D11.2 Demonstration of MAR effects on groundwater resources – development and application of different approaches for risk and impact assessment

The research leading to these results has received funding from the European Union Seventh Framework Programme (FP7/2007-2013) under Grant Agreement no. 308339 for the research project DEMEAU

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Summary:

This project report summarizes work conducted in work package 11. Along with the deliverable 11.1 and milestone report 11 it covers the tasks from work package 11 as formulated in the Description of Work (DoW). The content of the different sections is interrelated, but each section is organized as an independent part. Title of this report differs from DoW because recommendations for optimum design and operation will be handled in the deliverable 12.2. The sections in this report cover various topics and each section can be found as a stand-alone report in the DEMEAU tool box (http://demeau-fp7.eu/toolbox/) for download. Detailed summaries can be found for each section separately.

Grant agreement no:	308339
Work Package:	WP11
Deliverable number:	D11.2
Partner responsible:	KWB, KWR, Amphos21, HYDOR
Deliverable author(s) (alphabetical order):	Beatriz de la Loma González, Christoph Sprenger, Cornelia Kienle, Eszter Simon, Gesche Grützmacher, Harrie Besselink, Marta Hernández, Niels Hartog, Oriol Gibert, Wolfgang Seis
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Planned delivery date:	31. August 2015
Actual delivery date:	1.November 2015
Dissemination level:	PU

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1 Introduction, background and scope

The EU funded FP7 project DEMEAU is a three-year demonstration project on promising technologies that tackle emerging pollutants in water and waste water. Within the DEMEAU project one focus water treatment technology is Managed Aquifer Recharge (MAR). The following topics concerning the development of MAR can be found in this report:

- Definition and classification of managed aquifer recharge methods (section 2)
- Long-term effects and comparison of quantitative and qualitative data during MAR with aquifer baseline – generic approach development and site application in Berlin-Tegel (section 3)
- Approaches to estimate removal efficiency of emerging substances in MAR systems at The Hague (section 4)
- Risk assessment based on Australian guidelines at Berlin –Tegel (section 5)
- Summary of field investigations at the infiltration basins in Sant Vicenç dels Horts (section 6)
- Summary of field investigations in injection wells in Vall d'Uixó incl. risk assessment (section 7)

In section 2 a concise classification of the different MAR methods is described. This classification is based on the different recharge and storage techniques.

At an infiltration pond site in Berlin-Tegel the long-term effects of recharge on native groundwater is shown. First a generic approach is developed to compare the native groundwater baseline chemistry with water quality changes induced by the recharge activity. This approach is then applied at the groundwater replenishment site in Berlin-Tegel (section 3).

In The Hague (The Netherlands) two different approaches are developed to estimate the removal efficiency of micro pollutants (section 4). Because of the large variability of micro pollutant concentration and the difficulty of tracing back the original concentrations in the source water, these two approaches do not focus on the behavior of contaminants along a specific flow path. The first approach is based on long time series of analytical data, comparing the infiltrated and abstracted averaged concentrations as an overview of the reduction of the organic micro pollutant. The second approach consists of finding statistical relationships in source- and abstracted water between the micro pollutants and other hydrochemical parameters. The variation in these relationships that develop during subsurface passage gives information on the processes that are affecting micro pollutants attenuation.

This report contains risk assessment based on the Australian guidelines (NRMMC-EPHC-NHMRC 2009) for two MAR sites. In section 5 risk assessment is applied at an infiltration pond site in Berlin-Tegel (Germany) and section 7 presents the risk assessment for the Vall d'Uixó site near Castellón in Spain.

Another task of the project was the application of methodologies on site scale in order to optimize operational practice or develop new design. To this end, two Spanish sites have been assessed. At the Sant Vicenç dels Horts site near Barcelona (Spain) DEMEAU contributed by different techniques to assess the effects of MAR site on groundwater quality. Sant Vicenç dels Horts is an already operated infiltration system based in a settling pond and an infiltration pond. The objective in this case study was to provide additional information regarding the hydrochemistry, presence and elimination of emerging pollutants and the assessment of the effectiveness of the natural compost layer installed in 2011. Results are shown in section 6.

At the Vall d'Uixó site near Castellón (Spain) DEMEAU contributed to the Water Recovery Project to implement a new ASR (aquifer storage and recovery) site. To this end, Australian MAR Guidelines (NRMMC-EPHC-NHMRC 2009) have been applied, following the entry level assessment and the maximal risk evaluation. Entry-level risk assessment has been performed to evaluate the hazards of the injection of reclaimed water coming from the secondary effluent of the local WWTP. Results are presented in section 7. At each of the case studies three sampling campaigns have been carried out to characterize source- and groundwater and DEMEAU partner from other work areas collaborated with their analytical capabilities. Different bioassays have been applied to assess water toxicity caused by the presence of emerging pollutants. Samples from Vall d'Uixó and Sant Vicenç dels Horts were collected, shipped and analysed in BDS (The Netherlands) and EAWAG (Switzerland).

2 Definition and classification of managed aquifer recharge techniques

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The term Managed Aquifer Recharge (MAR) describes the intentional recharge (and storage) of water into an aquifer for subsequent recovery or environmental benefit. MAR is used to store and treat water in an appropriate aquifer from various sources, such as river water, reclaimed water, desalinated seawater, rainwater or even groundwater from other aquifers. It is an interconnecting technology equally applicable to water- and wastewater treatment and often combined with engineered treatment systems. With an appropriate pre-treatment before recharge and post-treatment (if necessary) after recovery it may be used for drinking water supply, process water for industry, irrigation, and sustaining groundwater dependent ecosystems. It found applications, sometimes since many decades, from village to large city scale supplies and offers opportunities for water supplies which have not yet adopted MAR. Aquifers have been used to store and treat water for centuries and along with climate change and increasing pressure on water resources through various factors, safe and reliable storage and treatment of water in the subsurface will gain more attention in the near future.

There are a large number and growing variety of techniques used for MAR, which can be classified based on the recharge respectively storage technique in four main groups:

- enhanced infiltration from or near the land surface by gravitation (e.g. surface spreading, point or line recharge, in-channel modifications)
- induced infiltration from stream or lake beds (bank- and lake filtration)
- well injection water in deep aquifers (e.g. aquifer storage and recovery)
- enhanced storage techniques (e.g. subsurface dams)

A concise classification of managed aquifer recharge methods is given in Table 2-1.

Table 2-1: **Classification and overview of MAR techniques**

Recharge technique	MAR type	
Enhanced infiltration	Spreading methods (areal recharge)	Infiltration ponds
		Soil-Aquifer treatment
		Excess irrigation, ditches, trenches
	Point or line recharge	Well/borehole infiltration
		Reverse drainage, shaft recharge
	In-channel modifications	Check dams
		Riverbed scarification
		Sand dams
Induced infiltration	Induced bank filtration	Riverbank filtration
		Lakebank filtration
Injection	Well injection	Aquifer storage and recovery
		Aquifer storage, transfer and recovery
		Aquifer storage (hydraulic barriers)
Enhanced storage	Aquifer storage	Sub-surface dams

Enhanced infiltration summarizes MAR techniques which rely on gravitational infiltration and percolation and consists of surface spreading, point or line recharge and in-channel modifications. Surface spreading is the simplest, oldest, and most widely applied method of MAR. With this technique, the source water is spread over a land surface and percolates to the target aquifer. Most of the existing large scale recharge schemes in western countries make use of this technique which typically utilises infiltration ponds to enhance the natural percolation of water into the subsurface. Surface spreading methods are used when the geology and hydrology allows the aquifer to be recharged from ground level or close to ground level and the MAR structures of this type are mostly above or near ground level. Infiltration ponds (IPs) are often operated until fully saturated conditions below the pond are developed, while Soil Aquifer Treatment (SAT) require unsaturated conditions below the infiltration basin. During SAT treated effluent is recharged through a biological active zone (soil), a vadose zone and finally to the saturated zone where the recharged water is usually recovered and reused. Both IPs and SAT are often operating in wet/dry cycles in order to allow for maintenance such as clogging removal. Excess irrigation in agriculture or forestry is also part of surface spreading.

During point or line recharge the source water is infiltrated either in elongated (e.g. shafts, drains) or punctual structures (e.g. abandoned dug wells or dry bore holes). Well, shaft, dam and borehole recharge comprise a wide range of types of recharge by gravitation in dug wells, shafts, pits or. MAR structures of this type are mostly below ground level and are also constructed to prevent or counteract seawater intrusion.

In-channel modifications are structures built in streams to intercept or detain the stream flow and enhance groundwater recharge. This type of MAR is more common in arid and semi-arid areas where intermittent or ephemeral stream conditions prevail. Sand dams e.g. are usually small structures built in non-perennial streams to store water during rainy season to overcome periods of drought. Check dams are used to stop part of the seasonally (e.g. storm events) occurring stream flow to enhance infiltration through the stream bed. The controlled discharge of the stored water through recharge releases provides additional options at times of limited infiltration upstream of check dam. The breakup of low conductive riverbed layer by heavy machinery (i.e. caterpillars) is also practiced in few countries (e.g. Spain, Italy) and is often called riverbed scarification.

Induced bank filtration (IBF) is a category by its own and describes the infiltration of surface water from a river or a lake induced by well pumping. Water quality improvement, which is commonly observed during the subsurface passage, is often the main objective of this MAR type. Main advantages of IBF include dampening of peak concentrations occurring in the surface water body of many dissolved components, substantially removing many micro pollutants and the efficient removal of pathogens and suspended solids.

Well injection techniques include wells which are either operated as subsequent injection and abstraction well (Aquifer Storage and Recovery, ASR) or multiple wells with spatially divided injection and abstraction wells (Aquifer Storage Transfer and Recovery, ASTR). During ASR the well is used for both injection and recovery of water. Many ASR sites are storing treated drinking water to provide drinking water to cities and communities, especially in times of peak demand. Groundwater levels can then be restored if adequate volumes of water are recharged to the target aquifer, which is sometimes used to counteract seawater intrusion in coastal aquifers. ASTR involves water injection through a well, and recovery from another, some distance away, to increase travel time and benefit from the attenuation capacity in the aquifer.

Subsurface dams (also called underground dams) do not enhance recharge but create additional water storage by stopping groundwater flow upstream of constructed impermeable subsurface barrier. Please note that in contrast to the classification by IGRAC (2013) underground dams are included here and not classified as in-channel modification. Rooftop water harvesting (also called rainwater harvesting) is a way to collect source water in the capture zone (rooftop) and can be combined with injection or infiltration techniques according to local conditions and requirements.

3 Comparison of quantitative and qualitative data during MAR with aquifer baseline data – generic approach and site application at Berlin-Tegel

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Managed aquifer recharge (MAR) is stipulated by the European Groundwater Directive (GWD) to be a supplementary measure to achieve ‘good status’ for ’all’ water bodies by 2015 (EC, 2006). A ‘good status’ means both good quantitative status and good qualitative status. Good quantitative status is stipulated to be achieved if natural groundwater recharge exceeds groundwater abstraction. A good qualitative status is stipulated to be achieved when, among other criteria, if certain measured values for pollutants and indicators are in compliance with the threshold values. These threshold values are currently in discussion and to fulfill the objective of ’good status’ in groundwater it is necessary to know the natural background values in groundwater, taking into account the geochemistry of the aquifer. Natural background values in groundwater can be defined as the regional (and depth dependent) background of a certain parameter, which would be present without any anthropogenic impact. In Germany, and especially in densely populated areas like Berlin, groundwater without any anthropogenic impact virtually does not exist. Therefore, it is important to differentiate between the natural and human impacted groundwater component.

In this section previously available methods to distinguish between anthropogenic and natural background level in groundwater are introduced. These background values, for selected inorganic and organic substances, from various studies are used and compared to measured values on site level in Berlin. Within this context, emerging pollutants are of special concern, since some have shown to be poorly degradable or may only be removed under specific redox conditions. The general approach followed in this report is described in Figure 1.

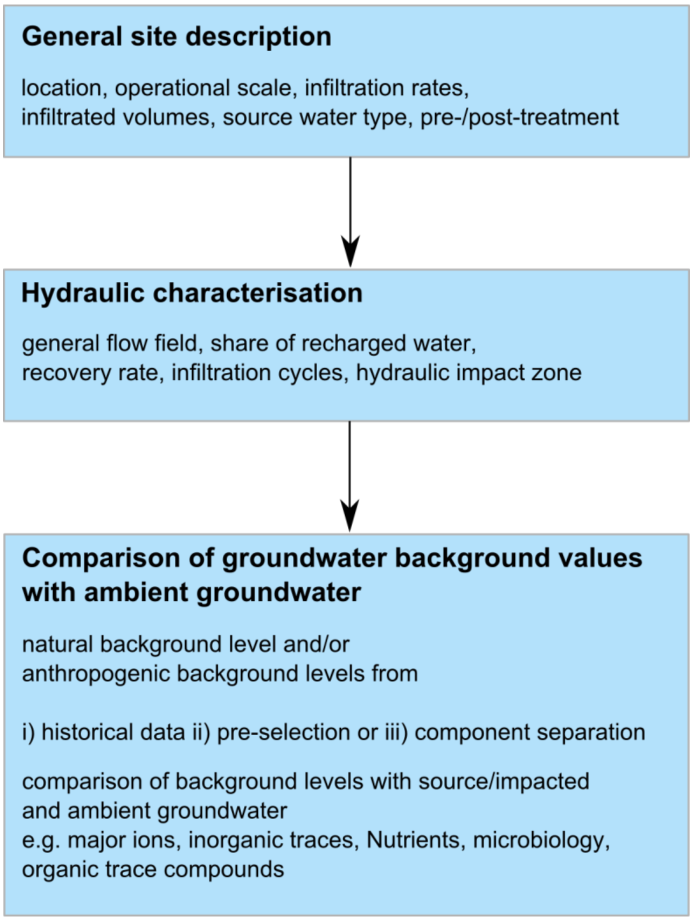

Figure 3-1: Description of approach to assess the impact of MAR on ambient groundwater.

3.1 General considerations on MAR impacts

The infiltration of water into an aquifer results in increased hydraulic pressure at the recharge zone. Depending on source water quality, travel time of infiltrated or injected water to the abstraction well, design of the MAR field site, and the purification capacity of the aquifer breakthrough of contaminants might be possible.

Impact zones of MAR structures can be divided into a) hydraulic impact zone and b) attenuation zone (Figure 2). Different transport processes of compounds during e.g. pond infiltration are exemplary shown in Figure 2.

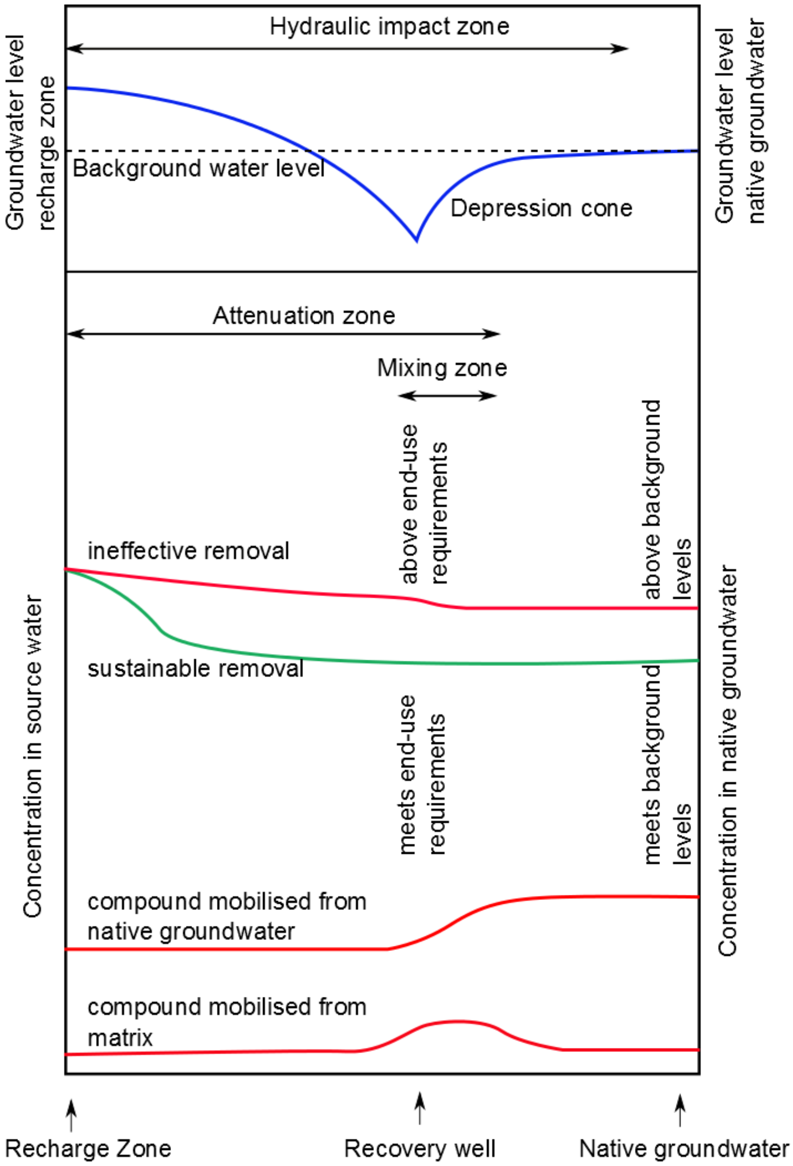

Figure 3-2: **Sketch of hydraulic and attenuation zonation during managed aquifer recharge.**

The hydraulic impact zone is characterized by measurable hydraulic changes derived from the MAR system. The spatial extent and shape of the hydraulic impact zone mainly depends on:

- spatial distribution of hydraulic properties in the aquifer
- ambient hydraulic gradient in the aquifer (simplified to horizontal background groundwater level in Figure 2)
- pumping rates and interferences by pumping from other wells

The impact zonation is elongated in the direction of the ambient groundwater flow, but the spatial extent and shape of the hydraulic impact zone might differ substantially from site to site. In fractured or karstic aquifers the hydraulic impact zonation is more complicated and not transferable from Figure 2. The hydraulic impact zone is usually many times larger than the water-quality impact zone, especially for confined aquifers.

The attenuation zone is the area surrounding the recharge zone where changes of the infiltrated water quality takes place due to natural processes in the aquifer. Depending on the compound and the geochemistry of the aquifer these processes include e.g. straining, degradation, sorption, dissolution/precipitation, inactivation (or die-off), decay and mixing. These natural attenuation processes may vary in time and space within the aquifer, particularly along the flow path from the area of recharge to the recovery well. Most attenuation processes in the subsurface occur at or close to the recharge zone. Part of the attenuation zone is the mixing, where ambient groundwater and the recharged source water mixes. Tracers are commonly used to distinguish between attenuation due to mixing and attenuation due to other reactions. A suitable tracer, or a set of tracers (e.g. chloride, δ18O, δD), occurs in different concentrations in the ambient and the source water and allows to calculate mixing proportions and, in case of time variant tracer concentration also travel times.

While many contaminants get attenuated during subsurface passage to background level or below detection limit, some persistent compounds may get transported to the ambient groundwater or are introduced by the ambient groundwater (Figure 2). Sustainable removal is achieved when the recovered water meets the end-use requirements (e.g. drinking or irrigation water) in the recovery well(s) and the ambient groundwater meets the background levels of the aquifer. Ineffective removal is found when the recovered water exceeds end-use requirements and ambient background concentrations are not met. Apart from ineffective removal of compounds introduced by the MAR activity, another possible release mechanism of contaminants is secondary mobilization from the ambient groundwater or aquifer matrix. An example of contaminant mobilization by MAR activity through changes in the redox environment resulted from the MAR activity is given by Arthur et al. (2003). During Aquifer Storage and Recovery (ASR) testing in Florida (USA) oxygen-rich source water was injected into a confined limestone aquifer. Both source water and ambient groundwater had As concentrations < 10 µg/l, but the concentrations in the recovered water were up to 112 µg/l. Arsenic release was explained by oxidation of arsenic bearing pyrite present in trace concentration of the aquifer (Arthur et al., 2003).

Hydraulic and water quality monitoring is essential to assess the impact of MAR. At least one monitoring well is required to evaluate the impacts on ambient groundwater. This monitoring well should be situated down gradient of the MAR structure beyond the attenuation and hydraulic impact zone. But because of heterogeneities in porous aquifers it is recommended to use more than one monitoring well. In complex flow regimes, such as fractured or karstic aquifers, more monitoring wells are obligatory.

3.2 Assessing the effects of MAR on ambient groundwater resources in Berlin Tegel

3.2.1 Site description and characterisation

The site is located in the northwest of Berlin, where 3 infiltration ponds in the catchment area of Tegel Water Works are surrounded by about 40 production wells (Figure 3). The site is operated by the local water supplier (Berliner Wasserbetriebe). Aquifer recharge started in the late 1950´s and from the 1960´s three infiltration basins have been continuously used for infiltration (Greskowiak et al., 2006; Möller et al., 2011). Surface water from the nearby Tegel Lake is used as source water, pre-treated during summer by filtering through a micro strainer (pore size diameter of 28 µm) to prevent clogging by algae.

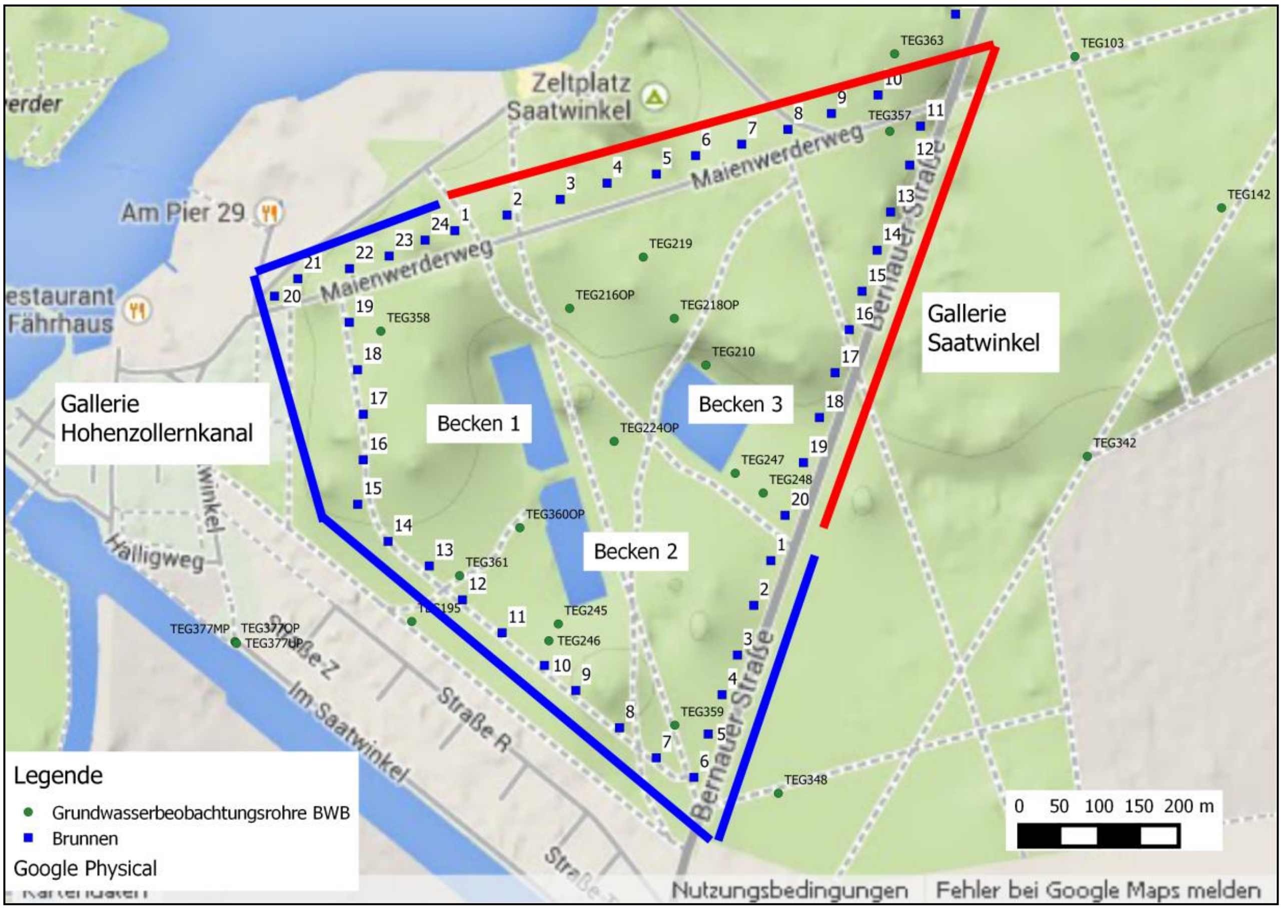

Figure 3-3: Overview of infiltration basins (Becken 1-3) and production wells (Brunnen) at the MAR site in Berlin Tegel with observation wells (Grundwasserbeobachtungsrohre).

The source water is influenced by treated wastewater from a wastewater treatment plant (WWTP) in the north of Berlin. The treatment process at the WWTP involves mechanical and biological treatment and additional chemical phosphate removal, nitrification and denitrification (Massmann et al., 2006). The share of treated wastewater in the infiltration pond is between 17-35 % (mean values from 1993-1998; Ziegler (2001)). The seven main components of the MAR site in Berlin Tegel are summarized in Table 1.

Table 3-1: Brief summary of the seven components of the MAR system in Berlin Tegel

Recharge technique	MAR type
1. Enhanced infiltration	Surface water (lake Tegel) with 17-35 % of treated effluent
2. Pre-treatment	Microstrainer
3. Recharge	3 infiltration basins, approx. 9 Mm3/a
4. Sub-surface	Fluvio-glacial sediments, ≥ 50 d residence time in the subsurface, oxic to Fe/Mn reducing conditions
5. Recovery	Fluvio-glacial sediments, ≥ 50 d residence time in the subsurface, oxic to Fe/Mn reducing conditions
6. Post-treatment	aeration, slow sand filtration
7. End-use	Drinking water

Impacted water quality is derived from samples taken from the monitoring wells situated inside the production well triangle (Figure 3). Ambient groundwater is derived from samples taken from the monitoring wells which are situated outside the production well triangle. The monitoring wells have filter screens at different depths (see Table 2 and Table 3) and the source water was monitored in pond 3.

Table 3-2: Monitoring well ID and filter screen depth of impacted water monitoring wells (location shown in figure 2; data source BWB).

Monitoring well ID	Filter screen depth (mbgl)
TEG357	22.5 – 25.5
TEG218UP	32-34
TEG368UP	12-14
TEG368OP	12-14
TEG364	5-7

mbgl = meter below ground level

Table 3-3: Monitoring well ID and filter screen depth of ambient water monitoring wells (location shown in figure 2; data source BWB).

Monitoring well ID	Filter screen depth (mbgl)
TEG342	18.4-19.4
TEG348	9.55-38.55
TEG332	6.8-15.5

mbgl = meter below ground level

Table 3-4: Classification and overview of MAR techniques

Parameter	Value/desciption
Enhanced storage	Approx. 12.000.000 m^3/year*
Horizontal aquifer passage	Shortest distance: 100 m*
Average infiltration rate	0.5 – 4 m/d*
Average injected or infiltrated volume	approx. 9 Mm3/a for all 3 basins (data from 2000-2010)*
Average abstracted volume	8.98 Mm3/a for Saatwinkel well field + 11.65 Mm3/a for Hohenzollern well field (data from 2006)**
Number of basins	3*
Infiltration area	8460 m2 + 8450 m2 + 8700 m2*
Source water type	Lake water (influenced by treated effluent (17-35%))***
Pre-treatment	Settling + micro strainer, pore dia 28µm *

* Möller et al. (2011) based on data from BWB; ** Möller and Burgschweiger (2008) based on data from BWB; ***Ziegler (2001)

Total annual abstraction from all wells in the well triangle is about 21 Mio. m3/a (Möller and Burgschweiger, 2008) and more than two times higher than infiltrated water volumes (Table 4). Apart from the infiltrated water from the recharge ponds, the well field also receives bank filtrate from the Tegel Lake and Upper Havel River (Pekdeger et al., 2006). From these data it can be concluded that the recovery rate for infiltrated pond water is 100 %.

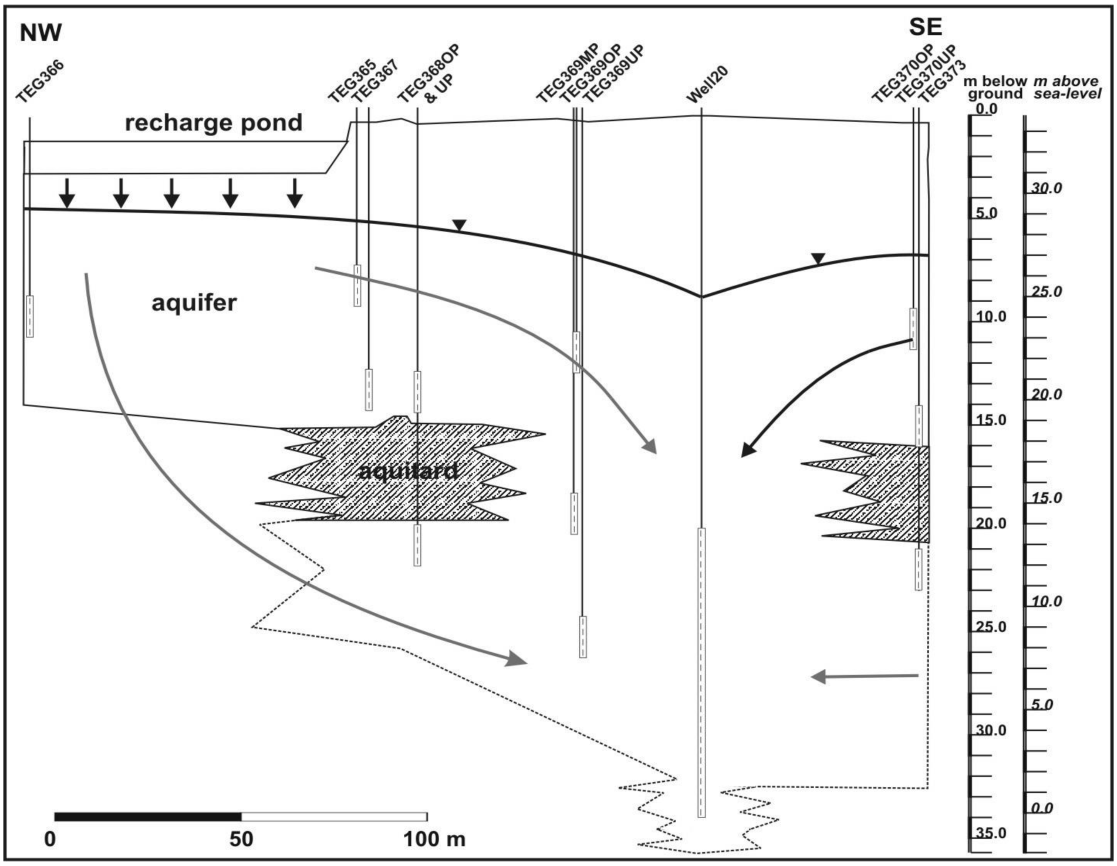

Figure 3-4: Semi schematic cross section between recharge pond, selected impacted water monitoring wells, production well and ambient groundwater wells (Saatwinkel well field) (Pekdeger et al., 2006).

At the recharge site the quaternary sediments consist mainly of fluvial and glacio-fluvial unconsolidated deposits. The aquifer is divided by discontinuously occurring glacial till layers of up to 5m thickness (Figure 4). At the recharge site the upper and lower aquifers are in hydraulic contact to each other (Pekdeger et al., 2006) and form a single hydrogeological unit.

3.2.1.1 General flow field/share of recharged water

In order to determine mixing proportions between source water and ambient groundwater environmental or anthropogenic tracers are often used. The ideal tracer is either of natural or anthropogenic origin, widely distributed in the regarded system, easy to detect and the geochemical behavior is conservative (non-reactive and non-retarding) or at least predictable. Considering a two end-member mixing of the abstracted water between the i) source water and the ii) ambient water the calculation of mixing fraction of recharge water in groundwater or recovered water is:

$$\mathrm{f} = \frac{\mathrm{C_r} - \mathrm{C_g}}{\mathrm{C_i} - \mathrm{C_g}} \times 100 \qquad \text{eq. 1}$$

where:

ƒ = fraction of recharge water present in the well water sample (as percentage)

Cr = tracer concentration in the well water

Cg = tracer concentration in the ambient groundwater

Ci = tracer concentration in the source water

The share of surface water in the individual production wells was determined by Pekdeger et al. (2006) using stable isotopes (δ18O, δD). An example of mixing calculation is shown in Figure 5.

At the recharge pond in Berlin Tegel the production wells in the eastern part of the well triangle are likely to be influenced by ambient groundwater and recharged water from the pond, while the production wells situated at the northern part of the well triangle are a mixture of the Tegel Lake water and the pond water (Pekdeger et al., 2006). Wells in the southern part of the triangle may contain proportions of groundwater which originates from the Havel River located > 1 km west flowing below the Hohenzollernkanal (Pekdeger et al., 2006).

