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Innovative reactive layer to enhance soil aquifer treatment: successful installation in the Llobregat aquifer (Catalonia, NE Spain)

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ABSTRACT

The *Life+* ENSAT project has demonstrated the effectiveness of a reactive organic layer on the improvement of recharge water quality in an aquifer recharge system. The vegetal compost layer was installed at the bottom of an existing infiltration pond in the Llobregat Lower Valley (Barcelona region) with the purpose of promoting biodegradation and improving the removal emerging micro-pollutants from Llobregat River water. A comprehensive monitoring of water quality including bulk chemistry, emerging micro-pollutants and priority substances indicated that hydrobiochemical changes within the organic layer enhance denitrification processes and reduce the levels of gemfibrozil and carbamazepine TP. This effect is due to the release of dissolved organic carbon which promotes biodegradation processes at local scale in the unsaturated zones, without affecting the furthest piezometers. The reactive layer is still active more than 3 years after its installation.
The economic assessment of this innovative reactive layer shows that it is a promising solution for the improvement of aquifer recharge with low quality waters, not only technically but also from the economic sustainability standpoint.

Key words: aquifer recharge, emerging pollutants, infiltration ponds, Llobregat River, reactive layer, soil aquifer treatment.

Capa reactiva innovadora para la mejora del tratamiento suelo-acuífero: exitosa instalación en el acuífero del Llobregat (Cataluña, NE España)

RESUMEN

El proyecto Life+ ENSAT ha demostrado la eficiencia en la mejora de la calidad del agua de recarga mediante la instalación de una capa reactiva en un sistema de recarga de acuíferos. La capa, constituida principalmente por compost vegetal, fue instalada en la sub-superficie de una balsa de recarga construida en el Valle Bajo del Llobregat (provincia de Barcelona), con el objetivo de promover la biodegradación y mejorar la eliminación de microcontaminantes emergentes del agua del Llobregat. El exhaustivo seguimiento de la calidad del agua que incluye química general, contaminantes emergentes y sustancias prioritarias, indica que los cambios hidrobiogeoquímicos con el sistema implantado mejoran los procesos de desnitrificación y la reducción de concentración de gemfibrozilo y carbamazepina- epoxy). Esta mejora se debe a la liberación de carbón orgánico disuelto, que promueve los procesos de biodegradación a escala local en la zona no saturada, sin efecto en los piezómetros de control más alejados. La capa reactiva sigue activa después de más de tres años desde su instalación.

La evaluación económica de la capa reactiva muestra que es una solución prometedora para la mejora de la recarga de acuíferos con aguas de baja calidad, no sólo desde el punto de vista técnico, sino desde el punto de vista de la sostenibilidad económica.

Palabras clave: Balsa de Infiltración, Capa Reactiva, Contaminantes Emergentes, Recarga de Acuíferos, Río Llobregat, Tratamiento Suelo-Acuífero.

VERSIÓN ABREVIADA CASTELLANO

Introducción y objetivos

En el Área Metropolitana de Barcelona (AMB), constituida por 36 municipios y una población total de más de 3 millones de habitantes, la recarga artificial juega un papel importante en la gestión conjunta de los recursos superficiales y subterráneos. El abastecimiento mediante aguas subterráneas supone un 11% del total y es estratégico en periodos de sequía (Figura 1). Históricamente se han llevado a cabo actuaciones de recarga por parte de la Agencia Catalana de Agua (ACA) y de operadores como SGAB (Sociedad General de Aguas de Barcelona) en la zona del Valle Bajo y Delta del Llobregat, como pozos de inyección, balsas de infiltración o la escarificación del lecho del río (Hernandez et al, 2010).

Conjuntamente con el agua regenerada producida por las depuradoras, los excedentes del río Llobregat también pueden ser recargados. El proyecto Life+ ENSAT busca la eliminación de las barreras actualmente existentes para hacer posible esta reutilización indirecta desde un punto de vista seguro para el medio ambiente y la salud humana. Para ello, es necesario conocer la evolución de las características del agua, no sólo delos parámetros legislados, sino también de los llamados "contaminantes emergentes", que aunque no están todavía regulados presentan un interés creciente en la comunidad científica y la sociedad en general. Se trata de fármacos, pesticidas, productos de limpieza y estrógenos, entre otras sustancias, que no son eliminadas completamente en las depuradoras, y que por tanto llegan a las aguas superficiales y subterráneas. El avance en las técnicas analíticas ha permitido su detección y cuantificación en concentraciones muy bajas (Kuster et al., 2008).

Numerosos estudios han reconocido las propiedades del tratamiento Suelo-Acuífero (SAT, Soil Aquifer Treatment, en inglés) respecto a la capacidad del subsuelo de reducir las concentraciones de estos contaminantes mediante la degradación natural (ex. biodegradación y adsorción) (Bosma et al., 1996). Estos procesos están vinculados a las condiciones físico-químicas del suelo, como la presencia de materia orgánica, condiciones aerobias o anaerobias, etc. Para promover la actividad microbiológica durante el SAT, es necesario disponer de una fuente de materia orgánica, para que los contaminantes emergentes en concentraciones de nano gramo por litro puedan ser eliminados como cometabolitos en los procesos de biodegradación El principal objetivo del proyecto Life+ ENSAT es mejorar la degradación de los microcontaminantes emergentes durante la recarga, mediante la colocación de una capa reactiva que aporte carbón orgánico y que promueva por tanto su biodegradación (Figura 5).

Descripción de la zona de estudio

El sistema de recarga se ubica en el término municipal de Sant Vicenç dels Horts, en la plana aluvial del margen derecho del Valle Bajo del río Llobregat. El espesor del acuífero aluvial en esta zona es de 20 metros de profundidad, donde se alteran arenas y gravas con finas capas de arcillas y limos (Pedretti et al, 2012) (Figura 2). El sistema de recarga fue construido en 2007, y consiste en una balsa de decantación de 4000 m^2 *y una de infiltración de 5600 m*^{2}*. Actualmente reciben agua directamente del río Llobregat por gravedad desde el azud de Molins de Rei, situado 2 km aguas arriba, pero el sistema está también preparado para recibir agua regenerada de la estación de tratamiento del Prat del Llobregat, mediante bombeo. La zona no saturada bajo la balsa de infiltración se encuentra entre 4 y 6 metros de profundidad. La tasa de infiltración es de 1m*^{3}*/m*^{2}*/día (ver otros parámetros operacionales en la Tabla 1). Este sistema de recarga está ampliamente instrumentado para su seguimiento, con una red de piezómetros ambientales y multitubos y cápsulas de succión para la toma de muestras (Figura 3).*

Metodología

Para el diseño de la capa reactiva a instalar en el sistema de recarga de Sant Vicenç dels Horts se realizaron ensayos de laboratorio de lixiviación de 4 materiales pre-seleccionados que cumplían alta disponibilidad, bajo coste y potencial de aporte de carbón orgánico en contacto con el agua de recarga. Se escogió el compost vegetal procedente de podas de bosque por su estabilidad en el tiempo en el aporte de COT (Carbón Orgánico Total). Posteriormente se probaron las características hidráulicas de una mezcla de 50% compost 50% material sedimentario de la balsa de recarga mediante un experimento en columna. Se simuló durante un mes el flujo natural de recarga de arriba abajo con un caudal de 2 L/día y se compararon los resultados de COT, carbón inorgánico (CI), pH, Eh y oxígeno disuelto en la columna reactiva y en la columna de control, formada 100% con material sedimentario de la balsa tamizado entre 2 – 5 mm. En la columna reactiva se observó un incremento de COT y CI a medida que el flujo de agua avanzaba a través de la columna, de acuerdo con mayores tiempos de residencia (Figura 4). Las propiedades hidráulicas de la columna reactiva se mantuvieron estables durante el experimento.

El diseño final de la capa reactiva consistió en 60 cm de una mezcla en volumen de 50% compost vegetal y 50% arenas locales a la que se añadió una pequeña proporción de 1% de arcillas rojas y un 0,1% de óxidos de hierro para aumentar la capacidad de adsorción. En la parte superior se dispusieron 5 cm de arenas locales para evitar la flotación de hojas o trozos de madera del compost vegetal (Figura 5). La instalación de la capa tuvo lugar en marzo de 2011,

Se realizaron un total de 25 campañas de muestreo (codificadas cronológicamente como C1, C2,… C25) entre octubre de 2010 y septiembre de 2012. Se tomaron 40 muestras de agua superficial en la balsa de infiltración, 177 muestras de agua subterránea en piezómetros y 30 muestras de agua intersticial en la zona no saturada mediante cápsulas de succión. La campaña C2 sirvió como referencia de infiltración en condiciones naturales, sin capa reactiva, y la campaña C3 de blanco, sin recarga. A partir de la instalación de la capa en marzo de 2011 se consideran dos periodos de recarga continuos en las campañas C9-C15 y C20-C25. Estos periodos permitieron evaluar el impacto de la capa reactiva a corto y medio plazo.

