Degradation of emerging contaminants in reclaimed water through soil aquifer treatment (SAT)

M. Hernández, C. Magarzo and B. Lemaire

ABSTRACT

Soil aquifer treatment (SAT) is considered to be an alternative technique able to enhance recharged water quality for aquifer recharge purposes. It allows the reuse of treated wastewater, which usually contains some recalcitrant organic micropollutants such as pharmaceutical and personal care products (PPCPs) and endocrine disrupting chemicals (EDCs). This study reports the removal capacity for a selection of organic micropollutants during SAT and the characterisation of the recharge system for the interpretation of the data. The experiment was performed in Angerville (France), where the treated wastewater effluent of the wastewater treatment plant (WWTP) is directly infiltrated through an excavated infiltration pond after biological treatment. The system was instrumented by installing piezometers downgradient of the infiltration pond, which were monitored, together with other reference points, and analysed for detailed interpretation. Results on the site characterisation allowed the quantification of the mixing proportion of the recharge water and groundwater and identification of the redox conditions encountered within the aquifer. With respect to the targeted micropollutants, results showed that they exhibited different behaviour during infiltration. Examples of atrazine, gemfibrozil and carbamazepine are discussed as a representation of the most characteristic patterns of organic contaminant fate after recharge.

Key words | aquifer recharge, organic micropollutants, reclaimed water, redox, soil aquifer treatment (SAT)

INTRODUCTION

The occurrence of endocrine disrupting chemicals (EDCs) and pharmaceutical and personal care products (PPCPs) in wastewater has become more easily detectable over the last two decades (Kuster et al. 2008; Arye et al. 2011). These and other synthetic compounds represent a relatively new threat to the environment and human health. Despite the apparently small risk of acute toxicity for humans at low concentration, effects may build up over a long period of time (Gilboa et al. 2011). However, and as reported by numerous studies, conventional processes developed in drinking and wastewater treatment plants (WWTPs) do not completely remove such products (Céspedes et al. 2005).

Soil aquifer treatment (SAT) constitutes an alternative practice to efficiently remove organic pollutants (including micropollutants such as EDCs and PPCPs) and improve water quality during aquifer recharge with reclaimed water. This improvement is achieved through a combination of processes such as filtration, precipitation, sorption and biodegradation (Bourg & Bertin 1995; Bosma et al. 1996). SAT techniques also imply economic advantages with respect to other technologies (Dillon et al. 2009). However, knowledge of the fundamental processes involved in SAT is still limited.

The lack of quantitative information about degradation trends of organic micropollutants in natural conditions encouraged the detailed study of how these compounds behave and the factors that control their degradation. Scientific literature supports the assertion that organic micropollutants behaviour and removal are affected greatly by redox conditions of the system (Lyngkilde & Christensen 1992). For this purpose, a field test was performed with the
objective of studying the removal trends of a selection of target organic micropollutants. The field test was carried out on an aquifer recharge system in Angerville (Beauce area, Paris), where the effluent of a municipal WWTP is infiltrated in a recharge pond on the treatment plant. After the instrumentation of the field site, analytical campaigns were performed and the results were interpreted and correlated with published studies.

SYSTEM CHARACTERISATION AND METHODOLOGY

Site description

The experimental field site is located in Angerville, about 80 km south of Paris (France), in a vast agricultural plain. The geology underneath Angerville WWTP is mainly composed of alternating chalks and marls with some interbedded levels of clay and sand. Together these constitute the Beauce aquifer, whose regional flow moves from NW to SE and has an estimated local permeability of 80 m/d. The site was selected considering the hydrogeological context and the configuration of the existing WWTP. The recharge system has been operating since 2002, so it is assumed that steady state flow conditions exist.

The WWTP effluent (6,000 population equivalent) is infiltrated integrally into the aquifer through a square-shaped pond of 2,500 m² (50 m × 50 m). The recharge water homogenises within the pond and settles for a few hours before infiltrating at a mean daily flow rate of 320 m³/d. The water level monitoring indicated that the infiltration capacity of the pond equals the discharge flow and, aside from the daily variations, the water column was about 30 cm in the pond. Figure 1 illustrates a scheme of the aquifer recharge system (showing the different inputs, outputs and monitoring locations).