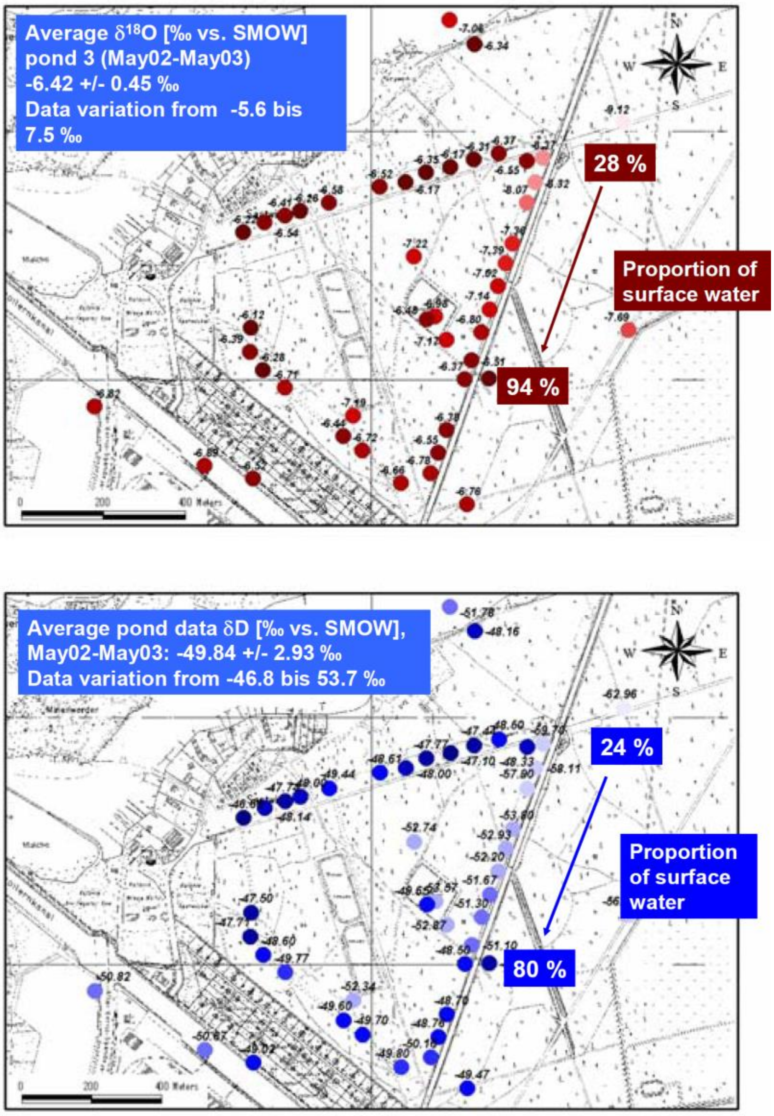

Figure 3-5: **Proportion of recharge water (surface water) in the abstraction wells (modified from Pekdeger (2006)).**

Water from the production wells close to the recharge basins (e.g. well 20) consists on average of 80-90% of recharged water (Pekdeger et al., 2006), while the wells in the northern corner of the well triangle abstract a higher share of ambient groundwater. Groundwater abstraction greatly exceeds the water volumes recharged by the infiltration ponds (see Table 4). Wells in the northern well field receive both water from Tegel Lake and from the recharge ponds. Frequent pumping at the well triangle causes a constant cone of depression, which induces lateral groundwater flow from all sides towards the well triangle. The average travel time from the pond to the production well 20 is given with ~50 days (Pekdeger et al., 2006).

Based on calculation (eq.1) with the two isotopes (δ18O, δD) the average proportion of source water in impacted water for all monitoring wells within the production triangle is approx. 98 - 99 % (Table 5). Therefore, groundwater in the well triangle up to a depth of 34 mbgl (maximal filter depth of impacted water monitoring well; see Table 2) consists virtually only of source water.

Table 3-5: Approximation of the proportion of source water in impacted water based on stable isotopes (given in mean isotope ratios).

Tracer	source water (n=26)	impacted water (n=30)	ambient groundwater (n=10)	Proportion of source water in impacted water (%)
δ18O	-6.25	-6.24	-7.57	99
δD	-49.15	-49.29	-56.49	98

3.2.1.2 Infiltration cycles

An infiltration cycle consists of 4 stages and the hydraulic behavior of the infiltration pond is described in detail by Greskowiak et al. (2005) and illustrated in Figure 6 and summarised in Table 6.

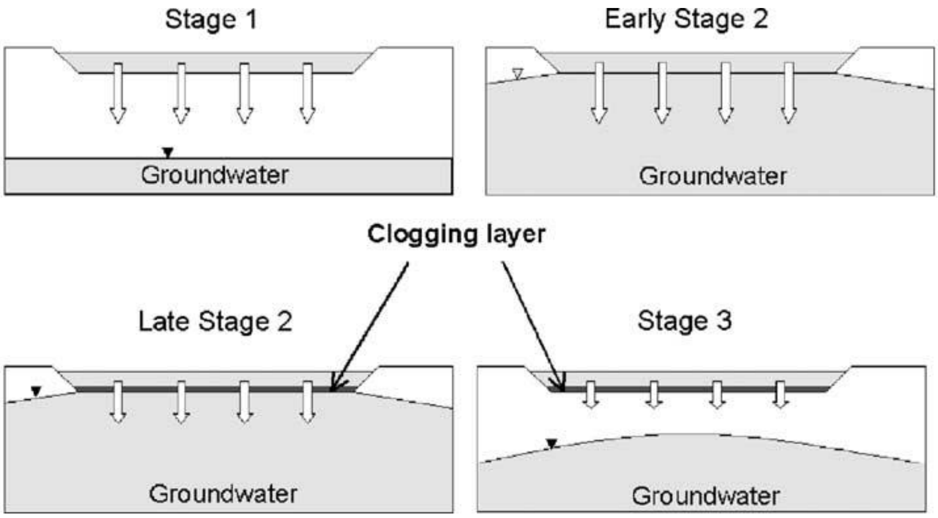

Figure 3-6: **Infiltration cycle at the Berlin Tegel MAR site (modified from Greskowiak et al. (2005).**

Table 3-6: **Brief description of hydraulics during infiltration cycle in Berlin Tegel (summarized from Greskowiak et al. (2005)).**

Stages during infiltration cycle		Description	Approximate duration (days)
Stage 1		steady increase of water saturation until full saturation beneath the pond	10
Stage 2	Early	saturated conditions prevail infiltration rate between 3.5 to 2 m/d	30
	Late	saturated conditions prevail but sharp decrease of infiltration rate to 0.3 m/d	20
Stage 3		unsaturated conditions prevail groundwater table dropped to approximately 5 - 6 m below the pond no recharge during late phase	40

If the infiltration rate for a given basin decreases to 0.3 - 0.5 m/d or at least three times a year the basin will be cleaned (Greskowiak et al., 2005; Möller et al., 2011). Cleaning is initiated by interrupting the inflow to the basin. After a drying period of a few days the clogged sediments from the basin up to a depth of 10 cm will be removed and washed (Greskowiak et al., 2005). After washing the sediments is refilled to the basin and distributed over the whole basin.

3.2.1.3 Hydraulic impact zone

The spatial extent of the hydraulic impact zone can be calculated by the empirical formula according to Sichardt (1928):

$$r = 3000 \times s \times \sqrt{k} \qquad \text{eq. 2}$$

where:

r = radius of the depression cone (m); s = drawdown in the production well (m); k = hydraulic conductivity (m/s) (please note: empirical formula is not unit conform!!!)

The recharge ponds in Berlin Tegel are surrounded by several production wells. The production wells are in distances of 50-100 m to each other and each cone of depression interferes with the neighboring depression cone. The resulting total drawdown in the production well is then used for s. Total drawdown is assumed to be 3-4 m (k = 6.05 × 10-4 m/s) and the hydraulic impact zone is then approx. 220 - 295 m around the well triangle. Ambient groundwater monitoring wells are therefore all situated within the hydraulic impact zone.

3.2.2 Characterization of MAR groundwater quality impacts

3.2.2.1 Hydraulic impact zone

How to distinguish between natural and anthropogenic groundwater?

Basically three methods are available to distinguish between natural and anthropogenic groundwater composition: i) statistical component separation (Kunkel et al., 2004), ii) data pre-selection (Mueller et al., 2006) and iii) historical data analysis (Griffioen et al., 2008).

For the component separation method the measured concentration frequency distribution of a chemical compound is separated in statistical components. The underlying concept is that the observed concentration frequency distribution is a result of the superposition of two components: the natural and the influenced component (Figure 7). Both distribution functions can be determined by statistical expressions (amplitude, median and variance), which are fitted by standard algorithms to the observed distribution function. After calibration, the upper and lower threshold of the respective component is then expressed by confidence intervals (usually 10th and 90th percentile).

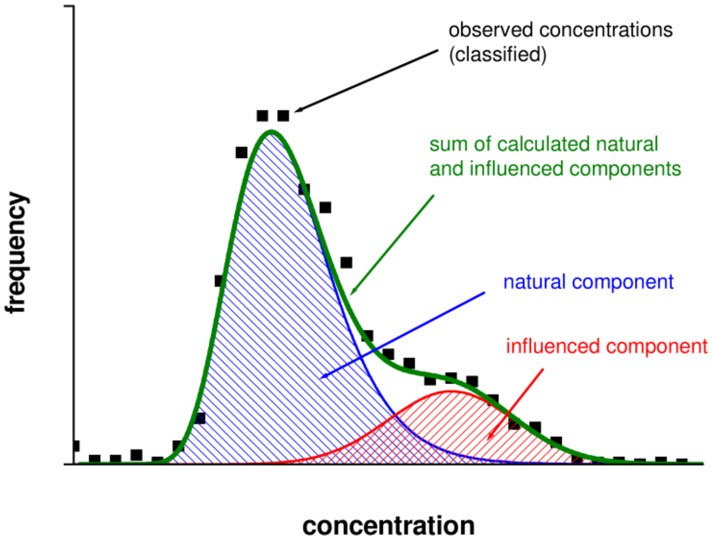

Figure 3-7: Separation of natural and anthropogenic influenced component from observed concentration distribution (Müller et al., 2006).

Müller et al. (2006) discusses pros and cons of this statistical approach and states that this method provides a sound scientific approach, but is not easy to use for non-experts.

The pre-selection method is based on the idea that certain chemical compounds can be used as tracers indicating exclusively anthropogenic influence. When these substances are detected or exceed certain thresholds the groundwater sample is regarded as anthropogenically influenced and excluded. Tracers are e.g. pharmaceuticals and pesticides which are exclusively of anthropogenic origin or tracers which usually occur in very low concentrations (i.e. nitrate, heavy metals). After the selection procedure, the upper and lower threshold of the regarded compound is then expressed by confidence intervals (usually 10 and 90 percentile). In Müller et al. (2006) pros and cons of the pre-selection approach is discussed. The authors state that this approach tends to exclude more samples than necessary. This method was further developed by the EU research project BRIDGE and proposed as the best procedure to obtain natural background levels for groundwater in Europe (Wendland et al., 2008).

The historical data analysis method is based on the idea that hydrochemical data analysed before a certain time (e.g. before World War II) represents near natural groundwater composition and can therefore be considered as natural background level. Historical chemical composition can either be obtained by hydrochemistry analysed many decades ago or by sampling and analysis of several decades old groundwater. Griffioen et al. (2008) argues that the historical data based on “antique” analysis is the most direct method to assess NBL´s. The disadvantages of this method are, amongst others, water conservation errors during sampling for redox sensitive compounds and that analyses are unlikely to be available for many trace elements (Griffioen et al., 2008). Moreover, it cannot be excluded that this “antique” data is in no way influenced by anthropogenic impacts (Griffioen et al., 2008). For a more detailed discussion of advantages and limitations of the different methods we refer to Griffioen et al. (2008).

3.2.2.2 Natural and anthropogenic groundwater in Berlin

In Berlin FUGRO and HYDOR (2002) distinguished between the natural and anthropogenic component in groundwater based on the pre-selection approach. The authors used selection criteria such as high salinity or presence of organic trace compounds to exclude samples. The resulting selection was then classified according to threshold values from the neighboring state of Brandenburg into natural and anthropogenic groundwater types. Threshold values are given for electrical cond., pH, TOC, Ca, Mg, Na, K, NH4, Fe, Mn, Cl, SO4, HCO3, NO3, NO2, PO4, B, Al for hydrostratigraphic units (aquifer wise) in 10th and 90th percentiles. For our study the threshold values (natural and anthropogenic) for the upper, shallow aquifer (Grundwasserleiter GWL 1) were used and compared with the measured concentrations from the MAR site.

A second study from Reinhardt and Hannappel (2003) regionalized eight parameters (electrical conductivity, SO4, Cl, NH4, K, chemical oxygen demand, PO4 and B) for the upper aquifer in Berlin based on a geostatistical interpolation method. After evaluation and omitting unreliable datasets the arithmetic mean of the respective parameter at the respective monitoring well is used for regionalization based on ordinary kriging. The concentration variance to distance relationship was analysed by variograms before regionalization. In this study it was not intended to differentiate between natural and anthropogenic background values and the results must be considered as the anthropogenically influenced background values. Anyhow, the good spatial resolution provides an additional reference for our study.

3.2.3 Comparison of qualitative data from the Berlin Tegel MAR site with natural and anthropogenic background values

Observed concentrations of major ions and physico-chemical parameters are compared with natural and anthropogenic values from FUGRO and HYDOR (2002) by box and whisker plots. The length of the box shows the 25th and the 75th percentile of the respective dataset. The median is indicated by the line in the box and the arithmetic mean is shown as a rectangle. The whisker indicates the 10th and 90th percentile. Minimum and maximum is indicated by small horizontal lines. Data which is used in this report was measured during the NASRI project and covers a time period from 2001 - 2004 (Heberer and Jekel, 2006; Jekel, 2006; Lopez-Pila and Szewzyk, 2006; Pekdeger et al., 2006).

3.2.3.1 Reliability check and pre-treatment

Before the hydrochemical database is used for interpretation a reliability check is performed in order to ensure a robust database. The amount of cations and the amount of anions with consideration of their valences should be balanced. The hydrochemical analysis of the major ions, given in mg/L, were transformed to mmol(eq)/l or meq/l and the ion balance was calculated according to DVWK (1992) :

$$balance\ (\%) = \frac{\Sigma\, cations - \Sigma\, \mathrm{anions}}{0.5\ \times (\Sigma\, cations + \Sigma\, \mathrm{anions})} \times 100 \qquad \text{eq. 3}$$

Ion balances above 10% are considered as not reliable. Figure 8 shows all measured samples for source-, impacted and groundwater. All samples are within the tolerance limits.

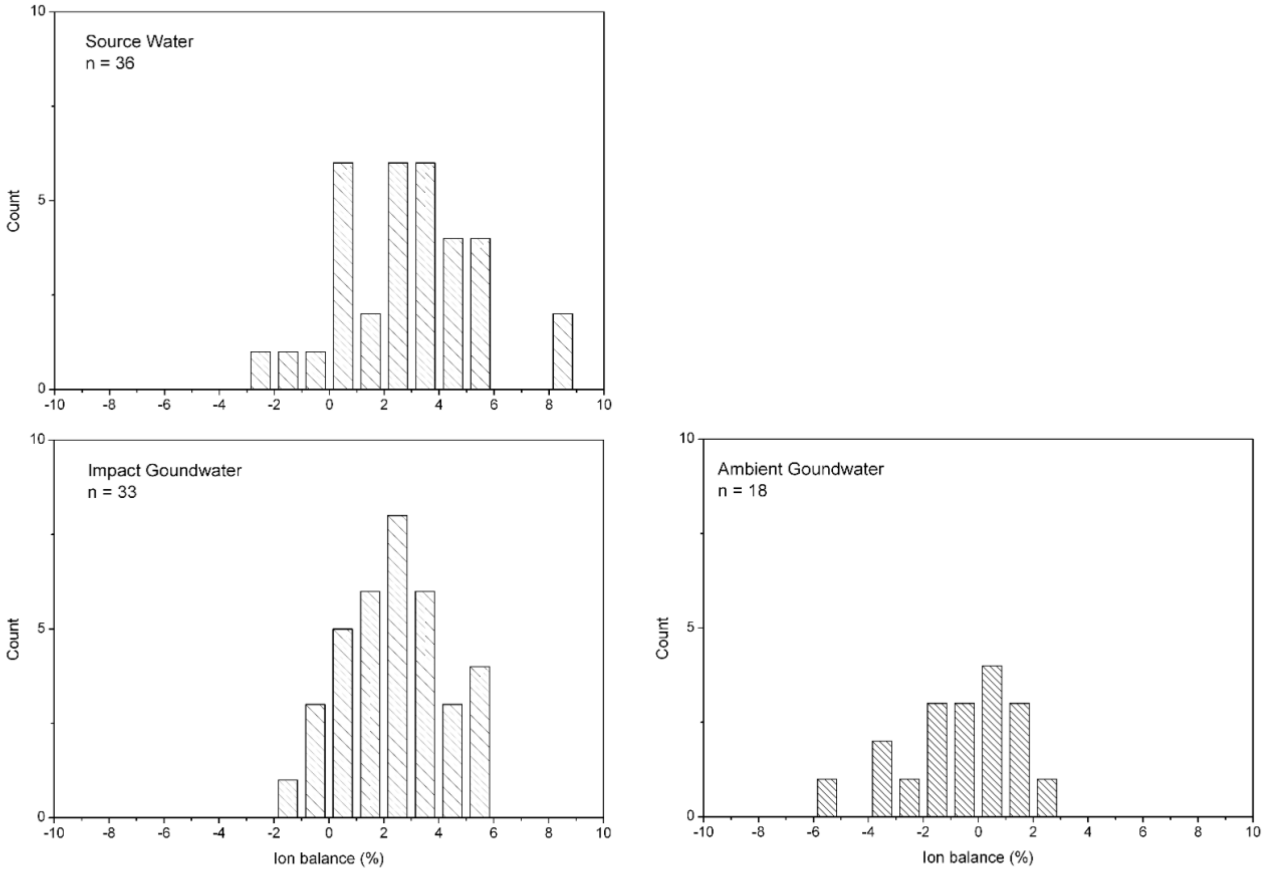

Figure 3-8: Ion balances for source water, impacted water and groundwater.

Measured concentrations below limit of quantification (LOQ) where set to half of the detection limit of the respective parameter whenever LOQ was available.

3.2.3.2 Major ions and physic-chemical measurements

The electrical conductivity of water is a function of the concentration of dissolved ions. It comprises the solute of inorganic salts (principally calcium, magnesium, potassium, sodium, bicarbonates, chlorides and sulfates) and small amounts of organic matter that are dissolved in water (WHO, 2006). In groundwater, the major part of the ions originates from natural sources (solution of salts, water- rock interactions, mixing etc.) or anthropogenic sources like seepage of agricultural runoff or urban wastewater.

Reinhardt and Hannappel (2003) discusses the variation of electrical conductivity in Berlin groundwater. The authors state that according to Schleyer and Kerndorff (1992) electrical conductivities > 840 µS/cm are considered as anthropogenically influenced. However, Kunkel et al. (2003) considers values up to 1000 µS/cm and FUGRO and HYDOR (2002) values between 352 to 608 µS/cm as natural background values. The spatial distribution of the electrical conductivity in Berlin shows high values in the densely populated city center (≥ 1000 µS/cm) and low values (≤ 750 µS/cm) in forested areas (e.g. Tegel forest). The influenced background electrical conductivity of groundwater in the area of recharge is in the range of 750-1000 µS/cm (Reinhardt and Hannappel, 2003).

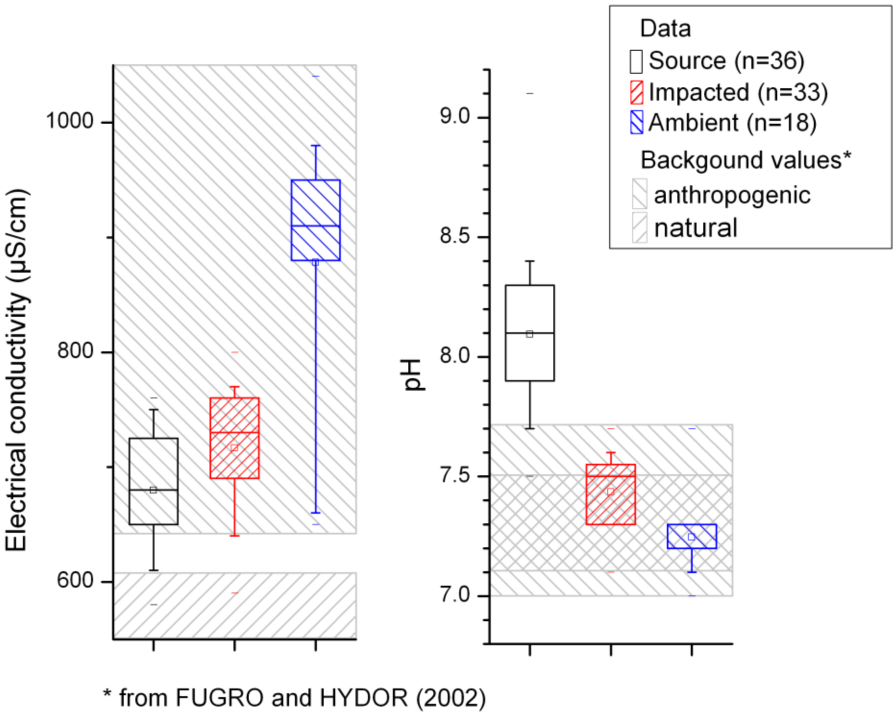

Figure 3-9: plots of electrical conductivity and pH from source, impacted and ambient groundwater compared with anthropogenic and natural background values. .

At the MAR site source water (median = 680 µS/cm) and impacted water (median = 730 µS/cm) is substantially lower mineralized than the ambient groundwater (median = 920 µS/cm) and impacted water shows higher electrical conductivity than source water (Figure 9). This increase of mineralization is commonly observed during MAR, since the recharge is associated with mineral dissolution. Median ambient groundwater mineralization is within the range of the anthropogenic background values from FUGRO and HYDOR (2002). However, considering the fact that forested areas in Berlin typically show values ≤ 750 µS/cm (Reinhardt and Hannappel, 2003), it cannot be excluded that the mineralization of ambient groundwater due to MAR activities in Berlin Tegel was increased (e.g. by mineral dissolution) in the hydraulic impact zone.

The pH decreases from source water (median = 8.1) to the impacted groundwater (median = 7.5) and further to the ambient groundwater (median = 7.2) as shown in Figure 9. Observed range in pH values of the ambient groundwater is within the proposed natural background values.

Major anions of source, impacted and ambient water are displayed by their concentration (mg/l) in Figure 10. In most of the cases source- and impacted water on the one hand and ambient groundwater on the other hand shows distinctly different ion concentration. Compared to source and impacted water the ambient groundwater shows higher concentrations of HCO3, SO4 and Ca. Cl, K and Na reach lower concentrations in the ambient groundwater, whereas Mg concentrations are similar.

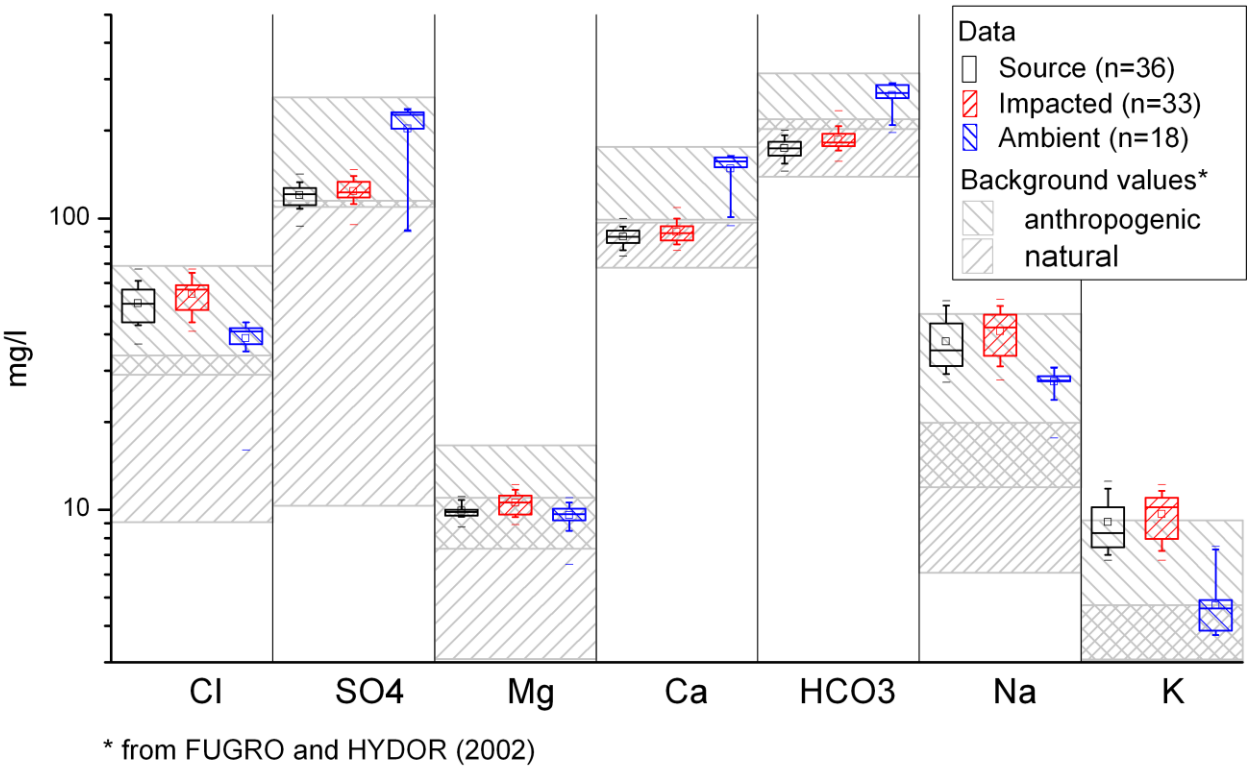

Figure 3-10: Box plots of major ions (Cl, SO4, Mg, Ca, HCO3, Na, K) from source, impacted and ambient groundwater compared to anthropogenic and natural background values.

Chloride concentrations in the range of 14-95 mg/l are considered to be general anthropogenic background values in Berlin groundwater (Reinhardt and Hannappel, 2003). At the area of recharge background values for chloride are in the range of 20-50 mg/l (Reinhardt and Hannappel, 2003). Chloride concentration in source water (median = 51 mg/l), impacted water (median = 57 mg/l) and ambient groundwater (median = 41 mg/l) are elevated compared to the natural background values, but within anthropogenic values.

Reinhardt and Hannappel (2003) showed that anthropogenic background values for sulfate concentrations typically found in Berlin groundwater are rarely below 100 mg/l. The authors argue that the sulfate is originated from diffusive sources of gypsum. The gypsum is a testimony of the destruction of buildings during the Second World War. Huge areas of the city were destroyed and during the reconstruction of the city the war debris was dumped wherever it was possible. Hence, high concentrations of sulfate (> 360 mg/l) are found nowadays in the densely populated city center (Reinhardt and Hannappel, 2003). At the recharge site background concentration are in the range of 50-120 mg/l (Reinhardt and Hannappel, 2003). Measured concentrations in source water (median = 121 mg/l), impacted water (median = 123 mg/l) and ambient groundwater (median = 227 mg/l) are within anthropogenic background values according to FUGRO and HYDOR (2002). However, the median concentration in the ambient groundwater of 227 mg/l appears to be strongly elevated compared to local anthropogenic background values according to Reinhardt and Hannappel (2003).

Ranges for natural and anthropogenic magnesium background concentrations show a wide overlapping zone (Figure 10). Magnesium concentration in source, impact and ambient groundwater are similar and plot within the ranges of the natural and anthropogenic background concentrations.

Calcium and HCO3 concentrations in the ambient groundwater are elevated compared to source and impacted water, but within ranges of anthropogenic background values.

Sodium concentrations in source and impacted water are elevated compared to the ambient groundwater but are within the anthropogenic background values and above natural background. The high proportion of treated effluent increases the sodium concentration in source water (Massmann et al., 2004).

General anthropogenic background concentrations of potassium in Berlin groundwater is given with 3-4 mg/l, while local background values are between 6-12 mg/l (Reinhardt and Hannappel, 2003). Both source- and impacted water are within the concentration ranges of local background values according to Reinhardt and Hannappel (2003), but exceed natural background values according to FUGRO and HYDOR (2002). Median concentration of ambient groundwater (4.5 mg/l) is similar to natural background values.

Except for K and Mg all other major ion concentrations in the ambient groundwater exceed proposed natural background levels, but are within anthropogenic values typically found in Berlin´s shallow groundwater. Still, especially SO4, Ca and HCO3 are at the upper edge of anthropogenic threshold values and may indicate an impact of MAR activities on ambient groundwater. As shown above, monitoring wells for the ambient groundwater are all situated within the hydraulic impact zone of the MAR site. Groundwater table fluctuations due to pumping introduce oxygen to the hydraulically impacted zone and the entrapped air is dissolved subsequently during stages of groundwater table rise and thereby oxidizing finely distributed Fe-sulphides commonly present in the sediments (Pekdeger et al., 2006). Oxidation releases acidity and would lead to additional calcite dissolution. These processes may lead to the observed lowered pH in the ambient groundwater and the elevated SO4, Ca and HCO3 concentrations.

3.2.3.3 Inorganic trace elements

Inorganic trace elements (Fetot, Mn, B) are displayed by their concentration (mg/l) in Figure 11 and compared to background values. The median concentrations of Fe and Mn in the source and impacted water are generally lower than in the ambient groundwater. Greskowiak et al. (2005) discusses the spatial and temporal changes in redox zonation at the site and states that the redox zonation at the recharge pond(s) is controlled by the transient hydraulic behavior of the system. Redox conditions below the infiltration pond are dominated by oxic conditions, but sub-oxic conditions develop especially in deeper part of the aquifer reaching Fe-reducing conditions (Greskowiak et al., 2005). The measured Mn/Fe concentrations in the impacted water are low and mostly below detection limit (Fe = 0.03 mg/l and Mn 0.005 mg/l). This is explained by rapid precipitation of amorphous Fe(OH)3 (Greskowiak et al., 2005). In the ambient groundwater Fe and Mn concentrations are elevated but within the natural ranges.

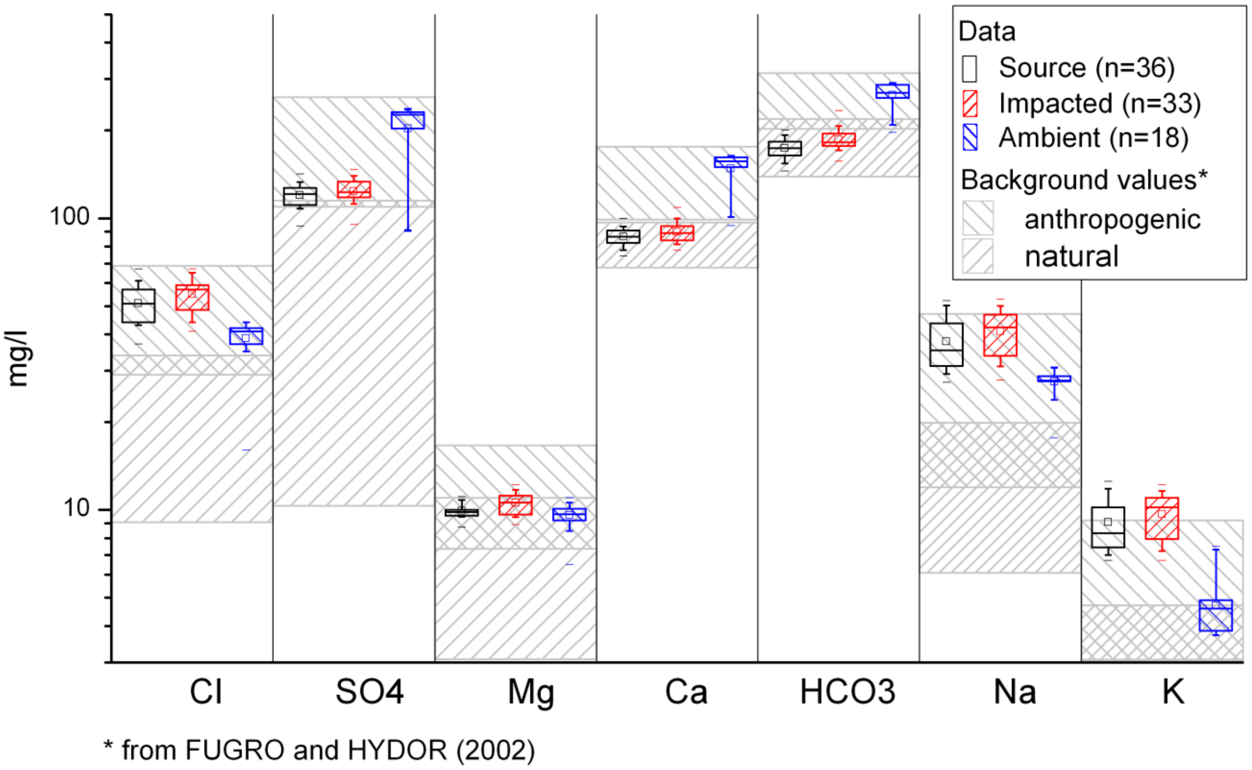

Figure 3-11: Box plots of inorganic trace elements (Fetot, Mn, B) from source, impact and ambient groundwater compared with anthropogenic and natural background values.