El laboratorio de AMB realizó análisis físico químicos para caracterizar los cambios hidrogeoquímicos durante la recarga, incluyendo indicadores del estado reductor como nitratos, hierro y manganeso. Además analizaron los compuestos orgánicos prioritarios de la Directiva 2008/105/EC, que incluyen pesticidas, hidrocarburos policíclicos aromáticos (PAHs) y disolventes.

El Laboratorio del IDAEA-CSIC aplicó cromatografía líquida y espectrometría de masas (LC MS/MS) (López de Alda et al. 2003) para la cuantificación de los contaminantes orgánicos emergentes seleccionados (incluyendo compuestos parentales y algunos productos de transformación): 4 herbicidas (diurón, simazina, hidroxi-simazina y deisopropilatrazina), 6 fármacos (ibuprofeno, carbamazepina, epoxi-carbamazepina, gemfibrozilo, atenolol, sufametoxazol) y un estrógeno (estrona). Esta selección se basó en la ocurrencia de los microcontaminantes en los recursos hídricos de la zona (Köck-Schulmeyer et al. 2011) y sus implicaciones en términos de salud humana y ambiental. Además se realizaron experimentos para determinar las propiedades de adsorción de los microcontaminantes seleccionados con los componentes de la capa (47 muestras).

Resultados

La Figura 6 muestra que los valores de COD en la zona no saturada aumentaron respecto la concentración del agua de entrada gracias al aporte de la capa reactiva. Se alcanzaron valores de 12 mg/L de COD, que son cuatro veces más la concentración en la balsa de infiltración. La concentración de COD se redujo en los piezómetros más alejados, sugiriendo un consumo mediante biodegradación. La desnitrificación se cuantificó en una reducción de concentración de nitratos inicial de 15-20 mg/L a valores por debajo de 1 mg/L por debajo de la capa reactiva. No se observó la reducción en la concentración de sulfatos, que indicaría unas condiciones reductoras más extremas en el medio. Respecto a las sustancias prioritarias analizadas se cuantificó una reducción del 75% en la concentración de los cinco PAHs regulados, y un 50% en el lindano. En la Figura 7 se muestra un ejemplo de la reducción de las concentraciones de tricloretano en el acuífero durante los periodos de recarga constante (campañas C6-C16).

Respecto al comportamiento de los microcontaminantes emergentes, la Tabla 2 resume los niveles muestreados durante el proyecto. Los compuestos gemfibrozilo y epoxi carbamazepina (producto de transformación del fármaco carbamazepina) mostraron una mejora en su eliminación tras la colocación de la capa reactiva. En el caso del gemfibrozilo la eficiencia de eliminación aumentó del 20 – 60% en condiciones naturales al 40 – 75% con la capa reactiva (Figura 8). Diurón, simazina, hidroxi simazina y carbamazepina no alteraron sus patrones de comportamiento en condiciones naturales tras la colocación de la capa reactiva. Los demás compuestos analizados fueron detectados esporádicamente, con lo que no pudieron ser evaluados: deisopropilatrazina, estrona, ibuprofeno, sulfametoxazol y atenolol. En general se observó que la concentración de emergentes en el acuífero disminuyó tras la instalación de la capa reactiva en la balsa de infiltración.

Los experimentos de adsorción con arcillas, óxidos de hierro y compost vegetal demostraron que los contaminantes emergentes se adsorben solamente en la superficie del compost vegetal, siendo los compuestos más adsorbidos estrona, hidroxi simazina, diurón y atenolol. Se realizó una tanda de experimentos con la capa reactiva después de su instalación y se demostró que las propiedades adsorbentes de la capa reactiva seguían presentes tras un año de infiltración.

Para finalizar, se realizó un análisis coste-eficiencia del sistema de recarga con capa reactiva, comparándolo con el sistema natural de recarga y con un tratamiento avanzado de ultrafiltración y ósmosis inversa para recarga profunda, con el mismo objetivo de recargar agua de baja calidad al acuífero, mejorando su calidad inicial (resumen en Tabla 3). Las ventajas de los tratamientos avanzados son su compacidad y una mayor eliminación de emergentes (más del 99% según Boleda et al., 2011). Los sistemas naturales presentan una clara ventaja en cuanto a costes, ya que la recarga tiene un coste unitario de 0.18 €/m^3 y 0.23 €/m^3 sin capa y con capa respectivamente, muy por debajo de los 0.41 €/m^3 de la inyección profunda.

Conclusiones

El proyecto Life+ ENSAT ha demostrado la eficiencia de la capa reactiva instalada en la balsa de infiltración de Sant Vicenç dels Horts en cuanto al incremento en la eliminación de contaminantes emergentes y la mejora de la calidad del agua subterránea (ex. desnitrificación, contaminación orgánica en el acuífero). El impacto de la capa reactiva se produce a nivel local, principalmente en la zona no saturada, siendo ésta una actuación segura de mejora de la recarga natural.

Este tipo de proyectos son necesarios para demostrar que se pueden "ingenierizar" los procesos naturales, maximizando su eficiencia y controlando su evolución. Reguladores, operadores y en general la sociedad necesitan este tipo de herramientas para incrementar la fiabilidad técnica y mejorar la percepción social de los sistemas de recarga, no sólo para el aumento del recurso hídrico, sino para mejorar la calidad a través de los procesos SAT.

La nueva tecnología de capa reactiva testada en Sant Vicenç dels Horts ofrece una nueva dimensión a los sistemas de recarga, demostrando que es una técnica coste-efectiva en comparación con sistemas avanzados de tratamientos ex situ para una recarga en profundidad. El siguiente paso será el estudio del mantenimiento y sustitución de este tipo de capas reactivas, para ofrecer esta solución a los operadores desde un punto de vista económica y técnicamente viable.

Introduction

MAR in a strategic area: the Barcelona Metropolitan Area

Managed aquifer recharge (MAR) is a technique widely used to increase groundwater resources and improve their availability and sustainability. In urban areas, MAR projects have many objectives in addition to water supply, and these vary from site to site (Dillon *et al.,* 2009): (1) securing and enhancing water supplies; (2) protecting aquifers against salinization; (3) freshening saline aquifers and assisting groundwater demand management; (4) mitigating floods and flood damage; (5) improving urban amenities, land value and biodiversity; (6) improving coastal water quality by reducing urban discharges and (7) enhancing environmental flow in original water supply catchments.

In the case of the Barcelona Metropolitan Area (BMA), MAR plays an important role in increasing storage capacity to help operators cope with the runoff variability in Barcelona catchments and unexpected changes in surface water quality which are exacerbated by climate change. Historically, public administration, the Catalan Water Agency (ACA), and water supply operators (the SGAB Company) have applied several techniques to improve artificially the groundwater resources in the Low Llobregat Valley and in the Delta of the Llobregat River such as injection wells, infiltration ponds or river bed scarification (Hernandez *et al,* 2010).

The BMA is made up of 36 municipalities with a total population of 3.23 million inhabitants, with an average density of 5,093 hab/km^2 (INE, 2012). Drinking water supply in the BMA needs approximately 8 m^3/s continuously, despite the low consumption per capita averages, 107 L/d/inhabitant, whilst the average for other European cities is over 150 L/d/inhabitant (AMB, 2011). The Llobregat River is currently supplying an average of 5 m^3/s from the inlet of the 3-reservoir system (see **Figure 1**). Whilst fresh water is considered an expensive and scarce natural resource, the biggest waste-water treatment plants (WWTPs) in the surroundings of Barcelona are El Prat and Besós WWTPs which are discharging respectively 100 hm^3/year and 137 hm^3/year into the sea. This situation shows the still heavy dependence on rainfall at headwater of the Ter and Llobregat Rivers and shows the difficulties for complying with the European Water Framework, which requires good ecological status.

In the framework of this complex scenario of water management, non-conventional water resources are intended to be used for direct and indirect water supply. The water reclamation treatment plant (WRTP) in El Prat del Llobregat reaches a production of 50 hm^3/year in drought periods, providing a significant potential of water reuse. Moreover, the Llobregat River surplus is susceptible to be used for aquifer recharge purposes. Reclaimed water and low quality surface water are considered a realistic option for feeding aquifer recharge facilities in the Llobregat area. Studies such as those presented in this paper aim at crossing barriers to make this possible, from the safety and health point of view.