Instrumentation of the experimental site

No observation wells existed downgradient from the infiltration pond prior to the project; therefore, the project’s scope of works included the construction of three piezometers which are aligned downgradient at increasing distances from the infiltration pond (10, 20 and 30 m, respectively) to assess water quality and changes in its composition while circulating in the aquifer. These new observation wells are represented in Figure 1 as P1, P2 and P3.

The unsaturated zone (UZ) and saturated zone (SZ) are considered to have an approximate depth of 23 and 17 m, respectively; thus the screened pipe of the piezometers remains almost 2 m over the water table.

Point A in Figure 1 corresponds to an existing private well located 1.2 km upgradient from the infiltration pond. Point E corresponds to Angerville WWTP effluent and IP

Figure 1 | Scheme of Angerville recharge system.
to the infiltration pond in which the effluent water is disposed of for aquifer recharge.

**Soil sampling methodology and analysis**

Taking advantage of the drilling works, three samples of drilled material from each constructed piezometer borehole (P1, P2 and P3) were collected, including the unsaturated and saturated zone. Their mineralogy was characterised using X-ray diffraction (CSIC-IDAEA facilities). Local pumping tests were performed for better estimation of hydraulic parameters of the aquifer.

A sample of settled sludge from the bottom of the infiltration pond was also collected in order to assess possible accumulation of target organic micropollutants within the pond over decades of continuous discharge by the WWTP. The settled sludge was visible/evident/apparent as a 20-cm layer of dark fine material. The analysis of micropollutants was done using accelerated solvent extraction (ASE) (LE Lab’Eau).

**Water sampling methodology and analysis**

Points A, E, IP and P1, P2 and P3 were monitored during four sampling campaigns between November and December 2010. The water analysis, performed by LE Lab’Eau (Le Pecq, France), targeted basic quality parameters (pH, conductivity, redox potential, dissolved oxygen), inorganic components (Cl, SO₄, Mg, K, Na, alkalinity, F, NH₄, orthophosphates, NO₃, NO₃, B, Fe, Mn, total P, dissolved organic carbon (DOC), As, S, chemical oxygen demand) and a selection of representative micropollutants in WWTP effluents (atrazine, simazine, carbamazepine, diclofenac, gemfibrozil, atenolol, metoprolol, iopromide, paracetamol, erythromycin, sulfamethoxazole, bisphenol A).

An automatic sampler was used to collect integrated 24-h samples from the main outlet (E). Each water sample collected from the pond was built from 10 samples taken all around the pond to ensure their representativeness (IP).

Water samples from piezometers P1, P2 and P3 were collected using a 76-mm submersible pump after emptying the equivalent of three times the water volume contained in the piezometer (French norm FD T 90-523-3 January 2009). As piezometers were totally screened in the saturated zone, the collected water samples were environmental (without any selection in the vertical profile as there was no stratification in the aquifer). Reference point A was sampled directly at the tap, using its pumping system.

**RESULTS AND DISCUSSION**

**Background groundwater characteristics**

The groundwater general composition was assumed to be constant in the surroundings of the WWTP, given its geological and environmental context. Aquifer geology was analysed by X-ray diffraction analysis of in situ soil samples obtaining calcite and quartz as the most abundant minerals, and some other trace minerals such as albite, chloride, gypsum or microcline at higher depths.

Field measurements at point A indicated circumneutral groundwater pH, conductivity around 500 μS/cm and Eh close to +150 mV. The analysed composition was, as expected, representative of a calcareous aquifer. Samples showed considerable calcium content (95.8 mg Ca/L). Nitrate (73 mg NO₃/L) also seemed to be well over the limit established by the European Drinking Water Directive (50 mg NO₃/L; DWD 98/83/EC), probably because of fertilisation of the agricultural area. The lack of DOC (0.35 mg C/L) in groundwater inhibits denitrification processes.