Boron is commonly used as a washing powder additive, not eliminated completely during wastewater treatment (Massmann et al., 2004) and used at the site as a tracer substance to identify mixing processes (Wiese et al., 2011). Boron concentrations in source, impacted and ambient groundwater are similar and within anthropogenic background values.

3.2.3.4 Nutrients

Data of NO3, NH4 and TOC for source water, impact- and ambient groundwater is shown in Figure 12. As for DOC no background values exist, measured PO4 concentrations are not available and NO2 was never detected, these parameters are therefore not shown.

When NH4 occurs in high concentrations in the water cycle, it is usually an indicator for untreated sewage, agricultural runoff or landfill leakage. It is only measured in anaerobic water because in the presence of oxygen it is converted to nitrite (NO2) and in a second step to nitrate (NO3) by microbiological oxidation (nitrification). The observed concentrations of N-species (NO3, NH4) at the MAR site are generally low. Nitrate (NO3) is elevated in source- and impacted water compared to ambient groundwater. The highest concentrations of NO3 can be found in the impacted water. Measured NO3 concentrations in the ambient groundwater are within the ranges of natural background values. NH4 is virtually not present in source water (median = 0.09 mg/l) and impacted water (median 0.12 mg/l, but with very low number of measurements n=3). Only in the ambient groundwater elevated median concentration of 0.66 mg/l can be observed, but are in the range of anthropogenic background values.

TOC is highest in source water (median = 7.7 mg/l) and lowest in impacted water (median = 5 mg/l). Measured DOC concentrations (not shown here!) are very similar to measured TOC, but slightly lower. A decrease of TOC in the source water compared to the impacted water is commonly observed during MAR. The biodegradable proportion of organic carbon is consumed by microorganisms, coupled to the reduction of terminal electron acceptors, such as O2, NO3, Mn, Fe.

Median concentration of measured TOC in source and ambient groundwater exceeds natural as well as anthropogenic background values, only the impacted water is within the anthropogenic background

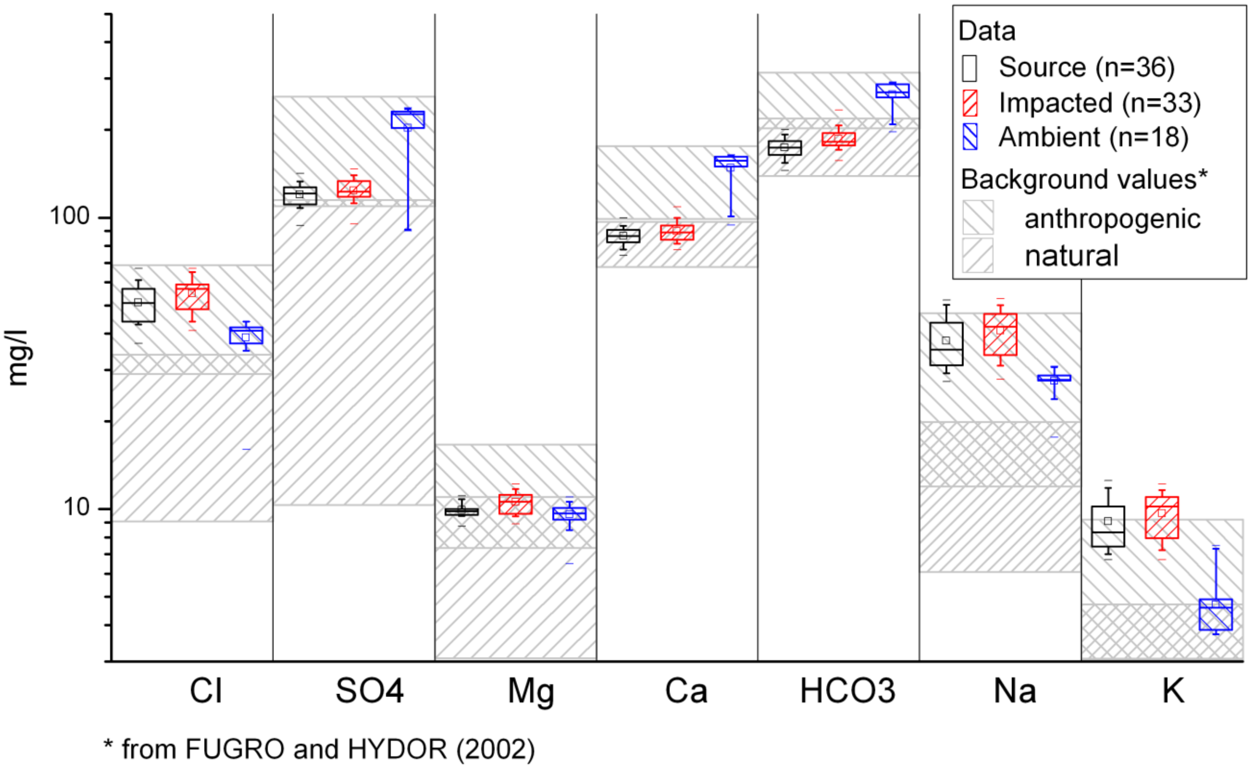

Figure 3-12: Box plots of nutrients in source water, impacted- and ambient groundwater compared with anthropogenic and natural background values.

3.2.3.5 Microbiology

The indicator microorganisms, Escherichia coli, intestinal enterococci, and coliphages measured in the source water, impacted water and in the ambient groundwater are shown in Table 7. Coliphages were found in the source water in concentrations between 2 and 26 pfu/100 ml, but not in the ambient groundwater samples. Concentrations of intestinal enterococci in pond water varied between 1 and 5 cfu/100ml and were not detected in ambient groundwater samples. E.coli was detected in the source water in concentrations up to 44 cfu/100 ml (average 13 cfu/100 ml) and was also found in the ambient groundwater but not in the impacted water.

Table 3-7: **Occurrence of somatic coliphages (pfu/100 ml), intestinal enterococci (cfu/100ml), E. coli (cfu/100 ml) in source, impacted and ambient groundwater samples (average concentration).**

Microoganism	unit	Source water	Impacted water**	Ambient groundwater
Somatic coliphages*	pfu/100 ml	11 (n=5)	<1 (n=10)	< 1 (n=5)
Intestinal Enterococci*	cfu/100 ml	2 (n=5)	<1 (n=10)	<1 (n=5)
E.Coli*	cfu/100 ml	13 (n=5)	2.2 (n=10)	10 (n=5)

*data from Lopez-Pila et al. (2011), detection limit: 1 pfu/100 ml; for colony counts 1 cfu/ml; **samples taken from shallow monitoring well TEG365 and TEG366, please note: monitoring wells not shown in figure 2

The results of the microbiological investigations indicate a comparably high hygienic quality of the source water at the recharge pond in Berlin-Tegel (Lopez-Pila et al., 2011). However, the authors state that during sampling secondary contamination, e.g. through not sterilized sampling equipment, cannot be ruled out completely and the source of the E.coli detection in the ambient groundwater remained unclear (Lopez-Pila et al., 2011).

Legislation of some countries with MAR systems assumes that an underground passage lasting, depending on the country, around 50 days will be free of pathogens (DVGW, 2006). Furthermore, assuming that the detection of E.coli in the ambient groundwater was caused by secondary contamination during sampling and the high recovery rate of infiltrated water by the surrounding production wells, it can be concluded that microbial contamination of the ambient groundwater by the MAR activities is very unlikely. However, considering the low frequency of measurements and low number of organisms it is recommended to improve the baseline data.

3.2.3.6 Organic trace compounds

Massmann et al. (2006) investigated the fate and transport of a wide range of organic trace compounds during bank filtration in Berlin. The authors state that “WWTPs (Wastewater treatment plants) receive a large spectrum of organic contaminants which are partly eliminated during treatment (Heberer, 2002a; Ternes, 1998), but several persistent organic contaminants are not removed. Adsorbable organic halogens (AOX) are, for example, present in the lake (Grünheid et al., 2005; Ziegler et al., 2002). Concentrations of anthropogenic Gadolinium (Gd), which is brought in as a contrast agent (Gd-DTPA), are strongly elevated (Bau and Dulski, 1996; Knappe et al., 2005). A number of pharmaceutically active compounds (PhACs) such as clofibric acid, diclofenac, ibuprofen, phenazone, propyphenazone, primidone and carbamazepine are not eliminated completely during the WW treatment process and have been detected in the surface water (Heberer, 2002a; Heberer et al., 2004; Reddersen et al., 2002; Zühlke, 2004).“

Pekdeger et al. (2006) described the different sources of organic trace compounds in the area of the recharge ponds. The authors state that: “While highest phenazone and AMDOPH concentrations are found in the south-west, highest propyphenazone (analgesic/anti-inflammatory) concentrations are found in the south-west and in the north, towards Lake Tegel. The phenazone-type pharmaceuticals and related substances originate from the surface water, where their presence is caused by their discharge from WWTP (Heberer, 2002a) or from former production spills of a pharmaceutical plant near Oranienburg on the Upper Havel, which produced phenazone-type pharmaceuticals. Reddersen et al. (2002) suspected that spills of the plant released into the environment in the past, when regulations were less strict, are the cause of some of today’s findings of PhAC residues. Because of the pharmaceutical plant, phenazone and dimethylaminophenazone (not detected) concentrations in the surface water of the Upper Havel were probably considerably higher in the past decades than they are today (exact values are not known). In addition, the production of dimethylaminophenazone was stopped in 1978 (Reddersen et al., 2002). Therefore, the high concentrations of phenazone and AMDOPH in the south-west indicate that the groundwater is probably older bank filtrate (similar to findings in greater depth at the bank filtration transects, where high phenazone and AMDOPH concentrations always corresponded to an older age of the bank filtrate). It infiltrated from the Upper Havel 1-2 km further west, passed the industrial contamination sites (thereby accumulating As, MTBE etc.) and is now abstracted by the production wells with a considerable time lag of a few years to a few decades. In addition, it appears that the share of “older” BF containing phenazone and, in particular, AMDOPH is getting larger with depth at all investigated sites (Figure 13).”

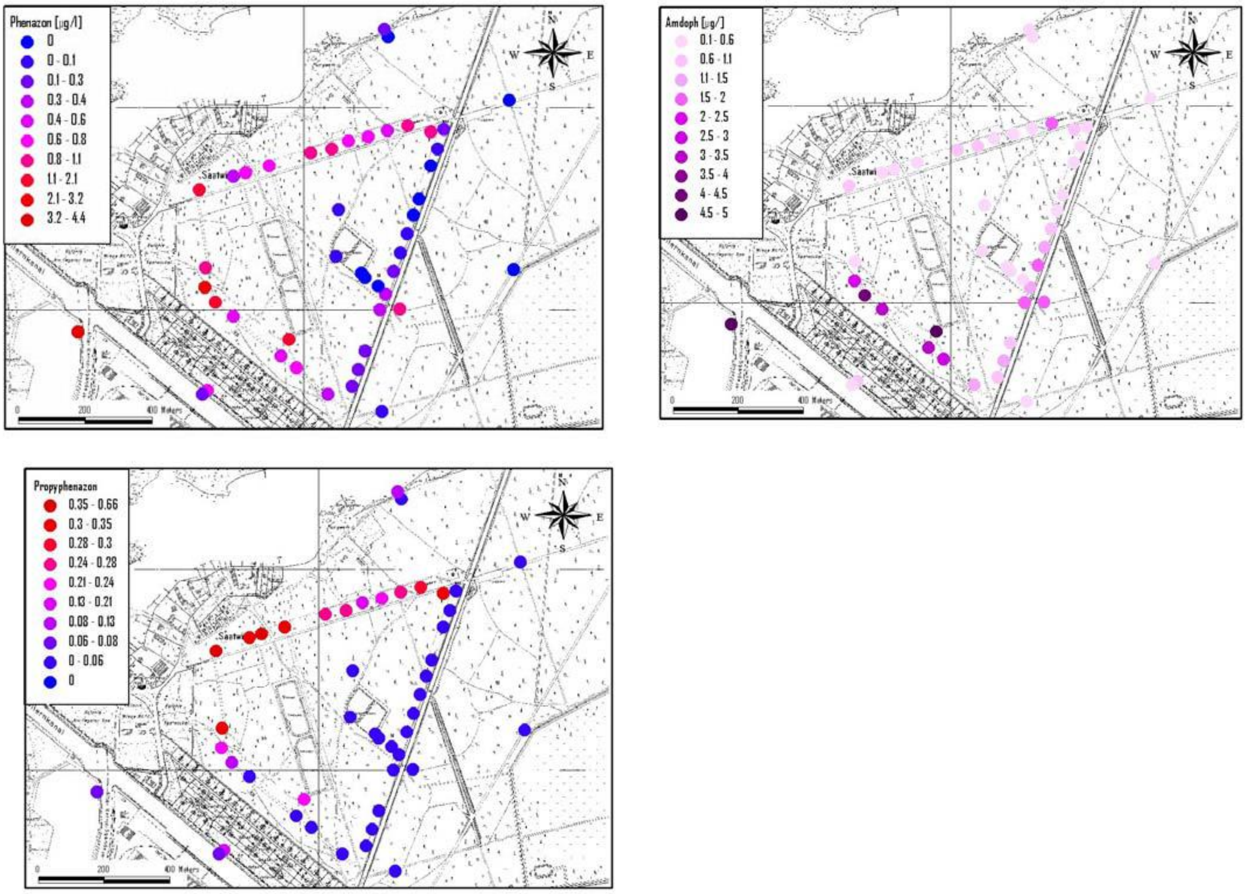

Figure 3-13: Spatial disctribution of Phenazone-type pharmaceuticals and residues phenazone, AMDOPH & propyphenazone (Pekdeger et al., 2006).

The authors summarized the main input paths for contaminants and water constituents as illustrated in Figure 13.

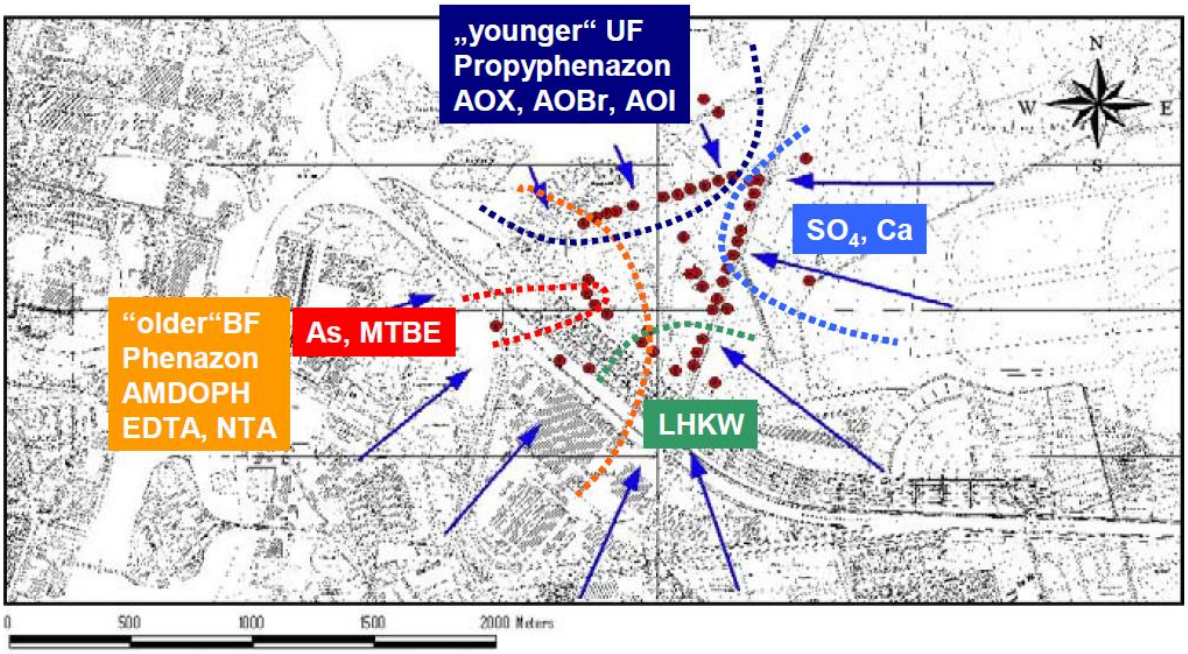

Figure 3-14: **Major input paths for various water constituents in the area of the recharge ponds (Pekdeger et al., 2006).**

Consequently, organic trace compounds are introduced by source and ambient groundwater to the MAR site in Berlin-Tegel. During the DEMEAU project ten priority substances were identified. The selection is based on the following criteria:

- Commonly found in wastewater / drinking water supplies
- Environmental relevance
- Broad spectrum of chemical and physical properties
- Covering a wide range of elimination potential
- Existence of analytical methods

Out of these substances only for Carbamazepine, Phenazone, Bezafibrate, Primidone and Diclofenac data was available. Additionally, AMDOPH was selected because of the local importance.

Carbamazepine is a drug primarily used for treatment of epilepsy and enters the environment through incomplete removal in WWTPs (Heberer, 2002b). Carbamazepine occurs in the Berlin´s surface water with maximal measured concentration of 1.87 µg/l (Adam, 2010). The measured maximum concentration in the source water was observed to reach almost 1 µg/l. In the ambient groundwater carbamazepine is mostly below the limit of quantification (LOQ), but found two times above the LOQ. Removal of Carbamazepine during subsurface passage is considered to be limited and seen as relatively persistent (Massmann et al., 2006). Consequently, Carbamazepine is introduced by source water, removed only marginally during subsurface passage and abstracted by production wells (further concentration decrease by dilution).

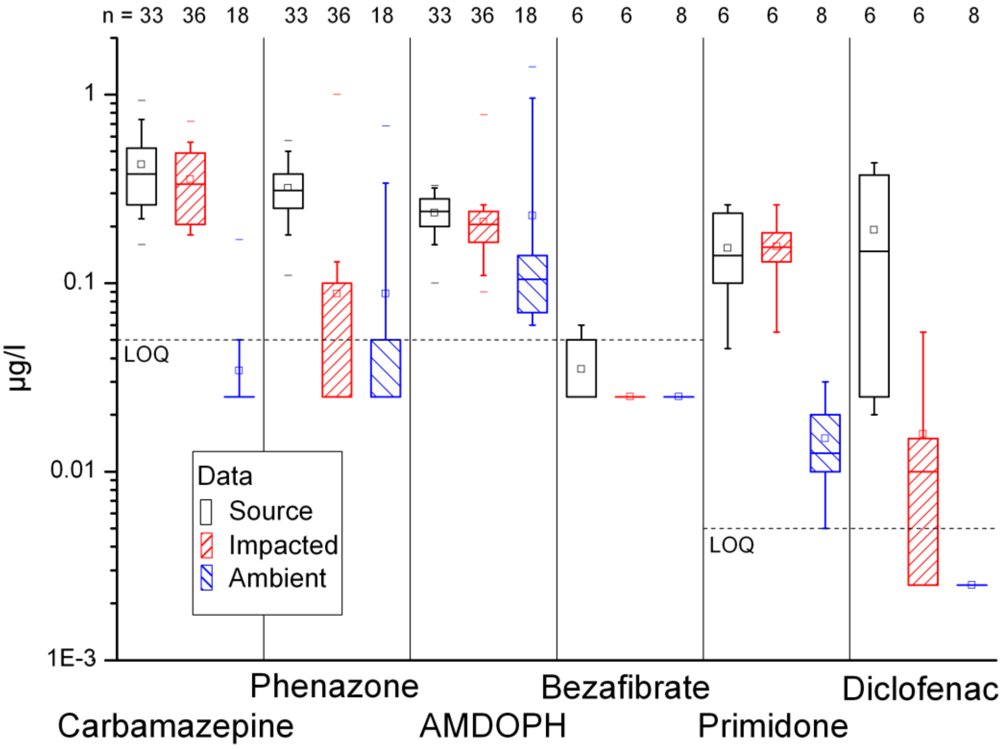

Figure 3-15: Box plots of Carbamazepine, Phenazone, AMDOPH, Bezafibrate, Primidone and Diclofenac (LOQ = limit of quantification).

The fate of the pharmaceutical residue Phenazone was investigated by Greskowiak et al. (2006) in detail at the MAR site in Berlin Tegel. The authors found that Phenazone breakthrough at monitoring wells within the well triangle were governed by warmer temperatures when anaerobic redox conditions developed. In winter, when aerobic conditions prevail, no breakthrough was observed. Hence, at the recharge site Phenazone is not completely removed during subsurface passage (Figure 15). In the ambient groundwater Phenazone is mostly below the LOQ, but detections above LOQ are explained to be originated from production spills of a pharmaceutical plant at the Upper Havel decades ago (Pekdeger et al., 2006).

The metabolite AMDOPH is measured in the Berlin surface water with maximum concentration of 5.3 µg/l (Adam, 2010). In Berlin drinking water it was measured with 3 µg/l (Reddersen et al., 2002). AMDOPH concentrations in ambient groundwater concentration show large variations and are also associated to be originating from production spills of a pharmaceutical plant at the Upper Havel River (Pekdeger et al., 2006).

Bezafibrate is detected only in source water, but mostly below LOQ. Impacted water and ambient groundwater is not affected by Bezafibrate.

The antiepileptic primidone occurs ubiquitarily in the Berlin water cycle and was measured in concentrations of up to 1.55 µg/l in Berlin´s surface water (Adam, 2010). At the recharge site primidone is detected in the impacted water in similar median concentrations compared to source water. Ambient groundwater concentrations are lower, but above LOQ. Sources of primidone in ambient groundwater are unknown.

Diclofenac is occurring at maximum concentrations of 2.36 µg/L in Berlin´s surface water (Adam, 2010). In the ambient groundwater at the Tegel site concentrations are always below LOQ. Compared to source water concentrations the impacted water concentrations are decreased and show a substantial removal during underground passage.

Among the selected organic trace compounds primidone, phenazone and phenazone-type metabolite AMDOPH are of relevance because of elevated concentration. Phenazone and AMDOPH are suspected to be originated from the Upper Havel River and transported as bankfiltrate to the MAR site. Primidone was found to be persistent during several studies (Heberer, 2002a; Heberer et al., 2004) and is also detected in the ambient groundwater.

3.3 Summary

This report assesses the impact of MAR on ambient groundwater in terms of hydraulic and water quality influences. Impact zones of MAR structures were divided into a) hydraulic impact zone and b) attenuation zone. Different transport processes of compounds during e.g. pond infiltration are schematically shown and explained. Within this report water quality data from one MAR site in Berlin Tegel are compared with natural and anthropogenically influenced background values in the aquifer. Common approaches to determine background values in groundwater are introduced and described. At the MAR site in Berlin-Tegel water quality parameter were observed in the infiltration pond (source water), in observation wells between the ponds and the production wells (impacted groundwater) and beyond the recovery wells (ambient groundwater). After hydraulic characterisation of the MAR site observed concentrations of major ions, physico-chemical parameters, inorganic trace compounds, nutrients and organic trace compounds were compared with natural and anthropogenic background values (if any) by statistical plots.

The recharge site in Berlin-Tegel is characterized by highly transient infiltration rates between 0.3-4 m/d, relatively short travel times of recharge water to the production well (~50 days) and seasonally changing redox conditions (oxic to Mn/Fe reducing) during subsurface passage. The share of recharged water in the production wells varies between 20 – 90 % and the recovery rate of infiltrated water is considered to be 100 %. The hydraulic impact zone was approximated to be 220 - 295 m around the production wells. Distance from the infiltration pond(s) to production wells varies between 100 – 400 m.

Source water (=pre-treated surface water from Lake Tegel) and ambient groundwater differ substantially in their major hydrochemical composition. Ambient groundwater is elevated in HCO3, SO4 and Ca and depleted in Cl compared to source water. Except for K and Mg all other major ion concentrations in the ambient groundwater exceed proposed natural background levels, but are within anthropogenic values typically found in Berlin´s shallow groundwater. Especially SO4, Ca and HCO3 are at the upper edge of the range of anthropogenic threshold values and may indicate an impact of MAR activities on ambient groundwater. Groundwater table fluctuations due to pumping introduce oxygen to the hydraulically impacted zone and the entrapped air is dissolved subsequently during stages of groundwater table rise, thereby oxidizing Fe-sulphides commonly present in the sediments (Pekdeger et al., 2006). Oxidation releases acidity and would lead to additional calcite dissolution. These processes may lead to the observed lowered pH in the ambient groundwater and the elevated SO4, Ca and HCO3.

In the ambient groundwater Fe and Mn concentrations are elevated but within the natural groundwater ranges. Boron concentrations in source, impacted and ambient groundwater are similar and within anthropogenic background values.

The observed concentrations of N-species (NO3, NH4) at the MAR site are generally low. Nitrate (NO3) is elevated in source- and impacted water compared to ambient groundwater. Median concentration of measured TOC in source and ambient groundwater exceeds natural as well as anthropogenic background values, only the impacted water is within the background values.

Microbial data suggest that microbial contamination of the ambient groundwater by the MAR activities is very unlikely. However, considering the low frequency of measurements and low number of organisms it is recommended to improve the baseline data.

Among the selected organic trace compounds carbamazepine, phenazone, phenazone-type metabolite AMDOPH and primidone are of relevance, as they are not removed completely during subsurface passage in the impacted groundwater. Phenazone and AMDOPH are suspected to be originated from the Upper Havel River, transported as bankfiltrate to the MAR site. Primidone was found to be persistent during several studies (Heberer, 2002a; Heberer et al., 2004) and is also detected in ambient groundwater. Of the selected trace compounds five were present in source water well above LOQ. Three of these showed little degradation during infiltration (carbamazepine, primidone, AMDOPH), while two (phenazone, diclofenac) showed substantial reduction. Bezafibrate is detected only in source water, but mostly below LOQ. Impacted water and ambient groundwater is not affected by bezafibrate.

This report shows that the MAR site in Berlin-Tegel shows substantial removal of many compounds (please note that total removal observed in the recovery well is higher). Compounds which were found to be persistent are abstracted by the production wells and a water quality impact of the infiltrated source water beyond the attenuation zone is unlikely. However, mobilization of SO4 and Fe by the MAR activity in the hydraulic impact zone cannot be excluded. Special attention must be paid to contaminants transported from the ambient groundwater to the production wells through various sources.

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4 Two approaches to estimate removal efficiency of emerging substances in MAR systems – Site application at The Hague, The Netherlands

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4.1 Introduction

4.1.1 Background

In the Netherlands, managed aquifer recharge (MAR) systems have been used for water supply for more than 70 years and currently account for up to 20% of the total water supply (Stuyfzand 2011). With MAR residence times ranging from 28 days to 70 days, the recharged water has substituted the natural background groundwater between the infiltration area and the abstraction area. It has been repeatedly demonstrated that through the subsurface passage of the infiltrated raw water quality is significantly improved by means of filtration, sorption and biodegradation (Bakker and Stuyfzand 1993; Stuyfzand 1993; Schmidt, Lange et al., 2007; Stuyfzand, Kortleve et al., 2007; Stuyfzand 2011). In addition, the quality improvement in MAR systems may be further supported through extensive pretreatment systems and controls (Lekkerkerker et al.2001; Stuyfzand et al., 2007; Lekkerkerker et al., 2009; Scheideler et al 2012). In particular, one of the challenges that MAR systems are facing is the removal of emerging organic substances (EOS) introduced in infiltrating water. Most of the MAR systems are overall effective in attenuating many of the unregulated trace organic chemicals or EOS (Hoppe-Jones et al., 2010). There are however some poorly degradable micro pollutants or pollutants that are only degraded under specific conditions. In this report an overview of the percentage of removal of micro pollutants is performed in two types of MAR systems in the Netherlands. These MAR systems are located in a dune area close to The Hague where pretreated river Meuse water is artificially recharged via infiltration basins (basin artificial recharge, BAR) since and deep wells (aquifer storage and recovery, ASTR).

In the context of the FP7 DEMEAU project about technologies that tackle emerging organic pollutants (EOCs) in water, the identification of the optimal conditions to face EOC removal in MAR systems is one of the key factors. The present study aims to determine the effective removal of EOCs in the two areas of study.

4.1.2 Objectives and work

To quantify long-term effect of MAR onto groundwater resources, the approach developed in the DEMEAU WP 1.2.1 (Vilanova et al., 2014) is applied on two Dutch cases. One of the main impacts here considered is the infiltration of emerging pollutants. This approach links the removal of certain emerging pollutants to specific key parameters of the MAR system itself, resulting in a suit of variables that can be site-dependent, such as redox conditions and the travel times in the MAR system in particular.

In order to relate the degree of removal per organic contaminant to the key parameters of the system, first the hydraulic and hydrochemical characterization of the system is performed and secondly the behavior of the contaminants during the passage through the soil is analyzed.

The site characterization includes the identification of the possible key parameters in the removal of emerging organic substances such as aquifer type, redox conditions, residence time and water types.

Quantifying removal of EOCs under field conditions is hindered by several factors such as scatter of the observed concentrations (temporal heterogeneity of the available data), mixing of different waters, threshold values (concentrations below which there is no removal), different analytical limits of quantification (LOQ) and site specifics like the travel times or the redox conditions (Wiese et al., 2011).Two approaches are here described: the first one studies the differences between the averaged concentrations of long time series in the infiltrating and abstracted water. Also a different approach is developed in this study that consists of finding relationships in the infiltrated water between the different EOS per sample. The variation in these relationships that develop during passage gives information on the processes that are affecting those EOS: conservation, dilution or degradation. Two approaches are here described: the first studies the differences between the averaged concentrations of long time series in the infiltrating and abstracted water. Also a different approach is developed in this study that consists of finding relationships in the infiltrated water between the different EOS per sample. The variation in these relationships that develop during passage gives information on the processes that are affecting those EOS: conservation, dilution or degradation.

4.2 Site description of MAR in the Meijendel dune area

4.2.1 Operational scale, history

The two artificial recharge areas studied constitute the most important part of Dunea's water production, the water supply company that delivers around 75Mm^3 of drinking water per year to The Hague and surrounding area (Lekkerkerker-Teunissen, 2012). The artificial recharge systems are located in the Meijendel dune area in the western parts of the Netherlands, directly north of The Hague , Figure 4-1left).

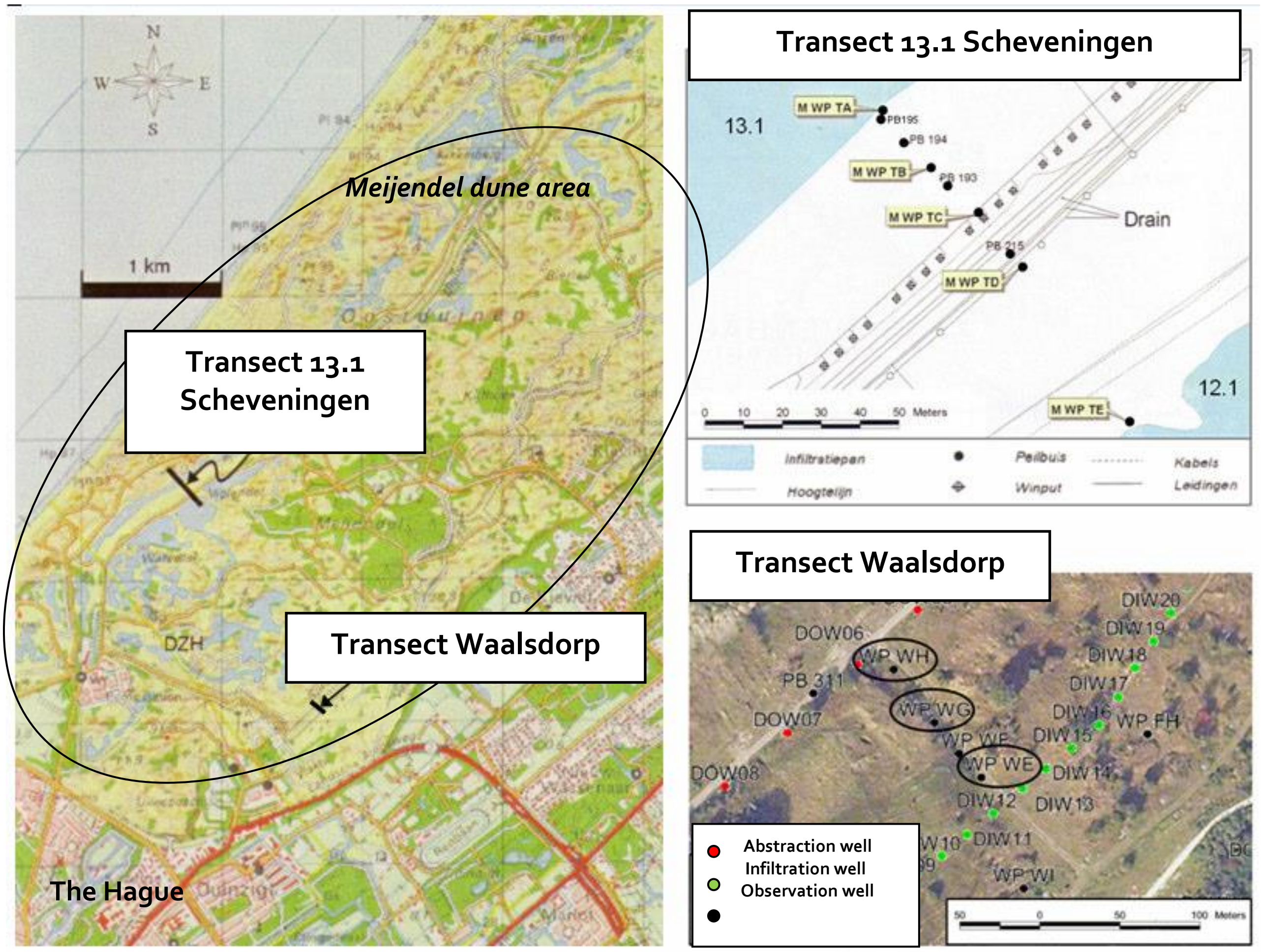

Figure 4-1: **Location of the transects subject to study in the present project. The left figure corresponds to an overview of the western coast of the Netherlands and the Meijendel dune area, with the North Sea bordering the dune infiltration area. The figures on the right side show the position of the wells along the transects of study.**

The transect located in the Scheveningen basin recharge starts in the infiltration basin 13.1 (see Figure 4-1, right side, above) and comprises six observation wells located between the infiltration pond and the abstraction drains. The transect studied in the deep injection recharge area covers two observation wells located between the injection and the abstraction well (see Figure 4-1right side below). The depth of the filters located in these observation wells and their distances to the infiltration pond or injection well are covered further in this section The Meijendel dune area has been used to supply drinking water ever since 1874. with a later infiltration of surface water in 1995 as an alternative to rain water and in an addition to natural groundwater recharge (Stuyfzand 1993), to restore and maintain the fresh water lens under the dune area (see fresh-salt water interface inFigure 4-3). Surface water is infiltrated through open infiltration basins and recharged through a system of drains and (small) vertical wells. In addition, since 1990, Dunea also runs a deep well managed aquifer recharge system in Waalsdorp, south of the open infiltration recharge system (Bakker and Stuyfzand 1993). The deep infiltration system in Waalsdorp was originally designed as a pilot that would eventually be extended with a second deep infiltration system (Waalsdorp 2). Due to a decreasing water demand, the second phase was not required but the deep infiltration system

Waalsdorp continues to be a very important production asset for Dunea with a capacity of 4 Mm^3 per year until 2010 and around 1 Mm^3 from 2010 onwards. The Meuse River is the source for drinking water produced in these two recharge systems. A multi-barrier approach ensures that the drinking water meets the high Dutch quality standards. The multi-barrier system consists of three treatment barriers: i) pre-treatment (coagulation, microstraining and filtration), ii) infiltration, subsurface passage and recovery from the dune MAR system, and iii) post-treatment (softening, activated carbon, slow and rapid sand filtration). The drinking water is then distributed chlorine-free to the costumers. The operational characteristics of the two MAR system types are compiled in table 4-1.