Emerging organic compounds in surface and reclaimed waters

Recharging with non-potable water such as reclaimed water or raw Llobregat River water requires the study of its evolution to evaluate its impact and ensure environmental and human health safety. It is essential not only to evaluate the behaviour of regulated parameters and/or compounds, but also to assess the

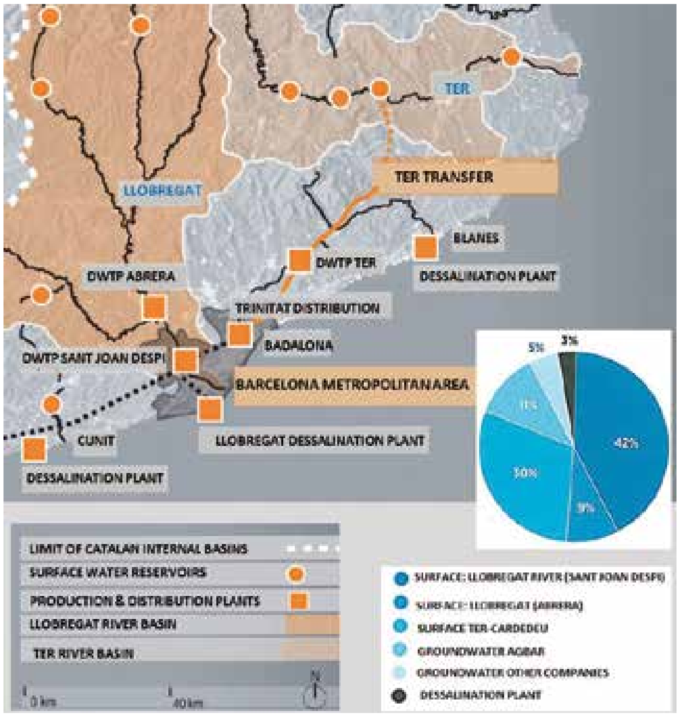

Figure 1. *Water management scheme in the Barcelona Metropolitan Area. In blue colour: percentages of the freshwater resources. Source: http://territori.scot.cat*

Figura 1. *Esquema de la gestión del agua en el área metropolitana de Barcelona. En color azul: porcentajes de los recuros de agua dulce. Fuente: http://territori.scot.cat*

fate of emerging pollutants in groundwater, and their changes throughout the subsoil passage.

During the last decades, the number of organic pollutants detected in the Llobregat River water has increased both in the river (Köck-Schulmeyer *et al.* 2012a; Köck-Schulmeyer *et al.* 2011; López-Serna *et al.* 2012; López-Roldán *et al.* 2010; Muñoz *et al.* 2009; Osorio *et al.* 2012; Ricart *et al.* 2010) and in the aquifer (Teijon *et al.* 2010; García-Galán *et al.* 2011; Köck-Schulmeyer *et al.* 2012b; López-Serna *et al.* 2013). Some of these chemicals are used in a wide range of applications, and have become indispensable to our modern society. Progress in analytical techniques has enabled the detection of more compounds at lower concentrations (Kuster *et al.*, 2008). The scientific community, as well as regulators and the general population are showing a growing concern about these substances, most of them not yet regulated, and the so-called "emerging pollutants", which comprise pharmaceuticals, personal care products, pesticides and estrogens, amongst others. The main reason for their presence in the Llobregat River is the discharge of treated wastewater and surface run-off from agricultural areas and effluents from different industries along the Llobregat river course. Water treatments applied are frequently not completely efficient, so natural water often contains many dissolved chemicals, which can affect ecosystems and impact drinking water supplies (Huerta-Fontela *et al.* 2008; Kampioti *et al.* 2005; Petrovic *et al.* 2003; Rodriguez-Mozaz *et al.*, 2004).

The ENSAT Project: a drive towards the improvement of groundwater through SAT

Soil aquifer treatment (SAT) has been widely applied since the 70's, and has been proven to be an effective technique for storing, treating and recovering a wide range of recycled water qualities. During infiltration and subsurface flow, the artificially recharged water usually undergoes quality changes. In general, they result from the interaction of physical (filtration, advection and dispersion), chemical (sorption, precipitation/dissolution) and biological (biodegradation) processes. A major aim of the research on artificial recharge of groundwater is to understand the potential key factors that control the water quality changes occurring between recharge/infiltration and recovery. The influence of these factors can be very different, depending on field site characteristics such as recharge water quality, composition of aquifer matrix, subsurface residence time and hydraulic conditions (Greskowiak, 2005).

Natural degradation processes (i.e., biodegradation and sorption) can help to remove dissolved (trace) organic compounds as well as pathogenic bacteria and viruses, and thus are of importance for the protection of ground- and drinking water quality in artificial recharge systems (Bosma *et al.*, 1996). However, the nature and reaction rates of these processes are strongly determined by physical and chemical conditions. The geochemical changes in a hydrogeological system are often to a large extent triggered and determined by microbial mediated redox reactions (Greskowiak *et al.*, 2006). These redox reactions are driven by the biodegradation of dissolved and/or sediment-bound organic matter and involve the consumption of so-called terminal electron acceptors such as oxygen and nitrate amongst others. The relation between biodegradation of trace organics at SAT sites and organic matter removal, under either aerobic or anoxic conditions, has also been assessed thus suggesting the possible role of cometabolism (Amy and Drewes, 2007).

Since certain pollutants are preferably removed under some particular redox conditions, such conditions could eventually be promoted in artificial recharge practices. Barbieri *et al.* (2011) proved at laboratory scale (batch tests) that different compounds were degraded under different redox environments, so they suggested that a water mass undergoing a sequence of redox states should maximise the removal of contaminants present.

To promote microbiological activity during SAT a source of organic matter should be present. Some of the emerging pollutants are used by microorganisms as cometabolites during the oxidation of easily degradable organic matter. Adding organic substrates to favour biodegradation processes has been widely tested mainly to stimulate NO_3^- and SO_4^{2-} reducing bacteria (Gibert *et al.*, 2004).

The *Life+* ENSAT project aims at incorporating an additional organic-carbon source to feed microorganisms, as it is a limiting factor for the biodegradation occurring in the subsurface in natural conditions. The ambitious challenge of the project lies in that it has been planned at full scale, using the existing infiltration pond of Sant Vicenç dels Horts. This system directly infiltrates raw Llobregat River water containing a wide group of emerging organic micro-pollutants which can be monitored during SAT. The innovative aspect of this project is the installation of an organic layer in the bottom of the infiltration pond in order to release dissolved organic carbon and enhance the biological activity and therefore the removal of organic micro-pollutants (see **Figure 5**).

Objectives

The main objective of this work is to demonstrate the effectiveness of an enhanced SAT to improve water quality, focused on the removal of organic micro-pollutants from Llobregat River water and the improvement of water quality in the aquifer (bulk chemistry and priority substances). The specific objectives of this paper are:

- Reporting the design and installation of the reactive organic layer in the recharge system of Sant Vicenç dels Horts, located in the Llobregat Aquifer (Barcelona), taking into account the geological characterisation of the site.
- Evaluation of the hydrogeochemical evolution of the recharge system after the installation of the reactive layer, to determine the spatial impact of the reactive organic layer and its durability / lifetime during the project.
- Assessment of the evolution of organic micropollutants through SAT in natural conditions and after the installation of the reactive organic layer.
- Cost-effectiveness analysis of the installation and operation of a reactive organic layer in existing or newly constructed aquifer recharge facilities compared to natural aquifer recharge systems and advanced treatments to eliminate organic micro-pollutants.

The *Life+* ENSAT project has other specific objectives not included in this article, such as the development of modelling tools using reactive transport numerical modelling and the transfer of the method to other European sites.

The experimental recharge site of Sant Vicenç dels Horts

Hydrogeology of the Low Llobregat Valley at Sant Vicenç dels Horts

The Llobregat Low Valley Aquifer is located before the Llobregat Delta plain, close to the Mediterranean Sea. There, the Llobregat River crosscuts the Catalan Coastal Ranges, made up of the Hercynian basement and Mesozoic to Cenozoic cover. The Hercynian basement consists of Palaeozoic metasedimentary rocks and late Hercynian granites, which were peneplaned prior to the Triassic, upon which the Mesozoic sedimentary sequences were deposited (Otero *et al*, 2008).