The analysis of organic pollutants at sampling point A showed that atrazine, simazine and bisphenol A were already present in the background groundwater, although their concentration was low (0.19, 0.04 and 0.02 μg/L, respectively) and quite close to the limit of quantification (0.02, 0.02 and 0.01 μg/L, respectively). No other organic micropollutant was detected in the groundwater.

**Recharge water characteristics**

Physicochemical parameters were measured during each sampling campaign. pH of the recharge water collected in the infiltration pond presented constant values close to 8, and conductivity remained around 1,000 μS/cm. Eh measurements were always positive at around 100–200 mV.

Chloride (~140 mg Cl/L) and sulfate (~35 mg SO₄/L) were found to be below the limit established by DWD 98/83/EC (250 mg/L for both species), and total P
(~3,800 μg P/L) was also relevant at values above the range stated by Directive 91/271/EEC for sensitive areas (>2,000 μg/L).

It should be taken into consideration that the variability in effluent quality was low over time, because of the operational criteria of the plant.

Characterisation of water blend

Both the recharge and the groundwater are supposed to mix underneath the infiltration pond (see Figure 1). The contribution of each source of water to the water blend depends on the volume of water that arrives at the mixing point.

Volume of the aquifer groundwater was estimated taking into account the general and local water flow, which had an average gradient of Δh = 1.2 × 10⁻³, and an estimated permeability of 80 m/d, obtained through a pumping test. Following Darcy’s law and assuming an average thickness of the aquifer of 17 m, the volume calculated corresponds to 1.6 m³/day per longitudinal metre of aquifer.

The volume of recharge water was estimated by the mean value of the infiltration rate. The infiltration rate indicated a value of 320 m³/day, which would correspond to 0.126 m³/day per m² of the infiltration area. Apparently, the contribution of groundwater was more relevant than the recharge water. However, in order to complete a better understanding of the system and confirm this assumption, chloride was selected as a conservative species to obtain a more accurate approximation of the contributions to the water blend. Figure 2 represents the values of the chloride concentration in the groundwater and recharge water to find the mixing ratio in the piezometers. The fairly constant concentrations along P1, P2 and P3 after the mixing points confirm that chloride behaves as a conservative species in the system of study. The contribution of recharge and groundwater can then be calculated from a mass-balance according to Equation (1).

\[ C_{P3} = x_A C_A + (1 - x_A) C_{IP} \]  

where C stands for the concentration of the aquifer (A) and the infiltration pond (IP), all of them measured in mg/L.

Calculations indicated a proportion of aquifer groundwater and recharge water of approximately 25% and 75%, respectively. Moreover, results showed that the recharge water volume is low with respect to the aquifer volume; nevertheless, the study focused on a small area close to the IP to evaluate its local effect, where the influence of infiltration seems higher.

Redox conditions identification

There are several mechanisms for contaminant removal reported in the literature. Bosma et al. (1996) and Bourg & Bertin (1993) specified the processes occurring during aquifer recharge in their field experiments: bacterial degradation of organic matter, filtration, sorption and redox conditions may play a crucial role in favouring the predominance of some mechanisms (i.e. biodegradation) over others. Lyngkilde & Christensen (1992) also found a considerable dependence of organic micropollutants behaviour and removal on redox conditions. Therefore, the identification

![Figure 2](http://iwaponline.com/jwrd/article-pdf/2/3/157/378330/157.pdf)
of the redox conditions became a very important premise in order to understand the processes involved.

Redox conditions were determined by field measurements and a group of redox-sensitive compounds. Field measurements taken during sampling campaigns did not obtain reliable values of dissolved oxygen but, in contrast, Eh was found to be more reliable. Eh values measured in the aquifer were around 200 mV which is considered to be within those expected for denitrification conditions (Christensen et al. 2000). On the other hand, the occurrence of a series of redox-sensitive compounds would also indicate the redox state in which the processes are taking place (Lyngkilde & Christensen 1992).

Considering both premises, it is possible that some organic degradation was happening in the system. The evolution of analysed nitrate and DOC suggested that denitrification conditions could be a probable redox state given the factors available.