Table 4-1: Overview of the characteristics of the two managed aquifer recharge systems subject of study.

Type MAR		**BAR**	**ATR**
Location		Scheveningen	Waalsdorp
Begin AR		1955-date	1990-date
Target aquifer	Depth	0-55	23-67
	Geological formation	Westland	Eemian, Urk/Sterksel
	Material	Dune sand / North see sand	North sea (coarse)Sand
	Kh (m/day)	10/15	15
	Vol. Inf iltration (Mm3/year)	45	Since 2010: ~1
	residence time in the subsurface (d)	70 (minimum 28)	100-200
Operation	distance to infiltration (m)	65	110
	Vol. Recovery (Mm3/year)	46	Since 2010: ~1
	Type recovery	drains+ wells	wells
	Nr wells infiltration	0	22
	Nr wells abstraction	12 km drains 1200 phreatic wells	24
Infiltrated water	type of water	Meuse water in Brakel Lekkanal as back-up (Rhine)	Meuse
	pre-treatment	C,MS, RF	C,MS,RF+C,FL,AC
Unclogging	methods	phreatic wells once every 2 – 5 years, high pressure water pump	no unclogging method

C=coagulation, MS=microsieve, RF=rapid filtration, AC=actived carbon filtration, FL=flotation, BAR – basin aquifer recharge, ATR – aquifer transfer and recovery

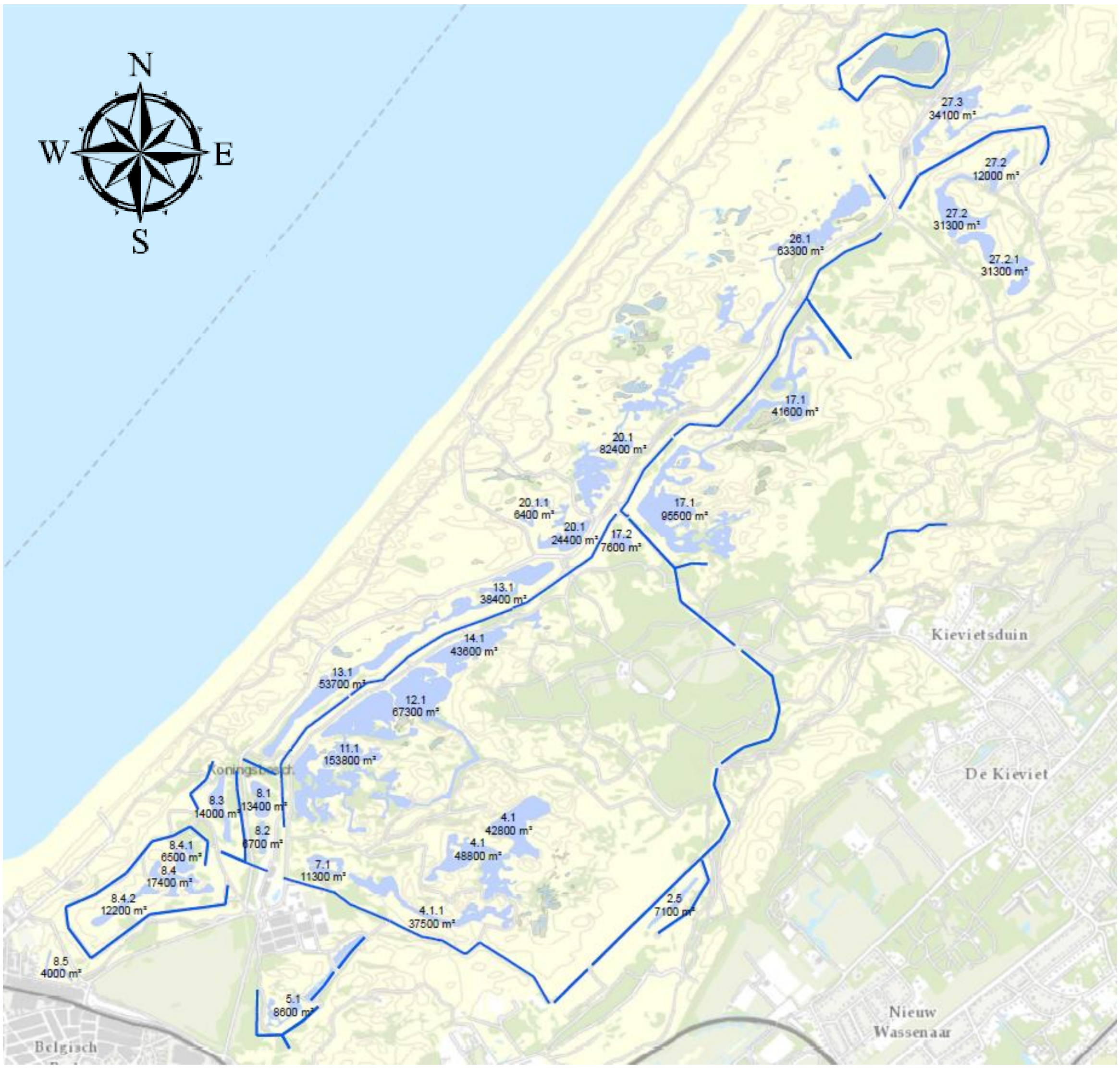

Figure 4-2: Infiltration ponds and drains in the BAR (Basin Artificial Recharge) in Scheveningen. The ponds are labeled with their number and the surface they occupy. The drains are indicated with blue lines.

The sampling locations in both transects is shown in Figure 4-3 and Figure 4-4. Figure 4-3 shows the observation wells along Transect 13.1, together with the abstraction well (Hoofdader). The abstraction well has two filter screens separated by a thin North Sea clay layer that confines the aquifer. The water is abstracted both from above and below the clay layer.

The 50 cm long filters of the observation wells Pb 193 - Pb 195 are placed in depth around 2m-NAP. Observation wells TA to TC have filters also around 2 m-NAP, 6m-NAP,12m-NAP and 16 m –NAP. The deepest samples available from these observation wells are from TA-filter 4 16m deep.

Figure 4-4 shows the transect of the deep injection system in Waalsdorp, with the injection well (DIW13 in the figure, also coded as SF-31-32 in the chemical analysis) , the abstraction well (DOW 06) between which the observation filters (WE -32 and WE -34) are placed in the second aquifer at a depth of around 30 to 35 meters.

Figure 4-3 and Figure 4-4 include the redox zonations in the transects according to Segers and Stuyfzand (2007), based on a sampling campaign performed in 2006 and following the criteria defined by (Stuyfzand 1993) (see 0 Annex A). The observation wells in Waalsdorp were unambiguously suboxic and anoxic, as expected in such a deep well injection recharge system. In the open infiltration system the shallow observation wells pb194 and pb193 showed concentrations of nitrate, ammonia and iron that corresponded to aerobic conditions. The reduced SO4 concentrations in the observation filters TA-2- well TA second filter starting from above, TA-4 and pb195 with respect to those in the infiltration pond indicate deeply anoxic conditions like in TC -1.

(Loma et al., 2013) similarly defined the redox zones of the top and the deep aquifer. In addition, they included a recent snapshot of the different water types that are found in the transect the water is fresh with chloride values between 37- 46 mg Cl/L and moderate alkalinity. The main anions are calcium and bicarbonate. In the top aquifer, the infiltrated water is gradually reduced along its flowpath: the oxic water in pond PAN13.1 transforms into suboxic at PB195 and PB193 (e.g., reduction of NO3) and is iron reducing at TC-F1. The sample taken at TA-F4, in the deep aquifer, indicated sulphate reducing to methane producing conditions. Various interesting downgradient quality patterns can be recognized that are all in line with earlier investigations as discussed by (Stuyfzand 1986).

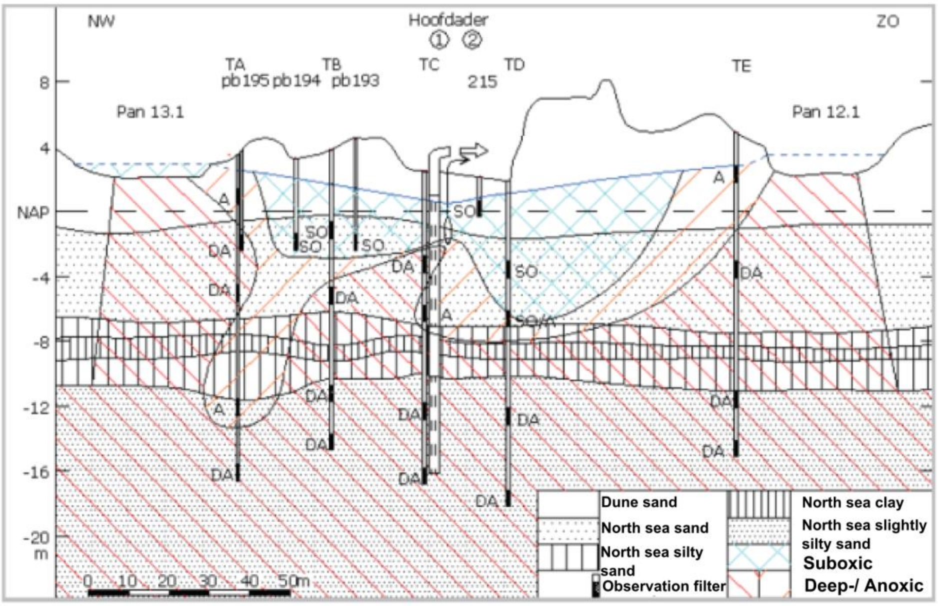

Figure 4-3: **Profile of hydrogeology and redox zonation along with observation wells, recovery wells of transect 13.1. from Stuyfzand et al(2007) Pan13.1 and 12.1 are the infiltration ponds, TA-TE the deep multilevel observation wells and pb the shallow observation wells. (SO = suboxic, DA = deeply anoxic; A = anoxic; NAP = sea water level)**

The water found in the artificial recharge system in Waalsdorp is fresh water with calcium as main cation and HCO3 as main anion. The water gets reduced along its passage according to the concentration of iron and sulfate. This classification is based on the sampling performed in the end of August of 2006.

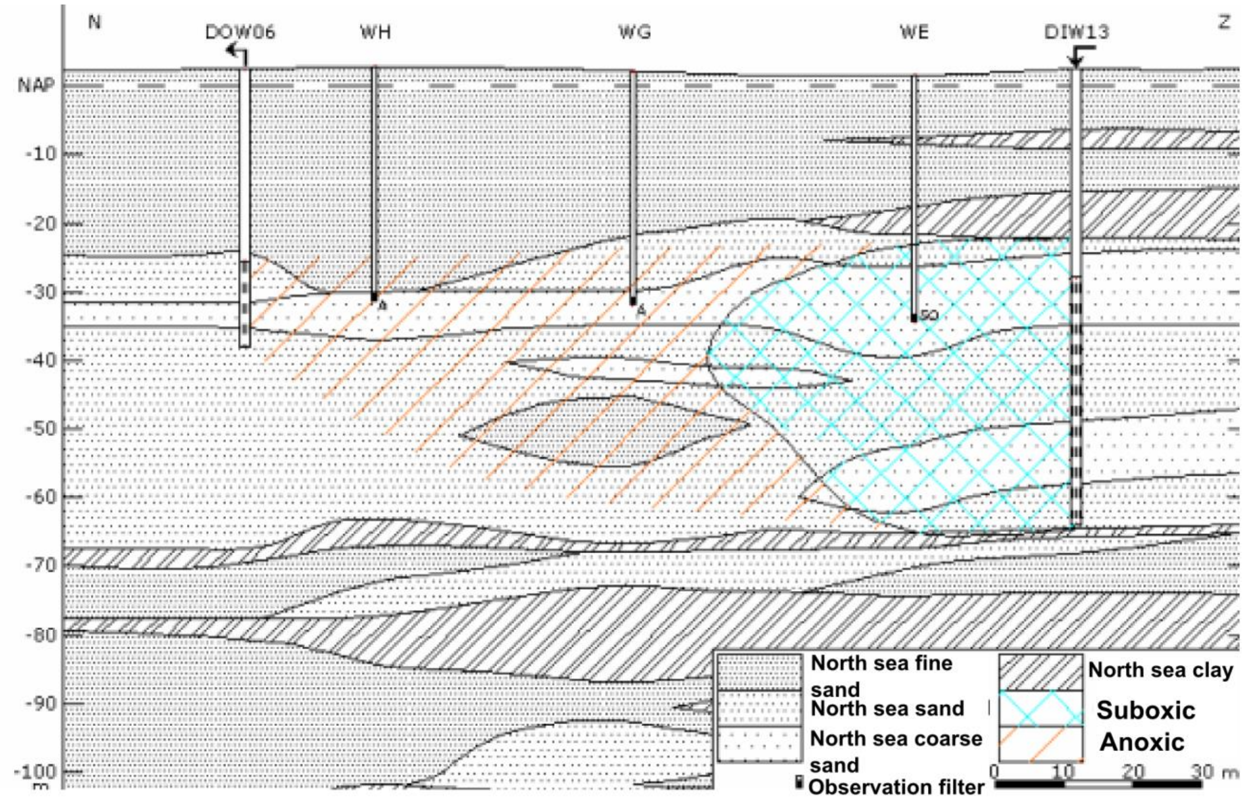

Figure 4-4: **Profile of hydrogeology and redox zonation along with observation and recovery wells of transect 13.1.(taken from (Stuyfzand, Segers et al., 2007)) DIW13 and DOW06 = injection and recovery wells, respectively; WE-WH = observation wells. (SO = suboxic, A = anoxic; NAP =sea level)**

4.3 Material and methods

4.3.1 Previous work

Most of the studies about removal of organic micro-pollutants is done in flow-path scale, and one of the most challenging elements for removal estimation is the scattered observations available. Previous studies calculated the removal efficiency through statistics (in a infiltration transect decreasing mean values would infer that removal processes are taking place, represented many times with box plots (Massmann, et al., 2008) (Eschauzieret al., 2010), or using frequency of detection (Stuyfzand et al., 2007). One of the most recent studies tracks back, with the help of the travel times, the original infiltrated concentrations through linear interpolation between surface water concentrations water since in most of the cases there was no measurement available for exactly the time when the water was supposed to be infiltrating (Wiese et al., 2011, Segers and Stuyfzand 2007). The interpolation of input signals with great variability can result in wrong or not accurate initial concentrations and therefore, false calculated removal rates when compared with the abstracted concentrations.

This approach is not possible with the data of the infiltrated water available from the river Maas. The broad variability of the input does not allow interpolation or averaging of the input concentrations. Houtman et al., (2013) studied the variation and trend of pharmaceuticals and pesticides measured in the intake Brakel at the Meuse river every four weeks from august 2010 to august 2012. The concentrations varied significantly between seasons depending on higher flows of the river Meuse or on higher consumption (for instance of caffeine or ibuprofen), also depending on environmental biodegradation.

Previous studies regarding urban ground water affected by waste water sources, introduced the concept of co-tracers to identify groundwater affected by waste water (Scheurer et al., 2011) or to identify single and multiple waste water sources (Van Stempvoort et al., 2013). In these studies correlation analysis and the spatial distribution of the co-tracers are studied in order to identify the changes in the relationships between them, providing information on degradation or in the case of ubiquitous co-tracers and the non-ubiquitous (plume-specific), to discern the effects of the different waste water plumes.

4.3.2 Investigation methods

Based on what is explained in the previous work section, the first approach here taken is, with the availability of long time series of data, instead of focusing in the behavior along the passage with help of the groundwater samples taken, to compare the average in time infiltrated with the average abstracted. It is considered then, that when using long databases the patterns observed between infiltrated and abstracted will be representative of the removal of contaminants, or of their persistence.

The second approach in the present study is thus a correlation analysis, which is run for each of the compounds found in the intake water (Brakel) and in the infiltrating water in the MAR systems. The ratio of two tracers that are linearly correlated in the infiltrating water, as seen for carbamazepine and acesulfame (Scheurer, Storck et al. 2011), is expected to be not affected by dilution with groundwater. In the absence of other contaminant sources, a ratio change suggests degradation or elimination of one of the compounds.

4.3.3 Data source and data processing

All available recent data (from 2003 to date) on organic and inorganic water chemistry was collected for the locations and observation filters listed in Table 3-1. Long time-series of data were obtained of the source water at the intake in the river Meuse, at Brakel pump station (Brakel intake). This data was provided by RIWA-MEUSE (source: RIWA database Nieuwegein). The available measurements since 2005 of the infiltrating water (source water) in Scheveningen and in Waalsdorp were provided by Dunea (seeTable 3-1). From the observation wells along the two transects, inorganic and organic water composition is available from the screenings performed in 2012 as part of the study by Loma et al., (2013), in 2006 by Segers and Stuyfzand (2007) and in 2005 by van Rooyen (2006). Groundwater data from the deep injection system Waalsdorp is available monthly from the 1990’s until 2000 and every four months since then. The bulk chemistry of the abstracted water was provided by Dunea. There is no information available of the abstracted water per transect or per well but as a mixture of the water collected by all the abstraction wells. The abstracted water from the open infiltration pond comprises thus, among others, the water infiltrated via pond PAN13.1 and PAN12.1 (Figure 4-2 and Figure 4-3) and the abstraction water from the deep injection system will be a mixture of the water abstracted by several wells in that system.

The mixing of different ground waters is disregarded in this study since the two recharge systems have been continuously in use, ensuring that the groundwater located along the passage is all infiltrated groundwater. The abstracted groundwater is recent infiltrated water, according to the spatial distribution of the ponds and drains and the hydrological models provided by the water company Dunea.

From the datasets only the macro and trace inorganic compounds together with the organic micropollutants are used for this study. The macro chemistry and trace inorganic considered are temperature, pH-Field, Na, K, Ca, Mg, Fe, Mn, NH4, SIO2, Cl, SO4, HCO3, NO3, PO4-T and TOC. Per dataset different EOS are found and not every sample was analyzed for all the parameters, the number of EOS analyzed varies thus greatly per sample and per sampling location.

Another challenge when working with long-term data is that different detection limits for the same compound are found due to rapid development of analytical procedures.

The different detection limits (DL) available can lead to "false positives" of removal when considering that a substance has been removed due to an increase in the detection limit because of a different analytical method (an increase of DL, like for example from DL=0.02 µg/l to DL=0.03 µg/l, which assuming constant concentration in source water, for instance 0.1 µg/l, would mean 80% and 70% removal respectively. This decrease of removal responds only to the increase in DL). Therefore when plotting the concentrations of substances, if one is under detection limit, the DL concentration will be indicated by a different sign. By doing this it is possible to have an overview of the different DL and to distinguish them from fake removals. Many studies (e.g. Wiese et al., 2001) calculate removal based on DL/2 or LOQ/2 which may lead to overestimation of removal.

Table 3 1: Water quality data of the MAR system in Scheveningen and Waalsdorp.

Location	Provided by	Sampling point ID	Number of samples	Initial sampling date	Final sampling date	Nr. of parameters analyzed*
Brakel intake (not treated)	RIWA Meuse	Brakel	1358	jan-03	dec-12	652
Source water Scheveningen (BAR)**	Dunea	PSC-SF3132-VEFF	190	feb-05	mar-12	428
Source water Waalsdorp (ATR)***	Dunea	WME-INF	875	jan-05	dec-13	420
Groundwater Scheveningen	Dunea	WME-PB195-F1	1	aug-12	aug-12	467
		WME-PB193-F1	1	aug-12	aug-12	467
		WME-WPTA-F4	1	aug-12	aug-12	467
		WME-WPTC-F1	1	aug-12	aug-12	467
	Older studies	Pond 13.1	2	jul-05	aug-06	136
		pb195	2	jul-05	aug-06	136
		pb194	2	jul-05	aug-06	136
		pb193	2	jul-05	aug-06	136
		TC-1	2	jul-05	aug-06	136
		TA-F4	2	jul-05	aug-06	136

Groundwater Waalsdorp	Dunea	WME-WWD-PPWG-32	137	may-90	oct-06	166
		WME-WWD-PPWG-34	6	jan-55	oct-06	166
Recovered water Scheveningen	Dunea	PSC-VK-VOW	742	jan-03	dec-13	620
Recovered water Waalsdorp	Dunea	WME-MPDIW_V	8	feb-07	may-13	88

* The total number of different parameters analyzed in each database includes physico-chemical on-site measurements, trace inorganics and organic trace compounds. Not every sample in the database was analyzed for all these parameters. RIWA Meuse is an international cooperation of drinking water companies, which use Meuse water as their source for supplying drinking water.

**BAR source water is pre-treated by $FeSO_4$

***ATR source water is pre-treated by $FeSO_4$ + $AlCl_3$

The site specifics are also taken into account in these plots since the removal of a certain organic contaminant can depend strongly on redox conditions but it also might be due simply to longer travel times (Wiese et al., 2011). Plotting the substances versus conservative parameters (such as Chloride) or plotting the substances versus parameters indicative of the redox status help to discern and take this processes into account when the percentage of removal.

Two approaches for the interpretation of long-term data at MAR sites are developed, described and applied in this report. The first approach calculates percentage removal based on average values measured in source and recovered water. The BAR site in Scheveningen is used for this approach (section 4.4.2). The Scheveningen data is chosen due to the sufficient amount of samples. A data table with all parameters used for this calculation can be found in 0.

For every sampling location (Brakel intake, source water Scheveningen and Waalsdorp, and recovered water in Scheveningen and in Waalsdorp) maximum, minimum and mean concentration per parameter are calculated (see 0). In 0 also the lowest detection limit for each compound is included and the amount of different detection limits found per parameter. The mean value calculated is the arithmetic average of the data values. It is the sum of the data values divided by the number of data values.

$$\mu = \frac{1}{N}\sum_{i=1}^{N} x_i$$

Where N is the number of data values.

When comparing statistically the input and the output if there is no information available of a certain abstracted parameter in the infiltrated water, this is looked for in the databases from Brakel. The database used for making this comparison consists of 89 substances defined as EOS. These substances have been divided in 4 groups: 57pesticides, 8 pharmaceuticals, 11 solvents and 13 others. The group others include substances such as volatile organohalogens, gasoline additives, and (poli) aromatic hydrocarbons.

In a second approach, a correlation analysis is done done, where the strength of a linear relationship between two compounds is quantified. This is, when there is no correlation between the concentrations of two compounds then there is no apparent tendency for the measured concentrations to increase or decrease concurrently.

To identify this behavior the square of the Pearson correlation coefficient is calculated for each possible combination of two parameters that were at least 10 times sampled at Brakel intake or in the source water of Scheveningen or Waalsdorp. The combination of parameters that showed Pearson coefficients higher than 0.6 were plotted against each other and visually inspected. For those parameters that showed real correlation (some of the high Pearson coefficients corresponded to combination with one parameter whose values were all under detection limit) all the individual measurements of the infiltrated water are plotted. The individual measurements of the abstracted water are also plotted and if they show a different rate (the trend line is higher or lower) then one of the contaminants is considered to be degraded or reduced. If the cloud of points plots in the same trend line but closer to the origin then dilution is expected or degradation at the same rate for both contaminants.

The basic idea of the second approach is to find indicators which can be used to estimate removal for a group of EOS with similar removal behavior during subsurface passage. Since many pharmaceuticals show a redox dependent removal the redox sensitive compounds indicated the redox zone may also be used to estimate removal of a certain group of EOS.

4.4 Occurrence, fate and transport of EOS in aquifer recharge systems of Scheveningen and Waalsdorp (The Netherlands)

4.4.1 Analysis of EOS concentration variability of the source water and redox conditions during subsurface passage

In some artificial recharge cases the seasonal variations in the input are dampened by mixing in the recharge basins or recharge lakes, resulting in groundwater concentrations that show average values of the concentrations of the conservative tracers measured at the source waters, as seen in an artificial recharge lake located in the province of Limburg, in the South East of the Netherlands (Hartog 2014). Initially, in both of the cases here there is no infiltration lake where the residence time is enough for the water to homogenize. To confirm this, the concentrations of chloride and sulfate in the intake of water in Brakel, the concentrations measured in the infiltration ponds and the concentrations in the groundwater and abstracted water were plotted. Figure 4-5 shows similar amplitude in the range of concentrations of Cl and SO4 in the intake as in the one observed in the abstracted water. However, if there would be mixing and homogenization during its distribution before being infiltrated, we would expect the groundwater and the abstracted values to vary along a smaller range towards the average of the infiltrating concentrations. This figure also shows consistently higher concentrations of sulfate in the water infiltrating in the open ponds in Scheveningen than the ones measured at the Brakel intake. This responds to the treatment with FeSO4 before recharge. The same accounts for increased Cl concentrations at Waalsdorp, where pre-treatment by coagulation with $FeCl_3$ or $AlCl_3$ is applied.

The concentration ranges of Cl as measured in the groundwater transect of Scheveningen 13.1 remains limited, while sulfate varies strongly. This is due to the different redox conditions that are found in that transect, sulfate is being reduced along the passage through the soil. The water abstracted however, since it is a mixture of different flow lines, shows higher sulfate concentrations.The sulfate concentrations of the water in Waalsdorp remain high in its passage through the soil, which is probably explained by the fact that there are no deep anoxic or sulfate reducing conditions in the deep injection passage (Stuyfzand,Segers et al, 2007).

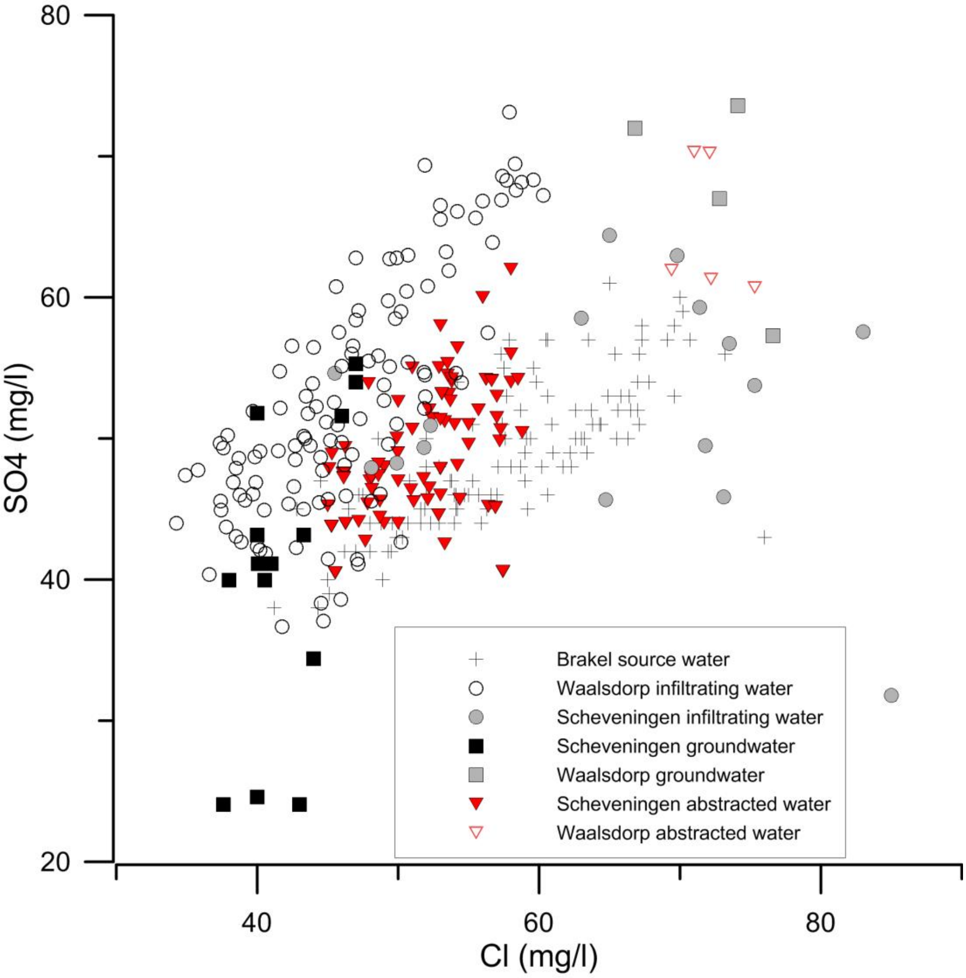

Figure 4-5: **Chloride and sulfate concentrations of samples taken in the water source intake (Brakel) in the infiltration ponds and infiltration wells (circles) and in the abstraction wells (inverted triangles) and in the groundwater (squares) of both Scheveningen and Waalsdorp.**

The concentrations measured at Brakel intake of some the compounds selected in DEMEAU task 1.2.1 BL are plotted as an example of input variability. These compounds were chosen for being commonly found in drinking water supplies, for being relevant environmentally, for their broad spectrum of chemical or physical properties and for their coverage of a range of elimination by O3 and/ur UV/H2O2 (Vilanova et al., 2014). From these compounds benzotriazole and epoxy-carbamazepine were not reported as analyzed in Brakel and unfortunately none of these compounds were analyzed for by Dunea in the MAR system, except for carbamazepine. This report focusses therefore on the most relevant compounds observed in the infiltrating water and in those compounds that are traced along the passage.

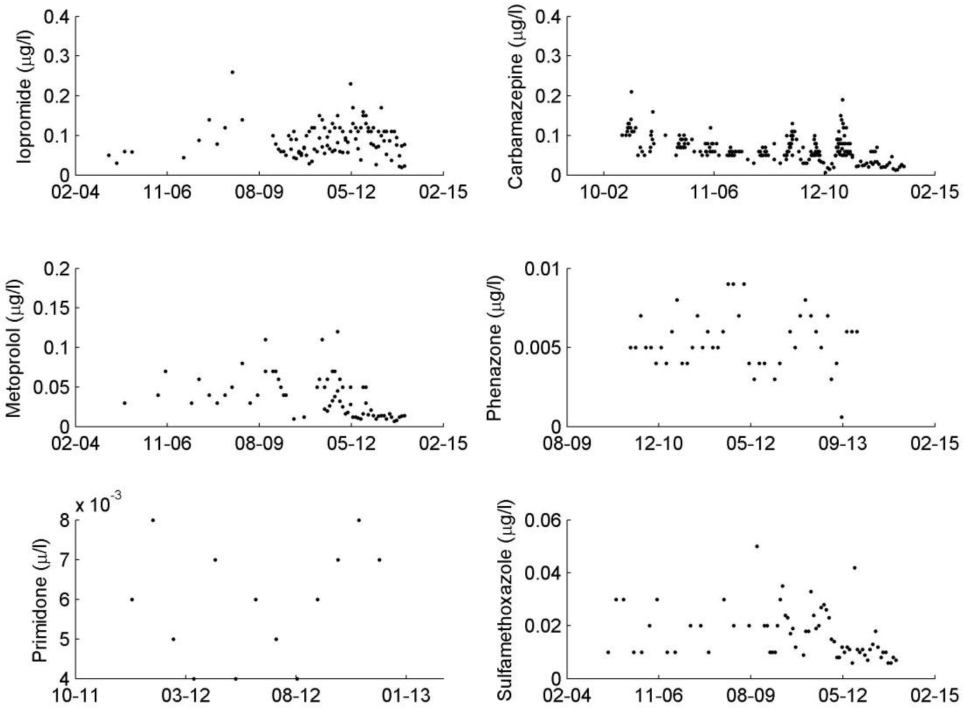

Figure 4-6: **Concentrations over time of selected EOS measured at Brakel intake (not treated).**

The overall analysis of the concentrations in Brakel over the last 10 years indicates also that the maximum measured concentration for the top 100 contaminants is poorly related with the frequency of detection (Annex B), illustrating the highly variable input signal to the MAR system.