The recharge system is located in the municipality of Sant Vicenç dels Horts in the floodplain on the right bank of the Llobregat River as it passes through the town. The geology of this area is a sequence of fine and coarse-grained facies of silico-clastic materials, deposited according to the evolution of the paleoriver. The deposition of fine-grained materials occurs in low energy streams (minimum on the alluvial planes), while coarser material needs higher transport efficiency (maximum along the channel). Therefore the hydrogeological setting is composed of sandy-gravel or gravelly-sand (depending on the proportion of the average grain sizes), separated by non-continuous

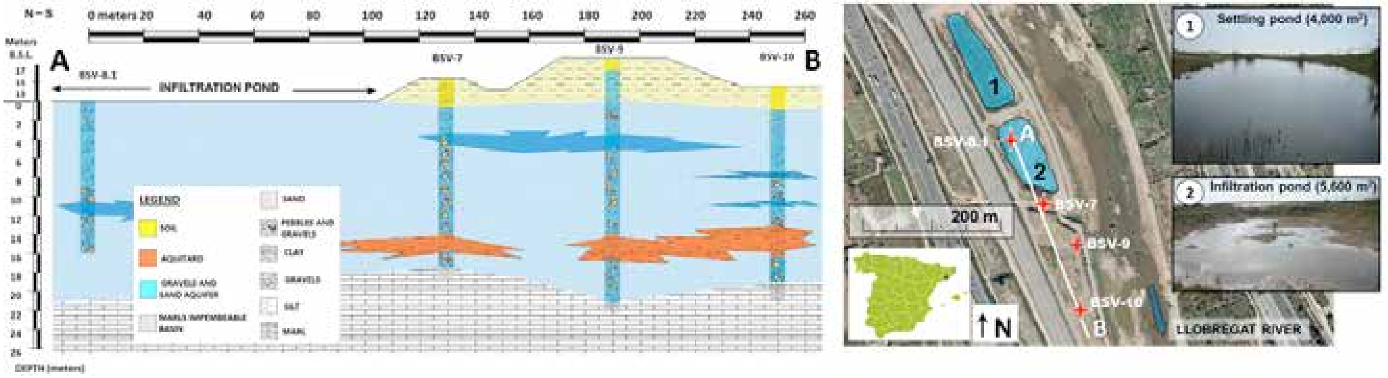

Figure 2. Sant Vicenç dels Horts geological characterisation and recharge system details.
Figure 2. *Caracterización geológica de Sant Vicenç dels Horts y detalles del sistema de recarga.*

fine-grained layers (Pedretti *et al,* 2012). The excavation of the pond ranges from 4 to 6 m below the ground surface, on the western edge of the Llobregat River. At the scale of the pond, the unsaturated zone had a thickness of around 4 metres during the project (2010 – 2012). The drilling works of 4 new piezometers in the infiltration pond (one: BSV-8 multitube) and downstream (three: BSV-7, BSV-9 and BSV-10) permitted the detailed geological section (A-B) illustrated in **Figure 2.** The saturated zone (aquifer) had an average thickness of between 10 – 12 metres.

Decantation and infiltration ponds for increasing water quality and quantity

The aquifer recharge (AR) system consists of a decantation pond (4,000 m^2) and an infiltration pond (5,600 m^2) connected by a 10 metre concrete tube (inner diameter of 1 metre) (see **Figure 2**). This AR system is prepared to receive not only Llobregat River raw water, but also treated water from the El Prat de Llobregat Reclamation Plant. Since 2008 it has been operated with Llobregat River water. The scale of the site is very useful for field experimentation since it represents an intermediate scale between laboratory and large scale systems.

Recharge water reaches the decantation pond by gravity from the inlet of Molins de Rei (a concrete pipe that conducts water from two kilometres upstream of the AR system). Residence time is about 3 days in the decantation pond, where the fine particles settle. Water passes by gravity to the infiltration pond, through a 1 cm light, plastic mesh. The water column is maintained at between 40 – 70 cm. Infiltration rate is about 1m^3/m^2/day. Control parameters and general data of the AR systems are described in **Table 1**.

General data	
Infiltration surface	5,600 m^2
Designed flow	250 (m^3/h)
Infiltration rate	1 m^3/m^2/day
Operational flow	200 – 500 (m^3/h)
Recharged volume and operation days	
2010 (01/01 – 31/12)	49,950 m^3 / 14 days
2011 (01/01 – 31/12)	1,163,885 m^3 / 169 days
2012 (01/01 – 30/09)	813,234 m^3 / 141 days
Control parameters	
Ammonia	1.5 mg/L
Electric conductivity	2.000 µS/cm
River turbidity	100 NTU
Entrance turbidity	25 NTU

Table 1: *Operational details of the recharge system during the project.*
Tabla 1. *Parámetros de operación del sistema de recarga durante el proyecto.*

Groundwater monitoring network

The studied zone is equipped with 16 control points where piezometric levels are measured both outside and inside the pond. At the end of 2010 a third measurement point inside the pond was added to the existing control equipment. The network of piezometers was also extended. Some of the piezometers installed are environmental piezometers, in order to obtain samples of the entire profile. Some other piezometers are multilevel piezometers, located at specific points to analyse the depth variation (codes "BSV" in Figure 3). In order to measure the chemical parameters during the recharge process, porous cups were buried under the pond at 1, 2 and 5 metres deep (CA, CB, and CC in **Figure 3**). These cups enable the collection of water samples in the unsaturated zone. Other devices such as tensiometers and humidity sensors were also placed to measure the saturation conditions of the soil.

Method

Selection, design and testing the reactive organic layer at laboratory scale

Leaching tests to select the best organic substrate

The objective of the leaching tests was to select the most suitable organic matter considering two main aspects: the dissolved organic carbon release and its low impact in other parameters such as pH. Moreover, other criteria for the final selection of organic substrate were the price (preferably a sub-product) and the availability. The pre-selected organic substrates according to literature and availability were: 15-day-old green grass (1), two-month-old vegetal compost from pruning material (2) and fresh grape skins (3 and 4). The fresh grape skins were tested alone and mixed with wood chips. To perform the leaching tests, organic substrates were mixed with distilled water. The ratios of solids to liquid were 1:10 for the first substrate, 1:20 for the grape skins and 1:2 in volume for the compost.

During the tests, water samples were collected to measure: total organic carbon (TOC analysed using a *Shimatzu TOC-Vcsh with IR detector* according to NPOC method); dissolved oxygen (analysed by the electrode *YSI, 550A*); pH and Eh measurements were done using an electrode from *Hanna Instruments*. Duplicate sets were performed for each substrate.

15-day- old green grass and grape skins provided a fast DOC release in the first two days, showing a too rapid releasing period. Furthermore, the grape skins led to pH values of around 3.5 and 4.0, which are too acid for the promotion of sustainable biological activity. In the light of these results fresh vegetal compost was selected.

Column experiment to assess the hydrogeochemical behaviour

The main aim of the column experiments was to quantify the amount of DOC released under continuous flow and to determine a proper proportion of organic substrate and local sediments to be mixed as filling materials which should fulfil requirements from both the chemical and hydraulic points of view.

Two 80 cm methacrylate columns were assembled, 60 cm of which were filled with different materials to study the behaviour of the organic substrate. Column I (control) was filled with local sediments from the pond with grain sizes sieved between 2 mm and 5 mm. This column was considered as a reference for natural conditions. Column II (reactive column) was filled with 50% selected organic substrate mixed with 50% of the same sieved local sediments. This column was considered as the representation of the reactive layer to be installed in the field.

Both columns were fed from top to bottom with Llobregat River water at a constant flow rate of 2 L/day (emulating the flow rate in the reactive layer during recharge in the bottom of the infiltration

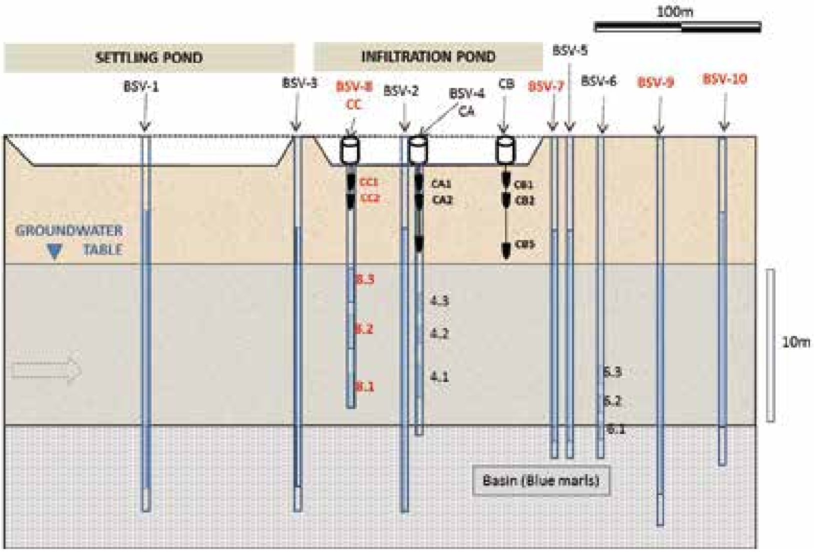

Figure 3. *Cross section of groundwater monitoring network (In red, new instrumentation acquired for the project in 2010).*
Figura 3. *Corte de la sección de la red de pozos de control (En rojo, la nueva instrumentación adquirida para el proyecto en 2010).*

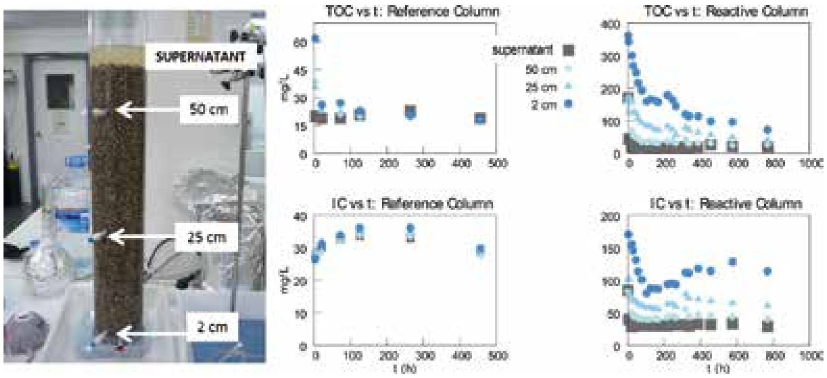

Figure 4. *Scheme of the column experiment (left) total organic carbon (TOC) and inorganic carbon (IC) measured in both reference and reactive columns.*
Figure 4. *Esquema de la columna experimental (izquierda) Carbono orgánico total (TOC) y carbono inorgánico (IC) medidos en las columnas de referencia y en la reactiva.*

pond (1m^3/m^2/day). Water from the columns was sampled through three sampling ports at different distances from the bottom: 2 cm, 25 cm and 50 cm (see **Figure 4**). The supernatant at the top was sampled as well.

