soil Aquifer Treatments (SAT) could be an approach since these treatments have demonstrated to be efficient to remove or decrease concentrations of such contaminants due to physico-chemical and biological processes occurring within the subsoil [3].

In the framework of the LIFE-ENSAT project, an organic substrate layer was installed in the basin of a recharge system located in the upper Llobregat delta aquifer. The aim was to enhance the degradation of contaminants through biochemical reactions on the reductive environment promoted in the unsaturated zone in order to improve the water quality of the system.

In this work, the efficiency of this organic layer to remove organic pollutants included in European directives (2000/60/EC-2008/105/EC), such as triazines, pesticides or polyaromatic hydrocarbons (PAHs), has been evaluated. More than 80 compounds were analyzed; among them, 27 were priority pollutants while 6 were classified as preference substances (RD 60/2011).

#### Method -

#### **SPE EXTRACTION**

SPE INSTRUMENT: SPE-DEX 4790 (Horizon Tech.)

CARTRIDGES: ATLANTIC C18 (Horizon Tech.)

**EVAPORATION:** miVac Concentrator(Genevac Inc).

#### GC/MS/MS

INSTRUMENT: 7000GC/MS/MS (Agilent Techn.)

**COLUMN**: HP-5MS (30 x0.250, 0.25um) (Agilent Tech.)

TEMPERATURE: 70-280 ° INJECTION VOLUME: 1 µL

#### Sampling Survey -

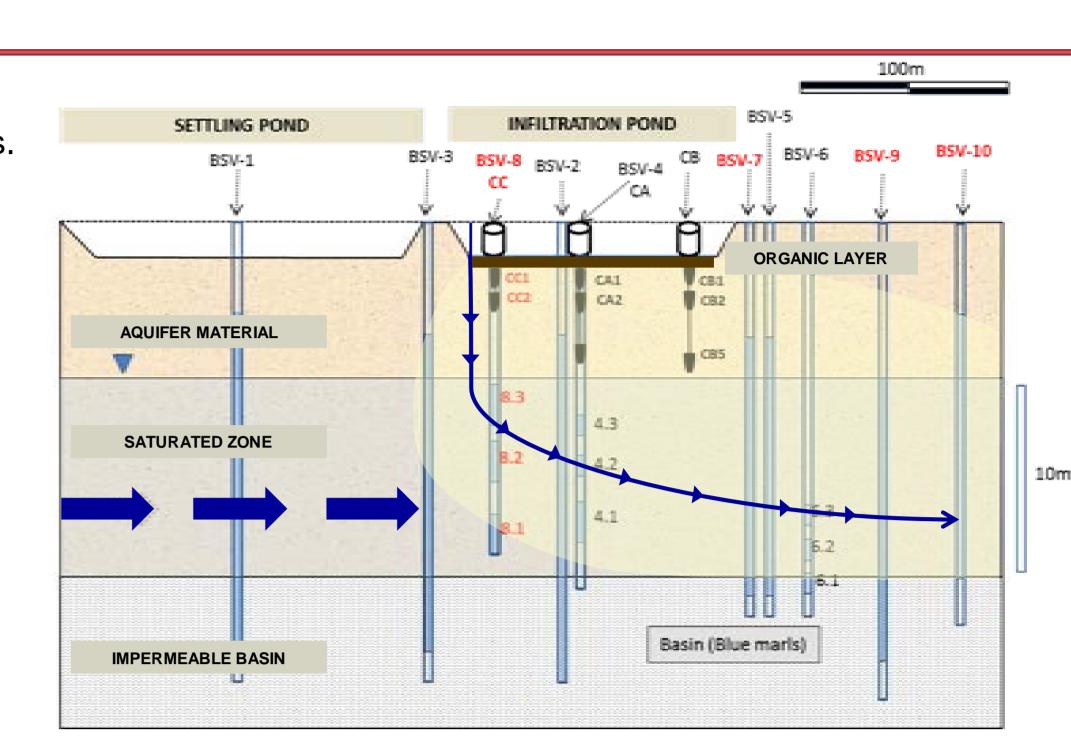
SITE: Llobregat River-St Vicenç dels Horts.
INFILTRATION SURFACE: 5600 m<sup>2</sup>
INFILTRATION RATE: 1 m<sup>3</sup>/m<sup>2</sup>/d
OPERATION FLOW: 200-500 (m<sup>3</sup>/h)

