Application of the guidelining soil-column study protocol: Soil-column experiments to assess the fate of emerging pollutants under MAR conditions

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Summary: This report corresponds to the second part of the D12.3. The document summarises the practical application of the guidelines presented in the D12.3(a), and corresponds to the experiment carried out in Barcelona, in the waste water treatment plant of El Prat del Llobregat to test the effectiveness of a natural and an enhanced simulated SAT system. 11 selected pharmaceuticals (target compounds of DEMEAU project) present in secondary effluent have been quantified in the inlet and outlet of the soil-column experiments to evaluate the fate of these compounds after a natural filtration process. Two parallel columns simulated the infiltration pond of Sant Vicenç dels Horts before the implementation of the reactive layer, while two additional doubled columns simulated the implementation of a compost-made reactive layer before the aquifer infiltration.

Results showed great differences in the elimiation of pharmaceuticals along the experiment in natural and enhanced conditions. 3 different groups have been created to summarise the behaviour of the 11 organic compounds. While 7 of them didn’t have a representative increase of elimination under enhanced conditions, 4 noticed better removal percentage in the enhanced system. Duplicated systems proved robustness in the acquisition of results, as both columns gave same results in terms of concentration and elimination of most of the parameters analysed. Comparison with field experiments have been already done. Elimination percentages reported in full-scale MAR systems are higher than those observed in the soil-column experiment. This is an important fact to take into account and reveals that soil-column experiments are quite limited to simulate MAR systems and their complexity.

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Deliverable author(s):	CETaqua: Marta Hernández , Oriol Gibert
Quality assurance:	Annette Wefer-Roehl (TUD, Technical University Darmstadt) Christine Kübeck (IWW, Rheinisch-Westfaelisches Institute for Water Research) Teresa E. Leitão (LNEC, Laboratório Nacional de Engenharia Civil)
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Summary

This report corresponds to the second part of the D1.2.3. The document summarises the practical application of the guidelines presented in the D1.2.3(a), and corresponds to the experiment carried out in Barcelona, in the waste water treatment plant of El Prat del Llobregat to test the effectiveness of a natural and an enhanced simulated SAT system. 11 selected pharmaceuticals (target compounds of DEMEAU project) present in secondary effluent have been quantified in the inlet and outlet of the column experiments to evaluate the fate of these compounds after a natural filtration process. Two parallel columns simulated the infiltration pond of Sant Vicenç dels Horts before the implementation of the reactive layer, while two additional doubled columns simulated the implementation of a compost-made reactive layer before the aquifer infiltration.

Results showed great differences in the elimiation of pharmaceuticals along the experiment in natural and enhanced conditions. 3 different groups have been created to summarise the behaviour of the 11 organic compounds. While 7 of them didn't have a representative increase of elimination under enhanced conditions, 4 noticed better removal percentage in the enhanced system. Duplicated systems proved robustness in the acquisition of results, as both columns gave same results in terms of concentration and elimination of most of the parameters analysed. Comparison with field experiments have been already done. Elimination percentages reported in full-scale MAR systems are higher than those observed in the column experiment. This is an important fact to take into account and reveals that column experiments are quite limited to simulate MAR systems and their complexity.

1. Introduction

Managed Aquifer Recharge is being widely applied worldwide to increase groundwater resources. Specifically in Europe, where more than 300 sites have been identified, MAR can be considered a well-established methodology for the increase of water resources. While in North East Europe River Bank Filtration is the most popular technique applied, in Spain infiltration ponds seem to be the most enduring system due to the low operational costs.

One example of MAR system in Spain under operation since 2008 is the MAR system of Sant Vicenç dels Horts (SVH) (Barcelona). Currently the system is being recharged with Llobregat river water, and it is almost prepared to receive reclaimed water from the waste water treatment plant (WWTP) of El Prat del Llobregat. In such a scarcity area this second option makes more sense, as it supposes closing the water cycle and the optimization of water resources.

Both Llobregat River and reclaimed water contain emerging compounds that have been reported in several studies (Kuster *et al.*, 2008; Teijon *et al*., 2010). In 2011, the ENSAT project installed in the bottom of the infiltration pond of SVH a reactive organic layer made by vegetal compost. The ENSAT project assessed the effectiveness of the reactive layer to eliminate emerging compounds. Conclusive results were obtained to gemfibrozil and epoxy-carbamazepine, which showed a higher percentage of elimination in enhanced conditions (Hernández *et al.,* 2014).

The work presented in this report goes a step further in the evaluation of the reactive layer installed in a MAR system. It was based on the recommendations and guidelines prepared in D12.3(a), and it consisted of the simulation of the MAR site using 2 parallel stainless columns, installed and operated in the WWTP of El Prat del Llobregat (Barcelona). The selected compounds corresponded to the list of 12 target substances selected by DEMEAU consortium, and the experiment was ongoing during 2013, in collaboration with the Technical University of Catalonia (assembling, operation and bulk chemistry) and the Göttingen University (chemical analysis of organic micropollutants).

The experimental work took place in El Prat del Llobregat (Barcelona, NE Spain) WWTP, which is the biggest in the Barcelona Metropolitan area, with 2,000,000 inhabitants-equivalent and a treatment capacity of 420,000 m^3/day (see location in Figure 1). This plant is one of the largest purification plants in Europe, after the WWTP was extended with a water reclamation plant (WRP), in 2006.

Since then the WRP has treated secondary effluent from the WWTP producing until the year 2010 a volume of 67.8 Mm^3. One of the end uses of reclaimed water of the plant are the artificial aquifer recharge schemes located in the Llobregat area: the deep barrier against the saline intrusion (14 injection wells installed in parallel to the coast line) and the aquifer recharge infiltration system located in Sant Vicenç dels Horts (SVH).

SVH MAR system is one of the most active aquifer recharge systems in the Llobregat area. It consists of a decantation pond (5600 m^2) and an infiltration pond (4000 m^2). The purpose of this aquifer recharge system is to increase groundwater resources at local scale, with an annual volume recharged of 1.11 and 1.16 million of cubic metres in 2011 and 2012, respectively, of raw surface water coming from the Llobregat River. In 2011 an organic layer of vegetal compost was installed on the bottom of the infiltration pond to enhance adsorption and degradation processes along the recharge, in what was the first experience worldwide in applying such an approach at such large scale (Hernandez *et al.*, 2011). Results demonstrated that this innovative technique indeed resulted in an enhancement of the elimination of some emerging pollutants (ENSAT, 2012). Specifically for gemfibrozil and carbamazepine epoxy, improvement in removal has been reported (Hernández *et al.*, 2014).

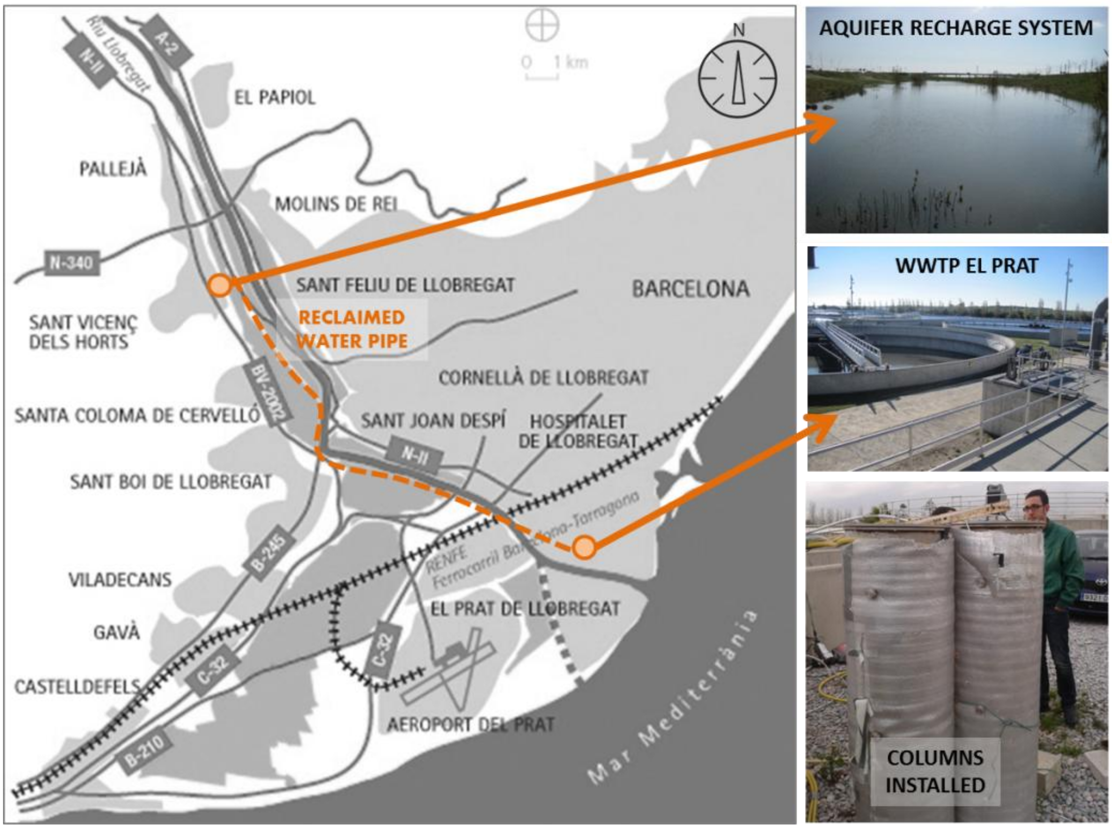


Figure 1: Location of the WWTP in El Prat del Llobregat and the MAR system in SVH
NOTE: Dashed line represents the connexion pipe between the WRP in El Prat del Llobregat and the MAR system in Sant Vicenç dels Horts.

Based on this experience and with the purpose of moving one step forward, the present study intends to apply secondary effluent from the WWTP, instead of river water, through the infiltration pond of SVH to assess the removal of emerging pollutants. The aim of this experiment was to evaluate the impact of the organic vegetal compost layer, installed on the bottom of the infiltration pond, on the removal of emerging pollutants coming from direct recharge of the secondary treatment effluent.

2. Objectives

The objective of this report is to apply in a real case the recommendations prepared as guidelines for the design, monitoring and interpretation of column experiments simulating MAR to evaluate the fate of emerging pollutants. D12.3(b) is the practical application of some of the recommendations prepared in D12.3(a).

Specifically, the objectives of the column experiment assessed are:

- Evaluate the effectiveness of removal of target emerging pollutants in an enhanced MAR system and compare it with a natural MAR system under controlled conditions.
- Compare results obtained in the experiment with reported removal percentages in literature (results presented in D12.1).

3. Methodology of the column tests experiments

3.1 Experiment location

Column experiments were installed in the waste water treatment plant of El Prat del Llobregat (Barcelona). This WWTP is the biggest in the Barcelona Metropolitan area, with 2,000,000 inhabitants-equivalent and a treatment capacity of 420,000 m^3/day. This plant is one of the largest purification plants in Europe, combining two large processes that operate in parallel: water line and sludge line (see **Figure 2**). The conventional treatment of the WWTP was extended with a reclamation plant, installed in 2006. Since July 2006, El Prat Water Reclamation Plant (WRP) treated secondary effluent from El Prat WWTP producing until the year 2010 a volume of 67.8 Mm^3. Nowadays the WRP is operating below its capacity due to economic restrictions.

The selected water to feed the columns for the experiments came from the secondary treatment effluent. The main advantage of working using real produced treated waste water is that the emerging pollutants studied are present in natural concentrations, and the water composition is representative of other WWTP effluents. Synthetic water, in contrast, presents the major advantage of the homogeneity along the experiment, which makes the interpretation of results easier. Contrary, results of experiments using synthetic water are less realistic and difficult to extrapolate to real conditions.

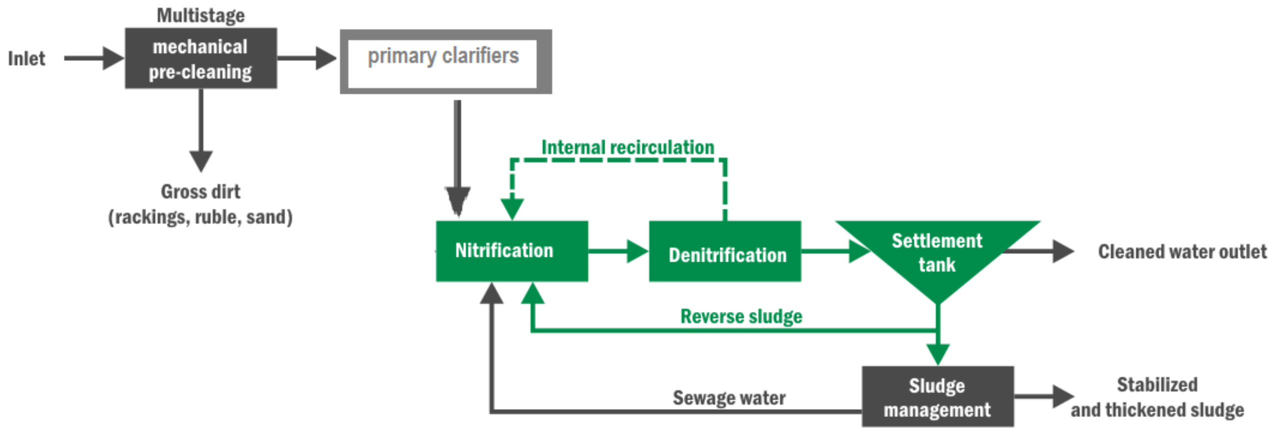


Figure 2: Treatment scheme of the WWTP of El Prat del Llobregat (Barcelona)

3.2 Inflow water characterisation

A previous analysis was performed to quantify the emerging micropollutants of the list of the DEMEAU project in the effluent of the secondary treatment. The following list indicates those that were naturally present in the effluent of the secondary treatment and those that were added on purpose (spiked) to the experiment. Concentration values represent the average concentration of the pollutants along the experiment:

Table 1: Concentration of micropollutants in WWTP secondary effluent (column inlet water)
NOTE: (a) detection frequency above LOQ, n= 21 samples. (*) spiked compounds

Compound INF1	Code	Mean [ng L-1]	Min [ng L-1]	Max [ng L-1]	Std. dev. [ng L-1]	QF[a] [%]
Diclofenac*	DCL	1334	876	1799	251	100
Phenazone*	PHEN	2170	1474	3043	381	100
Metoprolol	MET	48	23	121	27	76
Iopromide	IOP	740	317	1358	301	100
Sulfamethoxazole*	SMX	1443	1176	1759	131	100
Trimethoprim	TRI	207	17	1342	377	62
Bezafibrate	BZF	53	22	95	24	95
Gemfibrozil	GFZ	1052	504	2207	515	100
Carbamazepine	CBZ	242	199	270	19	100
Primidone	PRM	85	69	102	9	100
1H-Benzotriazole	BZL	2895	1829	4803	752	100
Compound INF 2	**Code**	**Mean [ng L-1]**	**Min [ng L-1]**	**Max [ng L-1]**	**Std. dev. [ng L-1]**	**QFa [%]**
Diclofenac*	DCL	979	680	1281	153	100
Phenazone*	PHEN	2278	1728	3018	304	100
Metoprolol	MET	59	35	112	23	95
Iopromide	IOP	747	227	1667	357	100
Sulfamethoxazole*	SMX	1448	1138	1747	133	100
Trimethoprim	TRI	122	62	711	138	100
Bezafibrate	BZF	39	19	80	18	100
Gemfibrozil	GFZ	1350	570	3261	735	100
Carbamazepine	CBZ	242	215	264	13	100
Primidone	PRM	89	64	125	15	95
1H-Benzotriazole	BZL	2471	1764	3831	540	100

3.3 Experiment set-up

Soil-column experiments were installed in the WWTP of El Prat del Llobregat, close to the secondary treatment effluent channel. An integrated volume of secondary treatment effluent was collected weekly and stored in glass container. There were two parallel systems to feed the columns. INF1 code corresponds to the inlet water of columns C1 and C2, while INF2 code corresponds to the inlet water of columns C3 and C4. Inlet water from INF1 and INF 2 containers were spiked with 1000 ng/L of phenazone, diclofenac and sulfametoxazole. The other target micropollutants were found naturally in the secondary treatment effluent water.

Columns C1, C2, C3 and C4 were stainless steel cylinders with an inner diameter of 0.5 meters and a total length of 1.5 meters. The total volume of each column is 300 L. The closing system of the column allowed a total tightness of the column, avoiding water losses and air entrance. The filling material of C1, C2, C3 and C4 was the same, using homogeneous silica sand (porosity 40%) mixed with 1% of organic matter. Columns were externally jacketed using a flexible hose with the continuous circulation of water from the closely channel of secondary treatment effluent.

Inlet INF1 and INF2 waters were pumped using a peristaltic pump to the 4 columns parallel systems. C1 and C2 received water that previously circulated along the compost columns. The 0.1 inner diameter compost columns had a total length of 0.6 meters and water circulated at 2.5 mL/min in saturated conditions. Outflow water from compost columns arrived to C1 and C2 by gravity. Entrance flow in C1, C2, C3 and C4 was fixed at 5 mL/min along the total duration of the experiment.

Table 2: Operational schedule of the soil-column experiment

Date	Actions	Comments
26/04/2013	Starting column infiltration (Line 1 of the WWTP effluent) Bulk chemistry analysis	High ammonium concentration. Inlet flow C1, C2, C3 and C4: 0.67 mL/min. Inlet flow in compost columns: 0.35 mL/min.
16/07/2013	WWTP effluent infiltration stopped	---
16/07/2013	Cleaning of the system by distilled water circulation	The objective of this action was to recover initial conditions of the filtering materials (desorption) and tubing materials. C1, C2, C3 and C4: 10 mL/min. Inlet flow in compost columns: 5 mL/min.
02/08/2013	Starting column infiltration (Line 2 of the WWTP effluent) Spike of DCL, PHEN, SMX. Bulk chemistry analysis Emerging pollutants analysis	Results of this phase are presented in this report. C1, C2, C3 and C4: 5 mL/min. Inlet flow in compost columns: 2.5 mL/min.
03/08/2013	Fluorescein tracer test in C4	Results of this test are presented in this report
15/11/2013	Infiltration stopped. End of the experiment	Columns were disassembled

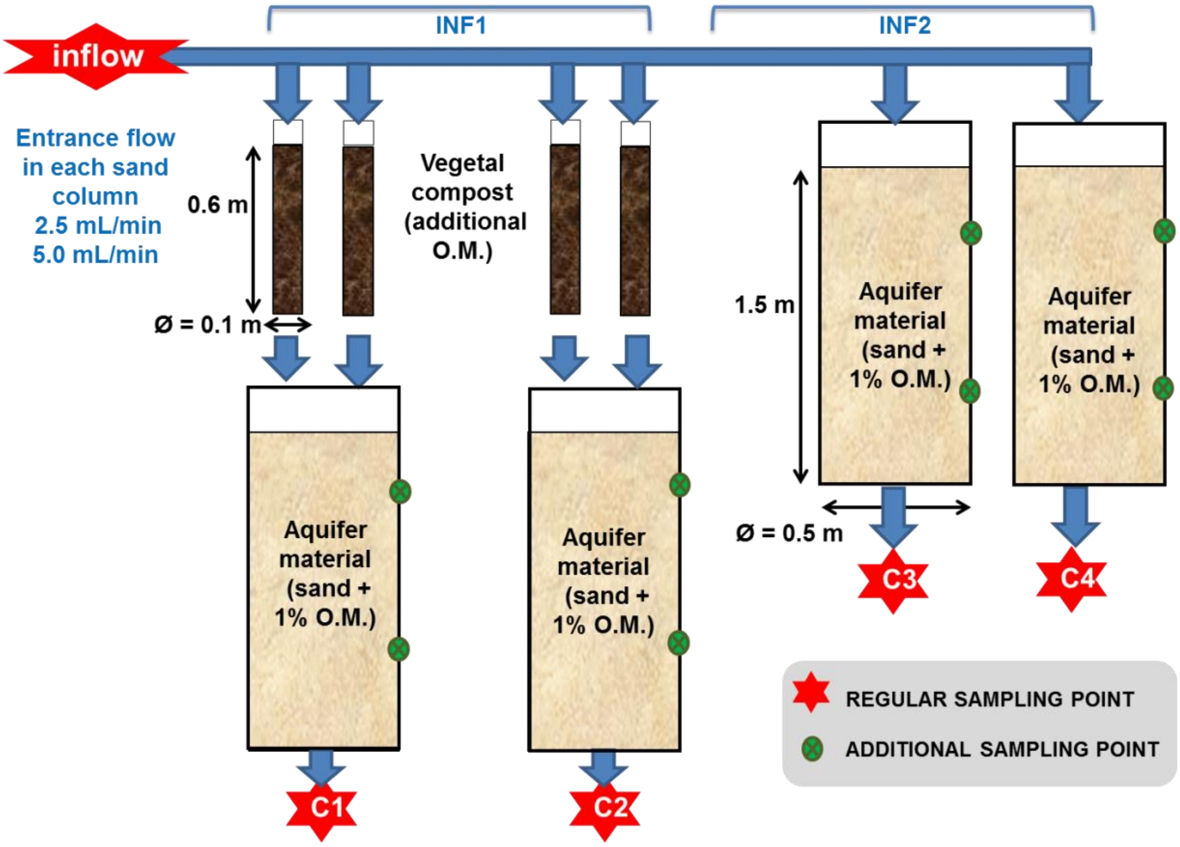


Figure 3: Operational scheme of the soil-column experiment

3.4 Chemical analysis methodology

3.4.1. Analysis of major inorganic ions and dissolved iron (UPC)

Analysis of bulk chemistry parameters were analysed by Technical University of Catalonia (UPC, Barcelona). Major ions (Cl^-, SO_4^{2-}, NO_3^-, Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+}) were determined by ion chromatography (IC). Samples were filtered with 0.45 µm nylon membrane filters and kept frozen until analysis. Cation samples were additionally acidified with HNO_3. Determination of anions was conducted with the DX-320 system (Dionex) with conductometric detection using the pre-column AG11-HC and the column AS11-HC. Separation was performed at 30 °C using 23 mM KOH as eluent. For the analysis of the inorganic cations the DX-500 system (Dionex) with conductometric detection and the pre-column CG12 combined with a CS16 column was used. Separation was performed at 44 °C using 20 mM methanesulfonic acid as eluent.

Water samples for analysis were filtered through 0.2 µm nylon filters, acidified to pH below 3 with HNO3 20% and kept at 4°C until analysis. The concentrations of dissolved Fe were determined by Inductively Coupled Plasma Atomic Mass Spectroscopy (ICP-MS) using an X-series II Thermo instrument. The reproducibility, accuracy and precision of results were ensured by analysing not only blank samples and laboratory standards, but also by duplication of experiments and samples. The total analytical error was estimated to be around 6%.

3.4.2. Analysis of organic micropollutants (Göttingen University)

Organic micropollutants were extracted by using the stacked-cartridges approach for solid phase extraction (SPE) similar to Nödler *et al.* (2013). In brief, the OASIS HLB (6 mL, 500 mg) and the OASIS WAX (6 mL, 150 mg; both from Waters) were connected for the extraction procedure with the HLB being first in contact with the sample. ACE was extracted by the WAX sorbent whereas all other compounds were extracted by the HLB sorbent material. After the extraction process, the cartridges were stored at −18 °C until analysis, which had been proved to be most suitable regarding analyte stability and recovery (Hillebrand *et al.,* 2013).

Prior to analysis the organic micropollutants were eluted as described earlier (Nödler *et al*., 2010; Nödler *et al*., 2013). The sample extracts were analysed by high-performance liquid chromatography coupled with tandem mass spectrometry (HPLC/MS-MS). Organic compounds were analysed as described by Nödler *et al*. (2010).

3.5 Tracer tests

3.4.3. Electric conductivity tracer test (C1, C2)

The average value of electrical conductivity of the effluent of the secondary treatment in the WWTP of El Prat is 2266 µS/cm (average value of 2012, n=345 measurements). Effluent of the secondary treatment (inlet water of column experiment) was used as a tracer at the beginning of the experiment. Previously, distilled water circulated along the columns to desorb any previous pollutant in the column. Literature review recommended the use of two orders of magnitude over the natural concentration for the performance of a reliable tracer test. Table 3 summarises initial conditions of the tracer test. Entrance flow was maintained at 5 mL/min along the experiment.

Table 3: Conditions of the tracer test using the conductivity of the inlet as tracer

	Starting date	Initial EC value [µS/cm]	Maximum EC value [µS/cm]
Column 1	03/08/2013 (12:00)	0.028	2.176
Column 2	03/08/2013 (12:30)	0.104	2.270
Column 3	03/08/2013 (12:30)	0.036	3.040
Column 4	03/08/2013 (12:30)	0.276	2.508

3.4.4. Fluorescein tracer test (C4)

A pulse of 1.0 mg of fluorescein was applied in the column 4 on the 15/10/2013 from 10:40 to 11:28. Flow in column 4 was 2.5 mL/min. Expected arrival time was therefore twice the arrival time observed in the electrical conductivity test in C1 and C2. Another difference between the continuous injection and a pulse tracer test is the curve obtained.