The reactive column was running for one month, whilst the reference column was running for 18 days. In both cases sampling was more frequent at the beginning. pH, Eh, dissolved oxygen, inorganic carbon (IC) and TOC were analysed using the methods listed in the description of the leaching tests.

In the reference column, TOC and IC trends in sampled points were close to the supernatant´s values in short time (**Figure 4**). The IC values increased during the first two days although it could not be caused by the TOC degradation because the increase also occurred in the supernatant´s values too, so the increase of IC is related to the initial washout. In the reactive column TOC and IC levels increased from the top to the bottom of the column. This was consistent because the samples taken at the lower port had a higher residence time, which means more contact with the substrate. During the first four days, i.e., during the transient state, TOC and IC levels decreased drastically (from initial concentration of 380 and 175 mg/L respectively. Afterwards the TOC level decrease is more regular.

A month later TOC and IC levels were still much higher in the reactive column than in the reference column. The results showed that the selected substrate released a significant amount of easily degradable organic carbon. The 50% - 50% proportion seemed to be adequate for increasing the organic carbon level without decreasing hydraulic soil properties.

Design of the reactive layer

Following on from laboratory feasibility experiments the reactive layer to be installed in the infiltration pond of Sant Vicenç dels Horts test site was designed (**Figure 5**). The total thickness of the layer was about 65 cm, consisting of 60 cm of reactive material at the bottom of the pond and an upper layer of 5 cm of inert material (sand and local gravels) to avoid flotation of small pieces of compost. The composition of the reactive layer was 50% vegetal compost (fresh gardening and forest pruning material such as the one tested in laboratory) mixed with 50% local sand and gravels to assure the permeability of the reactive layer. Red clay and yellow iron oxides were added at percentages of 1% and 0.1% respectively, with the purpose of contributing to the removal of organic micro-pollutants by sorption onto their surfaces (Feitosa-Felizzola *et al.*, 2009). The surface of the vegetal compost had an expected affinity for the neutral and lipophilic micropollutants (Maoz and Chefetz, 2010).

Application of the full-scale organic reactive layer in Sant Vicenç dels Horts

Installation of the reactive organic layer at the experimental site

In March 2011, the reactive layer was installed. 1,500 m^3 of compost was mixed with the local soil at a volume proportion of 50:50 using a backhoe loader and were spread at the bottom of the pond (**Figure 5**). Red clays were added at 1% to the fresh compost with a large compost mixer. Iron oxides were applied at 0.1% using a crane boom for a semi-homogeneous cover of the total surface of the reactive layer.

Monitoring of the hydrogeochemical system during the project

In order to analyse the impact of the reactive layer on the hydrogeochemical system, the supply of dissolved organic carbon (DOC) was monitored and the redox indicators were evaluated: DOC, nitrates, nitrites, ammonia sulphates, iron and dissolved manganese were analysed during the infiltration period on the non-saturated zone (NSZ are porous cup sampling points) and saturated zone (SZ) piezometers affected by the infiltration (BSV piezometers except BSV-1, see location in **Figure 3**). Average values were compared with infiltration water samples (INF) and the aquifer samples not affected by the recharge process (BSV-1).

An intensive monitoring programme was followed to analyse the efficiency of the reactive layer. Twenty five monitoring campaigns (referred chronologically to as C1, C2, ..., C25) were done between October 2010 until the end of the project (September 2012), with more than 300 samples analysed and 4,000 results processed. Samples of groundwater (177), surface water (Llobregat River) (40) and interticial water (30), were analysed.

At the beginning of 2011, monitoring campaigns were held to verify and understand the system's behaviour under natural conditions (C2 as example of recharge without reactive layer and C3 as blank without recharge). After the installation of the reactive layer in March 2011, measurements were performed to assess the chemical quality at strategic points of the monitoring network, especially in a period with continuous recharge (C9-C15). After a period without recharge (C16-C19), the monitoring restarted in July 2012 (C20-C25), following a half a year period of nearly continuous recharge. This allowed us to evaluate the impact of the reactive layer in the short and medium term.

The AMB (Metropolitan Area of Barcelona) laboratory performed the physicochemical analysis, including conservative parameters such as conductivity, alkalinity and hardness in order to characterise the water bodies involved, and others to demonstrate the redox conditions promoted by the reactive layer (nitrates, iron, manganese...). The analysis of organic priority substances (Directive 2008/105/EC) such as pesticides, PAHs and organochlorine solvents were also carried out to evaluate the effect of the reactive layer on the quality of the infiltrated water.

Emerging micro-pollutant surveillance and sampling campaigns

The IDAEA-CSIC laboratory worked on emerging pollutants using advanced techniques. The list of compounds monitored included four herbicides (phenylurea diuron, and triazine simazine with two transformation products, simazine hidroxy and deisopropylatrazine), one estrogen (the natural female sex hormone estrone), and six pharmaceuticals (the analgesic, antipyretic and anti-inflammatory ibuprofen, the psychiatric drug carbamazepine and its transformation product carbamazepine epoxi, the lipid regulator gemfibrozil, the β –blocker atenolol, and the sulfonamide antibiotic sulfametoxazol. The selection of these compounds was based mainly on their reported occurrence in the Llobregat river water (Köck-Schulmeyer *et al.* 2011; Osorio *et al.* 2012) and in the underlying groundwater (García-Galán *et al.* 2011; Köck-Schulmeyer *et al.* 2012b; López-Serna *et al.* 2013), their varying elimination in WWTPs (very low in the case of carbamazepine and very high in the case of ibuprofen) (Jesus García-Galán *et al.* 2012; Köck-Schulmeyer *et al.* 2011; López-Serna *et al.* 2012), their significance in terms of environmental and human health (estrone, for instance, is a potent estrogen that together with other estrogens has been associated with feminization effects in aquatic organisms (Solé *et al.* 2000; López de Alda *et al.* 2002), and

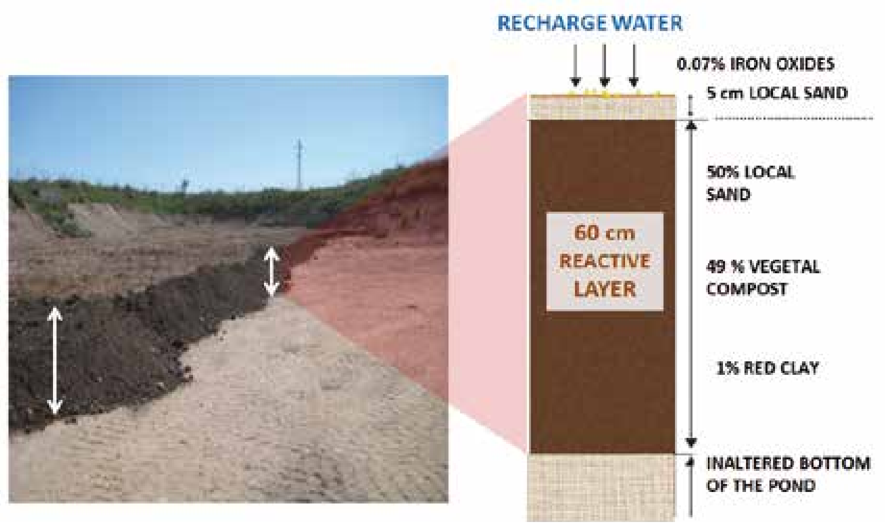

Figure 5. Details of the installation of the reactive layer (March 2011).
Figura 5*. Detalles de la instalación de la capa reactiva (Marzo 2011).*

the viability of their analysis by liquid chromatography-tandem mass spectrometry (LC-MS/MS) (López de Alda *et al.* 2003).

In addition to the samples taken on site (see previous chapter), adsorption tests were performed in the experimental platform on membranes laboratory (PEM) in Sant Joan Despí, to examine the behaviour of the emerging pollutants in contact with the components of the reactive layer (47 samples).