PONDS 2 PIEZOMETERS: 10 SURVEYS: 25 SAMPLES: >250

INFILTRATION SMP: 21

AQUIFERSMP: 36 PIEZOMT. SMP: 206

PERIOD: October 2010 – August 2012



#### **LLOBREGAT BASINS SURVEY**





- Recharge process (MAR) and organic layer (SAT) have demonstrated to improve the infiltrated water quality for several compounds found in raw waters.
- Comparison between infiltration water quality, aquifer water quality and mean values obtained from infiltration ponds have been selected to evaluate removal percentages and treatment efficiencies.
- Several **triazines** (Atrazine, Sebuthylazine, Simazine and Tertbuthylazine) were found in both infiltration and aquifer waters.
  - Mean concentrations ranging from 0.5 to 12 ng/L were found.
  - The organic layer effect was not remarkable for these compounds.
  - High stability of the heterocyclic aromatic ring.
- For **plaguicides**, hexachlorocyclohexanes were those mainly found in the analyzed samples, specifically,  $\gamma$ -HCH (lindane) and  $\beta$ -HCH.
  - Both were mainly found in infiltration water at trace concentration levels.
  - Infiltration process showed a decrease on these concentrations due to both dilution and organic layer effect.
  - Recharge (dilution with aquifer water) effect was observed in blank campaigns (no organic layer).
  - After organic layer installation, a more remarkable improvement was obtained due to the reduction conditions.
  - Considering the mixture ratio (20-40%), the organic layer accounts for reductions above 65% for both compounds.
- For **PAHs**, most of the selected PAHs were identified at different concentrations in the ng/L level, including the 7 regulated compounds.
  - All of them were found in infiltration water at similar concentration levels.
  - Recharge process showed an improvement for all PAHs (except for naphtalene) with concentrations lower than those found in infiltration waters.
  - Comparison between blank and organic layer campaigns, reductions due to the redox conditions were only obtained for chrsene, benzo-(a)anthracene, -(a)pyrene, -(b+k)fluoranthene, -(g,h,i)perylene and indeno (c,d)pyrene.
  - Considering the mixture ratio (20-40%), the organic layer accounts for reductions from 65% to 95% for these compounds.

#### Table 1. Results obtained for compounds found in infiltration waters. Evaluation of the involved effects. **RIVER-ORGANIC LAYER RECHARGE AQUIFER TOTAL COMPOUND** INF. **AFFECTED LAYER EFFECT EFFECT** (ng/L) **EFFECT** (ng/L) (ng/L) $1.34 \pm 0.20$ $2.43\pm0.37$ Acenaphtene $3.18\pm0.48$ $0.45 \pm 0.15$ Acenaphtylene $0.42 \pm 0.06$ $0.63\pm0.09$ **Anthracene** \* $4.64\pm0.70$ $0.87 \pm 0.13$ 1.14±0.17 X $9.87 \pm 1.48$ $9.43 \pm 1.41$ 23.6±3.53 Naphtalene\* 1.56±0.23 $3.51 \pm 0.53$ $1.18\pm0.18$ Pyrene $6.74 \pm 1.01$ $4.34\pm0.65$ $3.80\pm0.57$ **Phenantrene** $0.66\pm0.10$ Fluoranthene\* $1.72\pm0.26$ $0.55 \pm 0.08$ X $2.32 \pm 0.35$ $2.64\pm0.40$ $3.23\pm0.48$ Fluorene $0.82\pm0.12$ $0.39 \pm 0.06$ $0.19\pm0.04$ Chrysene $0.96 \pm 0.14$ $0.49 \pm 0.07$ Benzo(a)anthracene $0.94\pm0.14$ Benzo(b+k)fluoranthene\* $0.67\pm0.10$ $0.34 \pm 0.05$ $0.09\pm0.01$ Benzo(a)pyrene\* $0.27\pm0.10$ $0.13\pm0.05$ $0.03\pm0.01$ $0.02\pm0.01$ Benzo(g,h,i)perylene\* $0.12\pm0.12$ $0.06\pm0.01$ $0.10\pm0.12$ $0.05\pm0.01$ $0.01\pm0.01$ Indeno(c,d)pyrene\* X X $0.47 \pm 0.07$ $0.46 \pm 0.07$ $0.61\pm0.09$ Atrazine\* X X Sebutilazine $0.72\pm0.11$ 1.15±0.17 $0.65\pm0.10$ 1.61±0.24 4.75±0.71 $2.78\pm0.42$ Simazine\* Tertbuthylazine\*\* 12.4±1.86 21.1±3.16 17.1±8.22 β-НСН\* $0.38\pm0.06$ $\approx$ $0.03\pm0.00$ $0.10\pm0.02$

\*Prioritary pollutants( 2000/60/EC-2008/105/EC) \*\*Preference Compounds(RD 60/2011).

 $0.58 \pm 0.09$ 

# Conclusions

- The recharge effect together (MAR) with the organic layer treatment (SAT) have been evaluated for more than 80 organic compounds.
- The recharge dilution process has demonstrated to reduce the initial concentrations of all the compounds except for triazines and naphtalene.
- The organic layer effect was observed for 6PAHS and 2 plaguicides with removal rates ranging from 65 to 95%
- The global treatment effect accounted for the improvement of water quality for all the

studied compounds except for nahtalene with global reductions from 5 to 98%.

#### References

γ-HCH (Lindane)\*

[1] Petrovic, M., Diaz, A., Ventura, F., Barcelo, D., 2003. Environmental Science & Technology 37, 4442-4448.

 $0.10\pm0.02$ 

 $0.15\pm0.02$ 

- [2] Osorio, V., Marce, R., Perez, S., Ginebreda, A., Cortina, J.L. and Barceló, D., 2012. The Science of the total environment 440, 3-13.
- [3] Greskowiak, J., Grommer, H., Massmann, G., Nützmann, G., 2006. Environmental Science & Technology 40, 6615-6621.

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