The mixing ratios calculated above enabled the estimation of a theoretical concentration of nitrate and DOC to be found downstream of the mixing point, considering the previous calculation of 25% of groundwater and 75% of recharge water. Figure 3 shows the observed concentrations of nitrate and DOC.

In both cases, there is a depletion with respect to the theoretical water blend, a little in nitrate and more pronounced in DOC. Such a decrease could be due to a degradation process that may have occurred between the mixing point and the piezometer P3. DOC decrease is frequently caused by biological processes during SAT (Lin et al. 2008).

\[
\text{CH}_2\text{O} + 0.8\text{NO}_3^- + 0.8\text{H}^+ \rightarrow \text{CO}_2(g) + 0.4\text{N}_2(g) + 1.4\text{H}_2\text{O} 
\]

(2)

Considering that all nitrate depleted was reduced through denitrification (60 mmol/L NO₃), and taking into account the
stoichiometry in Equation (2) (Gibert et al. 2008), the theoretical N/C ratio of 0.80 could not account for the overall DOC consumption observed (400 mmol C/L, while the stoichiometry gives an expected value of 75 mmol C/L). This indicates that other processes need to be taken into account. The most probable is the aerobic respiration in the unsaturated zone, as this is the most favourable process according to Gibbs energy (Christensen et al. 2000).

The undetected values of NO2 indicate that the reduction of nitrate is totally complete, and no intermediate by-products were left. Lack of ammonium gave evidence that the reaction was hosted in a not very reductive system and, therefore, that nitrate was transformed to N2 (gas).

**BEHAVIOUR OF ORGANIC MICROPOLLUTANTS**

Once redox conditions were identified and the conceptual model was clear (Figure 1), then the results of the analytical campaigns regarding organic micropolllutants could be discussed. Just 12 out of 23 initial target compounds were detected over the limit of quantification. Those compounds were atrazine, simazine, carbamazepine, diclofenac, gemfibrozil, atenolol, metoprolol, iopromide, paracetamol, erythromycin, sulfamethoxazole and bisphenol A.

The mixing ratios estimated from chloride as a conservative compound were also used to establish a theoretical concentration value for each of those compounds. Thus, values below the theoretical prediction would imply removal of the compound. The 12 detected compounds presented different trends of removal, and some of them did not even appear at all after the mixing point. Those different behaviours could be synthesised into three groups or trends:

- **Group A**: in which removal was observed to a great extent and includes most of the detected compounds (concentrations of downgradient sampled points are under the detection level). An example of this trend is gemfibrozil (Figure 4(a)). Gemfibrozil presented a variable concentration in the recharge water (up to 0.13 μg/L) and below the limit of quantification (LOQ) (0.02 μg/L) in the groundwater upgradient of the infiltration pond. The predicted concentration for the water blend, represented

![Figure 4](http://iwaponline.com/jwrd/article-pdf/2/3/157/378390/157.pdf)

**Figure 4** | Examples of organic micropollutants evolution in Angerville system: (a) gemfibrozil; (b) atrazine; and (c) carbamazepine (GW, groundwater; RW, recharge water).
by a dotted line in the graphic, was quantified as well over the LOQ, suggesting that total removal of gemfibrozil occurred within the aquifer. Other studies (Drewes et al. 2003) support degradation of gemfibrozil under nitrate reducing conditions and also aerobic conditions, sometimes related to organic matter content.

- **Group B**: in which no decrease during aquifer recharge is detected or slight removal was observed. The group includes atrazine (shown in Figure 4(b)) and sulfamethoxazole.

- **Group C**: this group showed higher concentrations after the mixing point than the expected theoretical blend. Carbamazepine constitutes the only example (Figure 4(c)) of this unexpected trend; concentrations after the mixing point are higher than in recharge water. Nevertheless, if any kind of mixture had occurred, the expected concentrations would be lower than the recharge water. Some previous research studies reflect that carbamazepine is a recalcitrant compound (Rauch-Williams et al. 2010), and no degradation has been observed in SAT. Gibson et al. (2010) observed accumulation of carbamazepine in soils irrigated with WWTP discharges. They justified this phenomenon with sorption processes occurring for the retention of the compound. As carbamazepine is an emerging compound (not regulated), there are no historical data to review previous concentrations in the outlet of the WWTP of Angerville. Concentration of carbamazepine in the past could be higher, taking account that it was developed in the 1970s and its use had increased greatly by the 1980s (Gibson et al. 2010).