3.4.5. Calculation of residence time

Results of tracer tests using electrical conductivity in column C1 and C2 are represented in **Figure 4**. Using the maximum EC values detected along the experiment, it is calculated the $C_{max/2}$ and the interpolation in the curve shows T_{50}, representing the average of the residence time of the tracer along the column. This is the advection residence time. Column 1 showed a residence time of 7.57 days, and Column 2 showed a residence time of 7.51 days. The similarity of results obtained in C1 and C2 highlights the replicability of the experiment.

Regarding the residence time in column 4 obtained during the tracer test, **Figure 4** and **Figure 5** shows arrival time was determined to be 17 days. This can be explained as the flow in C4 was 2.5 mL/min and in C1 and C2 was 5.0 mL/min.

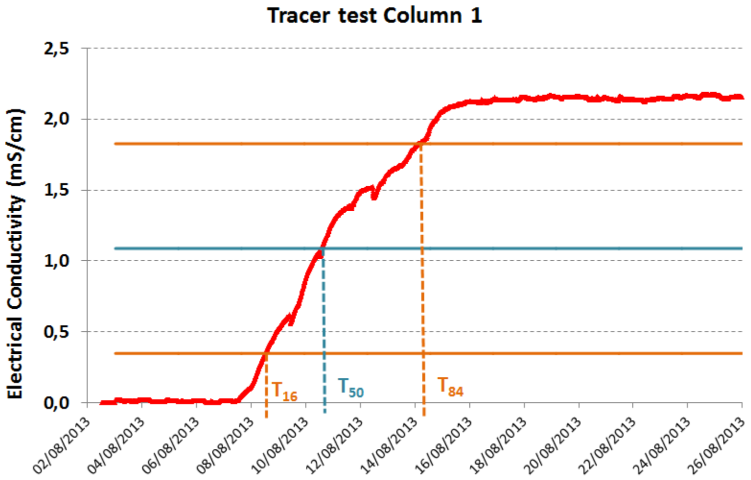


Figure 4: Tracer test C1 using Electric Conductivity

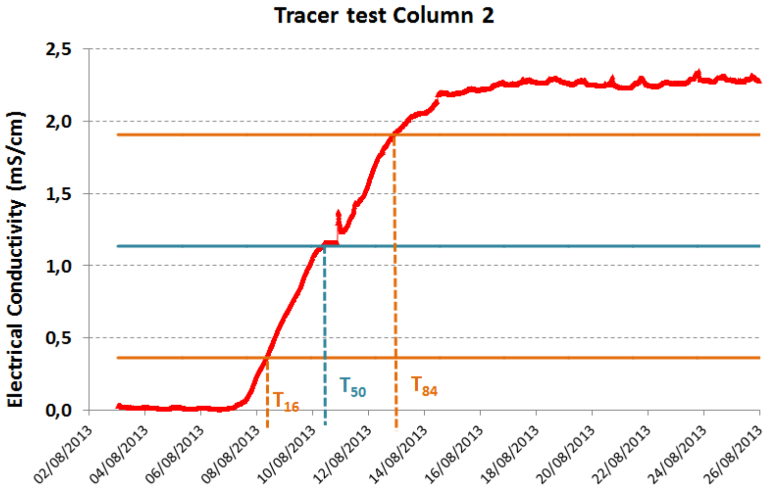


Figure 5: Tracer test C2 using Electric Conductivity

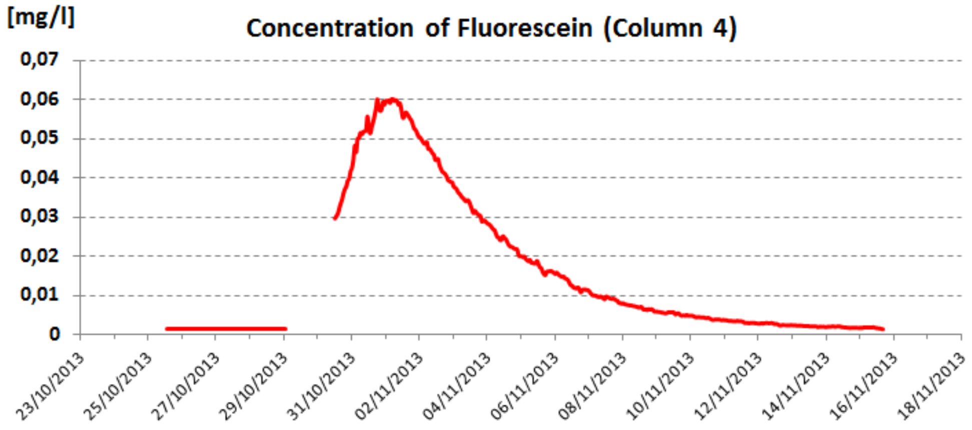


Figure 6: Fluorescein arrival curve (C4)

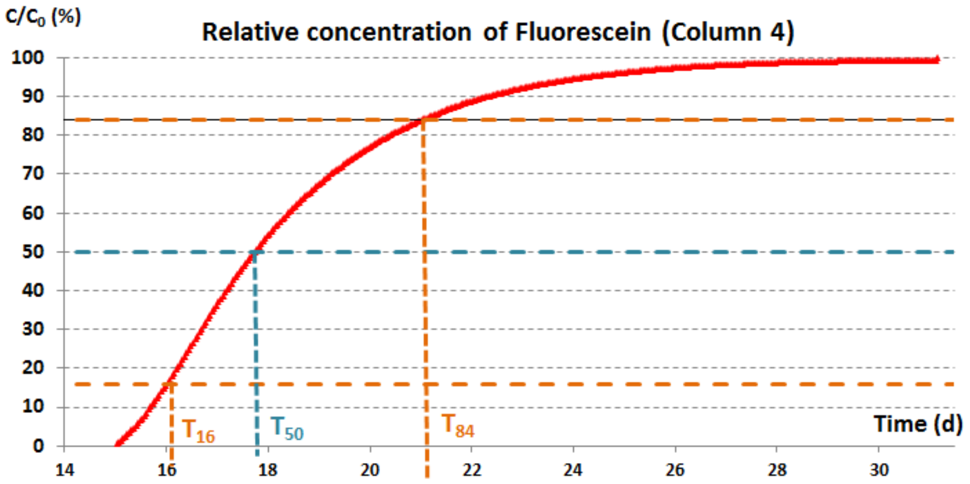


Figure 7: Fluorescein relative arrival curve (C4)

3.4.6. Calculation of dispersivity

Dispersivity is the temporal variation of C_r (relative conductivity). To calculate dispersivity coefficient it is necessary to calculate the typical deviation of the graphic in the C_r = 50%, where theoretically the curve is symmetric:

$$\sigma = \sqrt{\frac{2D_L \times T_{50}}{V_R^2}}$$

Where:

σ = Typical deviation of the curve [d]
D_L = Longitudinal dispersivity coefficient [m/d]
T_{50} = Arrival time of the 50% of the total relative conductivity [d]
V_R = Real velocity of water through the column [m/d]

Isolating D_L: $D_L = \frac{\sigma^2 \times V_R^2}{2\,T_{50}}$, and dispersivity “α ”is dimensionless → $\alpha = \frac{D_L}{V_R}$

Dispersivity can be calculated as: $\alpha = \frac{\sigma^2 \times V_R}{2\,T_{50}}$

Values of dispersivity of the 3 tracer tests performed are showed in **Table 4**.

Table 4: **Dispersivity values**

	Dispersivity (T_{16}-T_{50})	**Dispersivity (T_{50}-T_{84})**	**Dispersivity (average)**
Column 1 EC tracer test (5 mL/min)	0.063	0.0.167	0.108
Column 2 EC tracer test (5 mL/min)	0.050	0.092	0.070
Column 4 Fluorescein (2.5 mL/min)	0.007	0.025	0.014

4. Results of bulk chemistry

19 sampling campaigns were performed in the infiltration water (INF1 and INF2) and in the outflow water of the 4 large columns (C1, C2, C3 and C4). Samples were collected every two or three days from 2nd August 2013 to 27th September 2013. Bulk chemistry was analysed in CSIC-IDAEA laboratories (Barcelona). Water samples were filtered through 0.2 µm nylon filters, acidified to pH below 3 with HNO3 20% and kept at 4°C until ICP analysis. Concentrations of Al, Ca, K, Mg, Na, P, Si and Sr were measured by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES) using a Thermo Jarrel-Ash instrument with CID detector with detection limits of 10 mg L-1 for Fe and 500 mg L-1 for S. Trace metals Ba, Fe, Mn, Pb and Zn were determined by Inductively Coupled Plasma Atomic Mass Spectroscopy (ICP-MS) using an X-series II Thermo instrument and the detection limits for these elements were in the order of 1 mg/L. Calibration with sets of standards was performed for all the analytical techniques and regression coefficients exceeded 0.999.

The reproducibility, accuracy and precision of results were ensured by analysing not only blank samples and laboratory standards, but also by duplication of experiments and samples. The analytical error was estimated to be around 4% for ICP-AES and 6% for ICP-MS and FAAS measurements. The determination of the anions (Cl^-, SO_4^{2-}, NO_3^-) was conducted by ion chromatography with a Dionex DX-320 with conductometric detection using the pre-column AG11-HC, the column AS11-HC (stationary phase) and the suppressor ASRS 300, 2 mm, operated with a temperature of 30 °C, an eluent containing 23 mM KOH (mobile phase) and a flow rate of 0.38 mL/min. The injection volume was 10 µL. Prior to IC the samples were diluted with ultrapure water (1/4). Bromide was analysed with a specific electrode Hanna HI 4102. Dissolved Organic Carbon (DOC) was analysed with on line combustion-reduction-gas chromatographer Thermo EA 1108 from aliquots of water that were filtered through 0.45 µm nylon filters, acidified to pH below 3 with HCl 2N, and stored in a pre-combusted glass bottles at 4ºC.

Table 5 presents the mean values of bulk chemistry of the secondary treatment effluent of the wastewater treatment plant in El Prat del Llobregat. Some values were obtained using routine analysis done in the WWTP (example: pH, Electrical Conductivity) and the other were obtained by specific analysis carried out in DEMEAU project.

Table 5: Bulk chemistry in the inlet water (average value of INF1 and INF2)
[1] Daily monitoring WWTP plant (2012); [2] Data from column experiment (2013)

Parameter	units	n	Mean	Standard deviation
pH	-	345 [1]	7.47	0.19
EC	µS/cm	345 [1]	2266	225.6
TOC	mg/L	22 [2]	18.9	12.3
Nitrate	mg/L	13 [2]	13.0	2.7
Ammonium	mg/L	13 [2]	3.2	0.32
Chloride	mg/L	13 [2]	374.5	35.6
Calcium	mg/L	22 [2]	123.1	4.5
Magnesium	mg/L	22 [2]	37.9	2.2
Potassium	mg/L	22 [2]	33.1	1.4

Parameter	units	n	Mean	Standard deviation
Iron	µg/L	22 [2]	46.1	10.6
Manganese	µg/L	22 [2]	34.6	4.2
Sulphate	mg/L	13 [2]	172.2	10.5

Data analysis and interpretation regarding redox conditions in the column and behaviour of emerging pollutants along the experiment has been done using the results of the last 12 campaigns, corresponding to stabilized output conditions.

Regarding bulk chemistry, the average DOC concentration in the outlet from C1 and C2 was much higher (up to 30 mg/L) than that in the outlet from C3 and C4 (17 mg/L), showing that organic carbon was indeed being released by the organic layer (see **Figure 8**) .

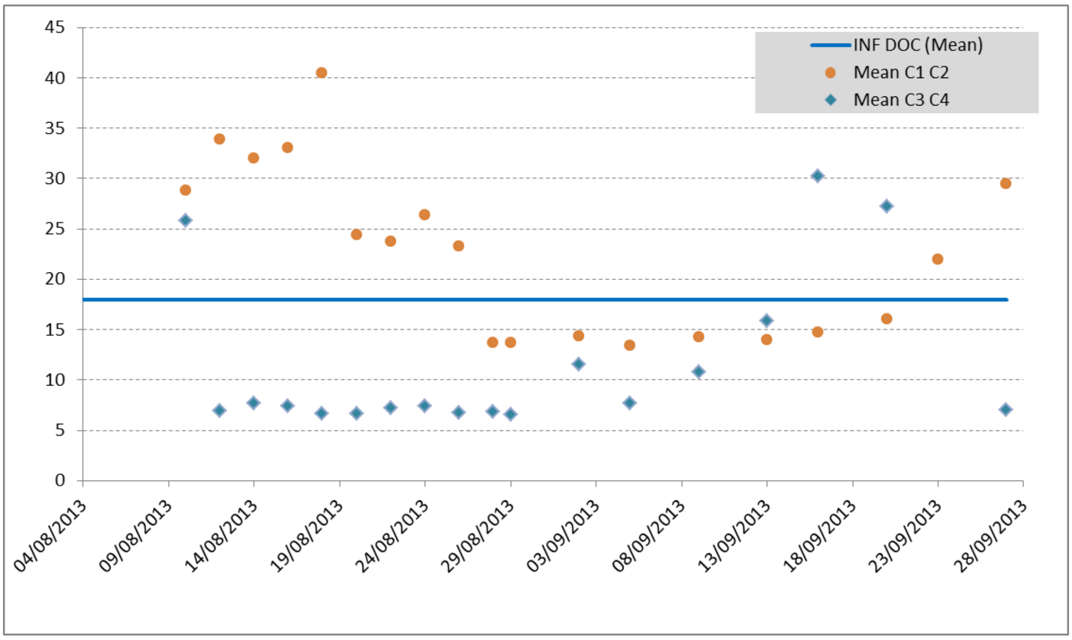
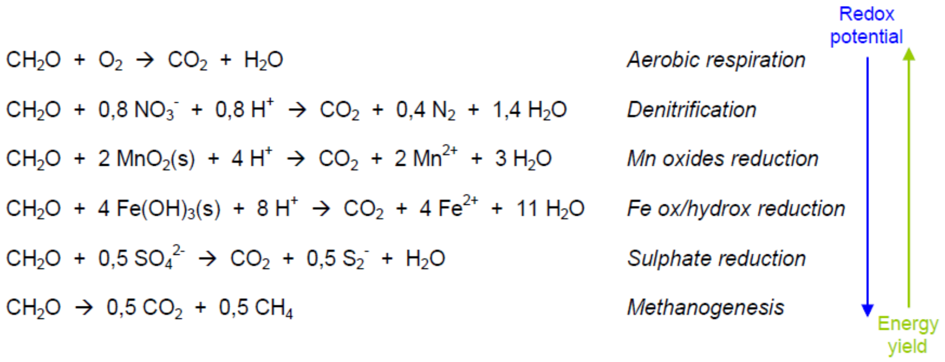


Figure 8: **Dissolved Organic Carbon evolution (Natural conditions C3&C4 vs enhanced conditions C1&C2)**

With regards to nitrate, results are presented in **Figure 10**. In the second part of the experiment, nitrate concentration in the outlet of columns C3 and C4 were higher than in columns C1 and C2. This is an indicator of denitrification processes occurring in the enhanced system. The reduction of nitrate concentration in the enhanced system can be related with the release of Dissolved Organic Carbon observed in **Figure 8**. The following sequences of reactions of reduction can explain the sequence produced in the experiment:



$$CH_2O + O_2 \rightarrow CO_2 + H_2O$$

$$CH_2O + 0{,}8\ NO_3^- + 0{,}8\ H^+ \rightarrow CO_2 + 0{,}4\ N_2 + 1{,}4\ H_2O$$

$$CH_2O + 2\ MnO_2(s) + 4\ H^+ \rightarrow CO_2 + 2\ Mn^{2+} + 3\ H_2O$$

$$CH_2O + 4\ Fe(OH)_3(s) + 8\ H^+ \rightarrow CO_2 + 4\ Fe^{2+} + 11\ H_2O$$

$$CH_2O + 0{,}5\ SO_4^{2-} \rightarrow CO_2 + 0{,}5\ S_2^- + H_2O$$

$$CH_2O \rightarrow 0{,}5\ CO_2 + 0{,}5\ CH_4$$

Figure 9: **Redox equations sequence**

The presence of organic matter and nitrate in inlet water allowed the occurrence of the denitrification process, which is shown in the second equation. As it occurs later in the redox sequence than aerobic respiration, denitrification starts when most of the dissolved oxygen is depleted from the water. Unfortunately, dissolved oxygen was not measured in the experiment, but indirectly it can be assumed a reduction on its concentration.

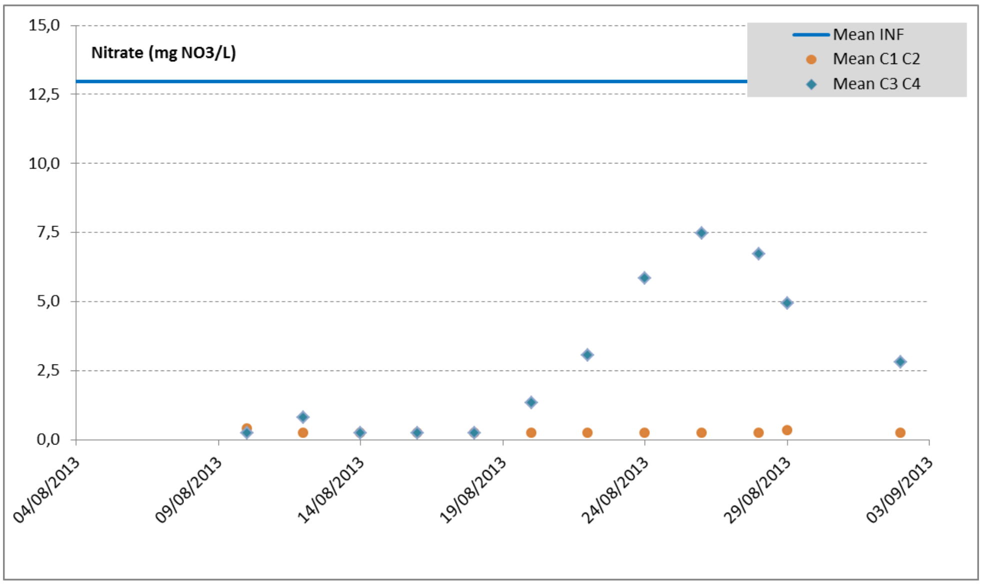


Figure 10: **Nitrate concentration evolution**
(Natural conditions C3&C4 vs enhanced conditions C1&C2)

No changes were observed in iron, manganese and sulphate concentrations, indicating that high reductive environments were not promoted. Figure 11 represents data of sulphate concentration in the experiment. As the entrance of sulphate in the system was constant and around 170 mg/L, the evolution observed the first 7 days of the experiment can be attributed to the acclimatising period. This trend was also observed in the emerging pollutants results, and it was really useful to discard Campaign 01 to Campaign 07 for further interpretation.

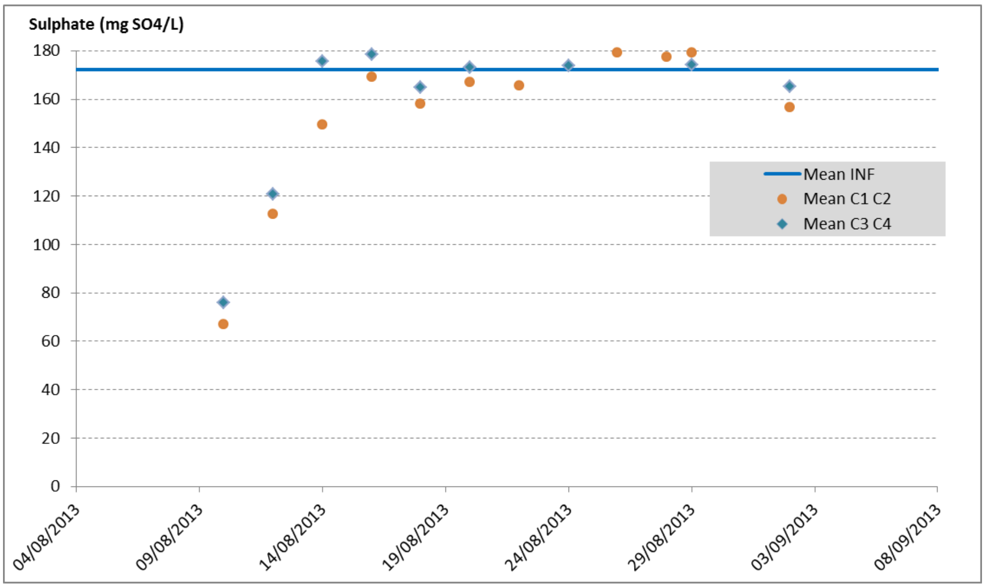


Figure 11: Sulphate evolution
(Natural conditions C3&C4 vs enhanced conditions C1&C2)

5. Results of emerging pollutants

5.1 Sampling campaigns of emerging pollutants

Water inlet and outflow of the 4 sand columns were regularly sampled. The INF and INF2 waters are quite similar, as both of them consist of the secondary treatment effluent of the WWTP and were spiked with DCL, PHEN and SMX separately. The schedule of the sampling campaigns is listed below (**Table 6**). A total of 21 samples were collected to characterize the inflow water, while outflow of each sand column was analysed in 19 campaigns. The average frequency of sampling was about 2 – 3 days:

Table 6: Schedule of emerging pollutants water sampling

Inlet water sampling		Outlet water sampling	
INF1 and INF2 Campaign 01	02/08/2013	C1, C2, C3, C4. Campaign 01	10/08/2013
INF1 and INF2 Campaign 02	04/08/2013	C1, C2, C3, C4. Campaign 02	12/08/2013
INF1 and INF2 Campaign 03	06/08/2013	C1, C2, C3, C4. Campaign 03	14/08/2013
INF1 and INF2 Campaign 04	08/08/2013	C1, C2, C3, C4. Campaign 04	16/08/2013
INF1 and INF2 Campaign 05	10/08/2013	C1, C2, C3, C4. Campaign 05	18/08/2013
INF1 and INF2 Campaign 06	12/08/2013	C1, C2, C3, C4. Campaign 06	20/08/2013
INF1 and INF2 Campaign 07	14/08/2013	C1, C2, C3, C4. Campaign 07	22/08/2013
INF1 and INF2 Campaign 08	16/08/2013	C1, C2, C3, C4. Campaign 08	24/08/2013
INF1 and INF2 Campaign 09	18/08/2013	C1, C2, C3, C4. Campaign 09	26/08/2013
INF1 and INF2 Campaign 10	20/08/2013	C1, C2, C3, C4. Campaign 10	28/08/2013
INF1 and INF2 Campaign 11	22/08/2013	C1, C2, C3, C4. Campaign 11	29/08/2013
INF1 and INF2 Campaign 12	24/08/2013	C1, C2, C3, C4. Campaign 12	02/09/2013
INF1 and INF2 Campaign 13	26/08/2013	C1, C2, C3, C4. Campaign 13	05/09/2013
INF1 and INF2 Campaign 14	29/08/2013	C1, C2, C3, C4. Campaign 14	09/09/2013
INF1 and INF2 Campaign 15	02/09/2013	C1, C2, C3, C4. Campaign 15	13/09/2013
INF1 and INF2 Campaign 16	05/09/2013	C1, C2, C3, C4. Campaign 16	16/09/2013
INF1 and INF2 Campaign 17	09/09/2013	C1, C2, C3, C4. Campaign 17	20/09/2013
INF1 and INF2 Campaign 18	13/09/2013	C1, C2, C3, C4. Campaign 18	23/09/2013
INF1 and INF2 Campaign 19	16/09/2013	C1, C2, C3, C4. Campaign 19	27/09/2013
INF1 and INF2 Campaign 20	20/09/2013	--	--
INF1 and INF2 Campaign 21	23/09/2013	--	--

The evolution of the concentration of each emerging pollutant is represented graphically in each section of the report. Inflow micropollutant concentration has been represented in red colour, and outflow organic micropollutant concentration has been represented in blue colour. Starting sampling campaigns form campaign 01 to campaign 07 where discarded for data interpretation, but their values are presented in the figures below the explanation. Green bars represent the percentage of micropollutant elimination, considering the difference between inflow concentrations and outflow concentrations. Residence time calculated using the tracer test was applied to correlate inflow and outflow samples.

5.2 Fate of Diclofenac (DCL) in the soil-column experiments

DCL was spiked in the storage tank as it was not detected in the secondary treated effluent water. Spiked concentration was 1000 ng/L, which supposed to be an initial concentration of 1334 and 979 ng/L in INF1 and INF 2respectively (Table 1). Parallel columns C1 and C2 showed similar results regarding an average elimination of DCL of 27% of the inflow concentration. C3 and C4 which operated directly without previous compost columns revealed to be ineffective in the elimination of DCL, as outflow concentration and inflow concentration did not show significant differences.

NOTE: Green bars show the removal percentage obtained for each organic micropollutant studied. This percentage corresponds to the difference between inlet concentration and outlet concentration, taking into account the residence time calculated with the tracer tests (7.5 days).