4.4.2 Overview of organic trace compounds in source water

Most of the organic contaminants with highest concentrations found in Scheveningen are pesticides (Figure 4-7) followed by solvents (Figure 4-9), pharmaceuticals (Figure 4-8) and others (many of which are PAHs, Figure 4-10). When comparing the averages of the infiltration compounds with the averages of the abstracted compounds in Figure 4-7, Figure 4-8, Figure 4-9, and Figure 4-10 and it appears that most of the contaminant concentrations (74% of the compounds analyzed) decrease to certain degree when being abstracted (being the average abstracted water marked by an inverted triangle). Taking into account that there is no dilution according to the Cl and SO4 concentration (see Figure 4-5) most of the reduction in concentration seen in the abstracted water should be due to the removal capacity of the MAR.

The contaminants that are being reduced the most (more than 75%) are all pesticides and in order of decreasing infiltrating concentration are: dimethomorph, flumioxazine, fenamidone, aldicarb-sulphoxide, butoxycarboxim, chlorobenzene, methiocarb, 3,4-Dichlorophenyl urea (DCPU) and methabenzthiazuron (see 0 with the detailed information on the concentrations and percentages). This accounts for 10% of the compounds.

Around 30% of the contaminants are being reduced by more than half of the concentration from which only 2 are solvents and four are others. Some of them (16%) show no decrease or even an increase in the averaged concentrations.

Most of the compounds that show stable or increasing concentrations after being abstracted do so based on averages of one or two samples that do show concentrations above detection limit in the abstracted water. Actually only the following persistent compound averages in the abstracted water were based in more than one sample with concentrations above the detection limit: naftalene, p-isopropylmethylbenzene, thiabendazole, 1,2-dichloorethane, 1,3,5-trimethylbenzene, metsulfuron-methyl, thiophanate-methyl, linuron, and phenanthrene. From these only thiabendazole and phenanthrene present higher averaged concentration values in the abstracted water than the maximum concentrations measured the infiltration water. This could imply that there are external sources of organic contaminants to the abstracted water. The compounds that show persistent or even increasing concentrations at abstraction account for 19% of the total.

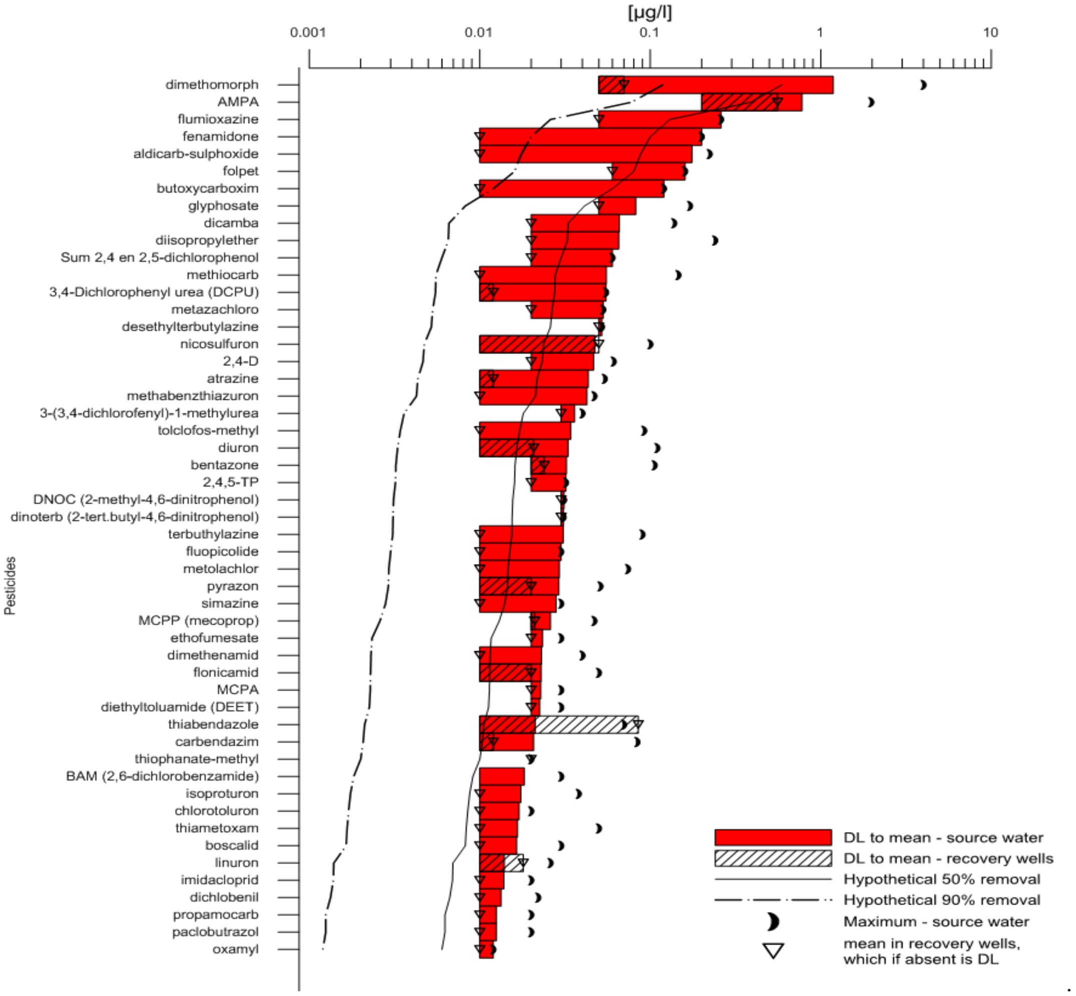

Figure 4-7: **Pesticides identified in source water (above detection limit) prior to its distribution to the infiltration ponds and recovered by the Scheveningen system (data from 1990 to 2013), ordered by average concentration in source water. The bars go from the lowest detection limit to the average infiltrated concentration measured. The maximum concentration detected is shown as a crescent. The small inverted triangles in the bars represent the average of the concentrations measured in the abstracted water, when the abstracted average concentration is over detection limit the bar is shown with diagonal lines from the detection limit to the average abstracted. If the abstracted concentrations were none above detection limit only an inverted triangle will be seen. Both averages of infiltrated water and abstracted water are taken of the values above detection limit, and from those species where no value was measured above detection limit in the abstracted water, the concentration shown is the detection limit.**

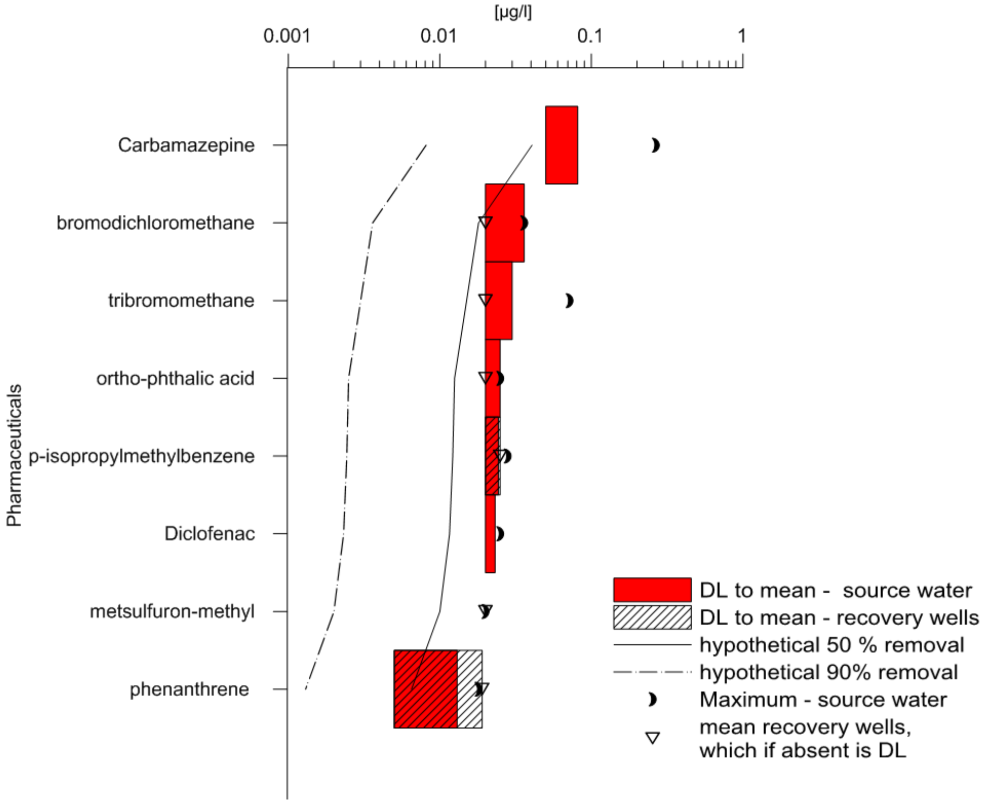

Figure 4-8: **Floating chart of all the pharmaceuticals identified in the water (above detection limit) in Scheveningen prior to its distribution to the infiltration ponds, since 1990 until December 2013, ordered by (averaged) infiltrated concentration. The bars go from the lowest detection limit to the average infiltrated concentration measured. The maximum concentration detected is shown as a small inverted moon. The small inverted triangles in the bars represent the average of the concentrations measured in the abstracted water, when the abstracted average concentration is over detection limit the bar is shown with diagonal lines from the detection limit to the average abstracted. If the abstracted concentrations were none above detection limit only an inverted triangle will be seen. Both averages of infiltrated water and abstracted water are taken of the values above detection limit, and from those species where no value was measured above detection limit in the abstracted water, the concentration shown is the detection limit.**

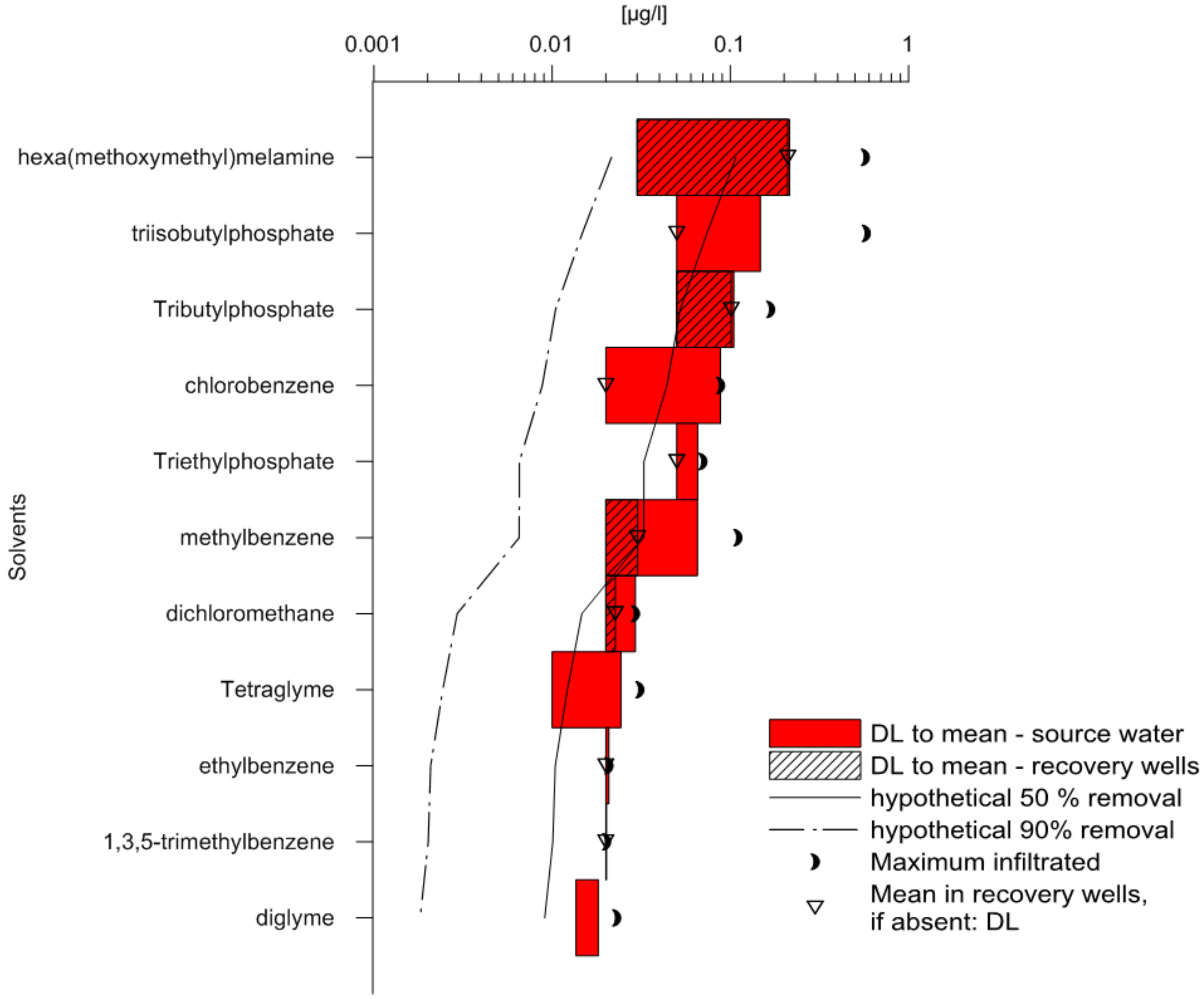

Figure 4-9: Floating chart of all the solvents identified in the water (above detection limit) in Scheveningen prior to its distribution to the infiltration ponds, since 1990 until December 2013, ordered by (averaged) infiltrated concentration. The bars go from the lowest detection limit to the average infiltrated concentration measured. The maximum concentration detected is shown as a small inverted moon. The small inverted triangles in the bars represent the average of the concentrations measured in the abstracted water, when the abstracted average concentration is over detection limit the bar is shown with diagonal lines from the detection limit to the average abstracted. If the abstracted concentrations were none above detection limit only an inverted triangle will be seen. Both averages of infiltrated water and abstracted water are taken of the values above detection limit, and from those species where no value was measured above detection limit in the abstracted water, the concentration shown is the detection limit.

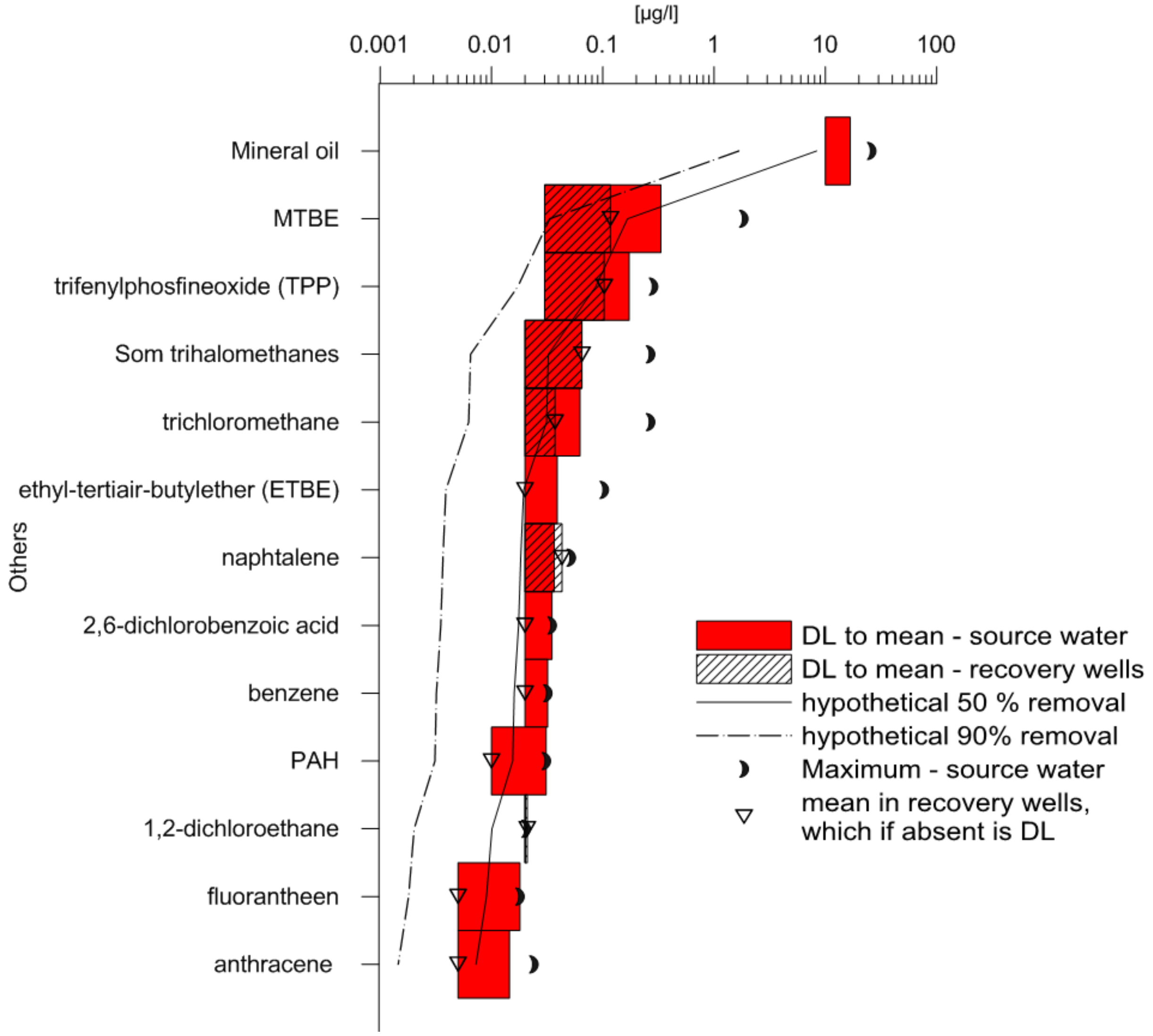

Figure 4-10: Floating chart of other organic compounds identified in the water (above detection limit) in Scheveningen prior to its distribution to the infiltration ponds, since 1990 until December 2013, ordered by (averaged) infiltrated concentration. The bars go from the lowest detection limit to the average infiltrated concentration measured. The maximum concentration detected is shown as a small inverted moon. The small inverted triangles in the bars represent the average of the concentrations measured in the abstracted water, when the abstracted average concentration is over detection limit the bar is shown with diagonal lines from the detection limit to the average abstracted. If the abstracted concentrations were none above detection limit only an inverted triangle will be seen. Both averages of infiltrated water and abstracted water are taken of the values above detection limit, and from those species where no value was measured above detection limit in the abstracted water, the concentration shown is the detection limit.

4.4.3 Correlations between contaminants

The large amount of data available from Brakel intake yielded significant correlations for many parameters. Following these correlations in the infiltration data from the MAR systems, the groundwater or the abstracted water proved to be more difficult since the amount of parameters that are regularly scanned is less. All the correlations found in the intake or infiltration water higher than 0.6 were visually supervised. From a total of 689 different parameters (organic and inorganic), the following figures contain those that showed linear relationship in the input and were analyzed in the groundwater or in the abstracted water of the MAR systems. PFBS, sotalol and amidotrizoic acid were only analyzed in Brakel and not in Scheveningen, that is why it is not included the floating charts from Scheveningen (Figure 4-7, Figure 4-8, Figure 4-9 and Figure 4-10).

Perfluoro-1-butanesulfonate (PFBS)

The perfluorobutanesulfonic acid (PFBS) has been widely used in the last years to replace the toxic PFOS in stain repellents because of its lower toxicity and bioaccumulation (Renner 2006) even though it is not easily removed by treatment facilities and is therefore environmentally widespread (Eschauzier et al., 2010; Eschauzier et al., 2012).

When comparing the PFBS with sulfate the linear relationship is of r2=0.78 (see linear fit PFBS-SO4 in

Figure 4-11).

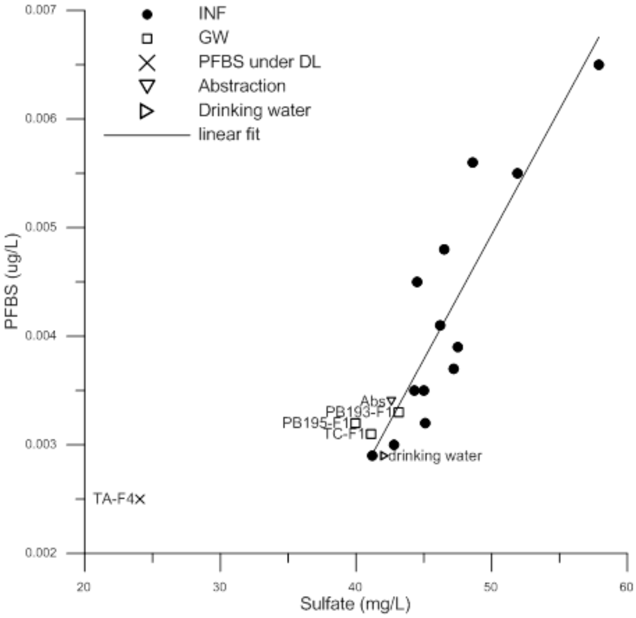

Figure 4-11: Perfluoro-1-butanesulfonate (PFBS) concentrations versus sulfate concentration. Where INF= source infiltrating water, GW=groundwater, Drinking water after post-treatment and abstracted means water from the recovery wells.

The relationship seen in the infiltrating water between PFBS and sulfate is maintained both in the suboxic groundwater samples taken in 2012 in filters PB 193 F-1, PB195 F1, TC-F1, and in the abstracted and drinking water (water obtained after post-treatment) sampled in that same campaign. It corresponds thus to what is expected from literature, where according to Stahl et al., (2012) the PFBS are short-chain molecules that pass quickly through the soil without retention times and behave almost conservatively.

Figure 4-11 includes the groundwater sample deep anoxic sample (TA-f4) where sulfate is reduced and PFBS concentrations were below detection limit (DL) (see point PFBS<DL).

PFBS and chloride are less strongly correlated in the intake water in Brakel. The groundwater samples taken in sampling locations PB 193-F1, PB 195-F1, and TC-F1 show chloride concentrations similar to the injected ones. The PFBS/Cl rate is maintained for those samples; they plot along the PFBS/Cl average concentration ratio of the infiltrated water. This is in keeping with Stahl et al., (2012) who found that PFBS molecules have a percolation time similar to chloride tracer ions in soil. The groundwater sample taken in the deepest filter of the observation well TA presents chloride concentration in the expected range but PFBS concentrations are under the detection limit (D.L) which could be due to the longer travel times. In the drinking water this ratio is reduced and this could be due to the relative removal of PFBS compared to chloride in the treatment processes.

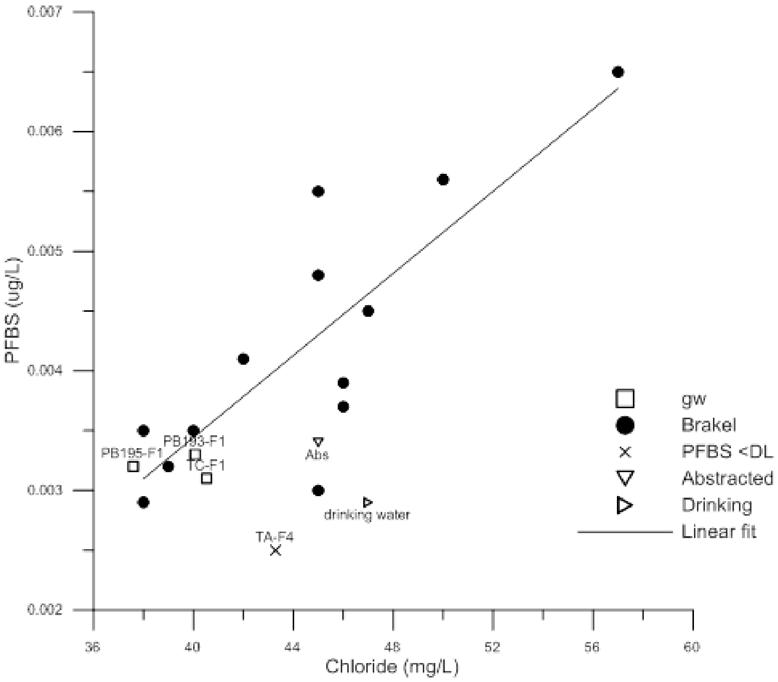

Figure 4-12: Perfluoro-1-butanesulfonate (PFBS) concentrations versus chloride concentrations. Where gw=groundwater, Drinking= water after post-treatment and abstracted means water from the recovery wells.

Sotalol

Sotalol is the beta blocker (pharmaceuticals for heart conditions) with the highest average concentration between 2010 and 2012 in the river Rhine (Houtman et al., 2013) Other pharmaceuticals with high concentrations are metoprolol, carbamazepine, iopromide, caffeine, metformin, oxazepam and sulfamethoxazole. Considering that PFBS behaves conservatively, the more strongly lowered sotalol concentrations in the MAR point towards removal of sotalol. This coincides with what was observed by Schmidt et al., (2007) where sotalol was removed in more than 80% in oxic, suboxic, anoxic and deep anoxic riverbank filtration zones. Being over the detection limit the three sotalol concentrations measured in the suboxic groundwater samples (PB 193 F1,PB195 –F1, TC F1).

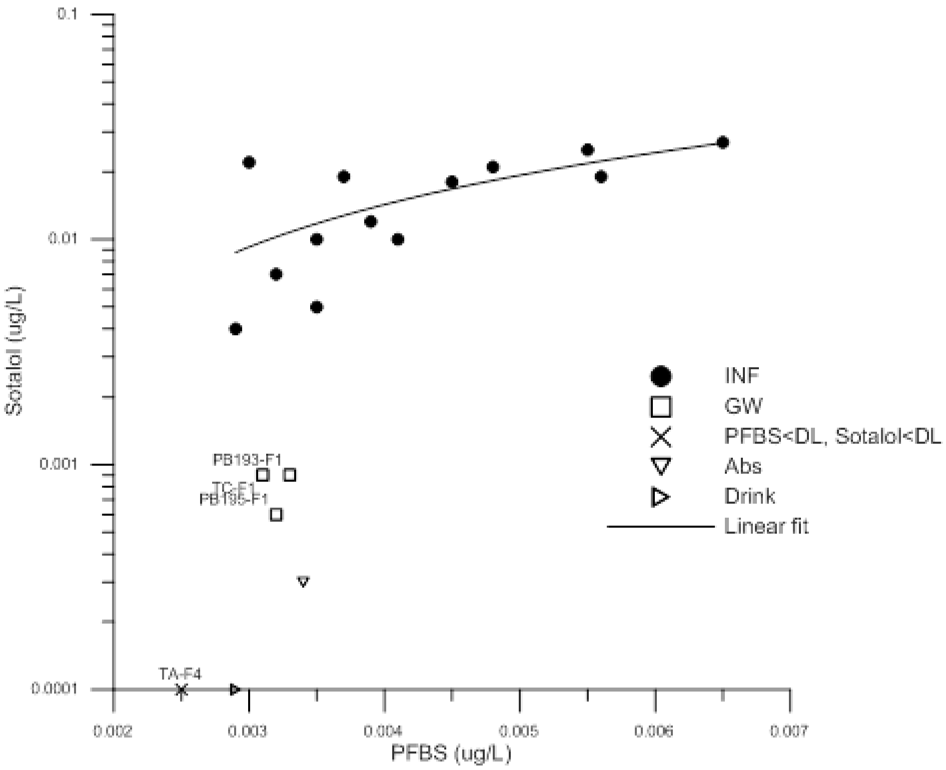

Figure 4-13: **Sotalol concentrations versus PFBS. Where INF= source infiltrating water, GW=groundwater, Drink= water after post-treatment and Abs= water from the recovery wells.**

Amidotrizoic acid

The amidotrizoic acid is an x-ray agent (like iopromide, iopamidol, iomeprol) with low removal rates in oxic and suboxic environment, however in anoxic environments the percentage of removal efficiency increases to 70 and 80% respectively according to Schmidt et al., (2007).

In the present study the ratio PFBS/Amidotrizoic acid remains similar along the different groundwater, abstraction and drinking water samples (Figure 4-14) indicating that in addition to PFBS, also amidotrizoic acid behaves conservatively. When plotting amidotrizoic acid versus Cl the linear relationship is weaker but the conservative behavior is still apparent. The groundwater samples taken in the 2012 campaign plot in the lower ranges of both inorganic and organic compounds in all the cases due to the infiltrating concentrations at that time.

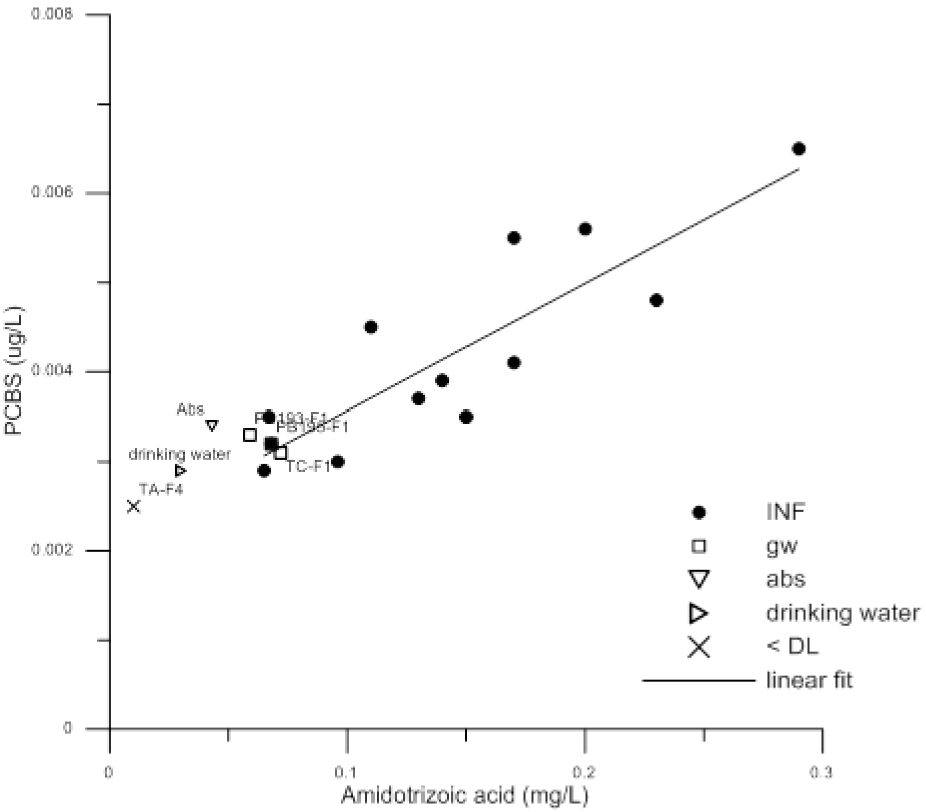

Figure 4-14: PFBS concentrations versus amidotrizoic acid. Where INF= source infiltrating water, gw=groundwater, drinking water= water after post-treatment and abs= water from the recovery wells.

<u>Carbamazepine</u>

Carbamazepine is a pharmaceutical used to treat epilepsy and bipolar disorders. It is regarded as one of the most persistent contaminants in the environment(Scheurer et al., 2011), and is used as a tracer for waste water input (Van Stempvoort et al., 2013). Schmidt et al., (2007) observed persistence of carbamazepine in aerobic and suboxic environment, certain reduction (26-50%) in anoxic environment and more than 80% of removal in deep anoxic environments.

When plotting carbamazepine versus sulfate(Figure 4-15), there is a general trend of decreased sulfate and carbamazepine in the abstracted water. The samples that show decreased sulfate compared to the input signal rare accompanied by a stronger reduction of carbamazepine, which means removal under SO4 reductions. The ratio however is conserved in suboxic groundwater samples, where the carbamazepine remained constant.