Regarding the extraction test performed with the sludge sample collected from the bottom of the infiltration pond, the only compound detected has been carbamazepine (limit of quantification for pesticides 0.4 μg/kg and for the rest of the substances 2 μg/kg). The measured quantity of carbamazepine analysed by ASE was 33 μg/kg. This is evidence of the carbamazepine recalcitrant behaviour and sorption affinity.

The behaviour of the whole group of the detected compounds is synthesised in Table 1. The description of the trend is qualitative, as most of the compounds were found under the detection limit in the piezometers downgradient.

### CONCLUSIONS

This study assessed the performance of a SAT system in Angerville (France) in removing a total of 12 targeted organic micropollutants.

From a hydrological point of view, the proportions of blended recharge water and groundwater after the infiltration were determined to be 75 and 25%, respectively. This is essential to determine how dilution accounts for the eventual decrease of concentration of the target micropollutants and, hence, to properly evaluate the performance of the SAT

**Table 1** | Behaviour trends of organic micropollutants

<table>
<thead>
<tr>
<th>Source of pollution</th>
<th>Observed trends</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atrazine</td>
<td>Agriculture + WWTP</td>
</tr>
<tr>
<td>Simazine</td>
<td>Agriculture</td>
</tr>
<tr>
<td>Carbamazepine</td>
<td>WWTP</td>
</tr>
<tr>
<td>Diclofenac</td>
<td>WWTP</td>
</tr>
<tr>
<td>Iopromide</td>
<td>WWTP</td>
</tr>
<tr>
<td>Metoprolol</td>
<td>WWTP</td>
</tr>
<tr>
<td>Paracetamol</td>
<td>WWTP</td>
</tr>
<tr>
<td>Erythromycin</td>
<td>WWTP</td>
</tr>
<tr>
<td>Gemfibrozil</td>
<td>WWTP</td>
</tr>
<tr>
<td>Atenolol</td>
<td>WWTP</td>
</tr>
<tr>
<td>Sulfamethoxazole</td>
<td>WWTP</td>
</tr>
<tr>
<td>Bisphenol A</td>
<td>WWTP and PVC interaction</td>
</tr>
</tbody>
</table>

Downloaded from http://iwaponline.com/jwrd/article-pdf/2/3/157/378390/157.pdf by guest
system. From redox-sensitive species and Eh analyses, results also showed that redox conditions were dominated by denitrification, although consumption of DOC beyond the stoichiometric ratio suggested that other mechanisms (i.e. aerobic degradation) were taking place too.

The targeted micropollutants exhibited different behaviours during the SAT system. Some micropollutants (gemfibrozil, diclofenac, iopromide, metoprolol, paracetamol, erythromycin and atenolol) were totally removed while others were not biodegraded and merely diluted by groundwater. Carbamazepine exhibited an unexpected trend as it showed concentrations downgradient higher than those in the recharge water and groundwater. This finding is likely due to desorption of the carbamazepine accumulated at the bottom of the infiltration pond over decades of continuous discharge by the WWTP. Detection of high contents of carbamazepine within the settled sludge collected from the infiltration pond corroborates this hypothesis.

This study has demonstrated that SAT technology can be effective at removing organic micropollutants from an infiltrated discharge of a WWTP. However, biogeochemical processes occurring during SAT need to be better understood to satisfactorily explain differences in behaviour observed among micropollutants and to determine how they are affected by redox conditions. For this purpose, the SAT system in Angerville will continue to be monitored in the future.

ACKNOWLEDGEMENTS

This work was supported by the R+i Alliance project WR0801 (DECRAT).

REFERENCES


First received 16 January 2012; accepted in revised form 20 April 2012