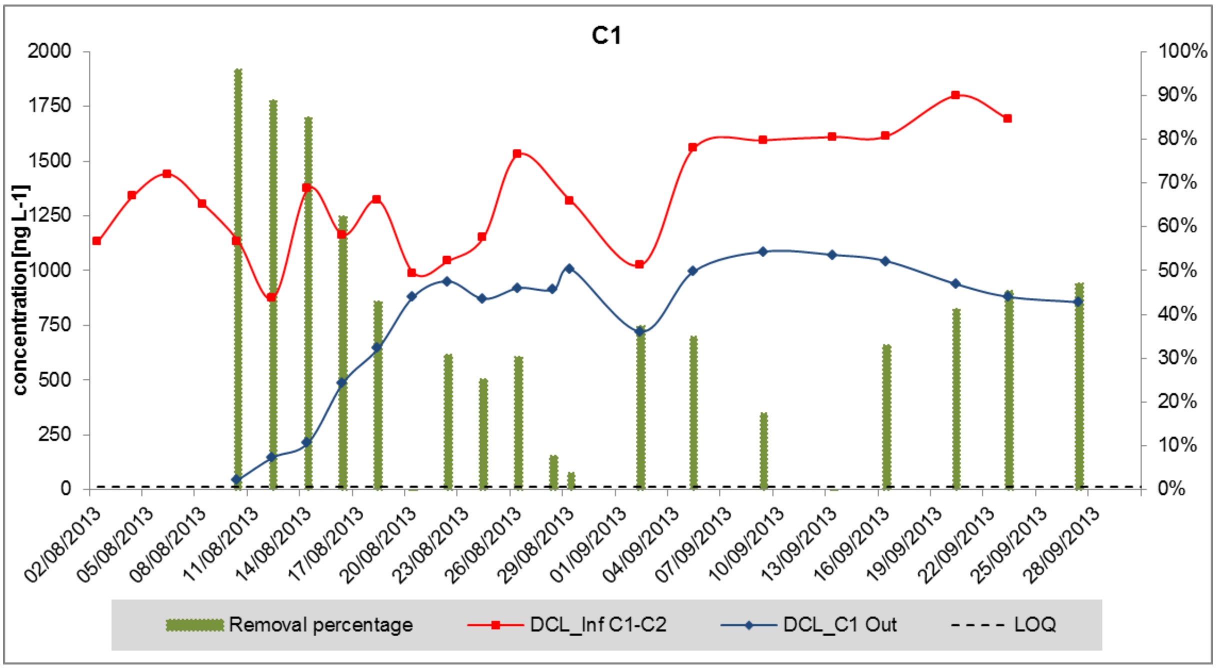


Figure 12: Results for Diclofenac (enhanced conditions C1)

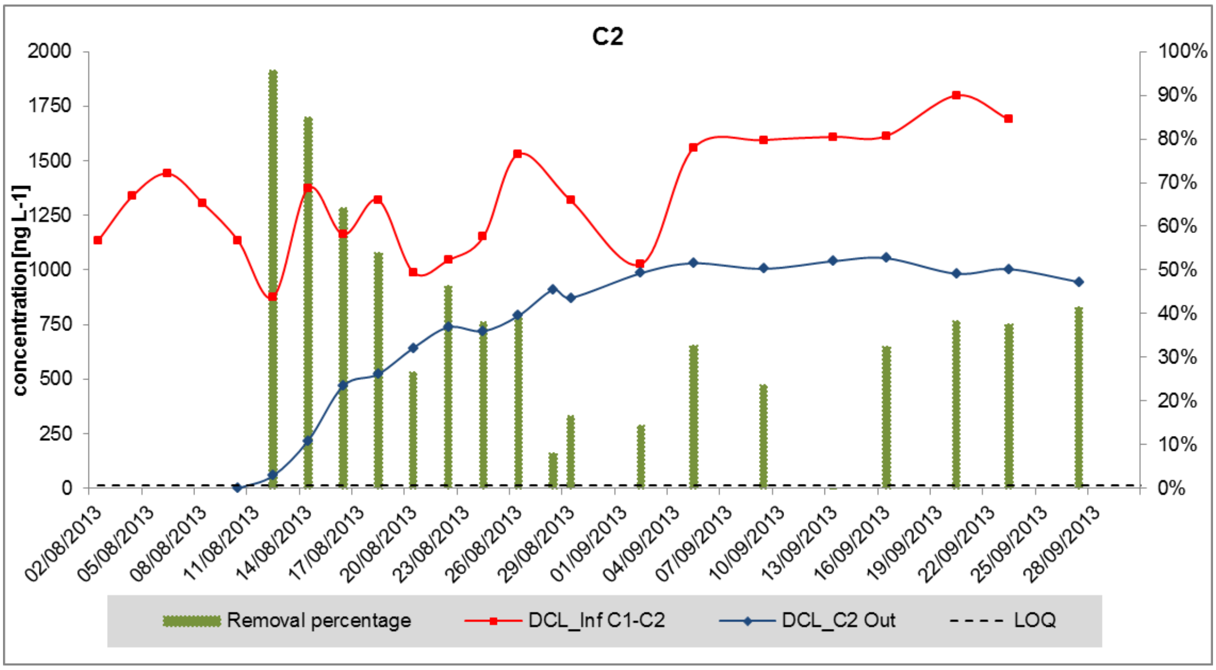


Figure 13: Results for Diclofenac (enhanced conditions C2)

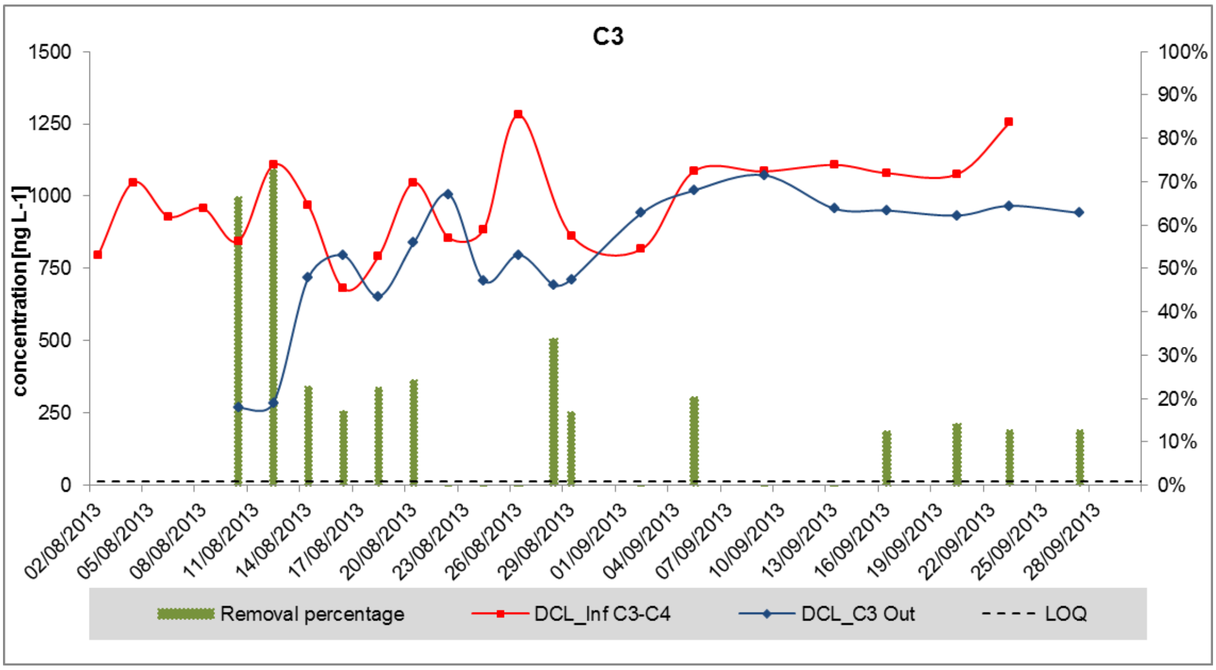


Figure 14: Results for Diclofenac (natural conditions C3)

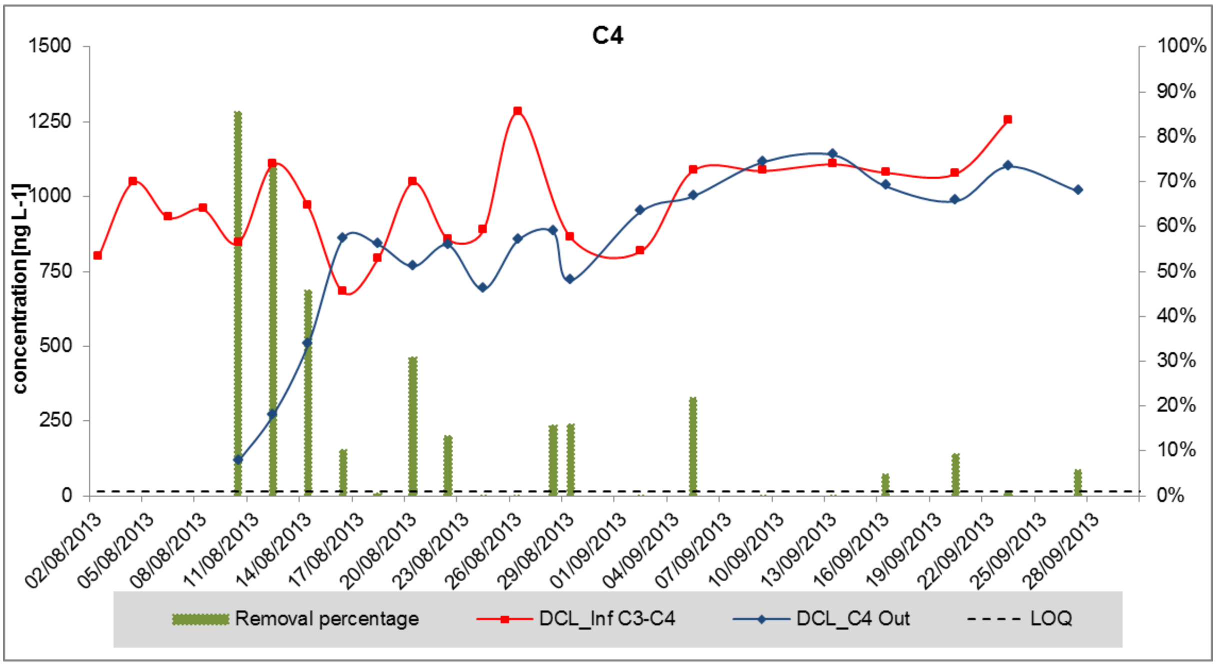


Figure 15: Results for Diclofenac (natural conditions C4)

5.3 Fate of Phenazone (PHEN) in the soil-column experiments

The initial concentrations analysed in INF1 and INF2 were 2170 ng/L and 2178 ng/L, respectively (Table 1). However, this compound was spiked to a concentration of 1000 ng/L in the inlet tank. Figure 16 to Figure 19 shows the evolution of the concentration during the experiment in C1, C2, C3 and C4. Output concentration in the four columns shows quite fluctuant values, corresponding to standard deviations from 14% to 25%. Differences between natural system and enhance system are not significant taking into account the standard deviation.

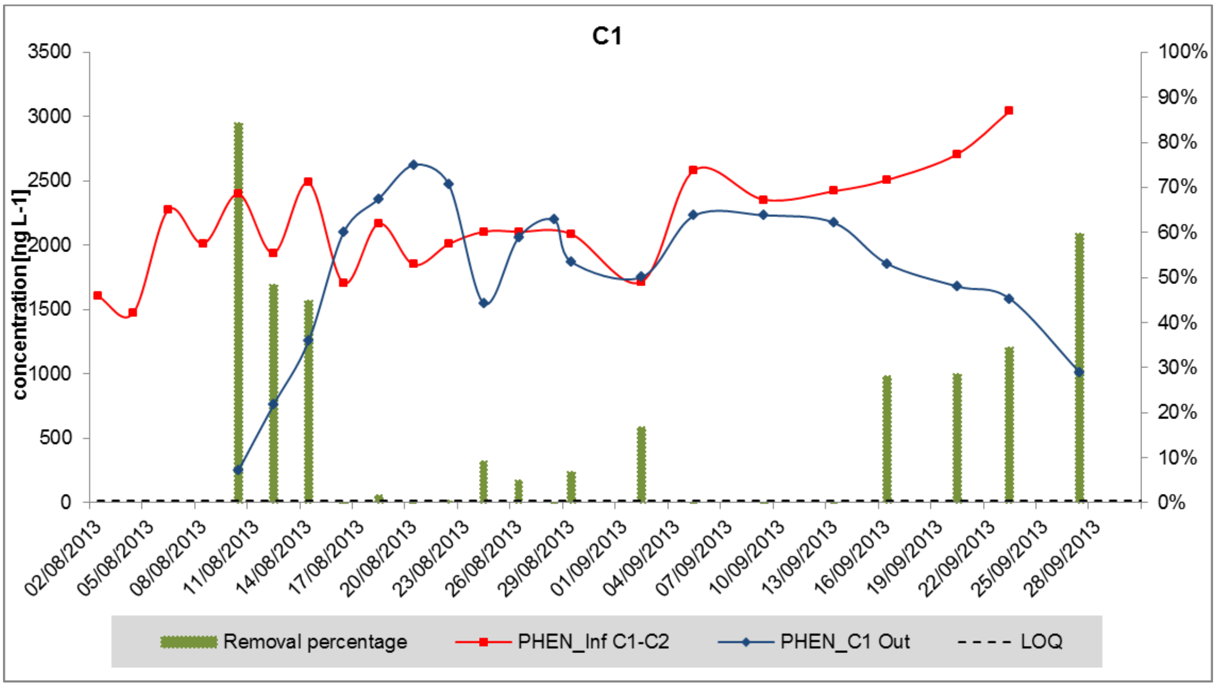


Figure 16: Results for Phenazone (enhanced conditions C1)

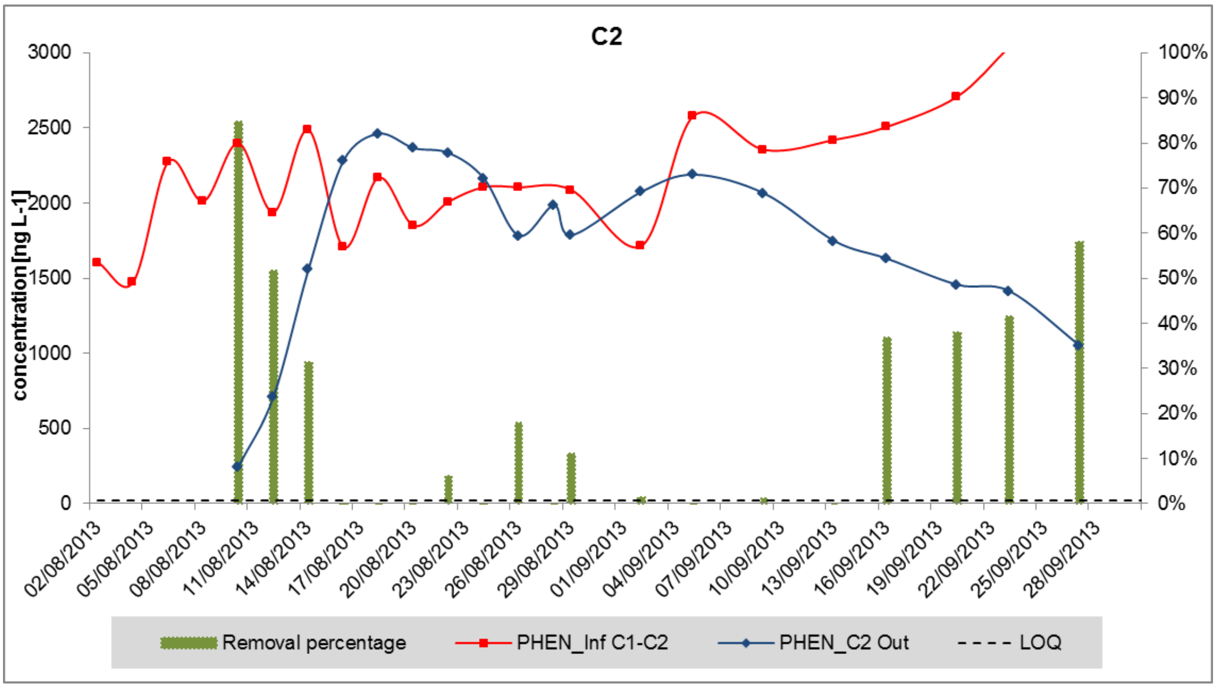


Figure 17: Results for Phenazone (enhanced conditions C2)

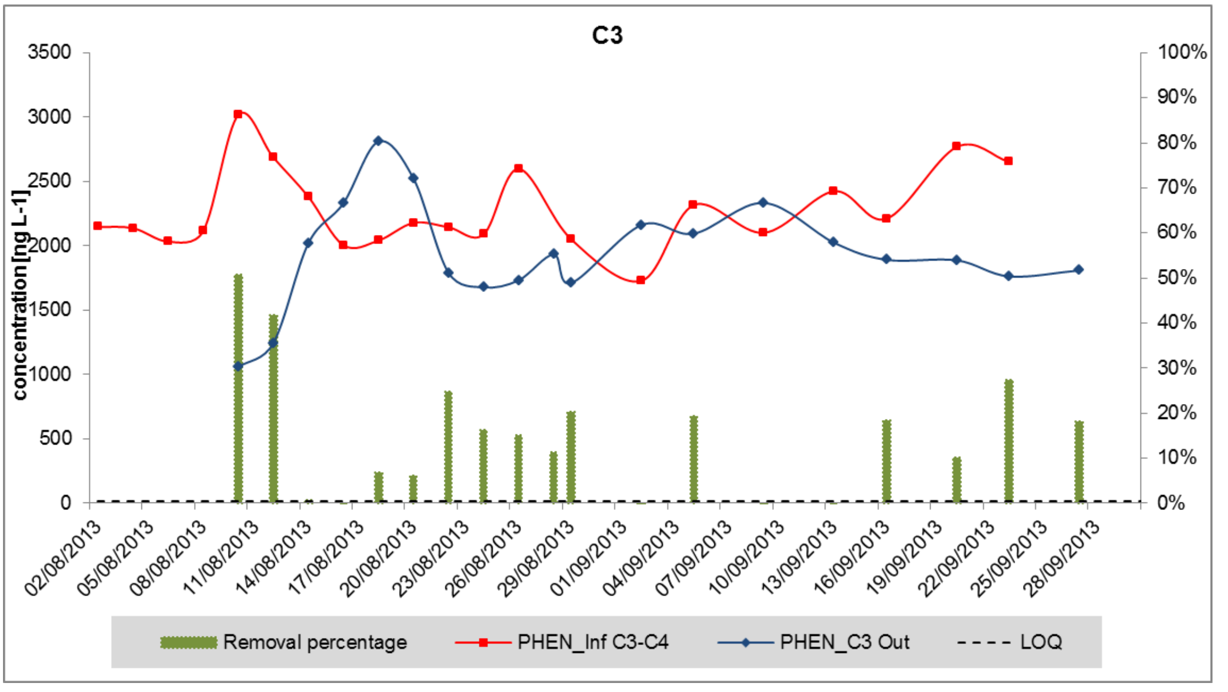


Figure 18: Results for Phenazone (natural conditions C3)

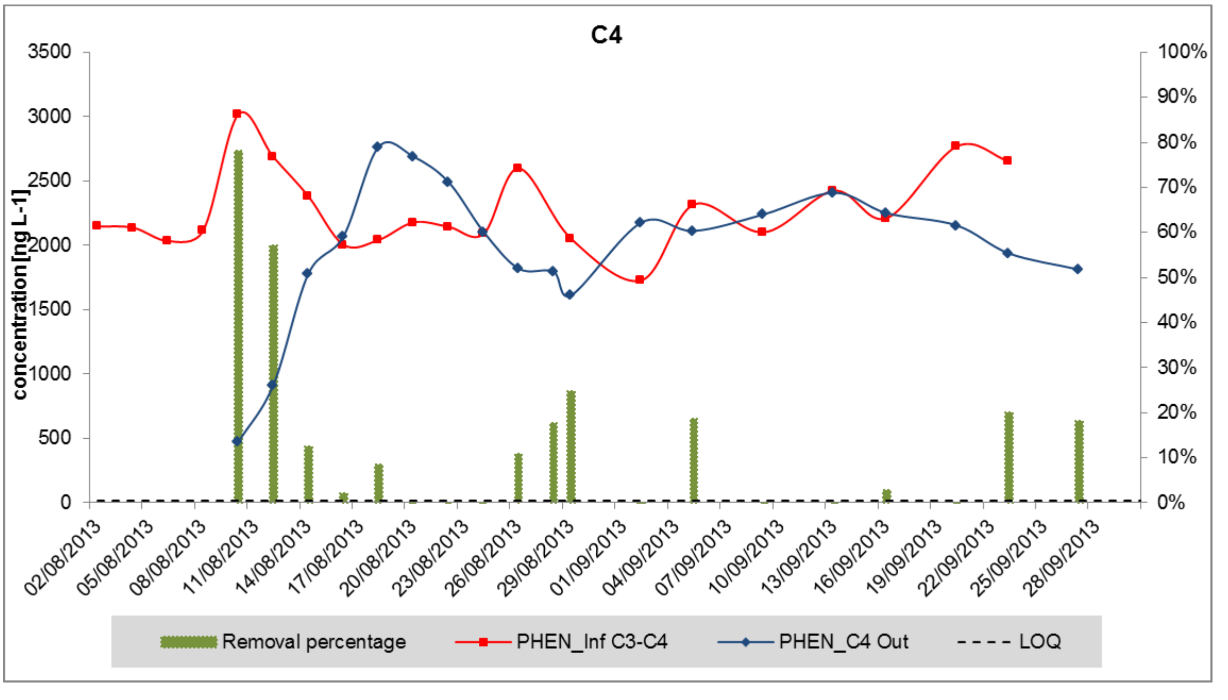


Figure 19: Results for Phenazone (natural conditions C4)

5.4 Fate of Metoprolol (MET) in the soil-column experiments

MET concentration in the secondary effluent was very low. In fact it is the compound with the lowest concentration quantified in the study jointly with BZF and PRM. The mean values in INF1 and INF2 were 48 ng/L and 59 ng/L respectively (Table 1). Results obtained in C1 and C2 revealed a total removal of Metroprolol in the columns with reactive layer, having a 100% of total removal in all the samples. In natural conditions, MET was found in most of samples, so the removal percentage was calculated. In column C4 some inlet samples showed higher concentration than the correlated outlet, giving an inconsistent negative removal percentage. This result has been discarded for further interpretation. C3 results seem to be more reliable, with a 20% of percentage of removal quantified in natural conditions.