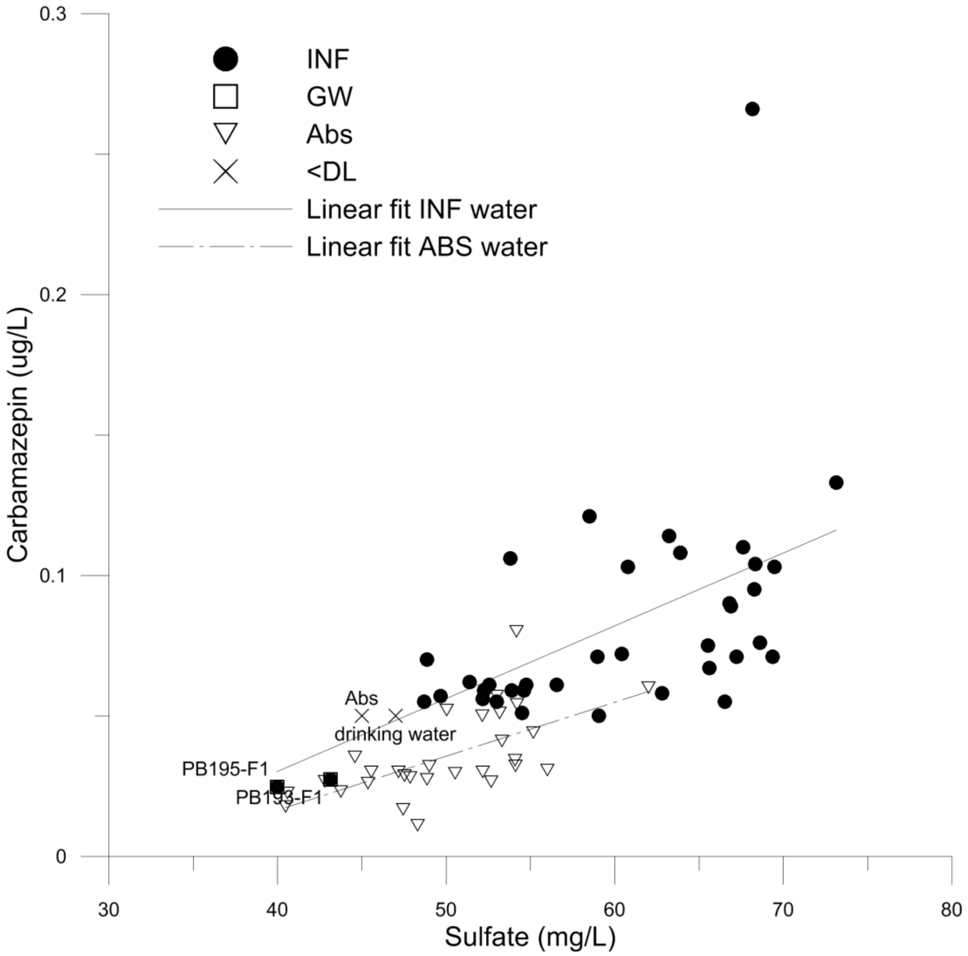

Figure 4-15: Carbamazepine versus sulfate concentration. Where INF= source infiltrating water, GW=groundwater and abs = water from the recovery wells.

Sulfamethoxazole

Sulamethoxazole is an antibiotic that according to the literature is removed in anoxic environments (Schmidt et al., 2007) or with long travel times (Laws et al., 2011). When plotting carbamazepine versus sulfamethoxazole the relationship found in the infiltrating water is replicated for many samples, although the abstracted water plots in the lower range of the infiltrated carbamazepine and the sulfamethoxazole in turn does the same, but it cannot be concluded that sulfamethoxazole is being more reduced than carbamazepine, but in similar rates. Which according to the previous plot (Figure 4-15) happens in anoxic environments.

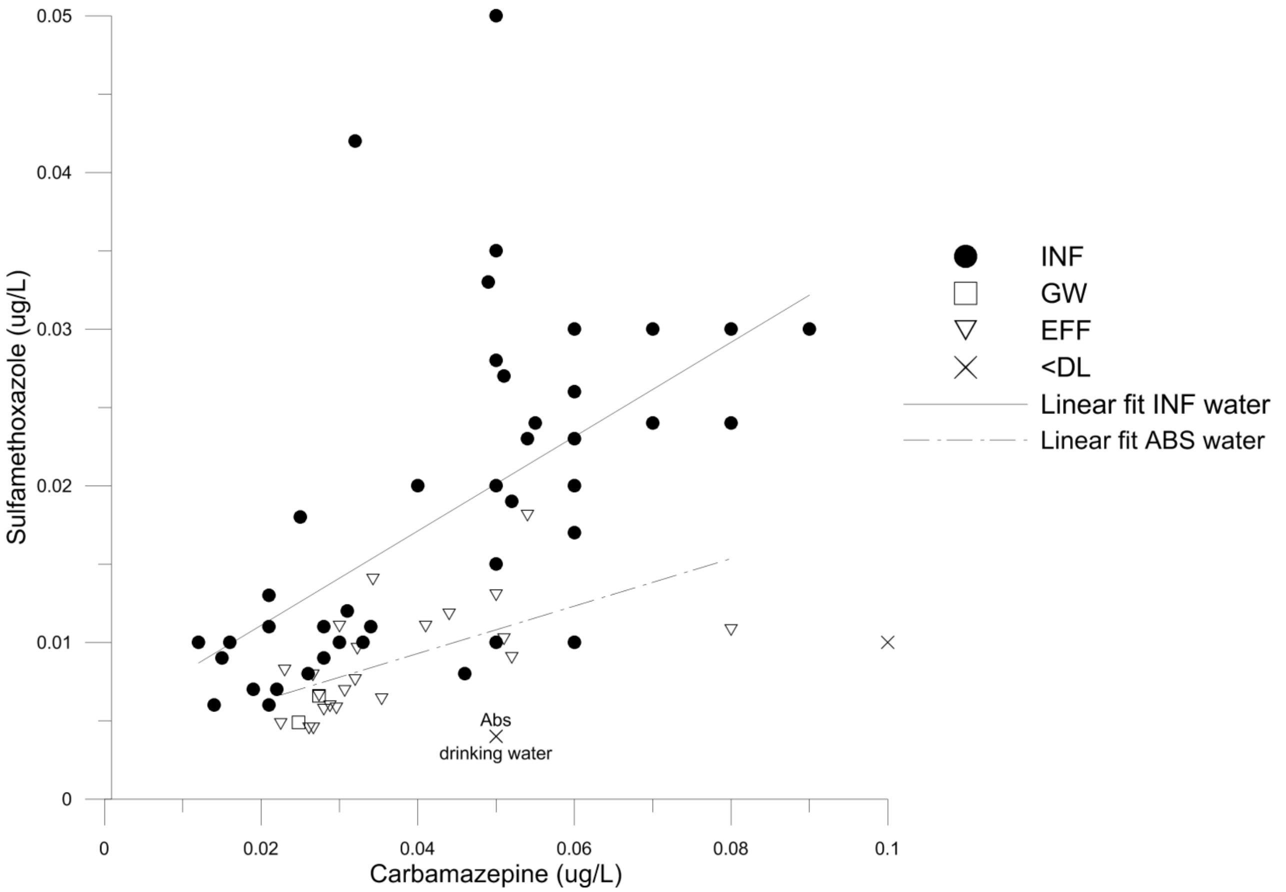

Figure 4-16: Carbamazepine concentrations versus sulfamethoxazole concentrations. Where INF= source infiltrating water, GW=groundwater, EFF= water from the recovery wells.

4.5 Summary of findings and conclusions

The high variability of emerging organic contaminants (EOC) concentrations in the infiltrating MAR water results in a very complex quantification of the effectiveness of MAR in removing EOC's. Determining the behavior of the EOC's based on the available data proved to be challenging also due to the spatial and temporal heterogeneity of the water quality data.

The infiltrating water in the MAR systems presents a wide range of EOCs and some of them can be found back in the groundwater. This naturally depends on the parameters that the water was analyzed for and the type of analysis done. The detection limits are also key factors when determining the actual removal of a substance.

In the present case-study two different approaches are taken to estimate the removal efficiency of MAR systems. These approaches do not focus on the behavior of contaminants along specific flowpaths, because of the variability of the input and the difficulty in tracing back the original concentrations when all that is available are snapshots of the contaminants in the system and not a continuous monitoring. The first approach here described is, when long time series of data are available, comparing the infiltrated and abstracted averaged concentrations as an overview of the reduction or persistence of the organic compounds.

In this case 30% of the contaminants are being reduced by more than half of their concentration through the MAR system. Removal rates of more than 75% are achieved only by pesticides, 10% of the compounds found in the infiltrating water. Almost 20 % of the compounds show no decrease in their concentrations. The compounds that are being degraded the most according to this are the following: dimethomorph, flumioxazine, fenamidone, aldicarb-sulphoxide, butoxycarboxim, chlorobenzene, methiocarb, 3,4-Dichlorophenyl urea (DCPU) and methabenzthiazuron.

The second approach aims to find correlations between the contaminants before their passage through MAR systems. Tracing this correlation along the passage is used to infer their behavior without using averages or interpolations of the infiltrated water. A script was run to find correlations between all the parameters measured in the infiltrated water and despite a wide range of correlations were found, those specific contaminants were not always analyzed in the groundwater or in the abstracted water. There are however some contaminants that were correlated and they were analyzed as well in the groundwater and abstracted water. One of them was PFBS (Perfluoro-1-butanesulfonate) that showed a conservative behavior, as expected from literature, and it was removed through the post treatment process. Sotalol on the other hand, was degraded during passage, as well as carbamazepine. Sotalol’s behavior was expected from literature but for carbamazepine a study was found were all the reduction was linked exclusively to dilution (Laws et al., 2011) which is not to be expected in Dunea’s setting. Sulfamethoxazole is seen to decrease in parallel with carbamazepine and amidotrizoic acid apparently moves through the soil in a conservative manner.

This approach also links the decrease in concentration of certain emerging pollutants to the location of the groundwater samples, which when available were specified in the analysis. These are related to specific key parameters of the MAR system itself, like the redox conditions and the travel times in the MAR system. In most of the cases the resulting behaviors fit with what was described in previous literature.

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5 Application of the Australian Guidelines for Water Recycling: Managing Health and Environmental Risks at Berlin-Tegel

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5.1 Introduction

During the last decade the Australian administration released a series of guideline documents in order to provide an authoritative reference that can be used to support beneficial and sustainable recycling of waters generated from sewage, grey water and storm water. The Phase 1 guideline is the overarching framework. The Phase 2 guideline refers to specific applications within the context of water recycling by Managed Aquifer Recharge (Figure 5-1).

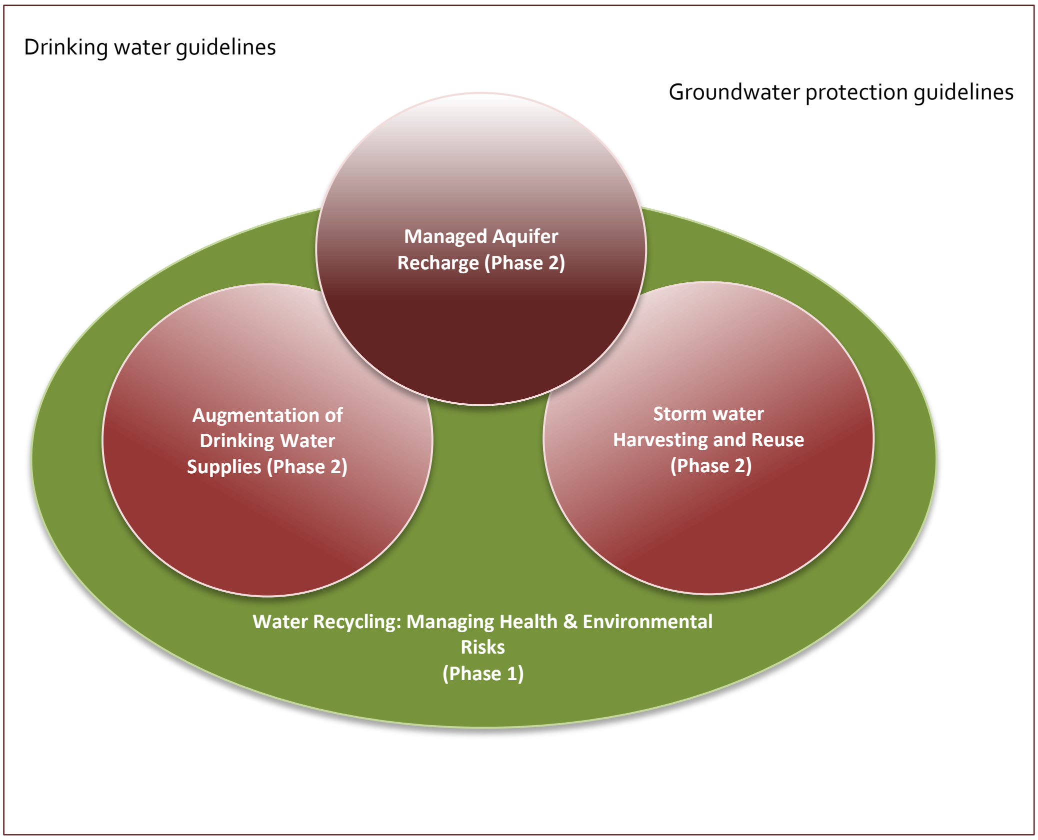

Figure 5-1: Overview of the series of guideline documents on water recycling released by Australian authorities (NRMMC-EPHC-NHMRC 2009).

Within this study these guidelines will be applied to the MAR site in Berlin-Tegel in order to demonstrate an additional methodological approach for impact assessment of MAR sites. In order to avoid redundancies, please see chapter 3 of this report for a detailed site description.

5.2 General approach

Within the Australian guidelines for water recycling a risk based and process oriented approach is promoted. The guidelines represent a practical guide to the planning and implementation of MAR projects, acknowledging that some developments cannot be predicted until full scale implementation. The assessment is based on a three level structure. Figure 5-2 shows the assessment levels and the objectives for the examined system.

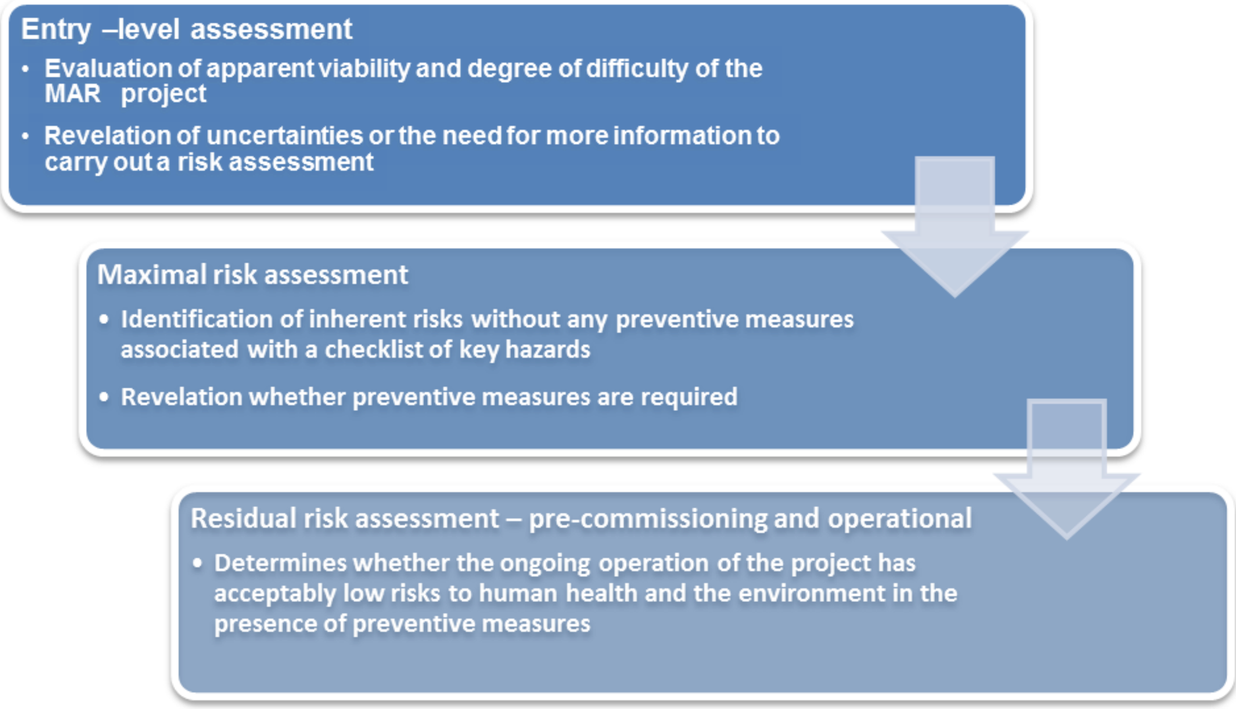

Figure 5-2: Overview and objectives of the general assessment stages (NRMMC-EPHC-NHMRC 2009).

Within this structure different assessment approaches are proposed in order to cover the full range of potentially important aspects when implementing a new MAR site. These include checklists, risk matrices, and simplified modelling approaches. During entry-level assessment a checklist approach is used to assess both viability and the degree of difficulty of the realisation of a new MAR project.

Moreover, a series of risk assessments that are designed to ensure protection of human health and the environment are foreseen. This includes an assessment of risks assuming the absence of any control measures (maximal risk assessment) and an assessment of the residual risk (both at a pre-commissioning and operational stage).

5.3 Application of Australian guidelines at Berlin-Tegel

This section demonstrates the application of the entry level assessment in Berlin-Tegel. Although Berlin-Tegel is an already running MAR project a periodic reassessment should be part of any proactive quality assurance. Entry level assessment may serve as a preliminary indicator of human health and environmental risks. Furthermore, it reveals existing knowledge gaps or the need for more information to carry out further risk assessment.

5.3.1 Entry level assessment of the MAR site in Berlin-Tegel

Entry-level assessment consists of a checklist approach for assessing viability the degree of difficulty of a MAR project (Table 5-1 and Table 5-2).

Table 5-1: Entry level assessment for Berlin-Tegel.

Attribute	Answer and Explanation
1. Intended water use	
Is there an ongoing local demand or clearly defined environmental benefit for recovered water that is compatible with local water management plans?	YES - About 70% of recovered water for drinking water comes from bank filtration (BF) or aquifer recharge through infiltration ponds (IPs) (BWB 2013) to ensure the supply of drinking water for about 3.5 million inhabitants in Berlin
2. Source water availability and right of access	
Is adequate source water available, and is harvesting this volume compatible with catchment water management plans?	YES - Lake Tegel water is readily available and is recharge through the river Havel, Tegeler Fliess and Nordgraben
3. Hydrogeological assessment	
Is there at least one aquifer at the proposed managed aquifer recharge site capable of storing additional water? **Is the project compatible with groundwater management plans?**	YES - The unconfined aquifer of Quaternary age is in connection with lake Tegel (for Induced Bankfiltration) as well as with the infiltration ponds (IPs). Also it is the main aquifer for recovery of Berlin's drinking water supply. YES - AR through ponds has been used in Berlin-Tegel since 1943 (Paproth et al., 2011) as essential part of the drinking water management
4. Space for water capture and treatment	
Is there sufficient land available for capture and treatment of the water?	YES - IPs have already been built in the forest in Saatwinkel near the WW Tegel. There is existing water treatment and supply throughout wells located around the ponds.
5. Capability to design, construct and operate	
Is there a capability to design, construct and operate a MAR project?	YES - The Berlin water company (Berliner Wasserbetriebe, BWB) has experience to operate and maintain IPs and recovery wells
➡ *Go to Table 5-2*	

Table 5-2: Degree of difficulty assessment of Berlin-Tegel

Attribute	Answers for Berlin-Tegel MAR site
1. Source water quality with respect to groundwater environmental values	
Does source water meet the water quality requirements for the environmental value of ambient groundwater?	**No** - The environmental value of the aquifer is drinking water production. The aquifer is the source of water for the Berlin drinking water supply. Investigations are required to assess risk.
2. Source water quality with respect to recovered water end-use environmental values	
Does source water meet the water quality requirements for the environmental values of the intended end uses of the water on recovery?	**No** - Lake Tegel water does not meet the German drinking water standards (TrinwV 2001) for turbidity, microbiology, organic micro pollutants and copper. Investigations are required to evaluate hazard attenuation processes during infiltration.
3. Source-water quality with respect to clogging	
Does source water have low quality; for example: **total suspended solids (TSS) >10 mg/L** **total organic carbon (TOC) >10 mg/L** **total nitrogen >10 mg/L?** **and is the soil or aquifer free of macropores?**	**No** - Source water is of good quality and additionally the clogging layer in the infiltration ponds is removed and washed and cleaned of finer grained material and algae periodically. No further investigations needed.
11. Fractured rock, karstic or reactive aquifers	
Is the aquifer composed of fractured rock or karstic media, or known to contain reactive minerals?	**Yes** - The aquifer can contain ferrous or manganiferous sediment. Investigations are required to assess potential consequences of iron and manganese dissolution.
12. Similarity to successful projects	
Has another project in the same aquifer with similar source water been operating successfully for at least 12 months?	**Yes** - Sites all around Berlin (mostly riverbank filtration, but IPs as well) are in operation for decades. No further investigations needed.
4. Groundwater quality with respect to recovered water end-use environmental values	
Does ambient groundwater meet the water quality requirements for the environmental values of intended end uses of water on recovery?	**No** - Ambient groundwater (TEG342) has evidence of of elevatediron and manganese concentrations. SO4 concentration is also punctually elevated (up to 240 mg/L). Contaminated sites nearby (e.g. Tegel airport, abandoned industrial sites). MAR site at risk of

Attribute	Answers for Berlin-Tegel MAR site
	contamination plume. Investigations are required to evaluate protective measures against contaminant input from shallow ambient groundwater.
5. Groundwater and drinking water quality	
Is either drinking water supply, or protection of aquatic ecosystems with high conservation or ecological values, an environmental value of the target aquifer?	**Yes** - The target aquifer is used for drinking water supply through wells. No groundwater dependant eco systems nearby. Investigations are required to assess the risk to groundwater quality and human health.
6. Groundwater salinity and recovery efficiency	
Does the salinity of native groundwater exceed either of the following: **(a) 10 000 mg/L** **(b) The salinity criterion for uses of recovered water?**	**No** - The mean value for TDS in TEG342 is 585 mg/L. This value is even lower in the source water. Also, sodium and chloride are below the guideline values. No further investigations needed.
7. Reactions between source water and aquifer	
Are redox status, pH, temperature, nutrient status and ionic strength of groundwater similar to that of source water?	**No** - Different water quality may lead to reactions. Investigations are required to evaluate geochemical reactions.
8. Proximity of nearest existing groundwater users, connected ecosystems and property boundaries	
Are there other groundwater users, groundwater-connected ecosystems or a property boundary within 100–1000 m of the MAR site?	**No** - The infiltration ponds are located within the catchment area of Tegel waterworks of the Berlin water company (BWB). Furthermore, the IPs are surrounded by recovery wells. No further investigations needed.
9. Aquifer capacity and groundwater levels	
Is the aquifer confined and not artesian? Or is it unconfined, with a water table deeper than 4 m in rural areas or 8 m in urban areas?	**No** - The unconfined aquifer has a water table of 4 m within the rural area of the forest, but in urban areas it may be higher than 8 m below ground. Investigations are required to assess risk of excessive groundwater mound height.
10. Protection of water quality in unconfined aquifers	
Is the aquifer unconfined, with an intended use of recovered water that includes drinking water supplies?	**Yes** - the aquifer is unconfined with recovered water for drinking water supply. Investigations are required to assess the protection of

Attribute	Answers for Berlin-Tegel MAR site
	groundwater quality.
13. Management capability	
Does the proponent have experience with operating MAR sites with the same or higher degree of difficulty, or with water treatment or water supply operations involving a structured approach to water quality risk management?	**Yes** - The proponents have a history of operating drinking water supplies and groundwater exploitation and the MAR site is in operation for decades now. In Germany, a high level of standardization is reality. The Berlin Water Utilities are the largest water supplier in Germany and have the German standard for securing drinking water quality implemented.
14.Planning and related requirements	
Question is not relevant, because the project is already in operation for decades.	

Both checklists represent a well-structured and comprehensible foundation for a first desktop assessment of available information. Since in Berlin the later use of the source water (lake water) is drinking water the non-compliance with some of the water quality related questions was expected and additional investigation and reduction measures are necessary. In summary, the assessment of degree of difficulty identified investigations needed for a continuing risk assessment, such as:

- Source water quality investigations (questions 1 and 2)
- Evaluation of the recovered water quality against the German TrinkwV (2001) (questions 4 and 5)
- A geochemical evaluation (questions 7 and 11)
- An assessment of groundwater levels (question 9)
- An assessment of urban land users and risks to groundwater quality (question 10).

According to the Australian guidelines water quality requirements should be reached prior to infiltration. In contrast, the Berlin drinking water purification systems strongly rely on the cleaning capacity of the underground passage as a major barrier for microbial and chemical constituents.

5.3.2 Identification of key hazards

Within the guidelines for managed aquifer recharge potential hazards are grouped into 12 categories, so called key hazards (see Table 5-3). For a detailed description of the potential adverse effects, which might be caused by the respective hazard, it is referred to chapter 5 of the guideline document.

For each key hazard, a clear entry-level acceptance criteria is defined in the guideline (Table 5-3). These acceptance criteria will serve for preselecting relevant hazards for the recharge system of Berlin-Tegel.

Table 5-3: **Summary of key hazards in source water, groundwater and aquifer materials for MAR projects, with examples of specific hazards.**

Key hazard	Estimated risk after entry-level assessment	Selected for further risk assessment	Reasons
Pathogens	High	**Yes**	Acceptance criteria not met: end use includes drinking water supply. Source water has high risk of pathogen contamination due to influence of treated wastewater
Inorganic chemicals	Low	**No**	Some calcite (CaCO3) and rhodochrosite (Mn-CO$_3$) dissolves during subsurface passage leading to an increase of Ca and decrease of pH (Greskowiak et al., 2006) The predominant aerobic subsurface passage does not pose a high risk for geogenic mobilisation of metals, concentration of metals in source water is low
Salinity and sodicity	Low	**No**	Acceptance criteria met: TDS source water < 500 mg/L. Source water in respect to salinity and sodicity of almost equal quality to the ambient groundwater quality, even better.
Nutrients	Low	**No**	Acceptance criteria met: source water nitrogen species meet with the TrinkwV 2001
Organic chemicals	high	**Yes**	Acceptance criteria not met: Occurrence of various organic chemicals is known (e.g. pharmaceuticals). Even if the concentrations of the measured and selected pharmaceutical active compounds are below guideline values (NRMMC-EPHC-NHMRC 2009) they still may pose a significant risk. Other literature provide much lower concentrations as a safe drinking water level based on TDI or maximum residue level, e.g. Mons et al. 2014 90 ng/L for carbamazepine in comparison to NRMMC-EPHC-NHMRC 2008 with guideline value of 100 µg/L (=100.000 ng/L)
Turbidity and particulates	low	**No**	Acceptance criteria not met: estimated values for Lake Tegel (Ø 2,5 ± 1,4 NTU > 1 NTU acceptance criterion of the entry-level assessment as well as the TrinkwV 2001 (1.0 NTU) Long term experiences at the demo site and pre-treatment to non-selection.
Radionuclides	Low	**No**	Acceptance criteria met: low-risk lithology in storage zone (i.e. no granite or coal deposits) No radioactive isotopes in the source water
Pressure, flow rates, volumes and levels (unconfined aquifer)	Low	**No**	Even though, some criteria are not met risk is estimated as low. Prevention of water contamination by operation of infiltration ponds and operation of different extraction wells at a time. Control of water table is given by an alternating well operation.

Key hazard	Estimated risk after entry-level assessment	Selected for further risk assessment	Reasons
			Also, there is no further investigation regarding this hazard because of already successful operation for so long.
Contaminant migration in fractured rock and karstic aquifers	Low	**No**	Not relevant since the aquifer is porous with sediments of Quaternary age that mainly contain glacio-fluvial sands with varying proportions of fine, medium and coarse grains.
Aquifer dissolution and aquitard and well stability	Low	**No**	Even though calcite dissolution occurs due to changing redox condition below the pond, at a larger scale influence of transient saturated or unsaturated conditions that lead to dissolution of calcite seemed not to be relevant (NUETZMANN ET AL. 2006)
Impacts on groundwater-dependent ecosystems	Low	**No**	There is no groundwater-dependent ecosystem within the area from infiltration pond to well 20.
Greenhouse gases	Low	**No**	The Berlin Water utilities fulfil entry-level assessment criteria with their environmental sustainability program (renewable energy use, energy efficient pumps, etc.)

5.3.3 Assessment of selected key hazards

The assessment of maximum and pre-commissioning risk provides information about the necessary treatment performance in the planning phase of an MAR project. In maximal risk assessment risk in the absence of any reduction measure is assessed. Crucial for the assessment risks of pathogens and chemicals in the aquifer is an estimation of travel times.

5.3.3.1 Estimating travel times during subsurface passage

Within the Australian MAR Guidelines for water recycling a simplified analytical modelling approach is proposed for predictions of the fate of organic and microbial hazards during MAR. The parameter values applied for the calculation of travel times are shown in Table 5-4.

Table 5-4: **Parameters values used for the calculation of travel times.**

Parameter	Value
Aquifer thickness (m)*	30-40
Porosity of the aquifer (%)	20-30
Distance between point of infiltration and recovery well (m)*	100
Average pumping rate of well 20 (m^3/d)	1920-2400
Minimum depth to the mounded water table beneath the infiltration basin or gallery (m)*	0-6
Saturated hydraulic conductivity (m/s)*	1.5×10^{-4}-1.1×10^{-3}

*from Greskowiak et al. (2005) and references therein

Within previous project and investigations at the site a travel time of 1-2 months (on average approx. 50d) was estimated. According to the methods proposed by the Australian Guidelines (NRMMC-EPHC-NHMRC (2009), Appendix 6) in combination with site specific parameter estimations (see Table 5-4) the modelled travel time lies between 28 and 59d with 50% of the values within an interval between 33 and 38d. Thus, although the results fall within the timeframe of 1-2 months the median or dominant travel time is 41d (Figure 5-3).

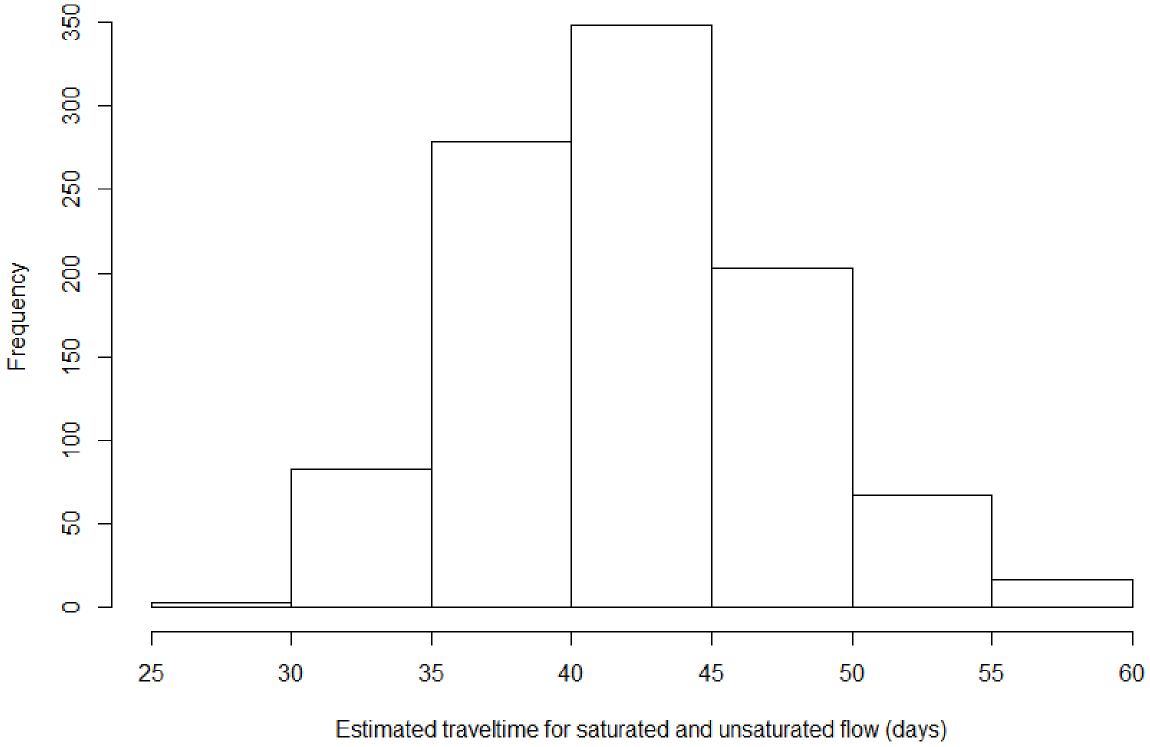

Figure 5-3: **Histogram of calculated travel times during subsurface passage.**

5.3.3.2 Organic chemicals

Organic substances are assessed at different stages of the overall assessment process. Table 5-5 gives an overview on the risk assessment and management approach regarding organic chemicals within the Australian guidelines.

Table 5-5: Assessment criteria for organic chemicals (NRMMC-EPHC-NHMRC 2009).

	Entry-level assessment and simplified assessment	Maximal and pre-commissioning residual risk assessment	Residual risk assessment (operational)
Acceptance criteria	Organic chemicals unlikely in source water at concentrations that would exceed acceptable concentrations for environmental values of aquifer or intended end uses Unlikely to be formed in the subsurface (no disinfection)	Any organic chemicals present in source water or formed in the subsurface are at or attenuate to concentrations that meet environmental values for aquifer beyond attenuation zone and in water recovered for use	As per pre-commissioning residual risk assessment
Preventive measures	na	Source control Pre-treatment, residence time in soil or aquifer or post-treatment	As per pre-commissioning residual risk assessment
Validation monitoring	na	na	- Determine organic chemical (hazard) and biodegradable organic carbon in: source water, attenuation zone, observation wells, recovered water - Analyze minimum period of aquifer storage using “natural” or introduced tracers - Evaluate physicochemical and redox conditions

The environmental values which would have to be applied at the case study in Berlin-Tegel would be the limit values of the German drinking regulation. Pharmaceuticals in Germany are addressed by the so-called health-oriented values (HoV), which apply a precautionary value of 0.1µg/L (0.01 µg/L for carcinogenic and endocrine disruptive chemicals) in case that no further information is available. HoV´s are recommended by the German Drinking Water Commission (Trinkwasserkommission) and are precautionary values for substances which either cannot or only partially assessed from a human toxicological endpoint. After testing several chemical properties and modes of action for the respective chemical less restrictive value may be applied.