All water samples were collected in amber glass bottles and were transported to the laboratory under cooled conditions (4 °C). Upon reception, samples were filtered and stored at -20 °C in the dark until analysis. Solid samples were also transported refrigerated at 4 °C to the laboratory where they were subsequently frozen at –20 °C, lyophilized, ground with a mortar, sieved through a 125 µm mesh to obtain a homogenous sediment material, and stored at –20 °C until analysis.

Analysis of the emerging micro-pollutants in the water samples was performed by on-line solid phase extraction-liquid chromatography-tandem mass spectrometry (SPE-LC-MS/MS) as described in Barbieri *et al.* (2011). Analysis of the emerging micro-pollutants in the solid samples was carried out by means of pressurized liquid extraction (PLE), followed by SPE purification and LC-MS/MS analysis.

Results and discussion on the performance of the reactive organic layer

Hydrogeochemical evolution of the system

The efficiency of the reactive layer in enriching groundwater with DOC has been demonstrated. DOC values reached 12 mg/L in porous cups, which means 4 times more concentration than the average value in the infiltration pond (**Figure 6**). In general terms, this finding suggests that quality parameters are maintained without the introduction of persistent or major changes into the system. DOC release is local, only detected in the NSZ of the system which means that the reactive layer only has an impact on the controlled zone of the aquifer.

Regarding nitrate concentration, whilst the concentration of nitrate in the aquifer water is around 15-20 mg/L and the infiltrated water has 5-8 mg/L, the samples affected by the infiltration through the reactive organic layer reached concentrations under 1 mg/L, thus showing a significant improvement on the aquifer water quality. This decrease is not observed when recharge is performed without the organic layer (C2) (**Figure 6**). During continuous recharge (C9-C15 and C20-C25) the decrease of nitrates is observed even at the deepest sampling points (at 16 metre depth). When the recharge stops (C16-C19), the usual levels are recovered quickly. Reduction of nitrates occurs concomitantly with the increase of nitrite and ammonia, which was observed only in the NSZ samples, demonstrating the anoxic conditions promoted. No decrease in sulphate concentrations was observed, probably due to the stronger reducing conditions needed.

The analysis of organic priority substances found in the infiltrated water has also shown the efficiency of the organic layer to remove some semi-volatile organic compounds. This study demonstrated that the 5 regulated PAHs [Benzo(a)Pyrene, Benzo(b)Fluoranthene, Benzo(ghi)Perylene, Benzo(k)Fluorantene, Indeno(cd) Pyrene] were removed with mean percentages values of 75% whilst lindane removals were above 50%. Another example is the reduction of tricloroethane in groundwater during recharge periods. This volatile organic compound has been present historically in the aquifer, and showed a significant decrease between

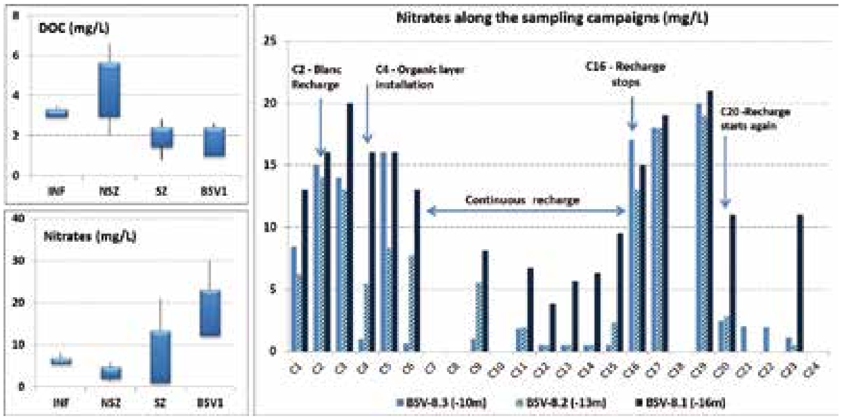

Figure 6. *Left: Comparison of DOC and nitrates maximum, minimum and average levels. INF = infiltration pond; NSZ = non-saturated zone; SZ = saturated zone; BSV1 = piezomer see location in Figure 3. Right: Evolution of nitrates with the recharge conditions at the different piezometric levels of BSV-8 (10, 13 and 16 meters depth, see location in Figure 3).*

Figura 6*. Izquierda: Comparación entre los niveles máximo, mínimo y medio de DOC y nitratos. INF = balsa de infiltración; NSZ = Zona no saturada; SZ = Zona saturada; BSV1 = ver localización de piezómetros en la figura 3. Derecha: Evolución de los nitratos bajo las condiciones de la recarga a diferentes niveles piezométricos del BSV-8 (10, 13 y 16 metros de profundidad, ver la localización de piezómetros en la figura 3).*

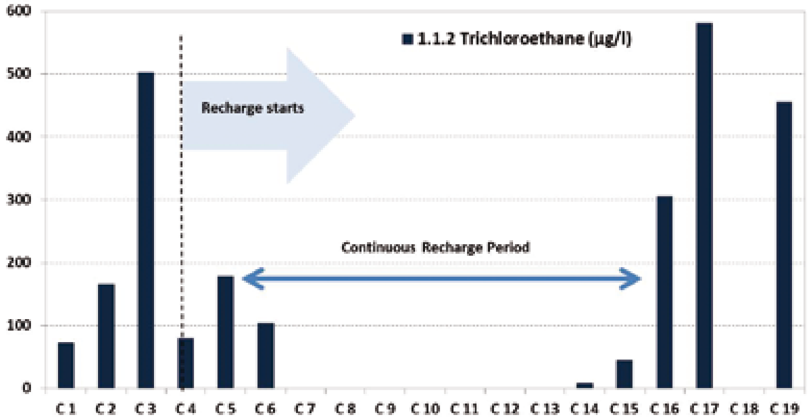

Figure 7. *Recharge helps the reduction of the aquifer's historical pollution (data from piezomenter BSV-8.2. See Figure 3 for detailed location).*
Figura 7. *La recarga ayuda a la reducción de la contaminación histórica del acuífero (datos del piezómetro BSV-8.2. Ver localización en figura 3).*

campaigns C6 and C16, when the recharge system was fully operational (see **Figure 7**).

Assessment of the emerging micropollutants

Table 2 summarizes the levels monitored for the various emerging micro-pollutants throughout the project, during campaigns C1 to C19, distinguishing only between surface (29 samples) and groundwater (173 samples). The purpose of this table is to give a general idea of the frequency of detection as well as mean, median and maximum concentrations of the compounds before (surface water) and after (infiltrated water) the infiltration. As can be seen, some compounds such as deisopropylatrazine, estrone, ibuprofen, sulfametoxazol, and atenolol were only seldom detected and hence their behaviour during MAR could not be assessed.

For the other compounds, two different patterns were observed. Compounds, such as gemfibrozil and the TP carbamazepine-epoxi, seem to be affected by the recharge (in the sense that their concentration in the groundwater becomes altered by the recharge process) whereas other compounds, such as diuron, simazine, simazine OH and carbamazepine, are not affected (see the example of gemfibrozil in Figure 8). Gemfibrozil and carbamazepine-epoxi experienced an improvement of their elimination with the reactive layer. In the case of gemfibrozil, the elimination varied from a range between 20% and 60% of removal in natural conditions to an enhanced elimination between 40% and 75% after the installation of the reactive layer (see evolution of gemfibrozil in Figure 8). Regarding the carbamazepine TP the elimination rate increased from 0% to 85%. The sampling points less affected by the recharge were those located upstream of the infiltration pond (BSV-1, BSV-3) or downstream but relatively far away and deep (BSV-9).

As a general conclusion, the concentration of emerging contaminants in groundwater was relatively high during recharge without the use of the reactive layer and decreased considerably thereafter with its use.

Regarding the carbamazepine TP the elimination rate increased from 0% to 85%. The sampling points less affected by the recharge were those located upstream of the infiltration pond (BSV-1, BSV-3) or downstream but relatively far and deep (BSV-9).