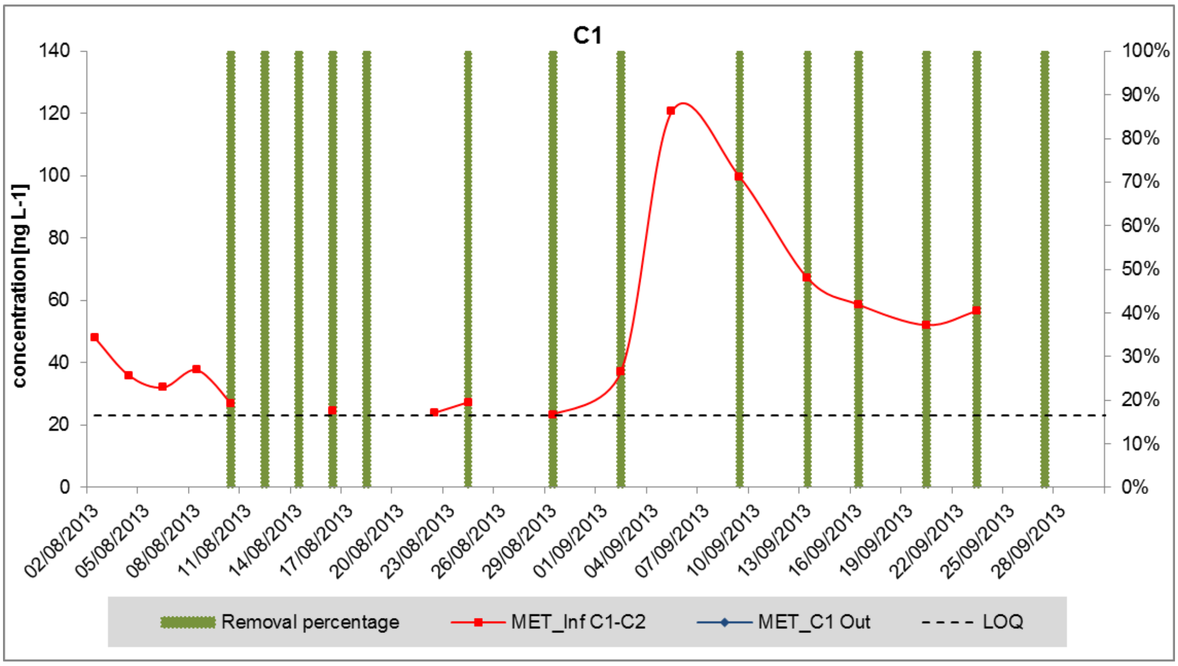


Figure 20: Results for Metoprolol (enhanced conditions C1)

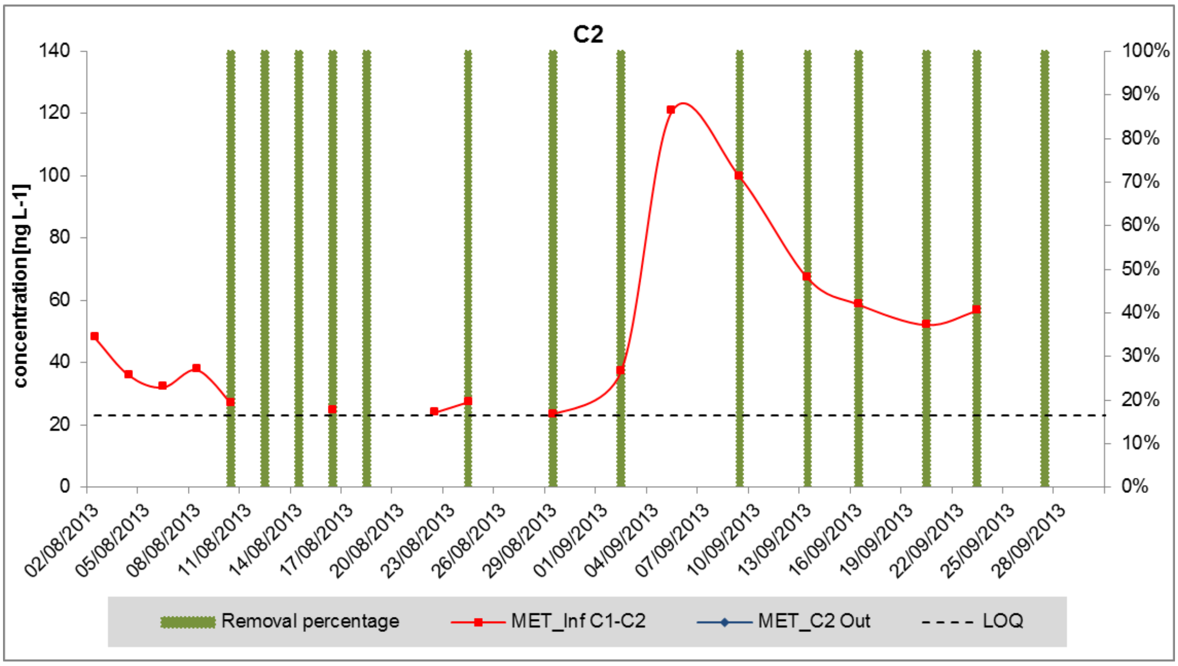


Figure 21: Results for Metoprolol (enhanced conditions C2)

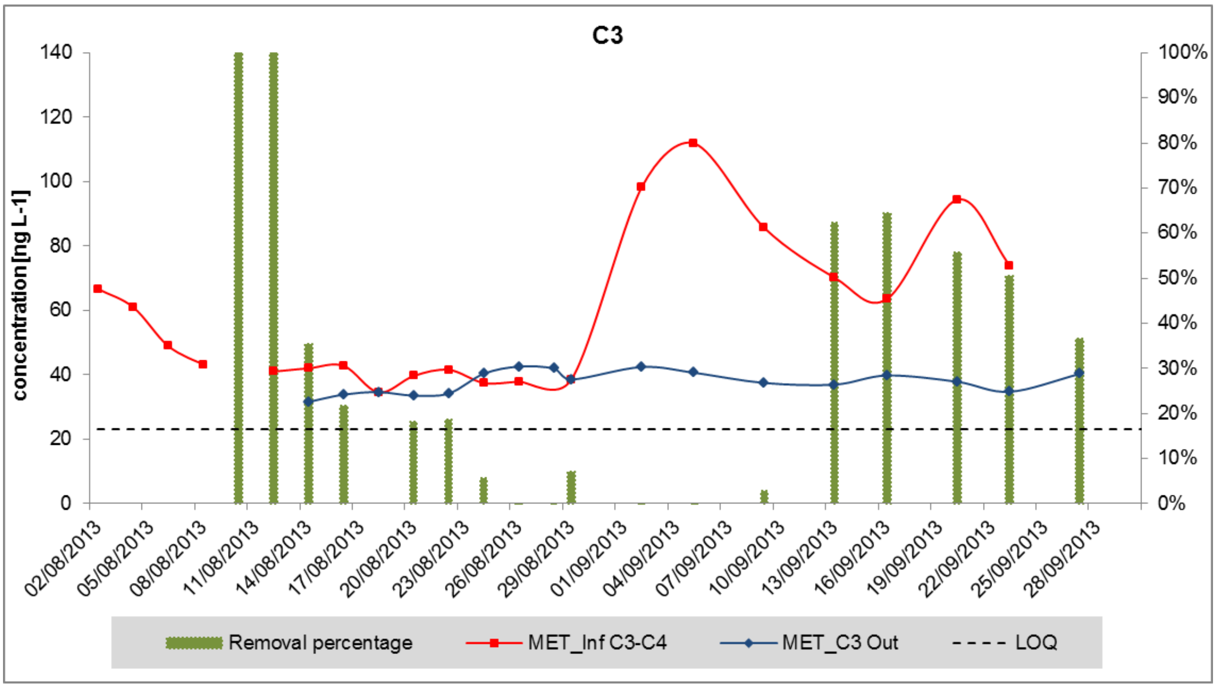


Figure 22: Results for Metoprolol (natural conditions C3)

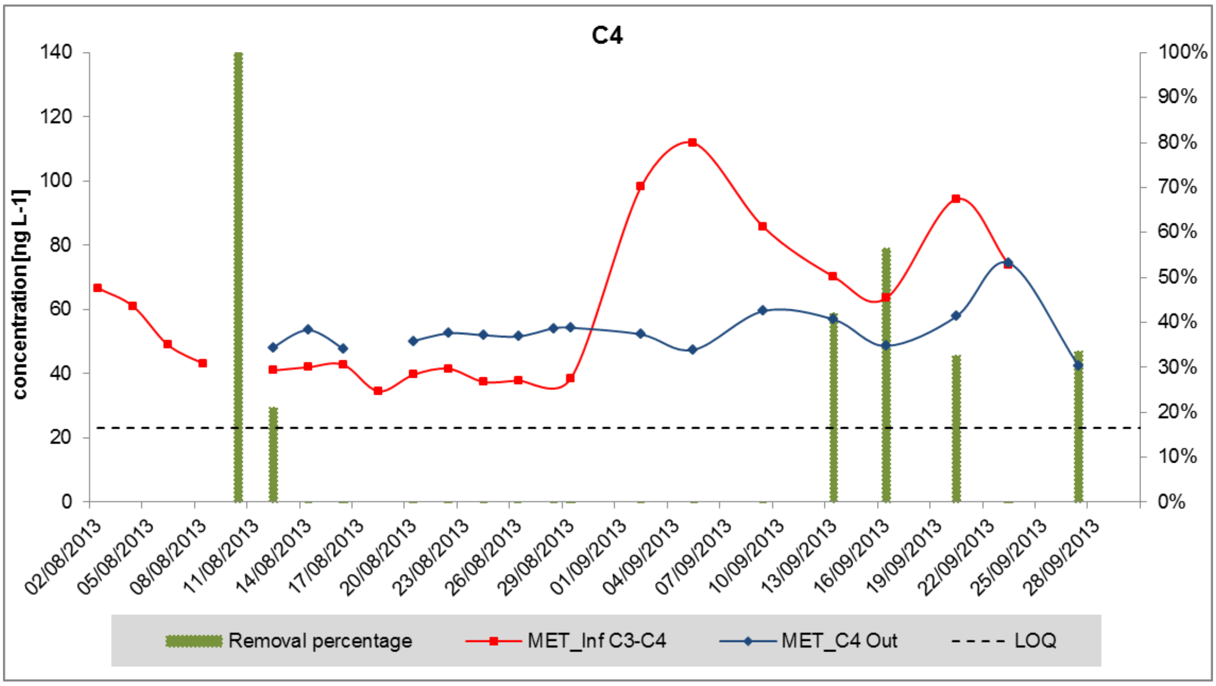


Figure 23: Results for Metoprolol (natural conditions C4)

5.5 Fate of Iopromide (IOP) in the soil-column experiments

IOP was found in similar concentration in the analysis of infiltration water, as INF1 and INF2 concentrations were almost the same: 740 ng/L and 747/ng/L respectively (Table 1). Results obtained along the experiment showed lot of variation in the infiltration water of the system, while the outflow showed more stable concentrations. C1 and C2 showed a percentage of removal of 59% and 62% respectively, while C3 and C4 46% and 69% respectively. This great difference between C3 and C4 which were expected to be a duplicated experiment makes it difficult to classify the behaviour of IOP in natural conditions.

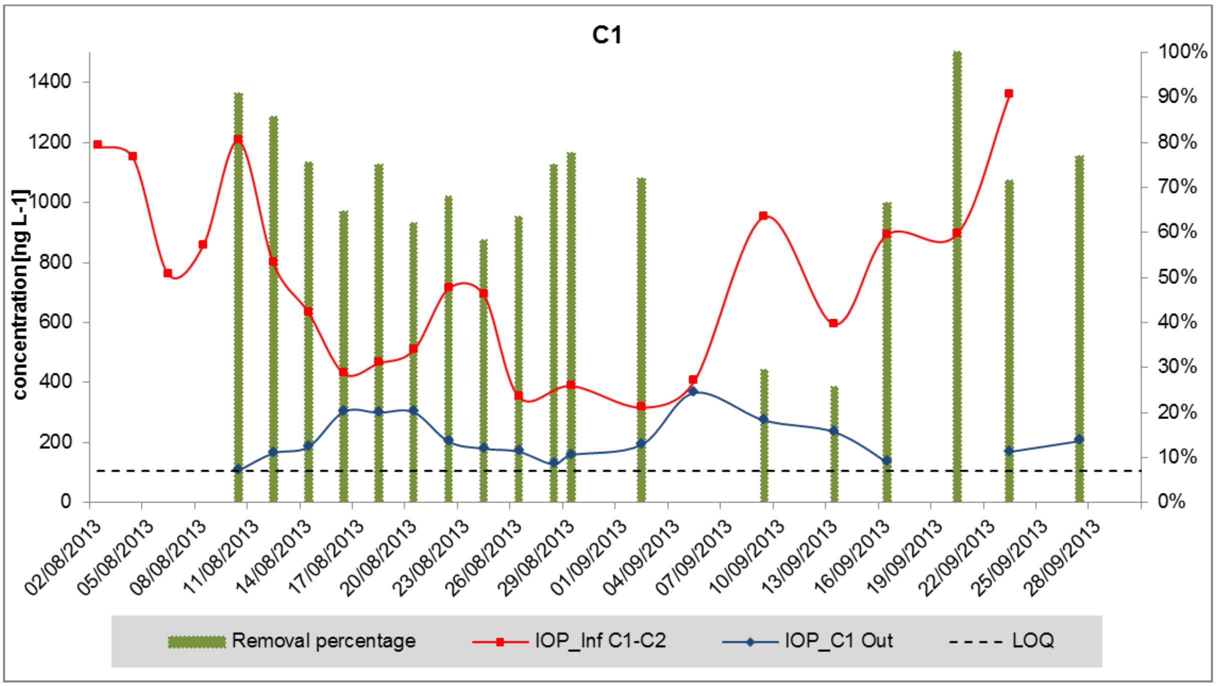


Figure 24: Results for Iopromide (enhanced conditions C1)

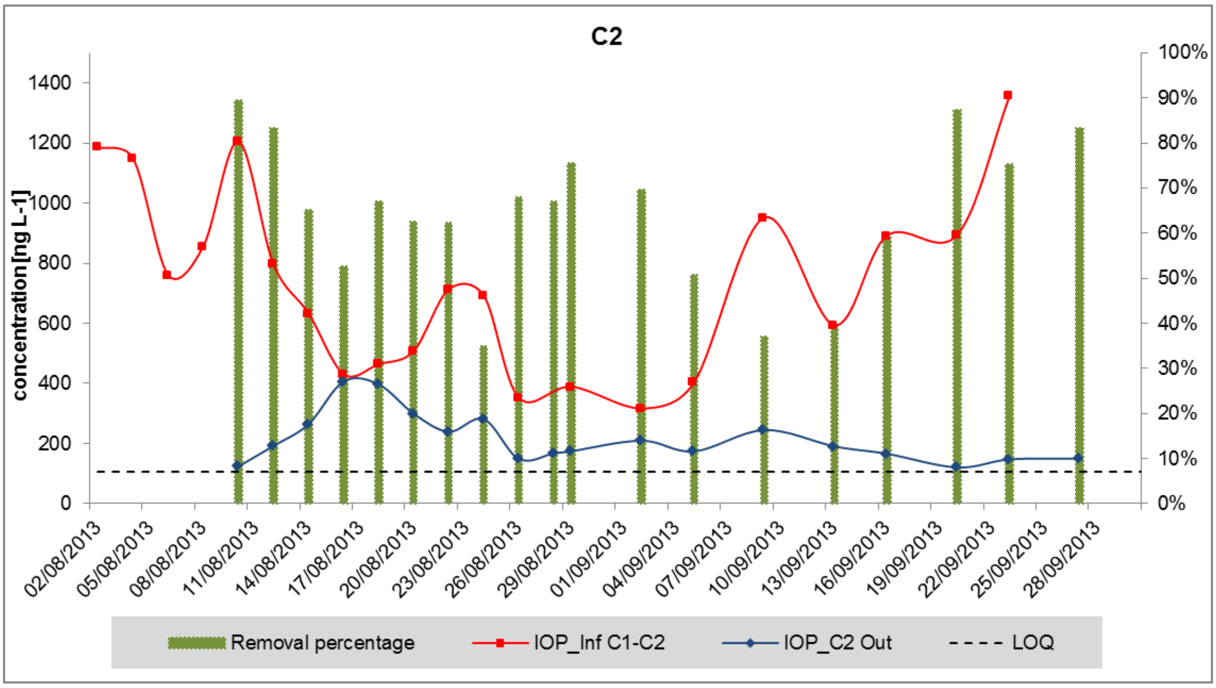


Figure 25: Results for Iopromide (enhanced conditions C2)

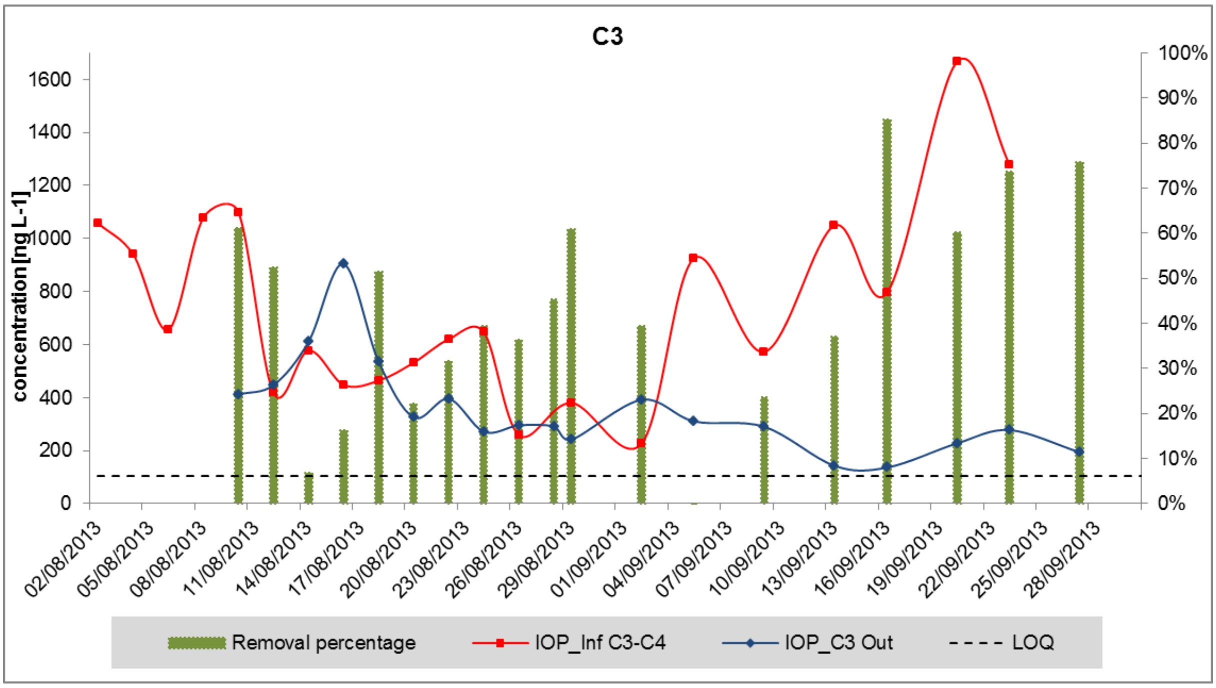


Figure 26: Results for Iopromide (natural conditions C3)

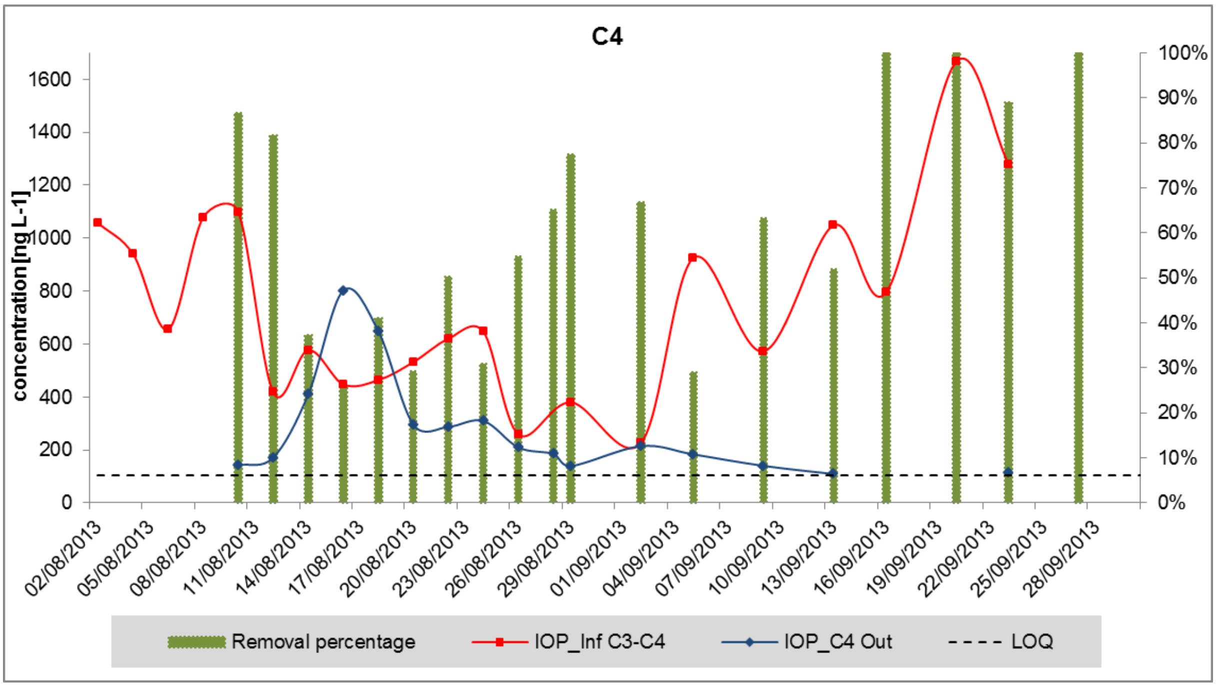


Figure 27: Results for Iopromide (natural conditions C4)

5.6 Fate of Sulfamethoxazole (SMX) in the soil-column experiments

SFM was almost totally removed in C1 and C2, while its presence was constant in C3 and C4, and with outflow concentrations similar than inlet concentrations, which was an evidence of no removal occurring in natural conditions. Sulfamethoxazole was spicked in the inlet tank with a concentration of 1000 ng/L, while analysis reported an initial concentration of 1443 ng/L and 1448 ng/L (Table 1).

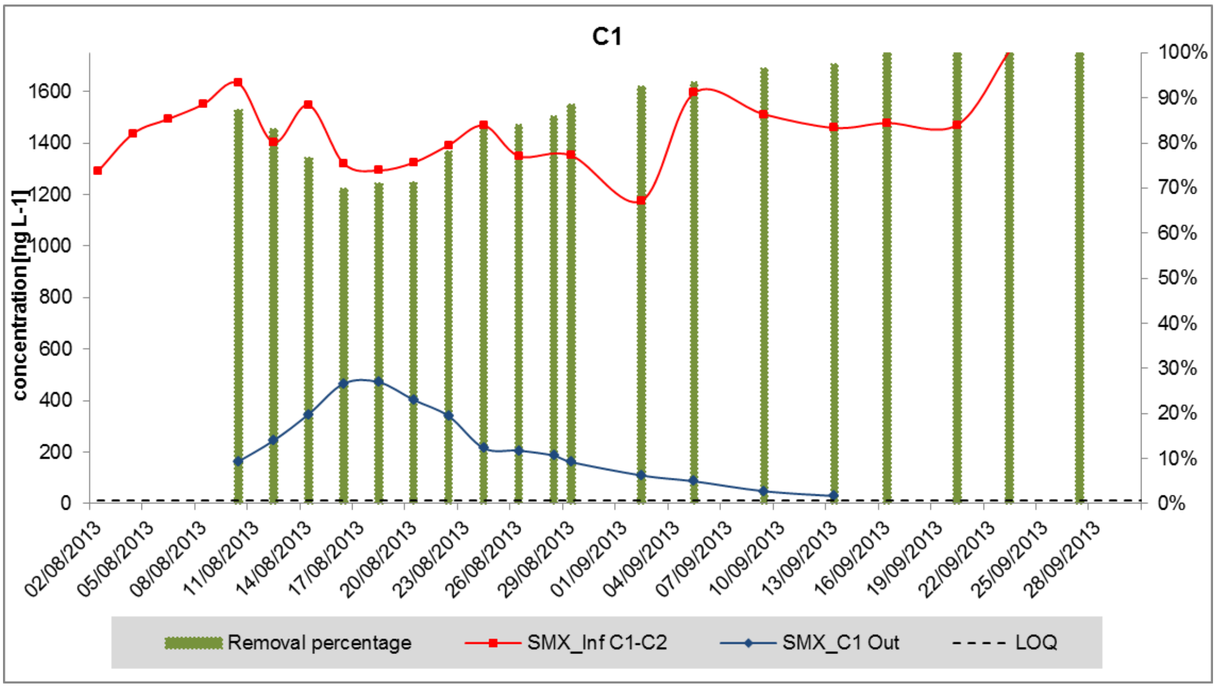


Figure 28: Results of Sulfamethoxazole (enhanced conditions C1)

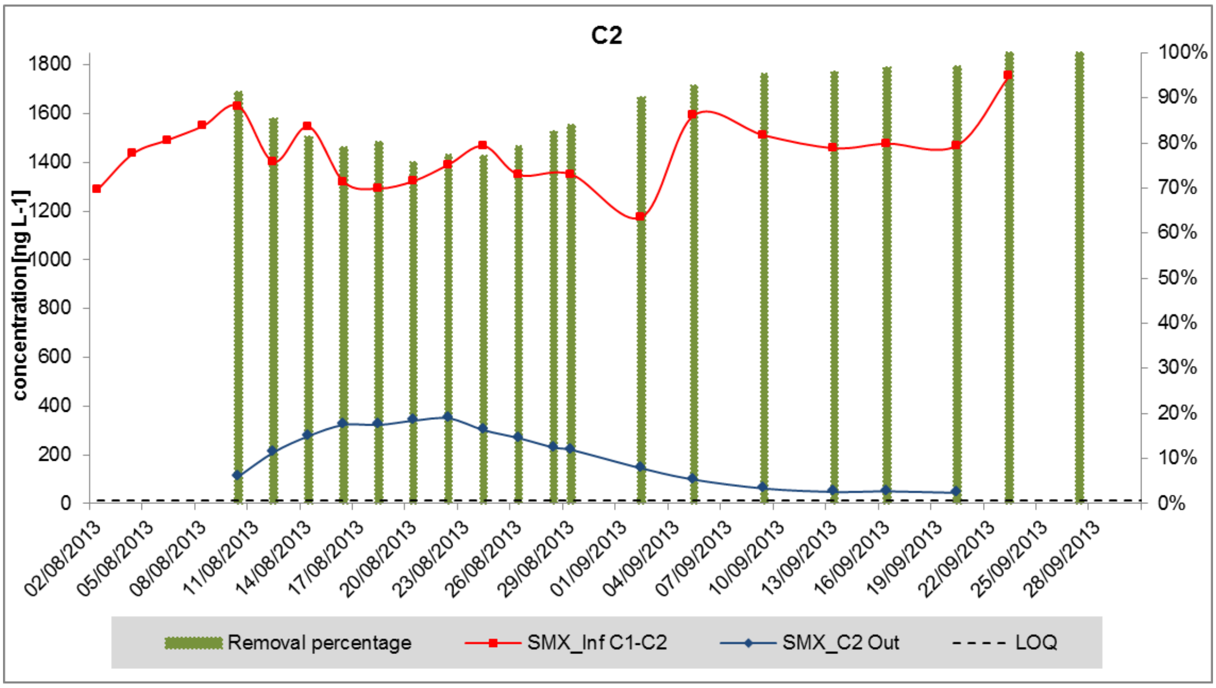


Figure 29: Results of Sulfamethoxazole (enhanced conditions C2)