In this study, measured data from source water (Lake Tegel) of five organic micro pollutants were used as an example. Measured substance concentration distribution was fitted to a gamma distribution for each data set using the “fitdistr” function in R for parameter estimation (www.r-project.org). Normal distribution was found to be not suitable as concentration will become negative. After fitting one thousand randomly distributed values were taken for further calculations.

The resulting concentrations in production well 20 were calculated using the equations outlined in the appendix 6 of the Australian guidelines (NRMMC-EPHC-NHMRC 2009) by:

1. Calculation of travel time of water from infiltration basin to production well (saturated and unsaturated)
2. Application of chemical specific retardation factors
3. Application of first order decay (dilution is not considered although the well 20 ab abstracts about 80-90 of infiltrate (Pekdeger et al., 2006))

Sorption processes during subsurface passage will retard the transport of chemical substances based on their physicochemical properties. The magnitude of the retardation factor is influenced by the partitioning coefficient (Kd) of the chemical substance and the fraction of organic carbon in the sediment. The soil organic carbon partition coefficients were determined by USEPA (1996) according to:

$$\log K_{OC} = 0.7919 \log K_{OW} + 0.0784$$

K_d is then calculated by multiplying K_{oc} by f_{oc} (the mass fraction of soil organic carbon content), according to:

$$K_d = f_{OC} \times K_{OC}$$

The log K_{OW} (Table 2) for the organic compounds can also be taken from the online database (www.chemicalize.org). Fraction of organic carbon in the sediments are f_{oc} = 0.02 – 0.08 wt % (Pekdeger et al., 2006). Table 5-6 gives an overview on the chemical properties used for transport calculation. The DT50 and log Kow values were previously determined by reactive modelling (Henzler et al., 2014) and represent the predominantly oxic to sub-oxic redox conditions at the site.

Table 5-6: Overview of chemical properties and drinking water benchmarks of different micro pollutants (from Henzler et al. (2014))

Substance	DT50 (days)*	Log Kow*
Carbamazepine	66	2.45
Diclophenac	36	4.01
Primidone	8022	1.12

Phenazone	57	1.22
EDTA	200563	-1.86

The retardation for each substance is calculated based on the following equation:

$$R_f = 1 + \rho_s \cdot K_d / ne$$

where

R_f	retardation factor [-]
n	porosity [-]
ρ_s	dry bulk density [g/cm³]
K_d	sorption isotherm [ml/g]

The effective porosity was assumed to vary between 0.2 -0.3. The dry bulk density varied between 1.450 - 1.900 g/cm^3, representing characteristic density for the porous aquifer. The retarded compound specific flow velocity is calculated by:

$$v_{compound} = \frac{v_{GW}}{R_f}$$

where

$v_{compound}$	flow velocity of compound [m/d]
R_f	retardation factor [-]
v_{GW}	flow velocity of groundwater [m/d]

The transport time for the compound for the distance between pond and abstraction well is calculated using the equation:

$$t_{compound} = \frac{x}{v_{compound}}$$

where

$t_{compound}$	compound specific transport time [d]
x	distance between recharge zone and abstraction well [m]
$v_{compound}$	flow velocity of compound [m/d]

The (biological) degradation for each compound during subsurface transport is calculated by first-order degradation term according to:

$$c = c_0 \cdot e^{-\lambda \cdot t_{compound}}$$

where

c concentration in abstraction well [µg/L]

c_0 initial concentration in source water [µg/L], gamma distribution of measured concentration in source water

λ decay constant [1/d]

with $\lambda = \frac{\ln 2}{DT_{50}}$

λ decay constant [1/d]

DT_{50} half-life time of the compound [d]

Dilution is not taken into account. Figure 5-4 shows the substance specific travel times.

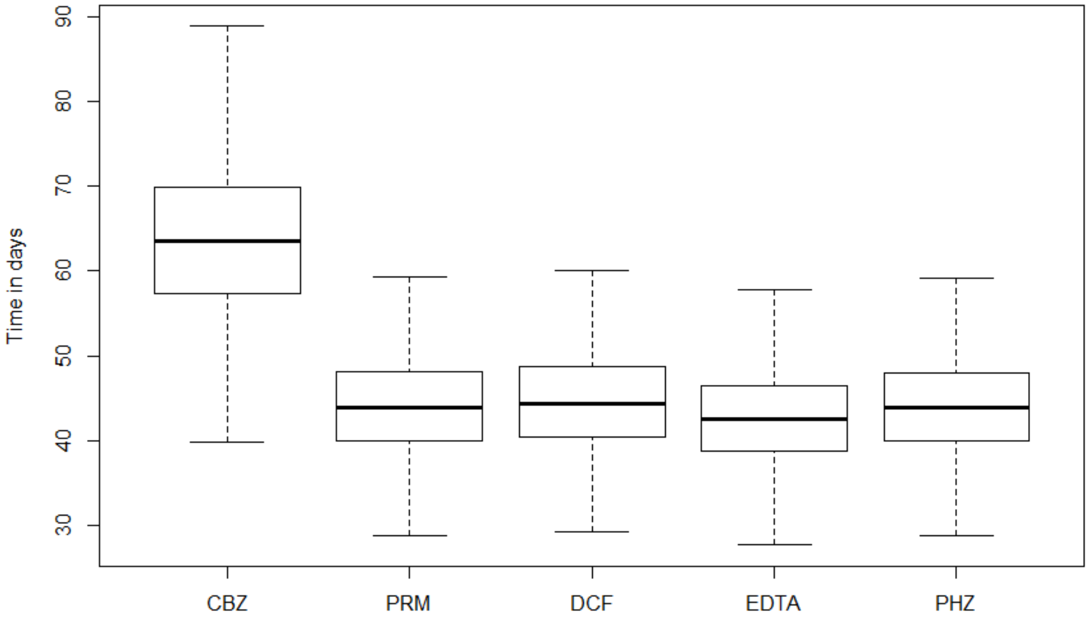

Figure 5-4: Substance specific travel time accounting for hydraulic and physico-chemical properties (Carbamazepine (CBZ), Primidone (PRM), Diclophenac (DCF), EDTA, and Phenazone (PHZ)).

Figure 5-5 shows the calculated and measured concentrations in production well 20. Upper and lower box shows the 75 and 25 percentile, maximum and minimum values are displayed by small horizontal lines at the end of the whiskers. Arithmetic average values are displayed by small rectangles and mean values are displayed by horizontal lines in the box.

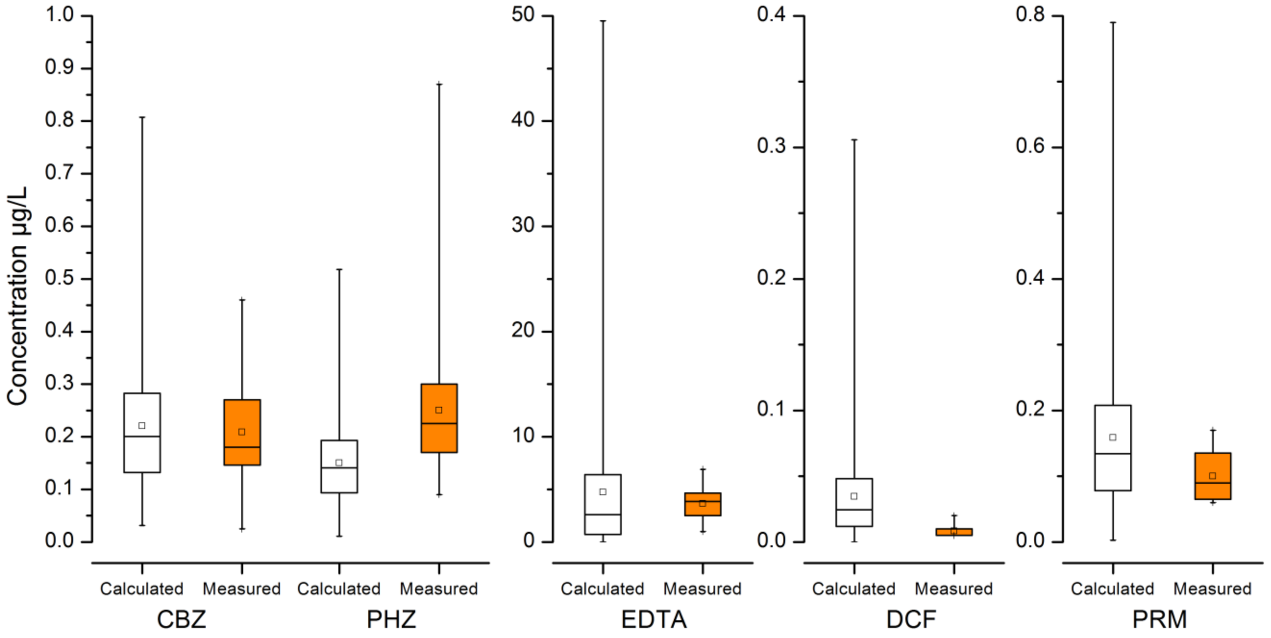

Figure 5-5: **Calculated (blank) and measured (orange) concentrations of micro pollutants in production well 20 (Carbamazepine (CBZ), Primidone (PRM), Diclophenac (DCF), EDTA and Phenazone (PHZ)).**

In general, the calculated concentrations show much larger concentration ranges compared to measured values. This is due to wide range of calculated travel times and the chosen distribution function of substance concentration. Calculated mean concentrations are higher compared to measured concentrations for CBZ, DCF and PRM, while PHZ and EDTA show lower calculated mean values, i.e. mean values do not represent a conservative value for risk assessment. However, considering the given input parameters and simple methodological approach the resulting concentrations are in a realistic range and represent a good approximation of attenuation processes in the subsurface.

Against the background of the used available information and assumptions the concentrations of DCF, PHZ, CBZ are not expected to exceed the benchmark of the HoV (0.1 µg/L and 0.3 µg/L). Although EDTA is expected to be present in the production well with a median value of approx. 2.4 µg/L the existing HoV threshold of 10 µg/L gives no reason for acute concern. However, this threshold is exceeded by calculated maximum concentrations by a factor of 5 approximately.

CBZ was measured at Berlin-Tegel with 0.47 µg/L in the source water and 0.21 µg/L in the abstraction well 20 (Heberer and Jekel 2006). The reduction of the concentration cannot be explained by dilution only (share of infiltrate 80-90%) and the measured concentration fits well with calculated values.

Calculated DCF values were mostly below limit of quantification (0.1 µg/L). As indicated by the high log Kow value (log Kow = 4.01) DCF shows a high affinity for sorption. Based on the assumed substance properties and the sake of risk assessment the resulting value adequately represents measured concentration. Measured PHZ concentrations are not adequately represented by this approximation and it is likely that native groundwater contribute to PHZ concentration.

5.3.3.3 Pathogens

For microbial hazards risk assessment via quantitative microbial risk assessment is proposed using the DALY (disability adjusted life years) indicator as a measure of risk. A health based target of 1 tolerable additional µDALY pppy is applied. This is in line with the current approach of WHO (WHO 2011). Risk is usually assessed for selected reference pathogens which cover bacterial, protozoan and viral pathogens. Here risk assessment is presented just for viruses, using Rotavirus as a reference pathogen.

For maximal risk assessment a rotavirus concentration of 1-10 virus particles per litre is assumed (WHO 2011). Assuming this concentration the risk resulting from Rotavirus without any reduction measures is calculated to be around 420 µDALYs per person per year (pppy) (see Figure 5-6). In order to be in compliance with the WHO standard of 1 µDALY pppy an additional reduction of 5-6 log units is necessary (Figure 5-7).

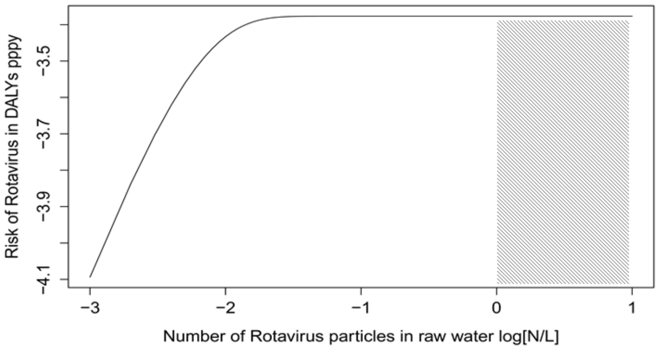

Figure 5-6: **Disease burden in DALYs without any reduction measures in place. Assumptions (1L drinking water consumption per day, disease per infection ratio (0.5), susceptible fraction (6%), dose response parameters for Rotavirus from (Haas et al. 1999), severity factor ($1.4*10^{-2}$ DALYs/case of disease)).**

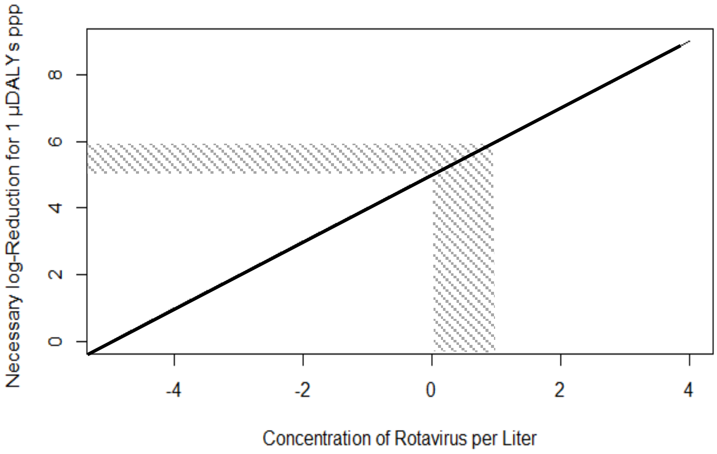

Figure 5-7: **Number of log removal (LRV) required to be in compliance with a tolerable level of risk of 1 µDALY pppy. Assumptions: 1L drinking water consumption per day, disease per infection ratio (0.5), susceptible fraction (6%), dose response parameters for Rotavirus from ((Haas et al., 1999)).**

5.3.3.4 Reduction measures in Berlin-Tegel and residual risk assessment

As described in chapter 3 of this report, drinking water treatment in Berlin-Tegel consists of an underground passage via bank filtration and groundwater recharge followed by aeration and rapid sand filtration before end-use. Regarding the effectiveness of the individual barriers with regard to virus removal the following values are given by WHO (WHO 2011) for bank filtration and rapid sand filtration (Table 5-7). It has to be mentioned that removal rates depend on the residence time, temperature, redox conditions and aquifer characteristics. Here, a stochastic approach is used to account for fluctuations and variation in pathogen removal.

Table 5-7: Barriers and assumptions of the effectiveness of virus reduction in Berlin-Tegel (WHO 2011)

Treatment	Log removal (LRV)	Remarks/assumption
Subsurface passage (assumption: effectiveness of comparable bank filtration for microbiological parameters)	2.1-8.3	Depending of the residence time in subsurface. Assumption used for calculation: 4-6 Log removal(LRV)
Rapid sand filtration	0-3.5	Depends on filter media and coagulation pre-treatment: Assumption used for calculation: 1-2 LRV

Following the assumptions made in the previous chapter an overall virus reduction potential of 5-8 LRV is assumed. In order to account for present uncertainties a Monte Carlo Simulation is conducted based on the made assumptions. The results are compared to the Australian and WHO standards of 1 additional µDALY per person per year (pppy). Results were grouped in five risk categories:

- A: risk exceeds tolerable WHO level by a factor of 10 or more
- B: risk exceeds tolerable WHO level by a factor of 10
- C: risk below tolerable WHO level by a factor of 10
- D: risk below tolerable WHO level by a factor of 100
- E: risk below tolerable WHO level by a factor of 1000

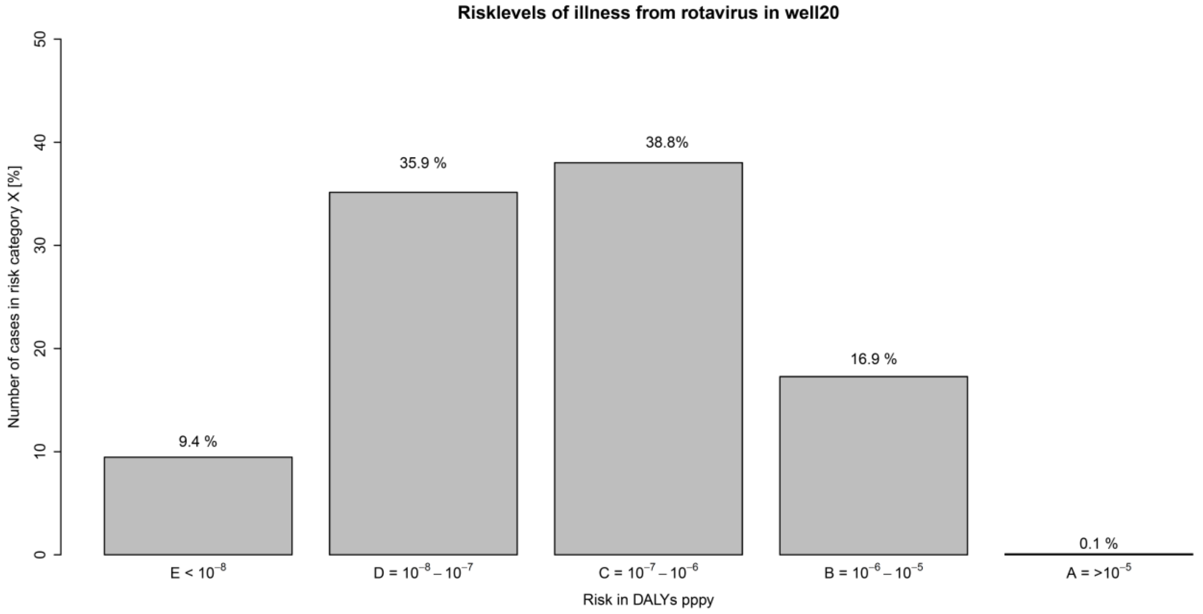

Figure 5-8: Results of risk calculation for drinking water production for well 20 at the MAR site in Berlin-Tegel.

The calculation reveals that against the background of the made assumptions the limit of 1 µDALY pppy is exceeded for about 17% of the calculated realizations. Both the mean and the median value are below this benchmark. An intolerable risk and an acute need for action can consequently not be postulated. However, as estimations of travel times in the aquifer indicate that a sufficiently safe residence time of 50 days cannot be guaranteed, it is recommended to further investigate the removal of viruses during subsurface passage and verify the residence time during MAR.

5.4 Summary and conclusions

The Australian Guidelines for Water Recycling – Managed Aquifer Recharge provide a ready-to -use and user-friendly compendium of knowledge. Practical instructions and checklists provide a step wise approach with a strong focus on implementation. The proposed models for water flow and substance transport allow a first tier estimation of present concentrations in ambient groundwater and the impacted zone in the aquifer. The use of stochastic models is not mandatory within the guidelines. A criticism which can be identified related to the use of models simply based on point estimates, is that especially in early stage risk assessments, where uncertainties are usually high, these models tend to pretend a level of certainty which often does not represent reality.

Risks associated to inorganic chemicals are required to be treated with more detail. Rigorous quantification of biodegradation kinetics (e.g. first-order rate constants) and adsorption parameters (e.g. linear distribution coefficients) for EOCs during subsurface passage determined on field scale are still scarce. It is clear that first-order rate constants and linear distribution coefficients provide only a simplified description of the removal mechanisms during subsurface passage, because they neglect spatial and temporal dynamics of physical and chemical conditions. Nevertheless, this approach often provides a good approximation and allows also for site independent comparison of removal processes.

Regarding the demonstration site in Berlin-Tegel the analysis showed that if the model of the Australian Guidelines is applied to the MAR system the travel time of 50d during subsurface passage cannot be guaranteed. In Germany, a residence time of 50d is usually considered to sufficiently reduce the risk of microbial hazards. Although risk calculations did not reveal immediate concern, it is recommended to develop and apply suitable verification monitoring techniques to quantify travel times and reduce present uncertainties. Moreover, this risk assessment and the study about the influence of the groundwater replenishment site on ambient groundwater (Sprenger and Grützmacher, 2015) clearly showed the need for protective measures against the input of undesired substances from shallow ambient groundwater.

References

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6 Summary of field investigations in Sant Vicenç dels Horts (Barcelona, Spain): MAR effects on groundwater resources

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6.1 Introduction

This report presents the work carried out at a groundwater replenishment site in Sant Vicenç dels Horts (Spain). The following topics are covered:

- Bulk chemistry: characterisation of infiltration and groundwater
- Assessment of emerging pollutants and their behaviour during MAR
- Using temperature of groundwater as a tracer to determine arrival time of recharged water
- Leaching test to assess the reactivity of organic layer (laboratory test)
- Bioassays of MAR samples

DEMEAU project has also contributed in the knowledge of the fate of emerging pollutants with a column experiment simulating the MAR system of Sant Vicenç dels Horts (Hernández and Gibert, 2014; Schaffer *et al.* 2015). A comparison between field results (this report) and column experiment from Hernández and Gibert (2014) and Schaffer *et al.* 2015 can also be found in this report.

6.2 Materials and methods

6.2.1 MAR profile

The infiltration system of Sant Vicenç dels Horts (SVH) was constructed in 2007 and started its operation in 2008. The main objective of the system is to introduce additional freshwater into the aquifer to gain an average extra volume of one Mm^3/year. The operation consists in a direct intake of Llobregat river water two km upstream of the ponds. The catchment area is an intake channel that has to be reconstructed from time to time according to rainy periods that can destroy totally or partially the intake channel. Collected water circulates downstream by a concrete pipe of an inner diameter of 1000 mm. the system is controlled manually by CUADLL (Association of users of the aquifer) according to quality alerts and meteorological forecast.

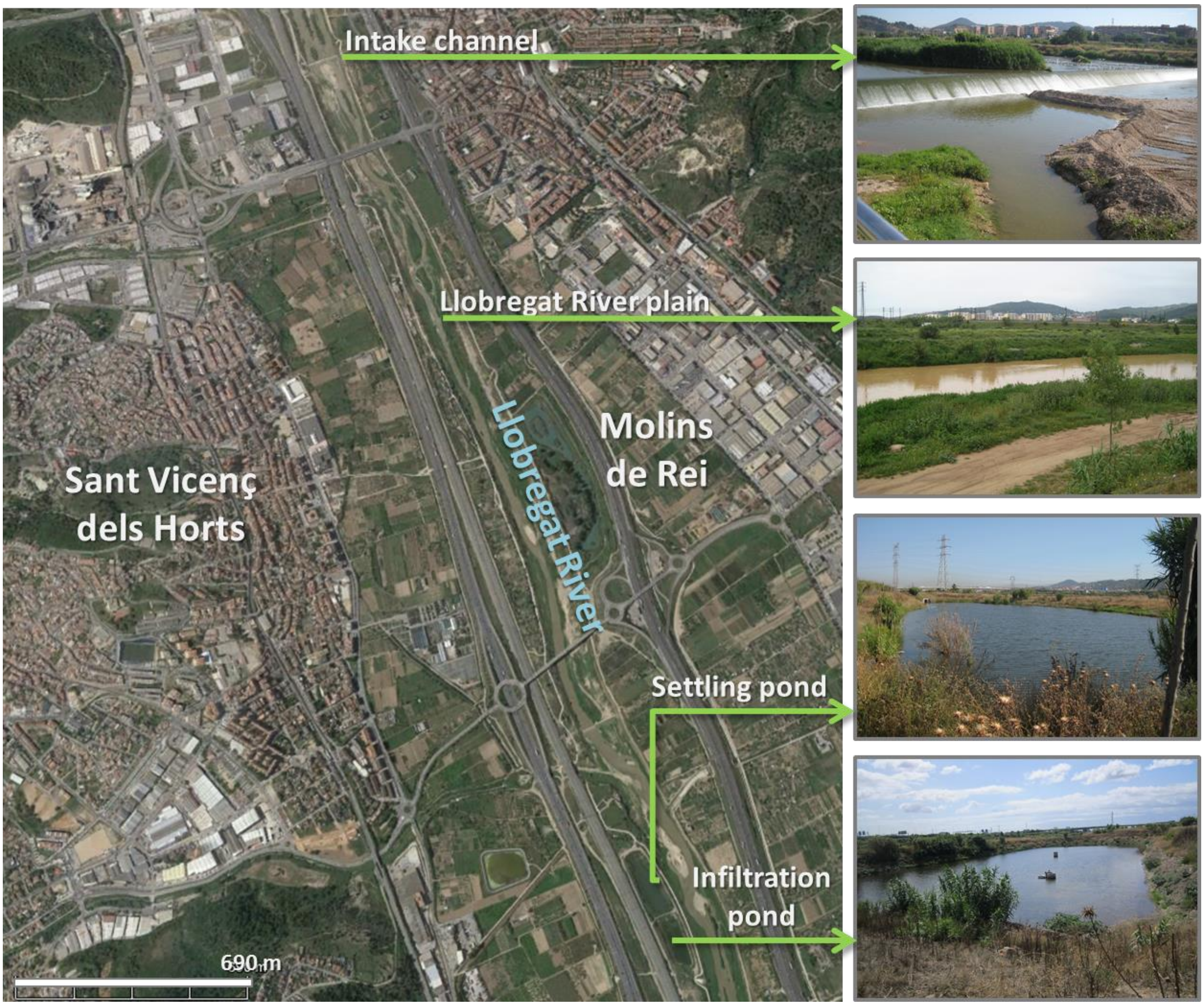

Figure 6-1: Overview of Llobregat area and SVH system location.

Water enters in the settling pond (6,000 m^2), with a residence time of about two or three days. Settling pond and infiltration pond are inter-connected by a concrete pipe of 1000 mm. The connection is instrumented with a flowmeter to quantify the volume of water introduced in the infiltration pond. Moreover, there is a datalogger installed in one of the concrete islands of the pond that gets automatic data of water level and temperature of the infiltration water. Spreading surface of the infiltration pond is about 5,600 m^2. In 2011 the infiltration pond was enhanced with a reactive organic layer compost-made. The compost was 100% vegetal compost and it was mixed half-and-half with local sand and gravels. The main objective of the installation of the reactive layer was the increase of removal of emerging pollutants. Effectiveness of the reactive layer was tested at field scale in the Life+ ENSAT project (results available at http://www.life-ensat.eu/). The reactive layer has been also tested in DEMEAU in a simulation of the real system of SVH at laboratory scale, by a column experiment (results available at http://demeau-fp7.eu/ and Schaffer *et al.* 2015).

SVH site is very well-known from previous projects carried out there[1]. The observation network is very completed. An accurate selection of groundwater observations wells has been done for the network of DEMEAU sampling campaigns. "INF" represents water entering in the infiltration pond. BSV-1 represents native conditions of the aquifer, and the rest of the points (BSV-5, BSV-8.1, BSV-8.3, BSV-9, and BSV-10) have the influence of the infiltrated water in different proportion according to the depth and distance to the infiltration pond.

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[1] ENSAT project: http://www.life-ensat.eu/
PREPARED project: www.prepared-fp7.eu
GABARDINE project: http://cordis.europa.eu/publication/rcn/13034_en.html

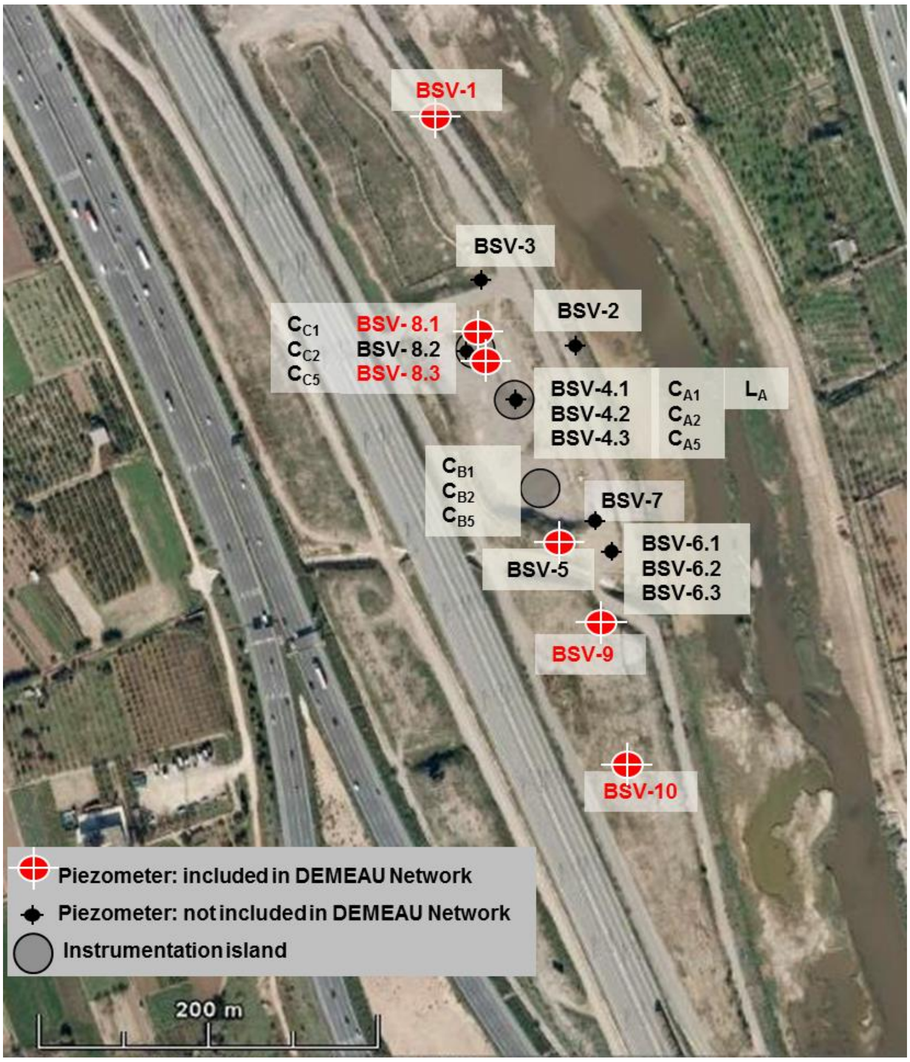


Figure 6-2: Aerial view of location of sampling points

Table 6-1 shows the location of the DEMEAU's sampling points and depths of filter screens. A profile with essential characteristics of the Sant Vicenç dels Horts groundwater replenishment site can be found in annex G.

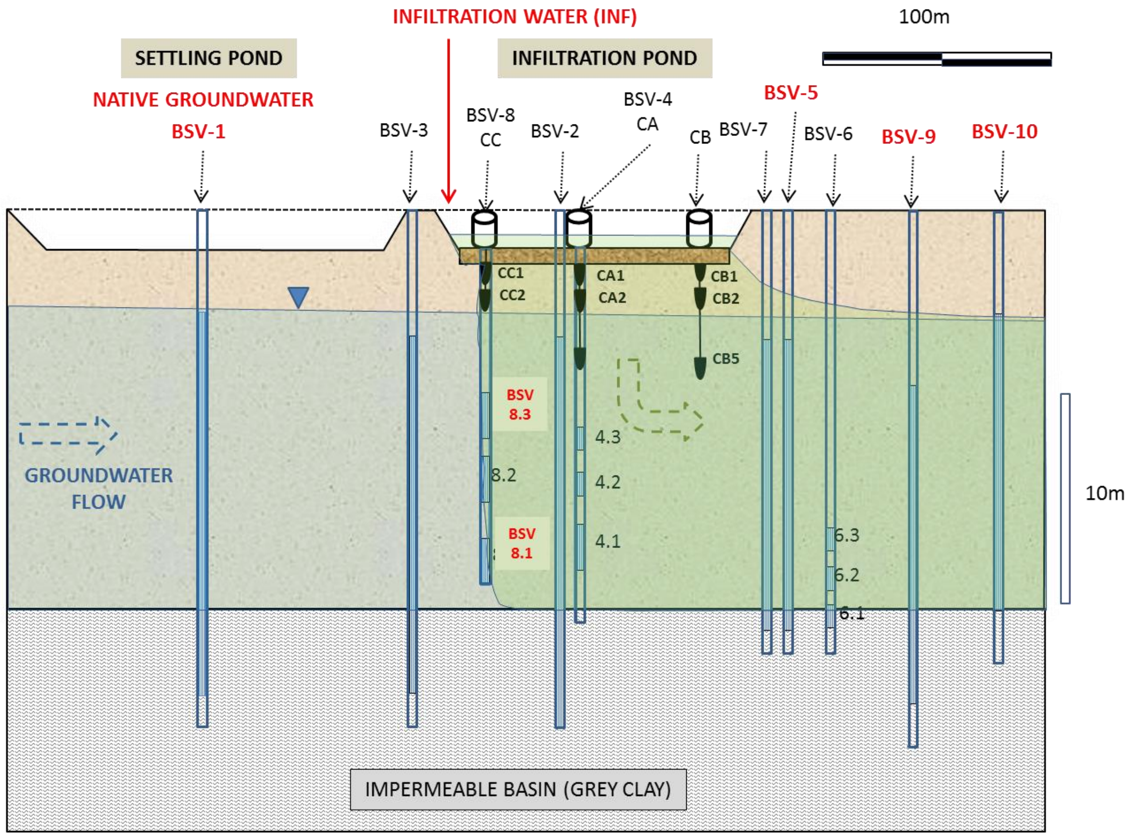


Figure 6-3: Hydrogeological profile section at Sant Vicenç dels Horts (red coloured observation wells were sampled in this study)

Table 6-1: Type, depth, filter screen position and hydraulics of sampling points.