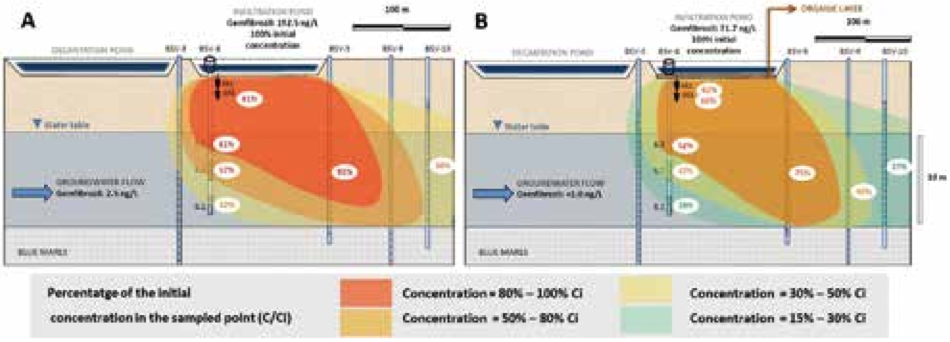

Figure 8. Improvement of the efficiency of the elimination of gemfibrozil during the recharge after the installation of the reactive layer (A) natural conditions; (B) after the installation of the reactive layer.
Figura 8. *Mejora de la eficiencia en la eliminación de gemfibrozilo durante la recarga, después de la instalación de la capa reactiva (A) condiciones naturales; (B) después de la instalación de la capa reactiva.*

Analytes	not detected (%)	median* (Ng/l)	mean*	± sd (ng/l)	max conc (ng/l)
Infiltrated surface water (29 samples – c1 to c19)					
Diuron	10	12,01	15,03	7,59	40,19
Simazine	79	5,41	5,83	1,48	8,56
Simazine oh	34	17,49	15,96	3,36	20,67
Deisopropylatrazine	100	-	-	-	-
Estrone	100	-	-	-	-
Ibuprofen	83	82,5	217,15	193,04	429,5
Carbamazepine	45	23,45	24,34	8,05	42,83
Carba epoxi	59	22,29	20,15	8,21	30,07
Gemfibrozil	10	58,43	65,08	31,18	192,47
Atenolol	72	16,88	19,06	9,57	41,99
Sulfametoxazol	66	52,21	55,4	13,53	80,36
Interstitial (capsules) and ground water (173 samples – c1 to c19)					
Diuron**	27	10,29	11,4	4,29	28,08
Simazine**	53	6,42	10,82	17,16	114,31
Simazine oh	18	12,5	14,46	13,96	162,64
Deisopropylatrazine	91	19,73	21,35	7,53	42,38
Estrone	98	12,69	14,99	12,26	28,24
Ibuprofen	98	57,75	67,96	29,71	111,56
Carbamazepine	27	22,73	23,5	6,57	63,25
Carba epoxi	53	14,81	17,05	11,61	64,83
Gemfibrozil	43	22,08	39,65	50,62	250,64
Atenolol	96	19,31	23,48	13,34	49,46
Sulfametoxazol	63	36,31	43,16	21,96	140,29

(*) of positive samples. (**) Regulated as priority substance Directive 2008/105/EC. *(*) de muestras positivas. (**) Establecidas como sustancias prioritarias según la Directiva 2008/105/EC.*

Table 2. Emerging micro-pollutants: descriptive analysis of the results of 19 water samples (C1-C19), distinguishing between surface water and interstitial (capsules) / groundwater.
Tabla 2. *Microcontaminantes emergentes: análisis descriptivo de 19 muestras de agua (C1-C19), distinguiendo entre agua superficial y agua intersticial (cápsulas) / subterránea.*

Sorption properties of vegetal compost

Sorption can play an important role in the retention of emerging pollutants and increase their residence time in the aquifer. Clay and iron oxide were added in very small proportions to increase the sorption capacity of the reactive layer (see the reactive-layer composition in Figure 5). Nevertheless, the sorption study conducted with clay, iron oxide and vegetal compost revealed the existence of sorption processes only with the compost for most compounds (all were adsorbed except deisopropylatrazine). Clay and iron oxides did not show evidence of micro-pollutant retention. The most adsorbed micro pollutants onto vegetal compost were estrone, hydroxy-simazine, diuron and atenolol.

A second sorption experiment was conducted with the reactive layer material after one year's recharge, to compare the sorption capacity of the installed vegetal compost with the fresh vegetal compost. Results showed that after one year of infiltration, the vegetal compost of the reactive layer maintained the adsorption properties.

Cost-effectiveness analysis

The reactive layer as an alternative to expensive advanced treatments

This paper presents an improved recharge system with a reactive layer as a promising approach to improve water quality and reduce the concentration of emerging micro-pollutants. This process could be an alternative solution to the conventional advanced treatments such as ultrafiltration (UF) and reverse osmosis (RO) seeking the elimination of organic micro-pollutants prior to aquifer recharge (e.g. the deep injection system for the saline intrusion in the Barcelona coastal area). Conventional advanced treatments (UF+RO) require more energy and reagents that raise the final cost of unitary cubic metre recharged in the aquifer. The main advantages are their compacity and almost total elimination of micro-pollutants, with over 99% removal in most cases, according to Boleda *et al.,* 2011. SAT systems require more detailed analysis to evaluate their removal efficiency. In the experimental phase, the removal of micro-pollutants has increased from 20 – 60% in natural conditions to 40 – 75% after the installation of the reactive organic layer.

Table 3 summarises the cost-effective analysis of these three potential recharge water treatments: (i) natural infiltration in a recharge pond, tagged as “conventional SAT”, (ii) enhanced infiltration taking into account the installation and operation of a reactive organic layer based on the characteristics of the one installed in Sant Vicenç dels Horts, and (iii) advanced treatments UF+RO as a previous step to deep injection. The final goal of the three alternatives is the same: to increase groundwater resources by assuring the quality of recharged volume of water. Cost calculations are based on a hypothetic volume of recharge of 15,000m^3/day. Economic data came from the administration, companies and organisations that are currently operating and budgeting for these kinds of facilities (ACA, AMB, CUADLL, SGAB) in the Llobregat area.

Conclusions

Aquifer recharge is a commonly used technique for increasing water resources with a low cost. There are many studies, including this study, which aim to prove these systems have another advantage: they can be useful for treating recharge water by taking advantage of the soil-aquifer processes.

The *Life+* ENSAT project proved the efficiency of the reactive layer in terms of reduction of emerging pollutants such as gemfibrozil and carbamazepine epoxy in recharge water. Moreover, it improves the aquifer water quality since it facilitates reaching lower nitrate concentration levels than in natural conditions. The processes responsible for the removal are the increase of dissolved organic carbon and the adsorption onto the compost. The impact of the reactive layer is local, limited to the non-saturated zone, whilst the good quality water remains available for future use in the aquifer.

	Conventional SAT	**/SAT with reactive layer**	**UF + RO deep injection**
Initial costing	5,028,738 €	5,322,432 €	18,345,210 €
CAPEX	0.0901 €/m^3	0.1366 €/m^3	0.1037 €/m^3
OPEX	0.0946 €/m^3	0.0946 €/m^3	0.3100 €/m^3
Unitary cost m^3	0.1847 €/m^3	0.2312 €/m^3	0.4137 €/m^3
Reagents consumption	None	None	Yes
Energy cost	None*	None*	0.0354€/m^3
Compacity	7.16 m^2/m^{3}d	7.16 m^2/m^{3}d	0.22 m^2/m^{3}d
Efficiency in micro-pollutant removal	20 – 60%	– 75%	>99%

(*) energy consumption does not take account the necessary power for recharge water production, only the energy during the AR process. *(*) el consumo de energía no tiene en cuenta la necesaria para producir el agua de recarga, solamente la energía consumida durante el proceso de recarga.*

Table 3. *Cost-effective analysis between conventional SAT, enhanced SAT using the reactive layer and advanced water treatment.*
Tabla 3. *Análisis de costes de los tratamientos SAT, SAT mejorado utilizando la capa reactiva y agua con un tratamiento avanzado.*

Regulators, operators and society in general need to have tools to monitor such systems and thus the "engineering development" of these processes needs to be focused on. This would increase the technical reliability and thrust and the social perception of recharge systems with reuse water or water of lower quality.

The development of a new technology such as the reactive layer tested in Sant Vicenç dels Horts offers a new dimension to the use of natural processes to eliminate pollutants. During this project, the efficiency of a reactive layer composed of vegetal compost was proven and in further projects, other materials should be tested, which answer the desired characteristics (price, availability, safety...). The most important objective would be to go further into analysing the maintenance and the replacement of such a layer in order to make this type of solution economically attractive for today's operators.

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References

AMB, 2011. Dades Ambientals 2011. 20/03/2013. http://www.dadesambientals.cat/

Amy, G; Drewes, J, (2007). Soil aquifer treatment (SAT) as a natural and sustainable wastewater Reclamation/Reuse technology: Fate of wastewater effluent organic matter (EfOM) and trace organic compounds. *Environmental monitoring and assessment* 129 (1-3) 19-26.

Barbieri, M., Carrera, J., Sánchez-Vila, X., Ayora, C., Cama, J., Koeck-Schulmeyer, M., López de Alda, M., Barceló, D., Tobella Brunet, J., Hernández García, M., 2011. Microcosm experiments to control anaerobic redox conditions when studying the fate of organic micropollutants in aquifer material. *Journal of Contaminant Hydrology* 126, 330-345.

Boleda, R. M., Galcedran, T., Ventura, F. 2011. Behavior of pharmaceuticals and drugs of abuse in a drinking water treatment plant (DWTP) using combined conventional and ultrafiltration and reverse osmosis (UF/RO) treatments. *Environmental Pollution* 159 (2011) 1584 – 1591.

Bosma, T. N. P., Ballemans, E. M. W., Hoekstra, N. K., te Welscher, R. A. G., Smeenk, J. G. M. M., Schraa, G., Zehnder, A. J. B. (1996). Biotransformation of Organics in Soil Columns and an Infiltration Area, *Ground Water*, 34(1), 49-56.