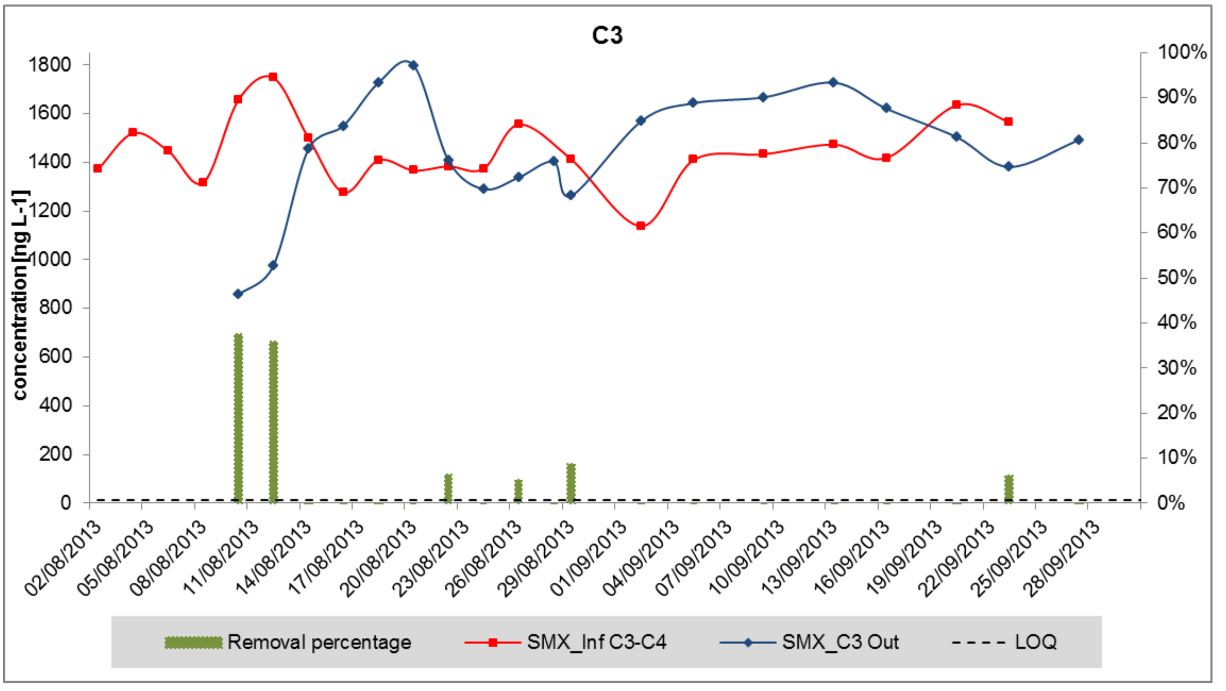


Figure 30: Results of Sulfamethoxazole (natural conditions C3)

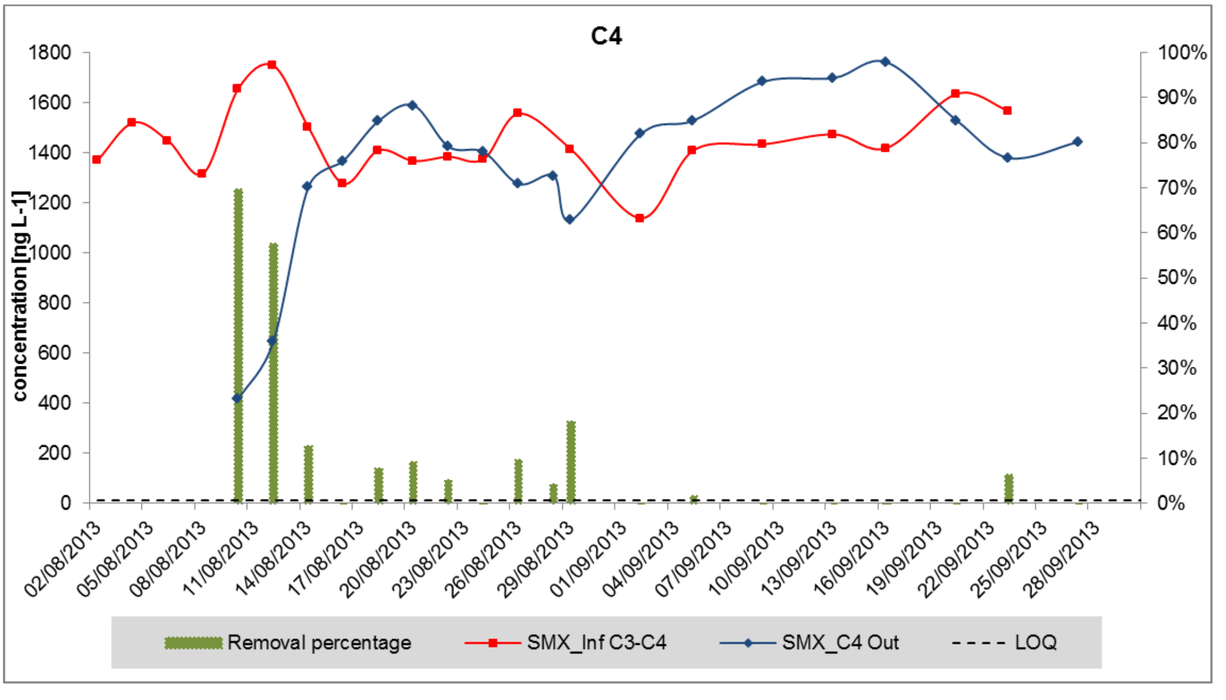


Figure 31: Results of Sulfamethoxazole (natural conditions C4)

5.7 Fate of Trimethoprim (TRI) in the soil-column experiments

Initial concentration of TRI was 207 ng/L and 122 ng/L in INF1 and INF2 respectively. TRI was not found above detection limit in any sample in the outlet of the column experiment. It has been reported a totally removal of TRI both in natural system (columns C3 and C4) and enhance system (columns C1 and C2).

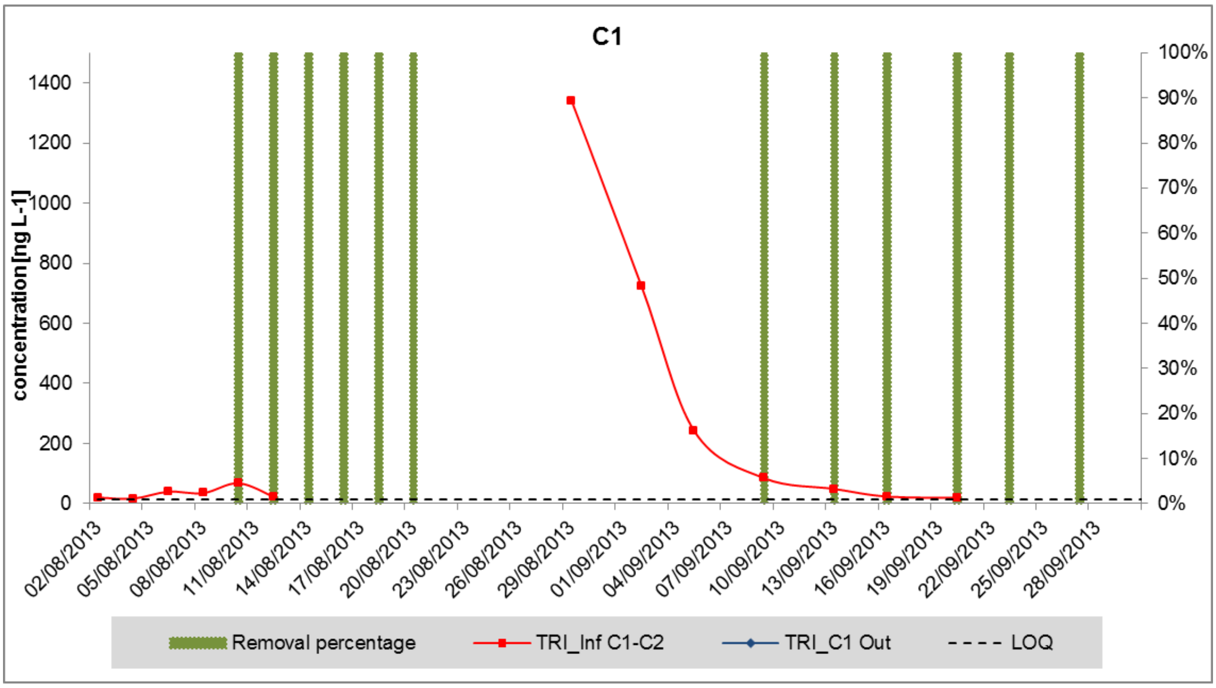


Figure 32: Results for Trimethoprim (enhanced conditions C1)

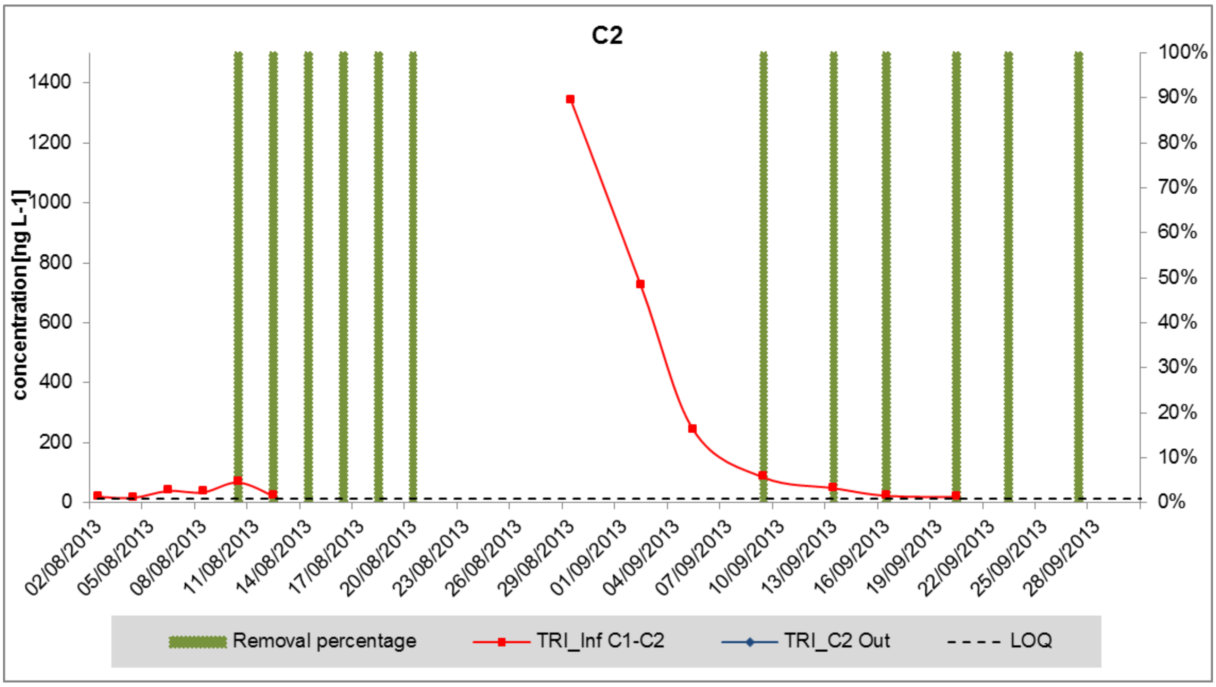


Figure 33: Results for Trimethoprim (enhanced conditions C2)

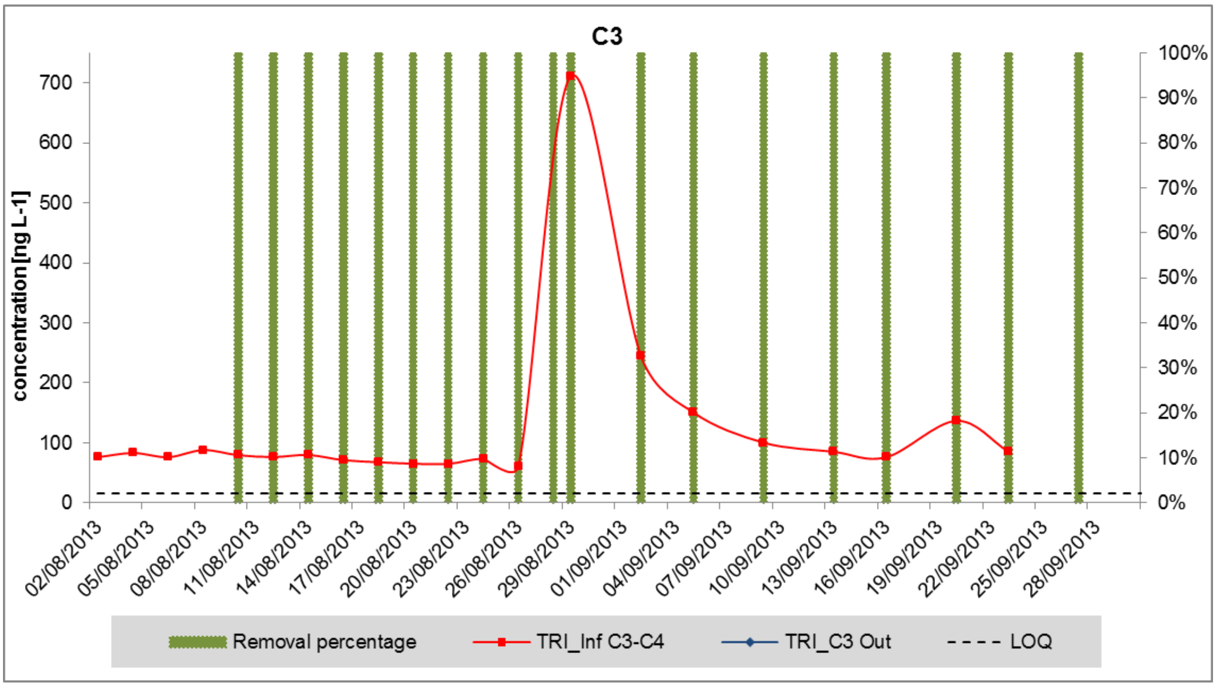


Figure 34: Results for Trimethoprim (natural conditions C3)

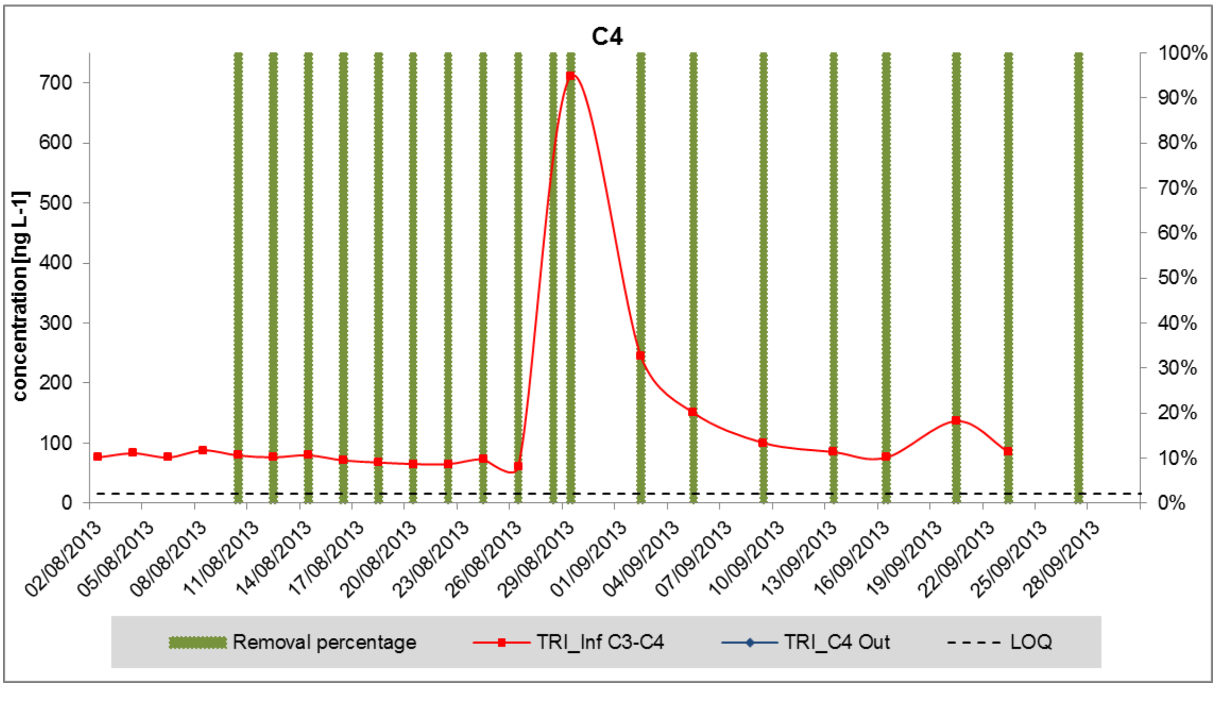


Figure 35: Results for Trimethoprim (natural conditions C4)

5.8 Fate of Bezafibrate (BZF) in the soil-column experiments

This compound was totally eliminated in C1 and C2 systems, corresponding to the enhanced system with reactive organic layer. In contrast, in C3 and C4 the average of removal was 57% and 39% respectively.

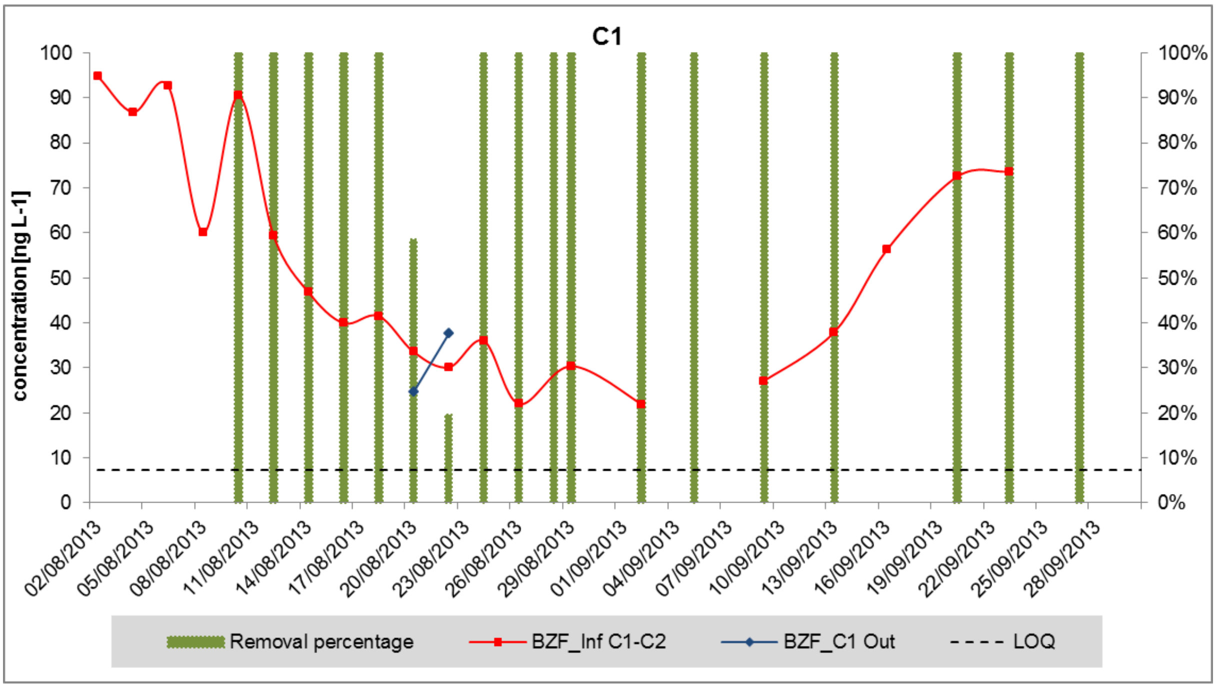


Figure 36: Results for Bezafibrate (enhanced conditions C1)

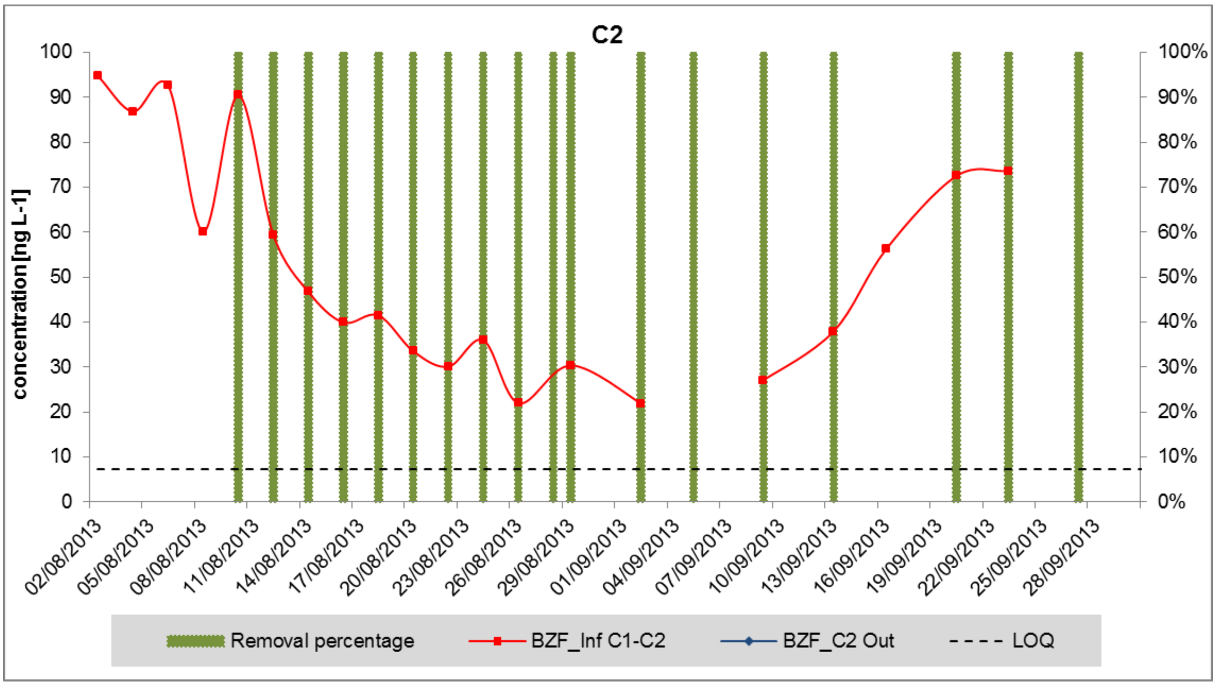


Figure 37: Results for Bezafibrate (enhanced conditions C2)

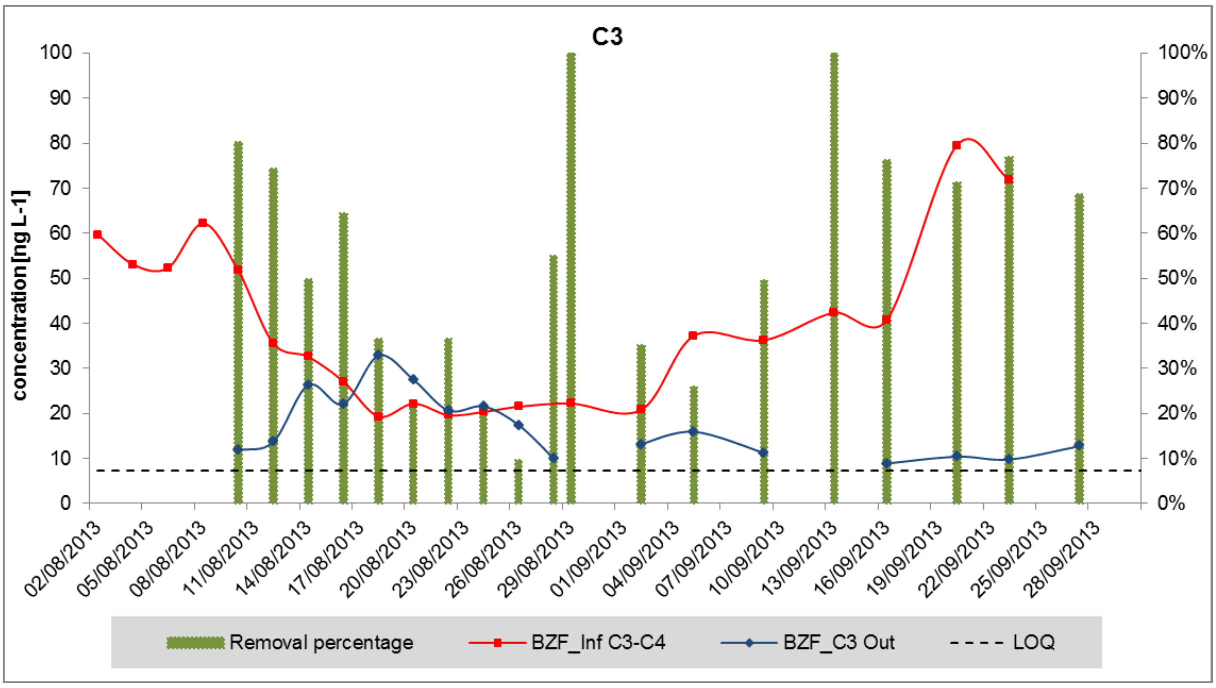


Figure 38: Results for Bezafibrate (natural conditions C3)