Dillon, P., Paveric, P., Page, D., Beringen, H., Ward, J. 2009. Managed Aquifer Recharge, an introduction. *Waterlines Report Series, No. 13,* February 2009. Australian Government, National Water Commission.

Feitosa-Felizzola, J., Hanna, K., Chiron, S. 2009. Adsorption and transformation of selected human-used macrolide antibacterial agents with iron (III) and manganese (IV) oxides. *Environmental Pollution* 157 (2009) 1317–1322

García-Galan, M.J., Garrido, T., Fraile, J., Ginebreda, A., Díaz-Cruz, M.S. and Barceló, D., 2011. Application of fully automated online solid phase extraction-liquid chromatography-electrospray-tandem mass spectrometry for the determination of sulfonamides and their acetylated metabolites in groundwater. *Analytical and Bioanalytical Chemistry* 399 (2), 795-806.

Gibert, O., de Pablo, J., Cortina, J. L., Ayora, C. 2004. Chemical characterisation of natural organic substrates for biological mitigation of acid mine drainage. *Water Research* 38 (2004) 4186–4196

Greskowiak, J. 2005. Reactive transport processes in artificially recharged aquifers. Field and modelling studies. PhD Thesis.

Greskowiak, J., Grpommer, H., Massmann, G., Nützmann, G., (2006) Modeling Seasonal Redox Dynamics and the Corresponding Fate of the Pharmaceutical Residue Phenazone During Artificial Recharge of Groundwater. Environ. *Sci. Technol.* 2006, **40**, 6615-6621

Hernández, M., Tobella, J., Ortuño, F., Armenter, J. Ll. 2010. Aquifer recharge for securing water resources: the experience in Llobregat River. *Water Science & Technology* 63.2 2011. IWA publishing.

Huerta-Fontela, M., Galceran, M.T., Ventura, F., 2008. Stimulatory drugs of abuse in surface waters and their removal in a conventional drinking water treatment plant. *Environmental Science & Technology* 42, 6809-6816.

INE, 2012. Instituto Nacional de Estadística. 20/03/2013, http://www.ine.es/

Jesus García-Galán, M., González Blanco, S., López Roldán, R., Díaz-Cruz, S., Barceló, D., 2012. Ecotoxicity evaluation and removal of sulfonamides and their acetylated metabolites during conventional wastewater treatment. *Science of the Total Environment* 437, 403-412.

Kampioti, A.A., da Cunha, A.C.B., de Alda, M.L., Barceló, D., 2005. Fully automated multianalyte determination of different classes of pesticides, at picogram per litre levels in water, by on-line solid-phase extraction-liquid chromatography-electrospray-tandem mass spectrometry. *Analytical and Bioanalytical Chemistry* 382, 1815-1825.

Köck-Schulmeyer, M., Ginebreda, A., Alda, M.L.d., Barceló, D., 2012b. Fate and Risks of Polar Pesticides in Groundwater Samples of Catalonia. In: Barceló, D. (Ed.). Hdb Env Chem, pp. 375–394.

Köck-Schulmeyer, M., Ginebreda, A., González, S., Luis Cortina, J., López de Alda, M. and Barceló, D., 2012. Analysis of the occurrence and risk assessment of polar pesticides in the Llobregat River Basin (NE Spain). *Chemosphere* 86 (1), 8-16.

Köck-Schulmeyer, M., Ginebreda, A., Postigo, C., López-Serna, R., Pérez, S., Brix, R., Llorca, M., Alda, M.L.d., Petrovic, M., Munné, A., Tirapu, L. and Barceló, D., 2011. Wastewater reuse in Mediterranean semi-arid areas: The impact of discharges of tertiary treated sewage on the load of polar micro pollutants in the Llobregat river (NE Spain). *Chemosphere* 82 (5), 670-678.

Kuster, M., López de Alda, M.J., Hernando M.D., Petrovic, M., Martín-Alonso,J., Barceló, D. (2008). Analysis and occurrence of pharmaceuticals, estrogens, progestogens and polar pesticides in sewage treatment plant effluents, river water and drinking water in the Llobregat river basin (Barcelona, Spain). *Journal of Hydrology* 358, 112– 123

López de Alda, M.J., Gil, A., Paz, E., Barcelço, D., 2002. Occurrence and analysis of estrogens and progestogens in river sediments by liquid chromatography-electrospray-mass spectrometry. *The Analyst* 127, 1299-1304.

López de Alda, M.J., Díaz-Cruz, S., Petrovic, M., Barceló, D., 2003. Liquid chromatography-(tandem) mass spectrometry of selected emerging pollutants (steroid sex hormones, drugs and alkylphenolic surfactants) in the aquatic environment. *Journal of chromatography.* A 1000, 503-526.

López-Roldán, R., López de Alda, M., Gros, M., Petrovic, M., Martin-Alonso, J. and Barceló, D., 2010. Advanced monitoring of pharmaceuticals and estrogens in the Llobregat River basin (Spain) by liquid chromatography-triple quadrupole-tandem mass spectrometry in combination with ultra performance liquid chromatography-time of flight-mass spectrometry. *Chemosphere* 80 (11), 1337-1344.

López-Serna, R., Jurado, A., Vázquez-Suñé, E., Carrera, J., Petrovic, M. and Barceló, D., 2013. Occurrence of 95 pharmaceuticals and transformation products in urban groundwaters underlying the metropolis of Barcelona, Spain. *Environmental Pollution* 174, 305-315.

López-Serna, R., Postigo, C., Blanco, J., Perez, S., Ginebreda, A., López de Alda, M., Petrovic, M., Munné, A. and Barceló, D., 2012. Assessing the effects of tertiary treated wastewater reuse on the presence emerging contaminants in a Mediterranean river (Llobregat, NE Spain). *Environmental Science and Pollution Research* 19 (4), 1000-1012.

Maoz, A., Chefetz, B. 2010. Sorption of the pharmaceuticals carbamazepine and naproxen to dissolved organic matter: Role of structural fractions. *Water Research* 44 (2010) 981–989.

Muñoz, I., López-Doval, J.C., Ricart, M., Villagrasa, M., Brix, R., Geiszinger, A., Ginebreda, A., Guasch, H., Jose López de Alda, M., Romani, A.M., Sabater, S. and Barceló, D., 2009. Bridging levels of pharmaceuticals in river water with biological community structure in the Llobregat river basin (northeast Spain). *Environmental Toxicology and Chemistry* 28 (12), 2706-2714.

Otero, N., Soler, A., Canals, A. 2008. Controls of d_{34}S and d_{18}O in dissolved sulphate: Learning from a detailed survey in the Llobregat River (Spain). *Applied Geochemistry* 23 (2008) 1166–1185.

Osorio, V., Marce, R., Perez, S., Ginebreda, A., Cortina, J.L. and Barceló, D., 2012. Occurrence and modeling of pharmaceuticals on a sewage-impacted Mediterranean river and their dynamics under different hydrological conditions. *The Science of the total environment* 440, 3-13.

Pedretti, D., Barahona-Palomo, M., Bolster, D., Sánchez-Vila, X., Fernández-García, D. 2012. A quick and inexpensive method to quantify spatially variable infiltration capacity for artificial recharge ponds using photographic images. *Journal of Hydrology* 430–431 (2012) 118–126.

Petrovic, M., Diaz, A., Ventura, F., Barceló, D., 2003. Occurrence and removal of estrogenic short-chain ethoxy nonylphenolic compounds and their halogenated derivatives during drinking water production. *Environmental Science & Technology* 37, 4442-4448.

Ricart, M., Guasch, H., Barceló, D., Brix, R., Conceicao, M.H., Geiszinger, A., de Alda, M.J.L., Lopez-Doval, J.C., Munoz, I., Postigo, C., Romani, A.M., Villagrasa, M. and Sabater, S., 2010. Primary and complex stressors in polluted mediterranean rivers: Pesticide effects on biological communities. *Journal of Hydrology* 383 (1-2), 52-61.

Rodríguez-Mozaz, S., López de Alda, M.J., Barceló, D. (2004). Monitoring of estrogens, pesticides and bisphenol A in natural waters and drinking water treatment plants by solid-phase extraction–liquid chromatography–mass spectrometry. *Journal of Chromatography A,* **1045** 85–92

Solé, M., de Alda, M.J.L., Castillo, M., Porte, C., Ladegaard-Pedersen, K., Barceló, D., 2000. Estrogenicity determination in sewage treatment plants and surface waters from the Catalonian area (NE Spain). *Environmental Science & Technology* 34, 5076-5083.

Teijon, G. Candela, L.,Tamoh, K., Molina-Díaz, A., Fernández-Alba. A.R. 2010. Occurrence of emerging contaminants, priority substances (2008/105/CE) and heavy metals in treated wastewater and groundwater at Depurbaix facility (Barcelona, Spain). Science of the Total Environment 408 (2010) 3584–3595.

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