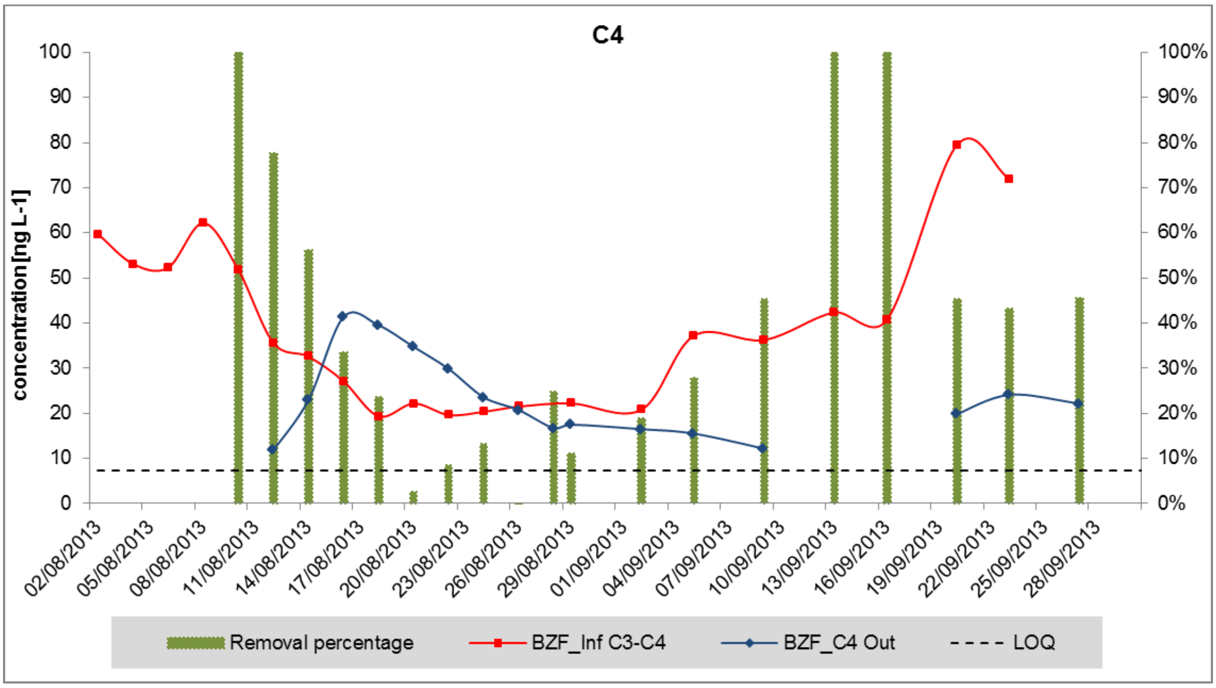


Figure 39: Results for Bezafibrate (natural conditions C4)

5.9 Fate of Gemfibrozil (GFB) in the soil-column experiments

GFB results are characterized by the lack of reproducibility between parallel assembled experiments. While C1 showed an average removal of 11%, results from C2 show a 26% removal of the compound. The same happened in C3 and C4, where removal of GFB was reported to be 14% and 1% respectively.

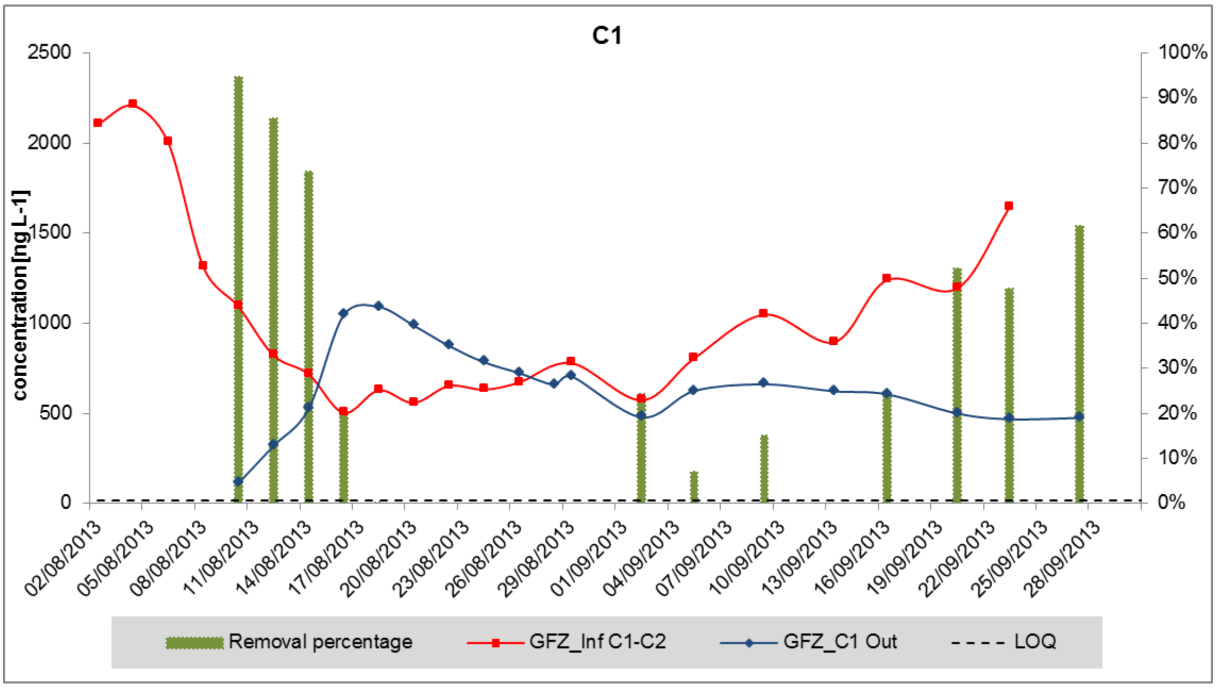


Figure 40: Results for Gemfibrozil (enhanced conditions C1)

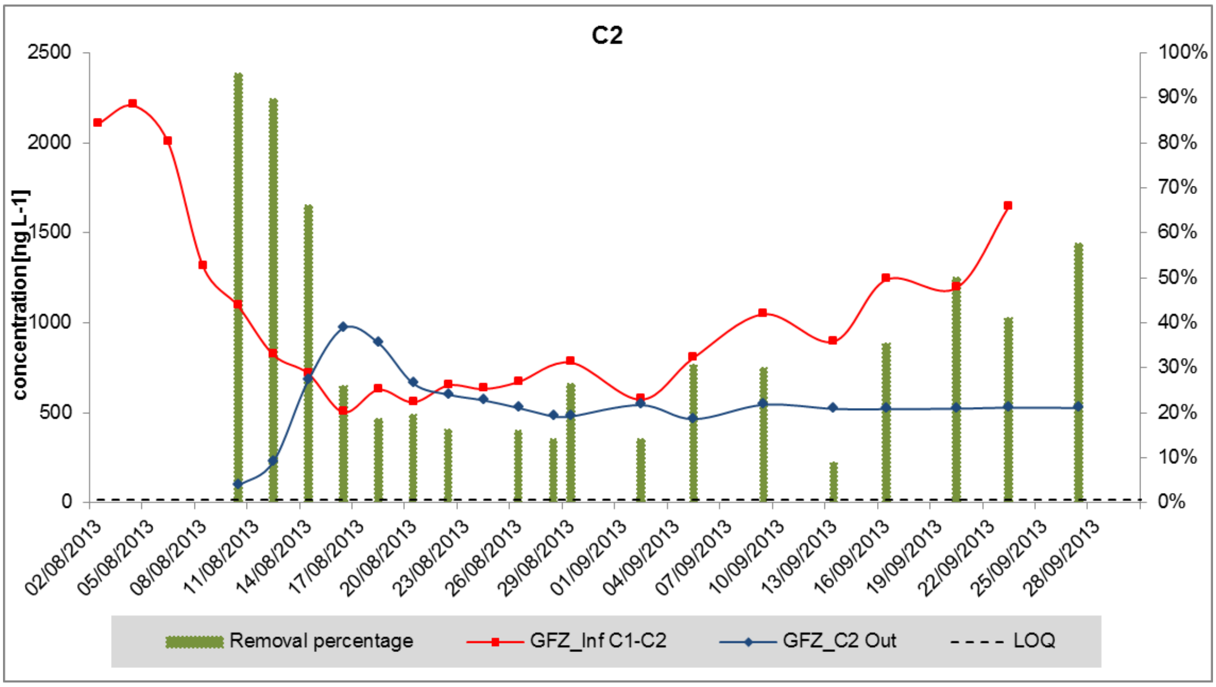


Figure 41: Results for Gemfibrozil (enhanced conditions C2)

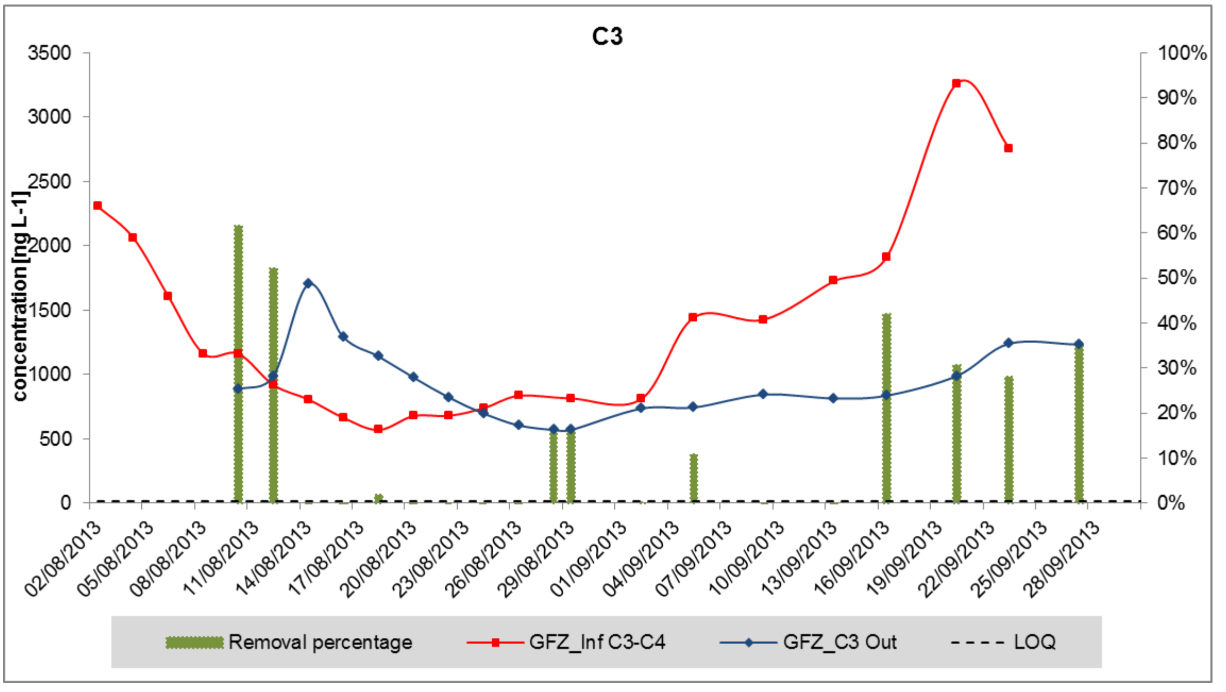


Figure 42: Results for Gemfibrozil (natural conditions C3)

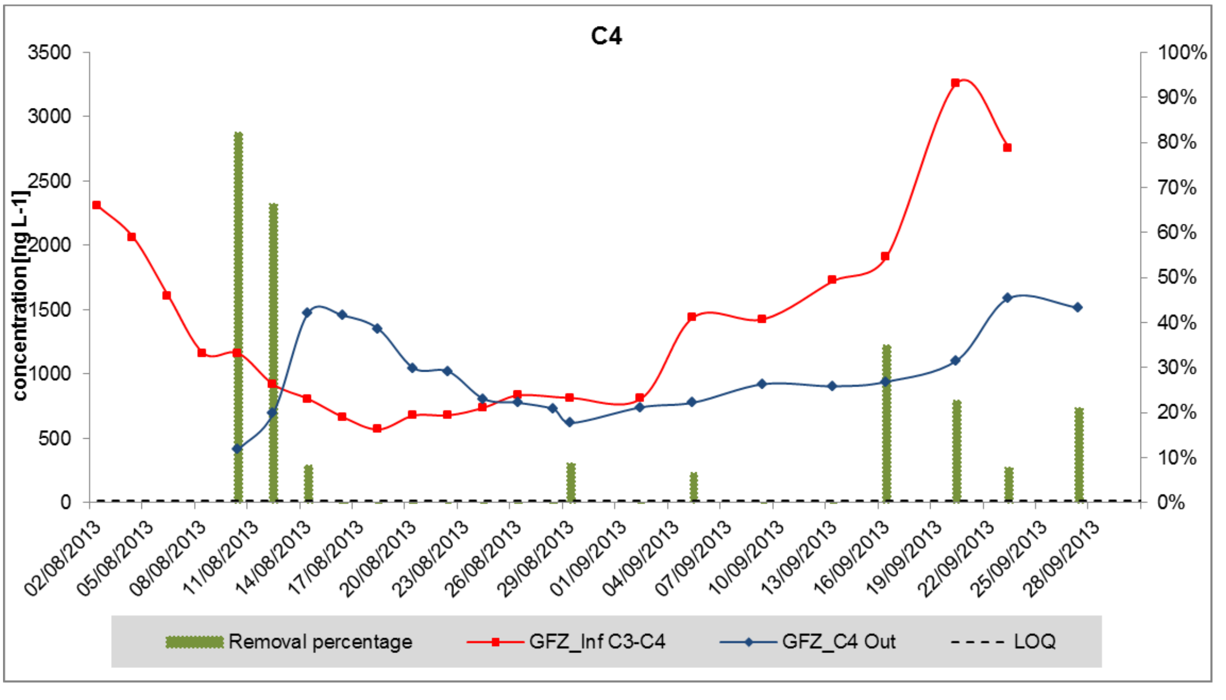


Figure 43: Results for Gemfibrozil (natural conditions C4)

5.10 Fate of Carbamazepine (CBZ) in the soil-column experiments

Carbamazepine was found in identical concentrations in samples INF1 and INF2, the concentration in the secondary effluent of the WWTP was 242 ng/L. No removal was observed in C3 and C4, while in C1 and C2 the percentage of elimination was 12% and 9% respectively. Anyway, the reported elimination in enhanced conditions is very low.

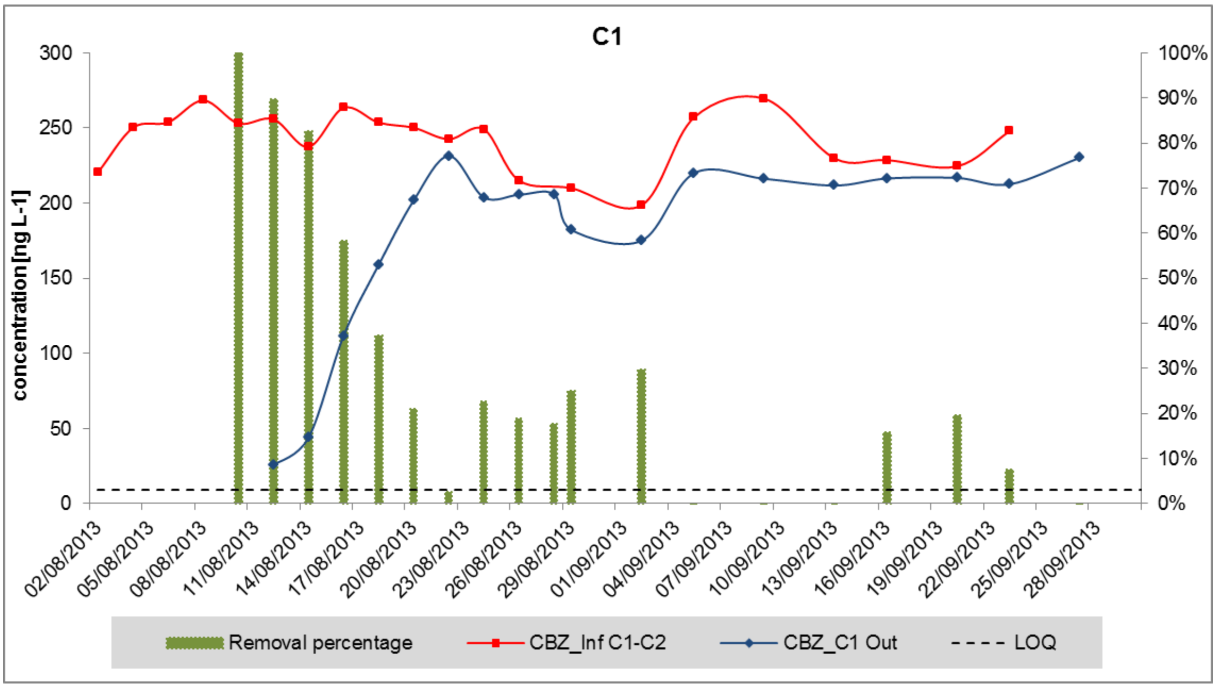


Figure 44: Results for Carbamazepine (enhanced conditions C1)

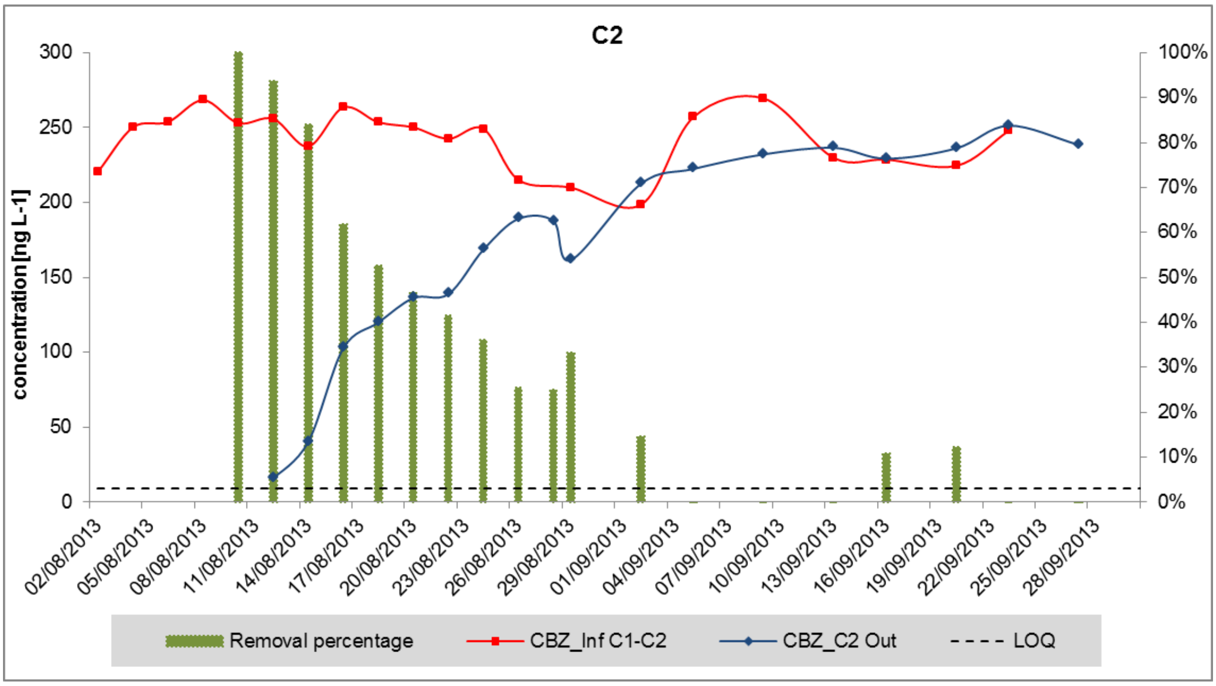


Figure 45: Results for Carbamazepine (enhanced conditions C2)

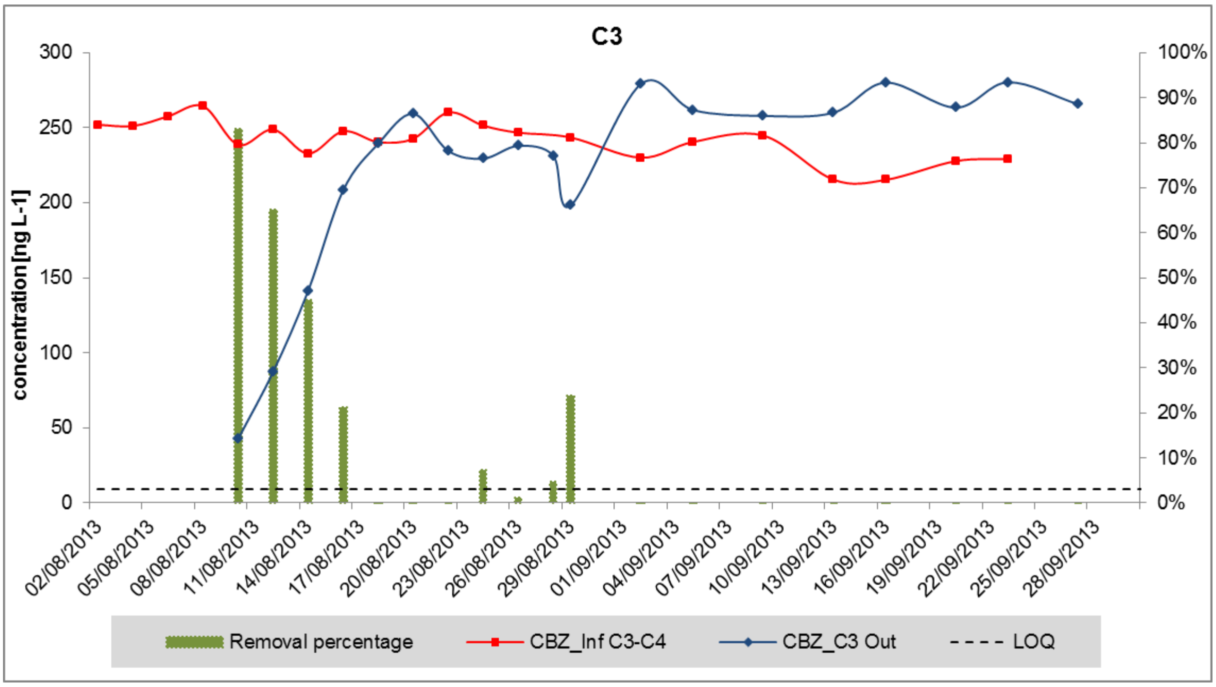


Figure 46: Results for Carbamazepine (natural conditions C3)

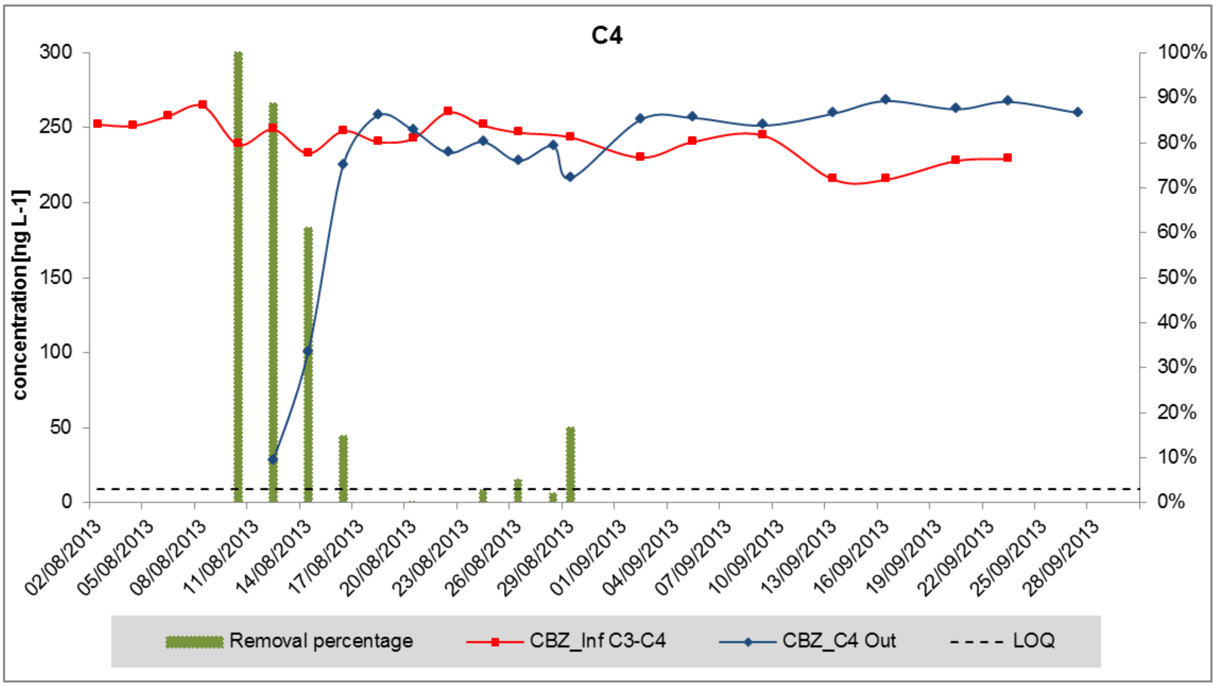


Figure 47: Results for Carbamazepine (natural conditions C4)

5.11 Fate of Primidone (PRM) in the soil-column experiments

PRM behavior is very similar to CBZ, as it has been quantified a slight removal under enhanced conditions (9% and 14% in C1 and C2), while the elimination in natural conditions have been reported below zero, which cannot be and therefore needs further discussion.

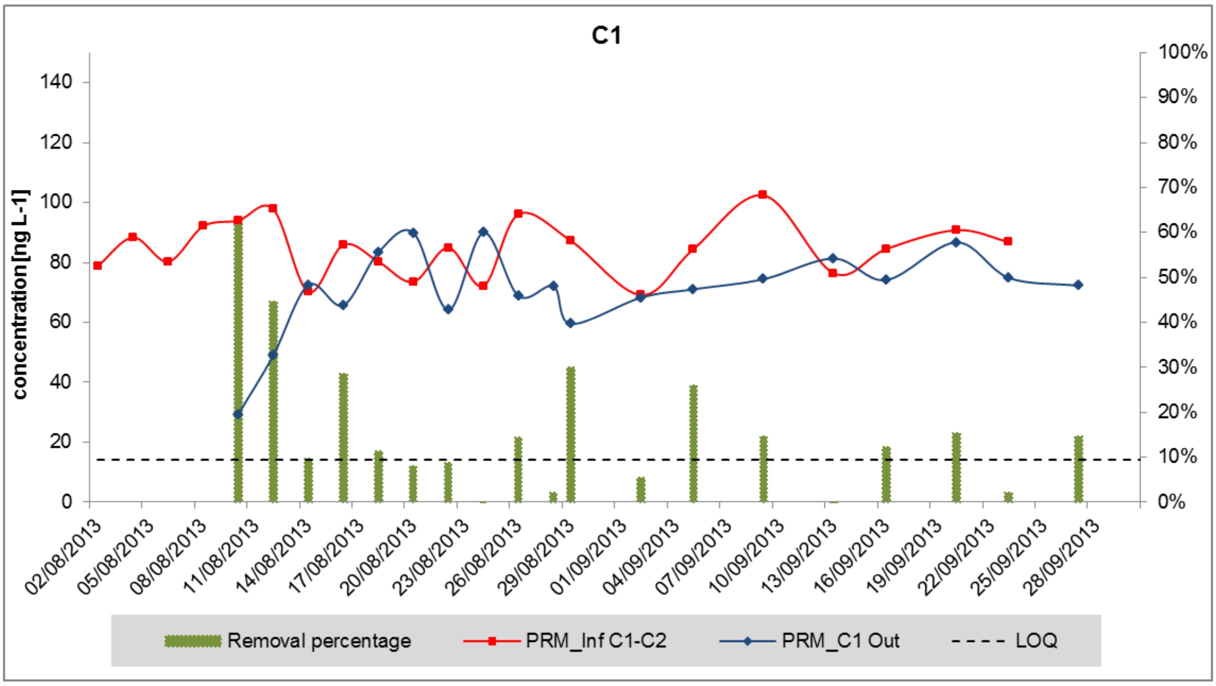


Figure 48: Results for Primidone (enhanced conditions C1)

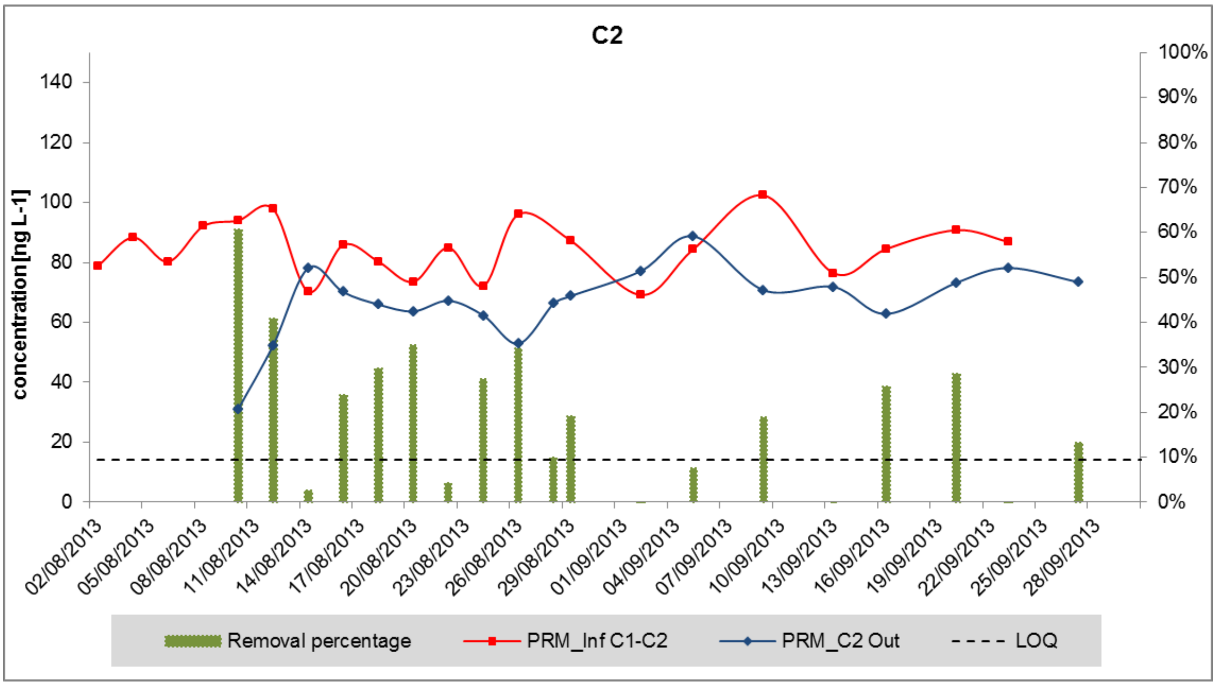


Figure 49: Results for Primidone (enhanced conditions C2)

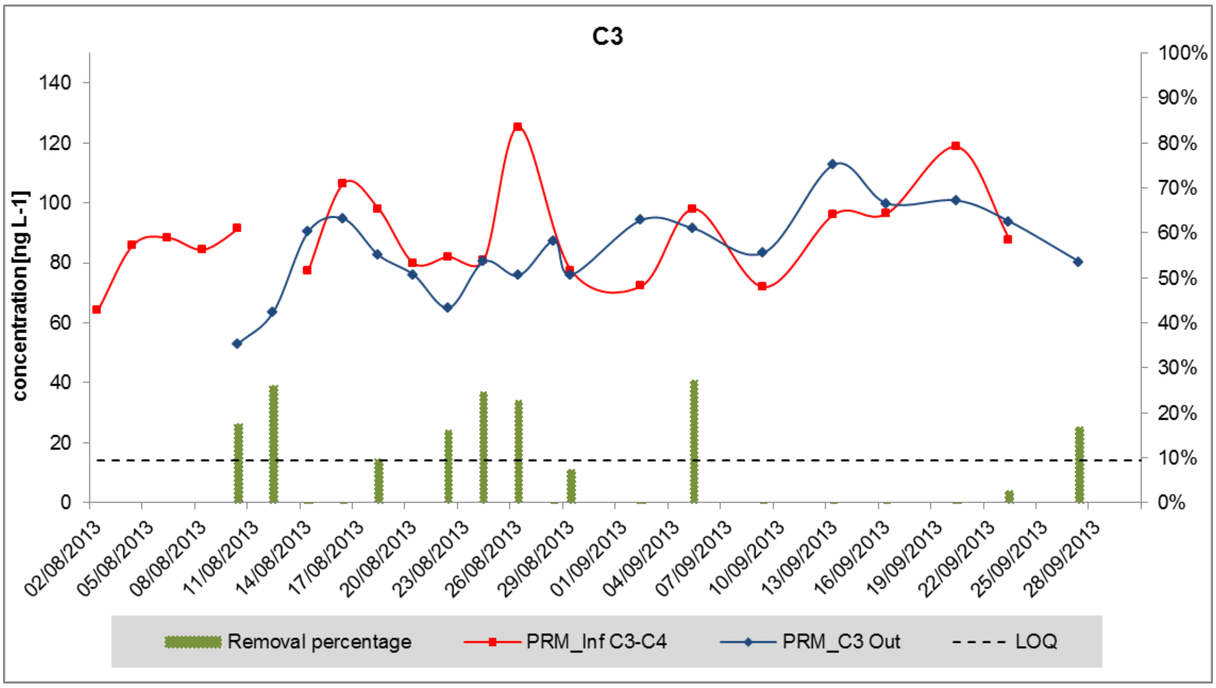


Figure 50: Results for Primidone (natural conditions C3)

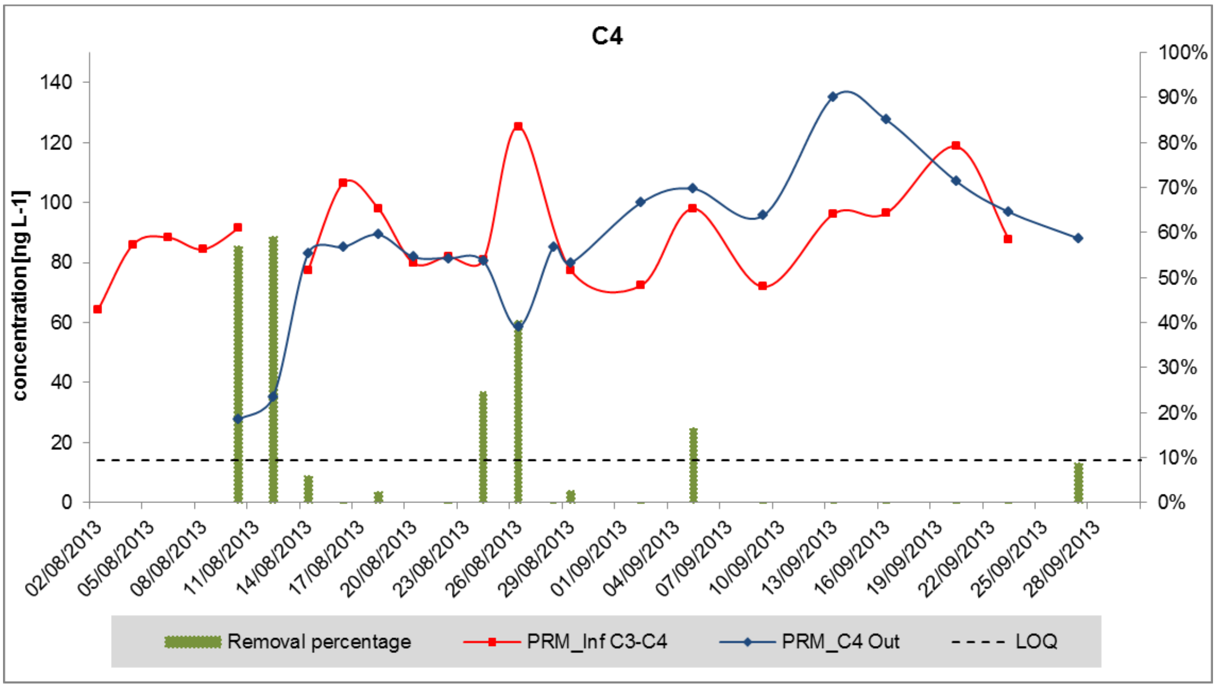


Figure 51: Results for Primidone (natural conditions CC4)

5.12 Fate of Benzotriazole (BZL) in the soil-column experiments

BZL is the compound with the highest concentration in the infiltration water. Initial concentration was reported to be 2895 and 2471 ng/L in INF1 and INF2 respectively. The best removal percentage have been obtained in the natural system, with a removal of 12% and 19%, while in the system enhanced with the compost layer the effectiveness of the BZL elimination has been less (0% and 4% respectively in C1 and C2)

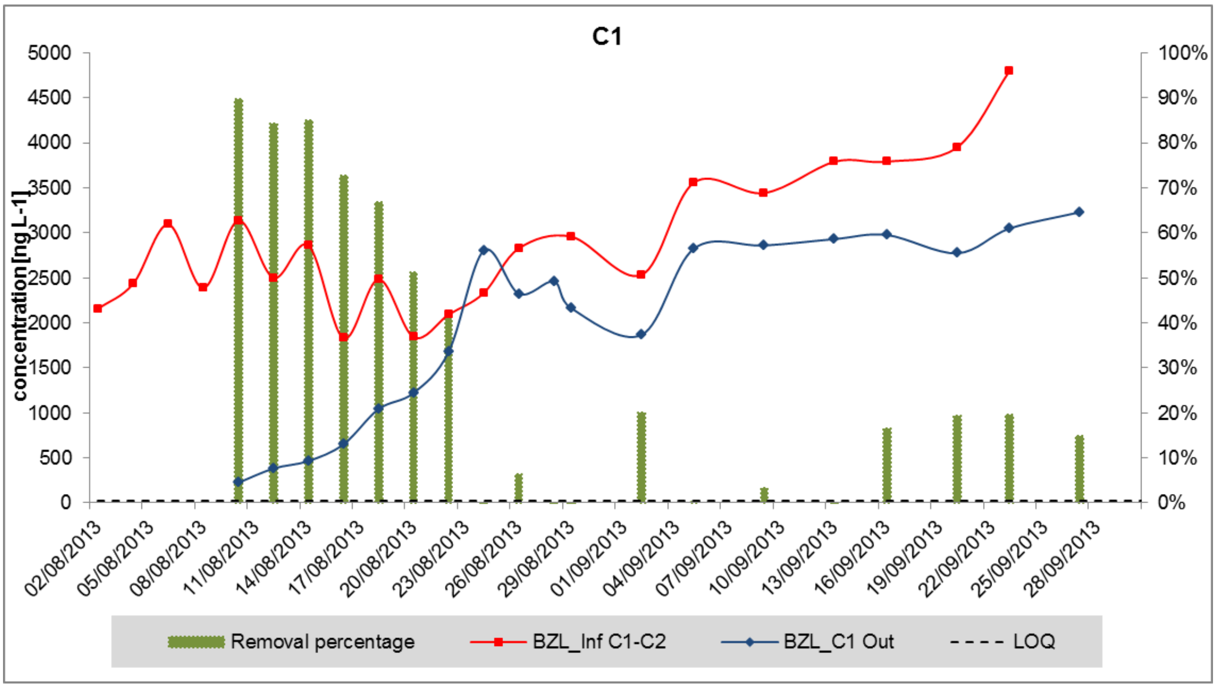


Figure 52: Results for Benzotriazole (enhanced conditions C1)

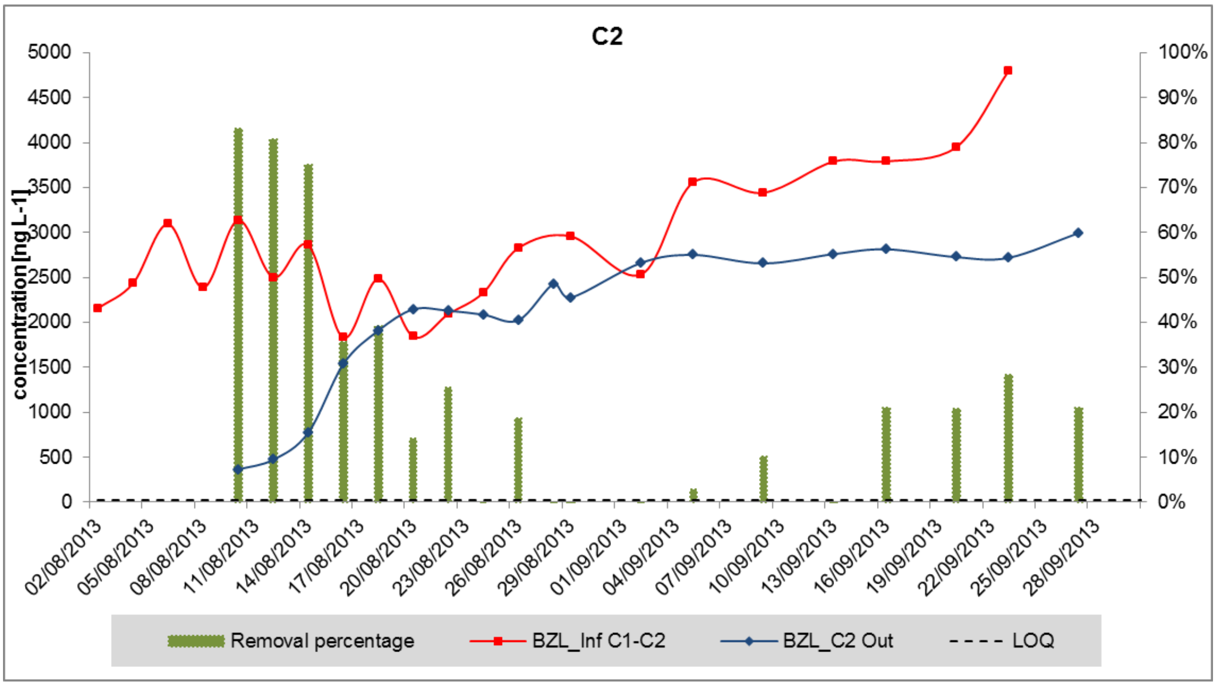


Figure 53: Results for Benzotriazole (enhanced conditions C2)

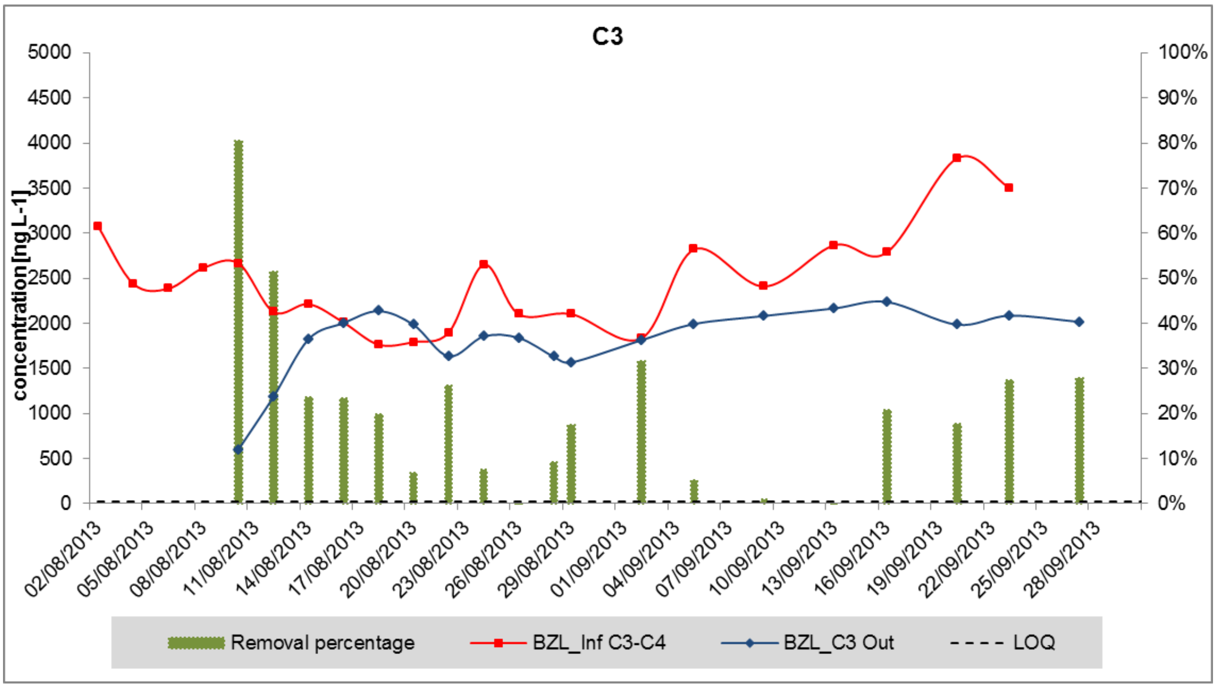


Figure 54: Results for Benzotriazole (natural conditions C3)

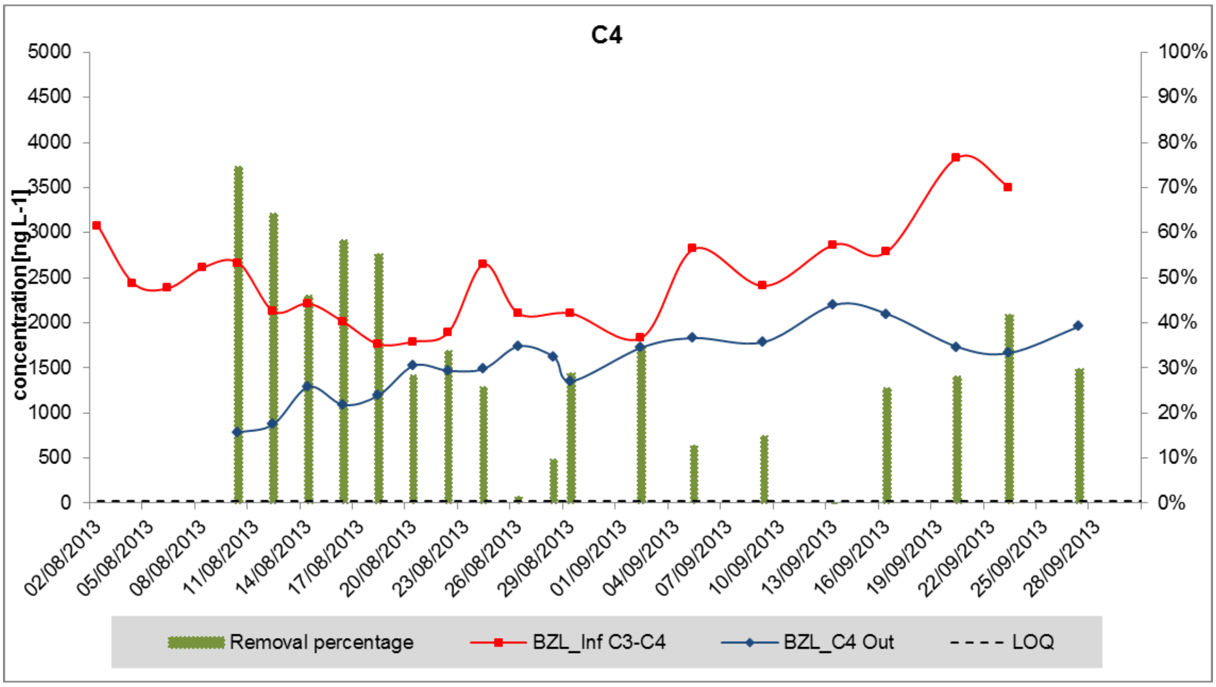


Figure 55: Results for Benzotriazole (natural conditions C4)

6. Summary of trends of emerging pollutants in soil-column experiments

Table 7 summarises the removal percentage obtained for each organic micropollutant studied. This percentage corresponds to the difference between inlet concentration and outlet concentration, taking into account the residence time calculated with the tracer tests (7.5 days). Same data have been represented graphically in Figure 56. According to the differences in the removal percentage under natural and enhanced conditions, three trends have been defined:

- **Trend A:** corresponds to emerging pollutants that are totally removed in both natural and enhanced conditions, reaching removal percentages of 100%. This trend is exemplified in the experiment by TRI.
- **Trend B:** this trend is characterised by an enhancement of the elimination percentage during enhanced conditions when additional DOC is provided by the organic layer. BZF, MET and SMX represent clear examples of Trend B. BZF and MET obtained a removal of 100% in columns C1 and C2, while the average removal percentage in C3 and C4 was 48% and 6%, respectively.
- **Trend C:** these micropollutants seem to be slightly eliminated in any experimental conditions (i.e. with or without the supply of organic carbon), with elimination percentage mostly below 25% (except IOP which showed an average of 58% and 61% of removal in natural conditions and enhanced conditions respectively). Taking into account the error bars for this trend, however, these results should be taken with caution and only as a qualitative indication rather than as a quantitative estimation. It is not possible to have a clear interpretation of the effect of the reactive organic layer in this last trend observed. Micropollutants classified as following trend C are: IOP, DCL, PHEN, GFZ, CBZ, PRM and BZL.

Table 7: Percentage of removal of emerging pollutants
Comparison between initial concentration in natural (blue) and enhanced conditions (brown)

		Enhanced conditions Reactive Layer + Sand Column				Natural conditions Direct Sand Column			
		ORGANIC C1	Desv. Stand	ORGANIC C2	Desv. Stand	NATURAL C3	Desv. Stand	NATURAL C4	Desv Stand
TRI	Trimethoprim	100%	0%	100%	0%	100%	0%	100%	0%
BZF	Bezafibrate	100%	0%	100%	19%	57%	30%	39%	33%
MET	Metoprolol	100%	0%	100%	0%	20%	32%	-8%	39%
SMX	Sulfamethoxazole	94%	6%	91%	8%	-8%	16%	-7%	18%
IOP	Iopromide	59%	28%	62%	18%	46%	28%	69%	25%
DCL	Diclofenac	27%	17%	27%	14%	6%	17%	-1%	18%
PHEN	Phenazone	11%	24%	14%	25%	10%	14%	4%	18%
GFZ	Gemfibrozil	11%	34%	26%	18%	14%	17%	1%	20%
CBZ	Carbamazepine	12%	12%	9%	14%	-6%	14%	-5%	11%
PRM	Primidone	9%	13%	14%	19%	-3%	26%	-11%	35%
BZL	1H- Benzotriazole	0%	23%	4%	14%	12%	15%	19%	17%

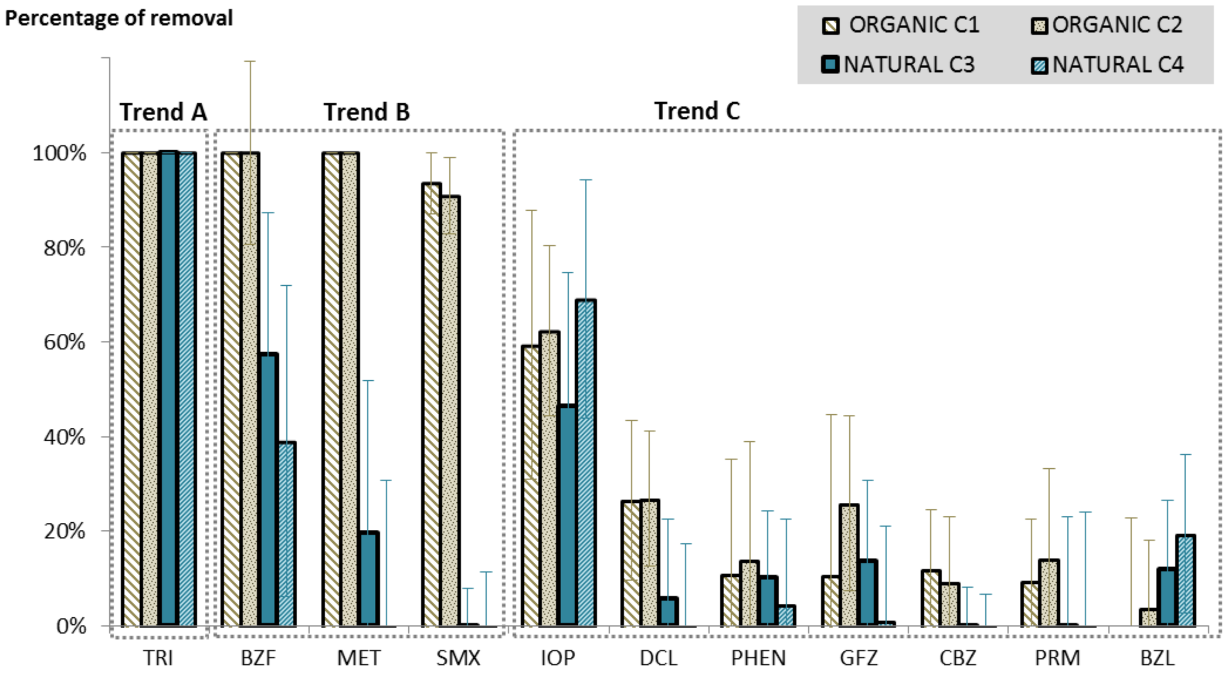


Figure 56: Classification according to the percentage of removal obtained in natural (blue) and enhanced conditions (brown)

7. Comparison to field tests

The report D12.1. includes an extensive literature review of MAR systems worldwide and the reported elimination of emerging pollutants. The most relevant aspect of this deliverable is that all the references cited are about field experiences, so the elimination of the emerging pollutants refers to natural conditions under non-controlled conditions: changes of temperature, long residence time, different DOC concentration…

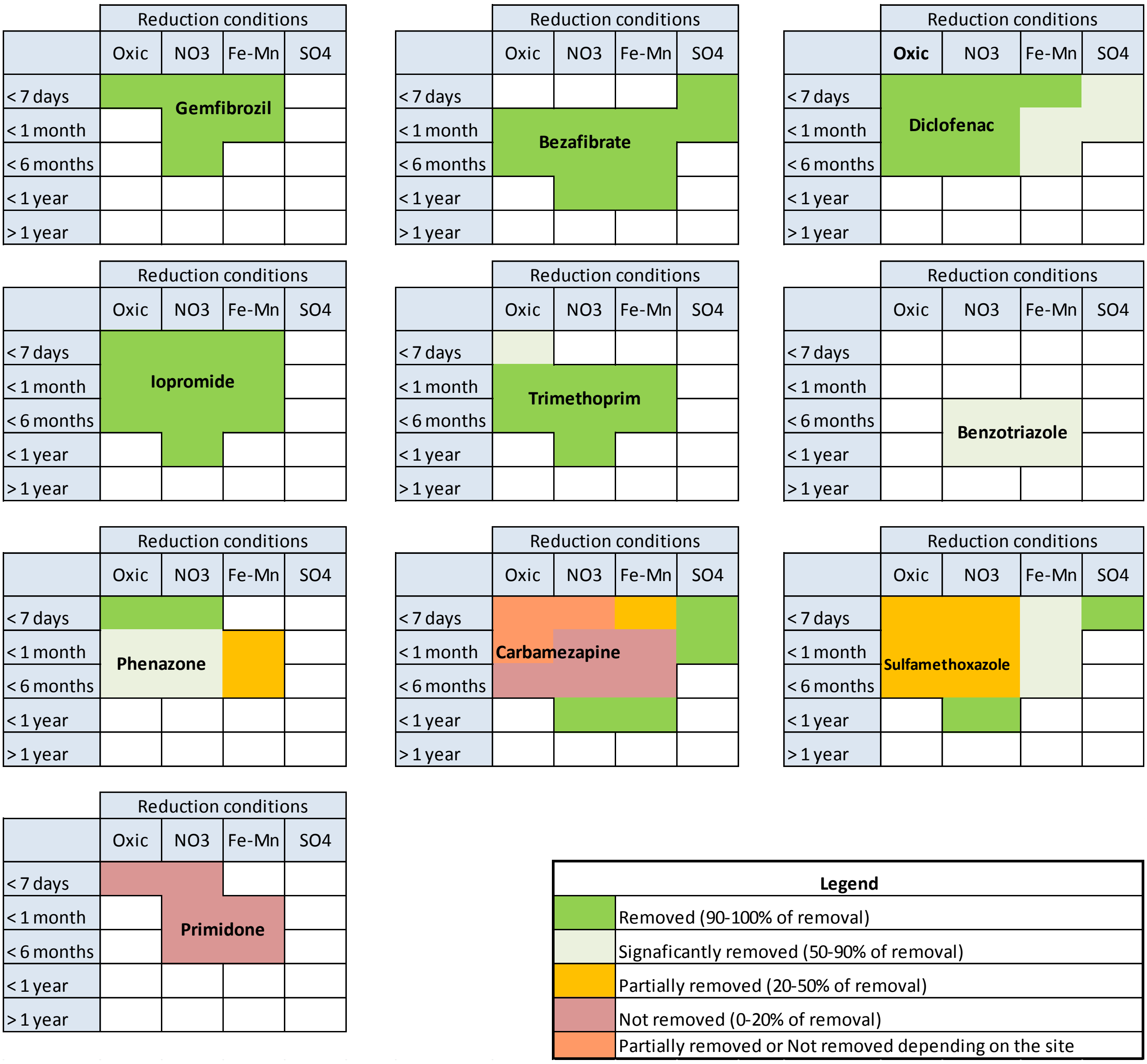
One of the most valuable outputs of the deliverable D12.1 is a matrix that reports the behavior of each target compound taking into account the following variables:

- **Redox State**: most of the field experiences of MAR cited in the literature specify the redox state, giving information of the aerobic or anaerobic conditions. Some studies analysed the behaviour of emerging pollutants according to the redox state. There is no preferred redox condition for the improvement of the elimination of micropollutants, as each family or single compound can be eliminated better or worse under one or several conditions. D12.1 classifies redox estates according to **Figure 9**. **Figure 57** summarises the findings obtained, with the following classification:

    - Aerobic conditions (Oxic)
    - Denitrification (NO3)
    - Iron reduction and Manganese reduction (Fe-Mn)
    - Sulphate reduction (SO4)

- **Residence time:** long residence time has been reported as one of the key factor for the successful elimination of most of emerging pollutants. Extended time in the aquifer favours biological processes, adsorption and consequently the degradation and elimination of the target micropollutants. D1.2.1 established 5 categories of residence time:

    - Less than 7 days
    - 7 days – 1 month
    - 1 month – 6 months
    - 6 months – 1 year
    - More than a year



Gemfibrozil

	Reduction conditions			
	Oxic	NO3	Fe-Mn	SO4
< 7 days	🟩	🟩	🟩	
< 1 month		🟩	🟩	
< 6 months		🟩		
< 1 year				
> 1 year				

Bezafibrate

	Reduction conditions			
	Oxic	NO3	Fe-Mn	SO4
< 7 days				🟩
< 1 month	🟩	🟩	🟩	🟩
< 6 months	🟩	🟩	🟩	
< 1 year		🟩	🟩	
> 1 year				

Diclofenac

	Reduction conditions			
	Oxic	NO3	Fe-Mn	SO4
< 7 days	🟩	🟩	🟩	⬜
< 1 month	🟩	🟩	⬜	⬜
< 6 months	🟩	🟩	⬜	
< 1 year				
> 1 year				

Iopromide

	Reduction conditions			
	Oxic	NO3	Fe-Mn	SO4
< 7 days	🟩	🟩	🟩	
< 1 month	🟩	🟩	🟩	
< 6 months	🟩	🟩	🟩	
< 1 year		🟩		
> 1 year				

Trimethoprim

	Reduction conditions			
	Oxic	NO3	Fe-Mn	SO4
< 7 days	⬜			
< 1 month	🟩	🟩	🟩	
< 6 months	🟩	🟩	🟩	
< 1 year		🟩		
> 1 year				

Benzotriazole

	Reduction conditions			
	Oxic	NO3	Fe-Mn	SO4
< 7 days				
< 1 month				
< 6 months		⬜	⬜	
< 1 year		⬜	⬜	
> 1 year				

Phenazone

	Reduction conditions			
	Oxic	NO3	Fe-Mn	SO4
< 7 days	🟩	🟩		
< 1 month	⬜	⬜	🟨	
< 6 months	⬜	⬜	🟨	
< 1 year				
> 1 year				

Carbamezapine

	Reduction conditions			
	Oxic	NO3	Fe-Mn	SO4
< 7 days	🟧	🟧	🟨	🟩
< 1 month	🟧	🟥	🟥	🟩
< 6 months	🟥	🟥	🟥	
< 1 year		🟩	🟩	
> 1 year				

Sulfamethoxazole

	Reduction conditions			
	Oxic	NO3	Fe-Mn	SO4
< 7 days	🟨	🟨	⬜	🟩
< 1 month	🟨	🟨	⬜	
< 6 months	🟨	🟨	⬜	
< 1 year		🟩		
> 1 year				

Primidone

	Reduction conditions			
	Oxic	NO3	Fe-Mn	SO4
< 7 days	🟥	🟥		
< 1 month		🟥	🟥	
< 6 months		🟥	🟥	
< 1 year				
> 1 year				

	Legend
🟩	Removed (90-100% of removal)
⬜	Signaficantly removed (50-90% of removal)
🟨	Partially removed (20-50% of removal)
🟥	Not removed (0-20% of removal)
🟧	Partially removed or Not removed depending on the site

Figure 57: Matrix of the elimination of emerging pollutants in MAR systems
Source: literature survey based on field experiences

According to the results obtained in the column experiments, the operation conditions of the simulated MAR system correspond to:

- Denitrification redox state
- Residence time: 7.5 days (more close to 7 days than to 1 month)

	Reduction conditions			
	Oxic	NO3	Fe-Mn	SO4
< 7 days		▨		
< 1 month				
< 6 months				
< 1 year				
> 1 year				

Figure 58: Selected operation conditions of the column experiment

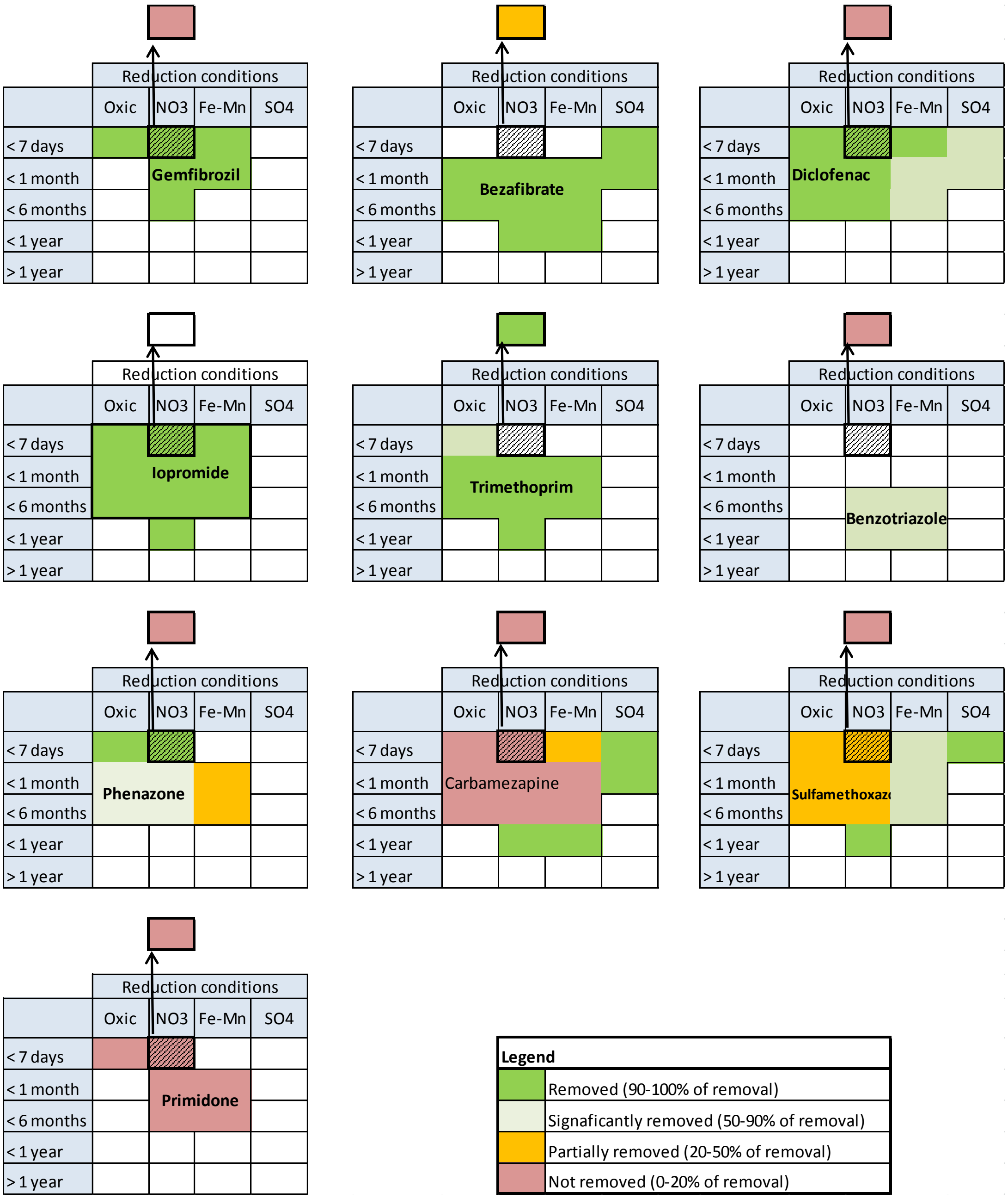


Figure 59: Comparison of column experiment results and literature review

Figure 59 compares graphically the elimination obtained in field experiences and the results of elimination obtained in the column experiments in natural conditions (results obtained in columns C3 & C4), using the mean value of Table 7 of C3 and C4. The effectiveness of elimination in the simulated system assembled in El Prat del Llobregat WWTP is notoriously lower than the one observed in field experiences under denitrification conditions and low residence time. Only Carbamazepine and Primidone showed same results in field experiences than in the column experiment, being not removed from the system.

These findings have been discussed in the working group, and some insights have come up:

- Column experiments are a good approximation to represent MAR and SAT systems, as it is the most extended technique applied worldwide. Nonetheless the values obtained in the column experiments regarding the effectiveness of elimination of emerging pollutants were below than the expected values. Some reasons could be:

    - The sand used as a filling material was not original from the aquifer. Adapted microorganisms were not present at the beginning of the experiment.
    - Acclimation period was only one week before the sampling campaigns. This time is not enough to develop microbiological activity.
    - Initial concentrations in the field MAR systems and the column experiments have not been compared. Different order of magnitude of initial concentrations could change the percentage of removal rates.
    - Despite in the articles and papers the dilution factor increasingly reported, it can cause a supra estimation of the removal percentage in natural systems, while in column experiments there is no possible dilution.

- Use column experiments as a tool for the prediction of field response add a safety factor, as it has been demonstrated that natural systems can eliminate more quantity of emerging pollutants than the simulations in laboratory.

8. Discussion and conclusions

Reduction of nitrate concentration along the infiltration and constant values of the other redox indicators (Fe, Mn, SO_4^{2-}) revealed that denitrifying conditions along the column experiments were achieved (Christensen *et al.*, 2000). Significant differences in the DOC concentration in the output of C1 and C2 (enhanced with the small pre-column filled with vegetal compost) and C3 and C4 (natural conditions) evidenced the achievement of the desired effect of the DOC release to enhance elimination of micropollutants.

Concentration of the DEMEAU target emerging pollutants in the columns outflow showed divergences among pollutants. Three trends in the removal of the analysed organic compounds were identified (see Figure 3). MAR systems seems to be a reliable alternative for the elimination of emerging pollutants as TRI, BZF, MET and SMX under the conditions of the experiment (denitrification) when these systems are enhanced with an additional input of dissolved organic carbon. For BZF, MET and SMX an increase of 52%, 94% and 92% respectively in the percentage of removal have been quantified during enhanced conditions compared to natural conditions.

Further evaluation has been done regarding the nature of the compounds in terms of polarity, Soil Organic Carbon-Water Partitioning Coefficient (K_{oc}), or functional groups of the target micropollutants, among others. All these specific information has been published in a scientific paper (Schaffer *et al*., 2015).

Previous literature review carried out in the DEMEAU project (Miret *et al.,* 2014) characterised European MAR systems and reported the percentage of removal obtained in MAR sites at full scale. Most of the data collected showed travel times above 6 months within the aquifer. The short residence time in the columns (7.5 days) and the lack of acclimatisation period during the recharge might have affected the poor elimination percentage observed for some of the emerging pollutants. Hoppe-Jones *et al*. (2010) reported a removal percentage of 99% for GFZ and 100% for DCL along the river bank filtration in 3 MAR sites based on River Bank Filtration in USA in a relative short residence time (10-20 days) under denitrifying conditions. In this case a high TOC in the river (between 7.6 and 10.5 mg C/L) was reported as an important factor for the biological activity in the MAR system. IOP, which has been classified as trend C according to the results of our experiment, was reported to be effectively removed (89-99% of elimination) along denitrification conditions at infiltration ponds located in Berlin Tegel (Germany) in 4-50 days (Grünheid *et al.,* 2005).

In general, MAR field experiences performed worldwide have reported higher percentage removal of organic micropollutants than those obtained in C3 and C4 of this study simulating natural recharge conditions. It can be interpreted as a positive factor, showing that MAR systems are more reliable at field scale than in bench- and column-scale simulations. Higher elimination percentages obtained in C1 and C2 highlighted the possibility of enhancing natural MAR systems with an additional source of organic carbon capable of increasing the natural capacity of micropollutants removal along SAT systems.

Better understanding of MAR systems at field scale should be necessary for the interpretation of the fate of micropollutants. DEMEAU project is currently on going, working on a deeper understanding of the behaviour of the target micropollutants. Another important line of action of the DEMEAU tasks is bringing these findings to decision makers, to position MAR as a reliable and potential alternative in combating the presence of undesired organic substances in the environment and in the full water cycle.

References

Christensen, T. H.; Bjerg, P. L.; Banwart, S. A.; Jakobsen, R.; Heron, G.; Albrechtsen, H. J. (2000) Characterization of redox conditions in groundwater contaminant plumes. Journal of Contaminant Hydrology 45 2000 165–241.

ENSAT, Enhancement of Soil Aquifer Treatment for securing Groundwater Resources in the Llobregat Aquifer. Life+ project code: LIFE08 ENV/E/000117 . Laymans' report. Published online December 2012. Accessible on-line: http://www.life-ensat.eu/

Grünheid, S.; Amy, G.; Jekel, M. (2005). Removal of bulk dissolved organic carbon (DOC) and trace organic compounds by bank filtration and artificial recharge. Water Research 39 (2005) 3219–3228.

Hernández, M.; Tobella, J.; Ortuño, F.; Armenter, J. L. (2011). Aquifer recharge for securing water resources: the experience in Llobregat River. Water Science & Technology 63.2 2011.

Hernández, M. Gibert, O.; Bernat, X.; Valhondo, C.; Köck-Schulmeyer, M.; Huerta-Fontela, M.; Colomer, M.V. (2014). Innovative reactive layer to enhance soil aquifer treatment: successful installation in the Llobregat aquifer (Catalonia, ne Spain). Boletín Geológico y Minero, 125 (2): 157-172.

Hillebrand, O., Musallam, S., Scherer, L., Nödler, K., Licha, T., (2013). The challenge of sample-stabilisation in the era of multi-residue analytical methods: A practical guideline for the stabilisation of 46 organic micropollutants in aqueous samples. Science of the Total Environment 454–455, 289–298.

Hoppe-Jones, C.; Oldham, G.; Drewes, J. E. (2010) Attenuation of total organic carbon and unregulated trace organic chemicals in U.S. riverbank filtration systems Original Research Article
Water Research, Volume 44, Issue 15, August 2010, Pages 4643-4659

Kuster, M.; López de Alda, M.J.; Hernando, M.D.; Petrovic, M.; Martín-Alonso, M.; 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 (2008) 358, 112– 123.

Miret, M.; Vilanova, E.; Molinero, J. (2014). DEMEAU Deliverable number D1.2.1 Identification of optimum conditions to face emerging pollutants removal in MAR systems. September 2013. Accessible on-line: http://demeau-fp7.eu/system/files/results/

Nödler, K., Licha, T., Bester, K., Sauter, M., (2010). Development of a multi-residue analytical method, based on liquid chromatography–tandem mass spectrometry, for the simultaneous determination of 46 micro-contaminants in aqueous samples. Journal of Chromatography A 1217(42), 6511-6521.

Nödler, K., Hillebrand, O., Idzik, K., Strathmann, M., Schiperski, F., Zirlewagen, J., Licha, T., (2013). Occurrence and fate of the angiotensin II receptor antagonist transformation product valsartan acid in the water cycle – A comparative study with selected β-blockers and the persistent anthropogenic wastewater indicators carbamazepine and acesulfame. Water Research 47(17), 6650-6659.

Schaffer, M.; Kröger, F.; Nödler, K.; Ayora, C.; Carrera, J.; Hernández, M.; Licha, T. (2015 in press). Influence of a reactive layer on the attenuation of 28 selected organic micropollutants under realistic soil aquifer treatment conditions: insights from a large scale column experiment. Water Research. In press.

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.