Sampling points	Type	Total depth (m)	Filter screen depth (m below surface)	Approximate travel time or recharged water (days)	Proportion of infiltrated water (conservative tracer test)*
INF	River water			0	100%
BSV-1	Groundwater	24.5	6-24	Not influenced	0%
BSV-5	Groundwater	21.5	5-23	6	98%
BSV-8.1	Groundwater	16.0	13-15	N.A.	57%
BSV-6.2	Groundwater	19	17.5 – 18.5		
BSV 6.3	Groundwater	17	15.4-16.6		
BSV-8.3	Groundwater	10.0	7 - 9	4	88%
BSV-9	Groundwater	26.6	9.5 – 24.4	13	96%

Sampling points	Type	Total depth (m)	Filter screen depth (m below surface)	Approximate travel time or recharged water (days)	Proportion of infiltrated water (conservative tracer test)*
BSV-10	Groundwater	22.5	6-20	17	98%

(*) this conservative tracer test was done in previous project ENSAT (2011) using chloride as a conservative tracer for the comparison between INF and BSV-1 (native groundwater)

6.2.2 Field sampling campaigns

Three sampling campaigns have been performed along the DEMEAU project: July 2014, January 2015 and May 2015. Different recharge conditions have been assessed, as the infiltration system was fully in operation in the first sampling campaign (July 2014), while in January 2015 the infiltration pond was dry. The last sampling campaign (May 2015) has been classified as “mixed conditions”, as there was partial infiltration due to the excavation of an infiltration channel to assess the infiltration rate in the pond.

Figure 6-4 shows the recharge conditions in each of the sampling campaign.

Figure 6-4: **Pictures of the infiltration pond in the 3 sampling campaigns** *Note: Left wet conditions July 2014; Middle dry conditions January 2015; Right mix conditions May 2015.*

The sampling points have been described in the MAR profile section of this document. Infiltration water was substituted by river water in the second sampling period in January 2015, as the system was in stand-by. Sampling bottles were provided by the laboratories. Groundwater samples were taken after a purge of one volume of the piezometers, using disposable 1L plastic bailers. Bottles and bottle caps were rinsed with sampled water. Samples were taken with gloves to avoid contamination. Plastic bottles for metal determination by ICP contained nitric acid for the direct acidification of the sample. No additional treatment was done (filtration, extraction, etc.) on site. Samples were directly analysed at the laboratory using standard methods. Table 2-2 lists the parameters analysed in the Laboratory of Aigües de Barcelona to assess the bulk chemistry.

Table 6-2: Summary of sampling campaigns and laboratories involved

Sampling campaign	Recharge conditions	Micropollutants laboratory	Bulk chemistry laboratory	Bioassays Survey
July 2014	Wet conditions (infiltration pond filled)	University of Göttingen 250 mL (WWTP effluent; 500 mL groundwater). Glass amber bottles	Aigües de Barcelona	YES (2 L frozen) Glass amber bottles
January 2015	Dry conditions (infiltration pond empty)	Kompetenzzentrum Wasser Berlin (KWB) 50 mL amber bottle	Aigües de Barcelona	NO
May 2015	Mixed conditions (infiltration channel in the middle of the infiltration pond)	Kompetenzzentrum Wasser Berlin (KWB) 50 mL amber bottle	Aigües de Barcelona	YES (500 mL refrigerated) Glass amber bottles

6.2.3 Temperature as a tracer

In this study a numerical approach is developed to investigate heat as a tracer for travel time evaluation during subsurface passage from the infiltration basin to the monitoring wells. Additional information on tracer studies related to MAR (Sprenger, 2015) can be found in the DEMEAU tool box (http://demeau-fp7.eu/toolbox). In this approach the numerical software VS2DH (Healy and Ronan, 1996) is used as a:

- pre-processor for setting up the model simulation
- numerical engine for computing flow and heat transport (VS2DHI 3.3) and solute transport (VS2DTI 3.3)

However, its pre-processor offers no advanced features, e.g. automatically changing model input parameters or performing batch runs, which is required for automatized model calibration. To overcome this drawback the programming language R (http://www.r-project.org) in conjunction with the user-friendly integrated development environment R-Studio (http://www.rstudio.org) is chosen for this study in order to perform:

- Data analysis: checking and visualising available monitoring data
- Data preparation: e.g. summarising of monitoring data (e.g. calculation of statistical parameters)
- Automatized numerical engine runs and result evaluation

6.2.3.1 Model structure

A two dimensional vertical cross section model was created. The model structure of the unsaturated zone, the aquifer and the filter screens of the observation wells (piezometers) are deduced from Figure 6-3 and implemented in the VS2DI model (Table 6-3).

Table 6-3: Temperature model set-up.

Model domain	Location Pond 1	Location Pond 2	Boundary conditions	Location observation wells
x=700 m z=35 m	x=140-315 m z=2 m	x=350-480 m z=2 m	X=0: constant head X=700: constant head	BSV3: x=330 m BSV2: x=404 m BSV4.1: x=406 m BSV5: x=515 m BSV6.3: x=525 m

The following boundary conditions are implemented in the numerical model:

- Specific flux boundary: infiltration from the infiltration pond to the unsaturated/saturated zone is calculated for each stress period by dividing the daily inflow rate through the infiltration pond surface area (5423.5 m^2) resulting in an average infiltration rate per unit area of 0.95 m/day. Note that this approach assumes that no water is neither lost through evapotranspiration nor stored in the pond, thus possibly overestimating the real infiltration rate,
- Constant head boundaries: upstream/downstream of MAR ponds.

Flow through the unsaturated zone is calculated based on the default values of the van Genuchten model (van Genuchten, 1980).

6.2.3.2 Calibration

The calibration period from 2/03/2009 to 11/04/2009 was subdivided into 41 stress periods, each one day long. The model is calibrated by fitting measured hydraulic heads and temperature to calculated values. During calibration the hydraulic conductivity was adjusted to achieve the best fit.

The calibrated heat transport model (VS2DHI) is then translated to a solute transport model (VS2DTI). The solute transport is used to approximate travel times and mixing proportions in MAR systems. In MAR systems the point of recharge (e.g. the infiltration pond) is assigned to species concentration C = 1, while the rest of the model domain is assigned to species concentration of C = 0. The resulting breakthrough curves for continuous infiltration are shown in Figure 6-5. The final hydraulic and thermal properties used for the calibrated model are shown in Table 6-4 and Table 6-5. Calibration results are shown in Figure 6-6 and Figure 6-7. Not all observation wells were equipped with data loggers and only observation wells with continuous measurements are used.

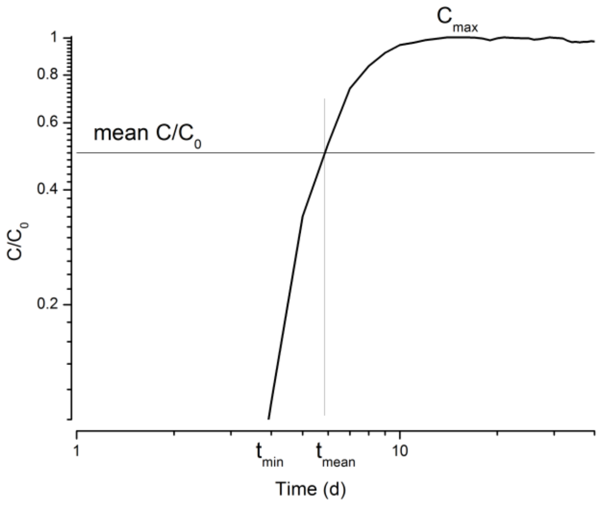


Figure 6-5: Log-log scale of an exemplary breakthrough curve (BTC) of an ideal tracer and calculation of minimum (t_{min}), dominant travel time (t_{mean}) and share of infiltrate (C_{max})

Table 6-4: Calibrated hydraulic parameters

Hydraulic conductivity (m/d)	Anisotropy (Kz/Kh)	Effective porosity (-)
850	1	0.35

Table 6-5: Calibrated thermal properties

Thermal conductivity (W/mK)	Heat capacity of sediment (J/m^{3}K)	Thermal dispersivity (m)*	Heat capacity of water (J/m^{3}K)
1.4 to 2.2	1×10^6	1	4.2×10^6

*thermal dispersivity is assumed analogues to solute dispersivity

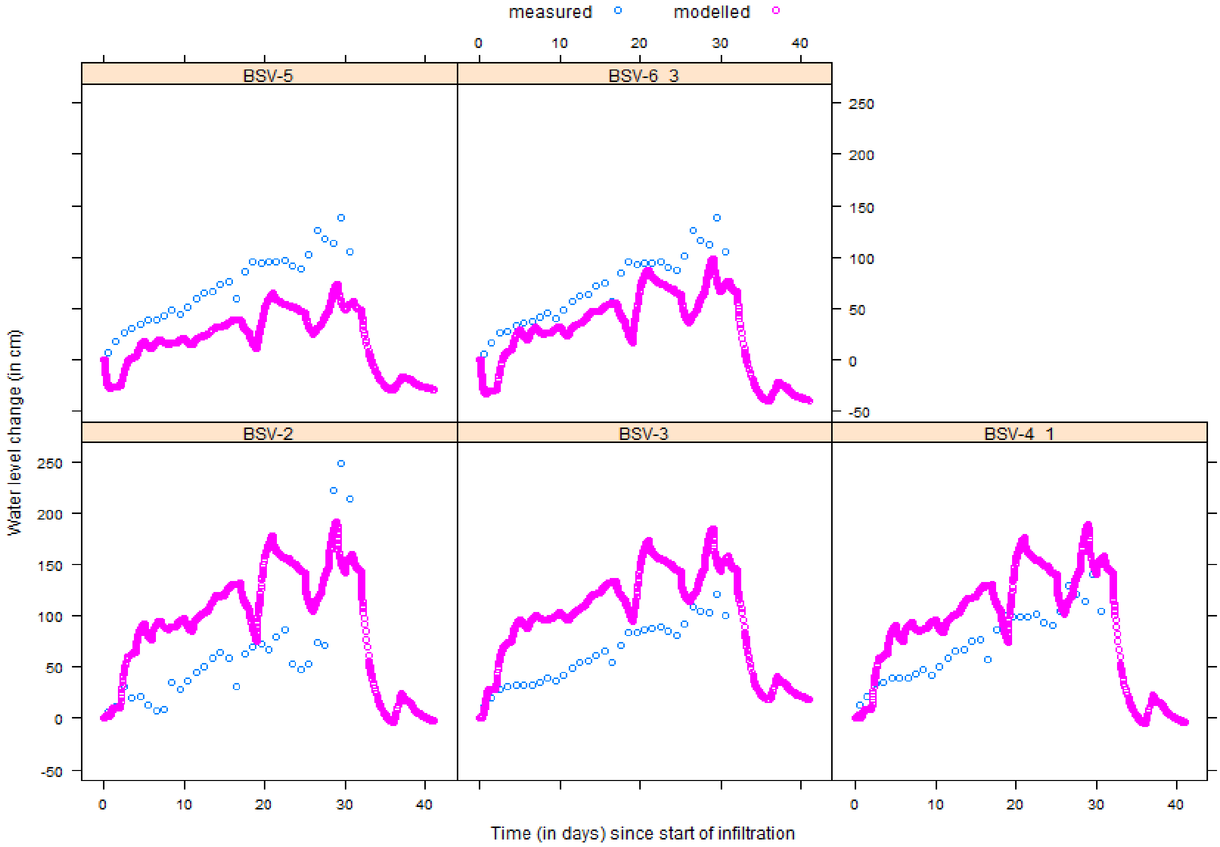


Figure 6-6: Measured (blue) vs. modelled (pink) hydraulic heads

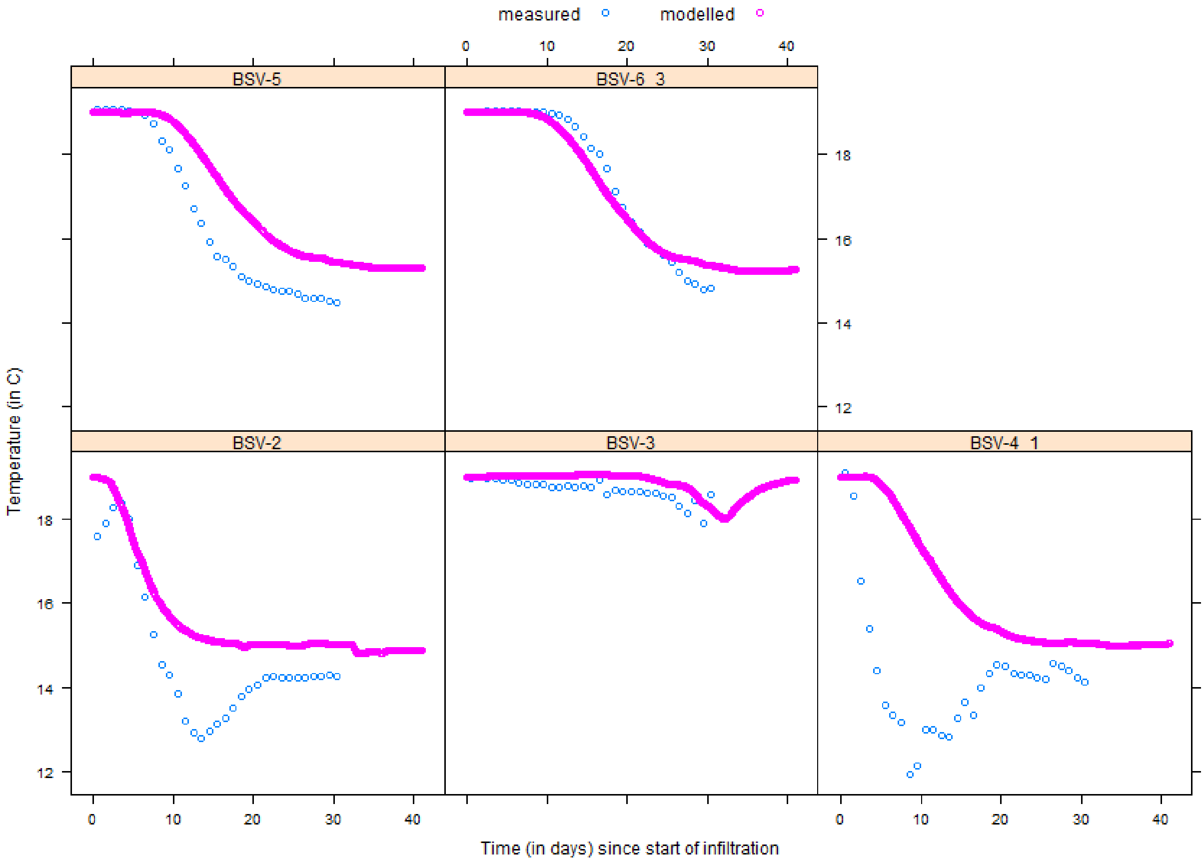


Figure 6-7: Measured (blue) vs. modelled (pink) temperature

A good fit was achieved for BSV5, BSV6.3 and BSV3. Other observation wells (BSV4.1 and BSV2) cannot be reproduced correctly, but show a similar trend of temperature variations. The resulting breakthrough curves for the conservative transport are then used to calculate the dominant travel time (t_{mean}).

6.2.4 Leaching test

The leaching experiment was designed to compare fresh compost and four year-old compost in terms of DOC release. The objective of this test was the evaluation of the long-term (purification) performance of the reactive layer after four years of operation under field conditions. The main indicator of the purification of the layer is the dissolved organic carbon (DOC) release. DOC was monitored during Life+ ENSAT project as a control parameter at laboratory and field scale. In brief, the enrichment of infiltrated groundwater in DOC creates an additional source of assimilable organic carbon for the microbiological community, increasing the biological activity and thus the removal potential of micropollutants present in recharge water.

Disturbed samples of the compost layer were collected in freshly excavated pits in the bottom of the infiltration ponds in 40 cm depth below surface (see Figure 6-8). Fresh vegetal compost was acquired from remainder stored compost in 2011 supplied by ECOMOIANES, the same supplier which provided the compost material for the reactive layer. The remaining compost in the collected material was carefully separated from sand and gravels to perform the leaching test.

Leaching test consisted in mixing 40 gr of selected compost (sample 1, sample 2 and fresh compost) with 400 mL of river water in three beakers to obtain a ratio 1:10 solid-liquid[2]. A fourth beaker was filled only with 400 mL of river water as a control experiment. Beakers were gentle removed with a spatula to favour the solid/liquid contact at the beginning of the experiment. After 2 hours of contact, 100 mL supernatant was collected using a plastic syringe and filtered (pore size 1.2 µm). This procedure was done repeated for all beakers. The supernatant samples were analysed in the laboratory of Aigües de Barcelona for DOC.

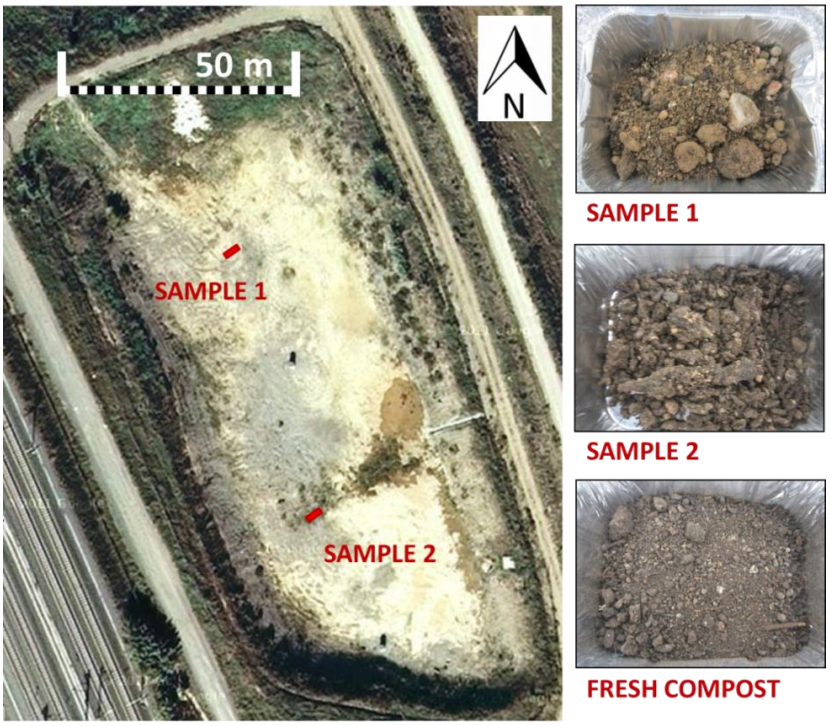
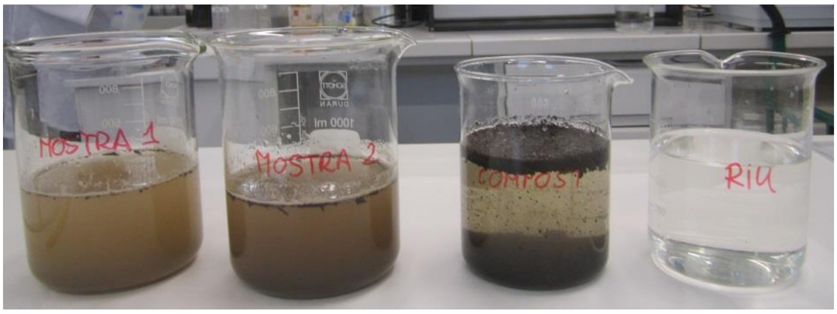


Figure 6-8: Location of the excavated pits for compost collection and pictures.



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[2] Ratio 1:10 is recommended for this type of testing, according to UNE-EN 12457-4

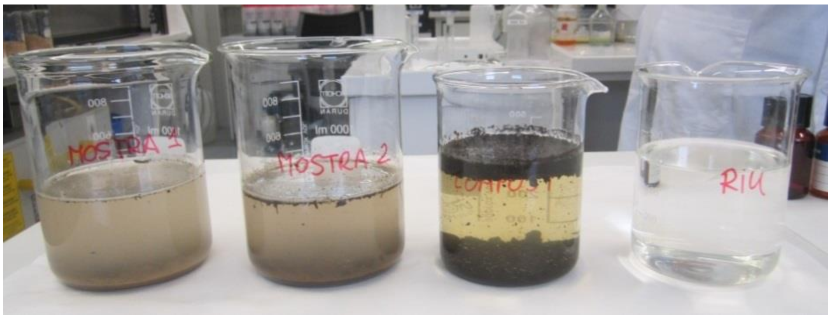


Figure 6-9: **Leaching test performance,** *Above, in the initial shake gently; below after two hours*

6.2.5 Emerging pollutants

At each sampling campaigns a different set of micropollutants was analysed. An overview of substances which were analysed for each campaign can be found in annex2. Laboratory analyses of the emerging pollutants have been carried out by Göttingen University (GU) and Berliner Wasserbetriebe (BWB) in Germany.

6.2.5.1 Berliner Wasserbetriebe (BWB)

The BWB laboratory uses German standard methods for the examination of water, waste water and sludge according to DIN 38407-F36 (Determination of selected active substances of plant protection products and other organic substances in water) using a high performance liquid chromatography and mass spectrometric detection (HPLC-MS/MS or -HRMS) after direct injection. List of analysed parameters and limit of quantification for each substance is found in annex E.

6.2.5.2 Geoscience centre of Göttingen University (GU)

Emerging pollutants 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 emerging pollutants 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).

6.2.6 Bioassays

Bioassays allow the identification of the observed biological effects caused by environmental chemicals and the mixtures that contain them. Recent technological developments have provided powerful quantitative in vitro bioassays to effectively measure a wide range of major classes of toxicants (i.e. acutely toxic compounds, endocrine disrupting substances and genotoxic agents) in the water cycle. As part of the DEMEAU project, scientists recently developed the CALUX cell panel, a type of bioassay panel with the ability to run in an efficient and automated way (Van der Linden et al., 2008). In order to show the potential of these integrated techniques in the field of MAR, collaboration was done between La Vall d'Uixó test site and the laboratories developing and testing these techniques.

MAR samples from two sampling campaigns - conducted in July 2014 and May 2015 - were subjected to sample preparation (i.e. extraction) and screening with selected bioassays to characterize their toxicity profile and investigate the impact of micropollutants present in these water samples. Table 6-2 summarises the sampling conditions in Sant Vicenç dels Horts. The aim of this duplicated experiment was to compare results obtained in the same season to assess the replicability of the bioassays. Techniques applied are listed below:

- **CALUX®-panel** consisting of 9 assays (covering toxic endpoints found to be relevant for water quality benchmarking indicated by the toxicity profiling of the DEMEAU compounds and other case studies (see references van der Linden, 2014; Leusch *et al.* 2014 and Escher *et al.* 2014).
- **Combined algae assay** assessing both photosystem II-inhibition and effects on algae growth
- **Bacteria luminescence inhibition** evaluating acute toxicity of the samples.

Prior to the bioassay analyses samples were concentrated by various extraction methods allowing for enriched pollutant concentrations in the extracts and thereby enabling their better detection in the bioassays. It also limits the impact of the matrix components and metals, which are partially separated during the extraction (Macova *et al.* 2010).

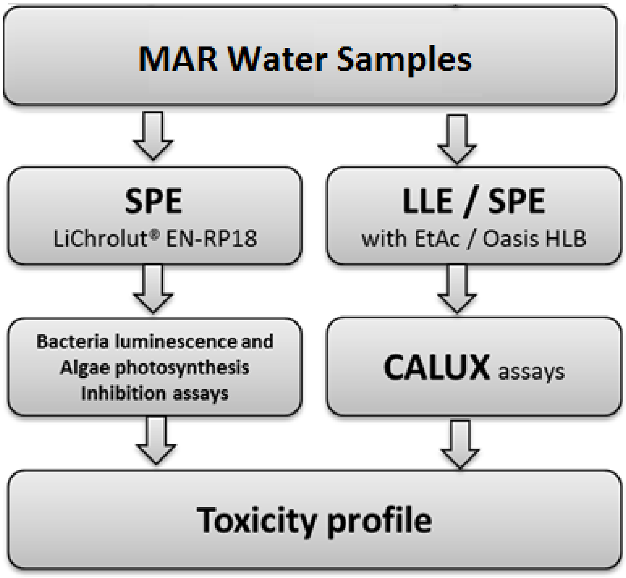


Figure 6-10: Schematic study design of bio screening.

Table 6-6 lists the sampling points Sant Vicenç dels Horts for the performance of bioassays. Additional information as the total depth of the wells of geographical coordinates can be found in Table 6-1, and aerial view for their location is shown in Figure 6-2.

Table 6-6: Sampling points selected for the bioassays.

Code	Type of water
INF	Surface Water
BSV-1	Groundwater
BSV-5	
BSV-8.1	
BSV-8.3	
BSV-9	
BSV-10	

6.2.6.1 Sample workup

Samples were transported to the partners (BDS, Amsterdam and Ecotox Centre – EAWAG, Dübendorf) for bioassay analyses either frozen (1st campaign done in July 2014) and refrigerated (2nd campaign done in May 2015) and subjected to extraction as soon as possible.

Prior to the combined algae and bacteria luminescence inhibition (Ecotox Centre-EAWAG, Dübendorf) the sample enrichment was done by solid phase extraction (SPE), which allows for increased pollutant concentrations in the extracts and thereby enables a better detection in the bioassays. Briefly, 500 mL was enriched 500 times using LiChrolut® EN-RP18 cartridges (Merck, Germany) after filtration and pH adjustment (pH=3) of the samples. For each SPE a blank is prepared and treated in the same way as the samples, including filtration and pH adjustment. The volume of the SPE blank (ultrapure water) corresponded to the highest sample volume (i.e. 500 mL). Extracts were then stored in 1 ml of a solvent mixture (~50% ethanol, ~50% acetone and methanol) at −20 °C until analysis following the method described by Escher *et al.* (2008b).

Prior to CALUX analysis (BDS, Amsterdam) samples of the first sampling campaign (06/2014) were liquid-liquid extracted (LLE) following the in-house standard operation protocol (SOP) of BDS (p-BDS-053). Briefly, from each sample 250 mL was extracted three times with ethyl acetate (200, 50 and 50 mL). All three ethyl acetate fractions were collected, combined and evaporated under a gentle stream of nitrogen till almost dryness and taken up in a final volume of 100 µL of dimethyl sulfoxide (DMSO). DMSO is a suitable solvent for the CALUX screening. All extracts were stored at -18 °C until analysis.

From the samples of the second campaign (05/2015) somewhat different volumes were worked up due to the various sample volume availability. 600 mL from the Sant Vicenç dels Horts samples were extracted by SPE using Oasis HLB cartridges. During the time between the two sampling campaigns BDS modified his in-house extraction method and stepped over from LLE to SPE with Oasis HLB cartridges. The two methods were fully compared and evaluated and resulted in no changes in extraction efficiency. Similarly to the sample handling in the first campaign, extracts were dissolved in 100 µL of DMSO and stored at -18 ⁰C until analysis.

Taking into account all the sample manipulation steps (concentration during extraction and then dilution in the bioassay) during the analysis, 25 times (samples from the first campaign) and 60 times (samples from the second campaign enriched samples were tested in the CALUX bioassays.

6.2.6.2 Combined Algae Assay

The Combined Algae Assay on the green algae *Pseudokirchneriella subcapitata* was conducted as described by Escher *et al. (*2008a). The photosynthesis inhibition was measured by means of effective quantum yield (after two h of exposure) and the inhibition of the algae growth by means of absorbance at 685 nm (after 24 h of exposure). The herbicide diuron served as the reference substance and ethanol as the solvent control (30 and 80 µl/well, respectively with a setup of 8wells/plate). The reference substance in duplicate and the extracts of the water samples in triplicate were tested in a 1:2 dilution series, with the highest concentration of diuron being 3×10^{-7} M (69.9 µg l^{-1}, in ethanol). Maximum enrichment factors of the water samples in the assay were 133 times. The toxicity of the water samples was expressed as diuron-equivalent concentrations (DEQs) for the endpoint “inhibition of Photosystem II” and toxic equivalent concentrations (TEQs, virtual baseline toxicant) for growth inhibition.

6.2.6.3 Bacteria luminescence inhibition assay

The inhibition of the luminescence of the bacterium *Aliivibrio fischeri* (bacteria luminescence inhibition assay) is a commonly used bioassay for screening of surface waters to detect non-specific effects of toxicants. The extracts were added in microtiter plate wells, a geometric dilutions series in ethanol was done and the solvent left to evaporate to dryness. The residues were redissolved in a NaCl buffer solution and added to the reconstituted freeze-dried bacteria (Dr Lange, Düsseldorf, Germany) in another microtiter plate. The bacteria luminescence output was measured prior to addition of sample and after 30 min incubation and the inhibition of bioluminescence was reported as toxic equivalent concentrations for baseline toxicity (baseline-TEQ) (Escher *et al.*, 2008b).

6.2.6.4 CALUX reporter assays

All CALUX reporter assays used for this screening are stable cell lines based on the human osteosarcoma U2OS cells with a luciferase gene under the transcriptional control of responsive elements for activated hormone receptors. These cell lines allow sensitive and specific measurements of hormone receptor action by complex mixtures of compounds. In short, cells were seeded in 384-well plates and cultured for 24 h, after which they were exposed to a dilution series of 13 dilutions with 0.5 log unit increments of the compound or extract in DMSO (final concentration in the well was 1 %). Along with the test samples, a concentration series of a reference compound was included on the same well plate. After 24 h of exposure cells were lysed, and luciferase activity was quantified using a luminometer (Berthold Technologies, Bad Wildbad, Germany) that adds substrate to each well and subsequently measures luminescence for 1 s per well. Only dilutions that were negative in the cytotoxicity test were used for quantification of the response (Pieterse *et al.* 2015 and van der Linder *et al.* 2008).

6.2.6.5 Data analysis

6.2.6.5.1 Hormone assays, PPARγ-CALUX assays, bacteria luminescence inhibition assay and combined algae assay

For these assays (showing and S-shaped dose-response curves), the measured activity is expressed as being equivalent to a reference compound concentration in the sample, which is determined by interpolating the response of the extract into the concentration-response curve of the reference compound (generally at 50 % effect level) and further back-calculation taking all previous dilution and concentration factors into account. Equivalent concentrations are expressed ng or µg reference compound-Eq/L water.

6.2.6.5.2 P53 (+/-S9)-CALUX and Nrf2-CALUX

For these assays (showing other type of dose-response relationship, i.e. no S-shaped curve) induction factors (IF) were calculated by dividing the level of response (relative light units [RLU]) in the assay by the average RLU level of the solvent control wells (DMSO only). Samples were considered to be positive in the assays when the response of at least one concentration showed an increase of at least 50% (i.e., a 1.5-fold induction compared to the negative control). This effect level of the sample was then interpolated from the reference dose-response curve and back-calculated taking all previous dilution and concentration factors into account. Equivalent concentrations are expressed ng or µg reference compound-Eq/L water. Table 6-7 summarises the ecotoxicological effects detected by the in vitro bioassays performed.

Table 6-7: In vitro bioassay panel used for the characterisation of the activity profile of the MAR samples received from two sampling campaigns

Toxic pathway	Pertinent in vitro bioassay	Possible adverse health/ecotoxicological effects
Cell viability	Cytotox-CALUX	General (non-specific) toxicity
Hormone mediated mode of action (MoA)	ERα-CALUX, (anti)AR-CALUX, (anti)PR-CALUX, GR-CALUX	Tumor development, Birth defects, (Sexual) developmental disorders
Lipid metabolism	PPARγ-CALUX	Obesity and inflammatory diseases
Reactive MoA	P53-CALUX, P53 S9-CALUX	Tumor development
(Oxidative) stress response	Nrf2-CALUX	Inflammation, sensitisation and neurodegenerative diseases
Inhibition of the luminescence of the bacterium	Bacteria luminescence inhibition assay	General (non-specific) toxicity

Toxic pathway	Pertinent in vitro bioassay	Possible adverse health/ecotoxicological effects
Inhibition of the photosystem II	Combined algae assay	Photosynthesis inhibition linked to reduced algae/plant survival and growth

6.3 Results

6.3.1 Temperature as a tracer

The first step in understanding a MAR site is the hydraulic characterisation. This can be done in various ways and tracer tests are one way (Sprenger, 2015). Without a proper understanding of the temporal and spatial dynamics of subsurface flow the interpretation of contaminant transport is very challenging.

Modelling results of temperature transport are shown in Table 6-8. Compared to travel time estimations based on Darcy´s law the modeled travel times show large differences. In general Darcy´s law estimation overestimate the travel time compared to modelled values based on transport BTC´s.

Table 6-8: Dominant travel time and share of infiltrate for observation wells.

Monitoring well ID	Calibrated dominant travel time (d)	Dilution ratio
BSV-3	11.5	1
BSV-6.2	9.5	1
BSV-2	5.8	1
BSV-5	8.9	1
BSV-4.1	3	1

The resulting BTC is shown exemplary for the observation well BSV-6.2 in Figure 6-11. The red curve is the previously calibrated temperature BTC (see Figure 6-7 for calibration results). It starts from the initial temperature (19 °C) and decreases as the colder (15 °C) infiltrate reaches the observation well. The black curve describes the BTC of the artificially introduced conservative species which is used for the travel time calculation. The mean thermal travel time is about two times longer than the mean conservative travel time.

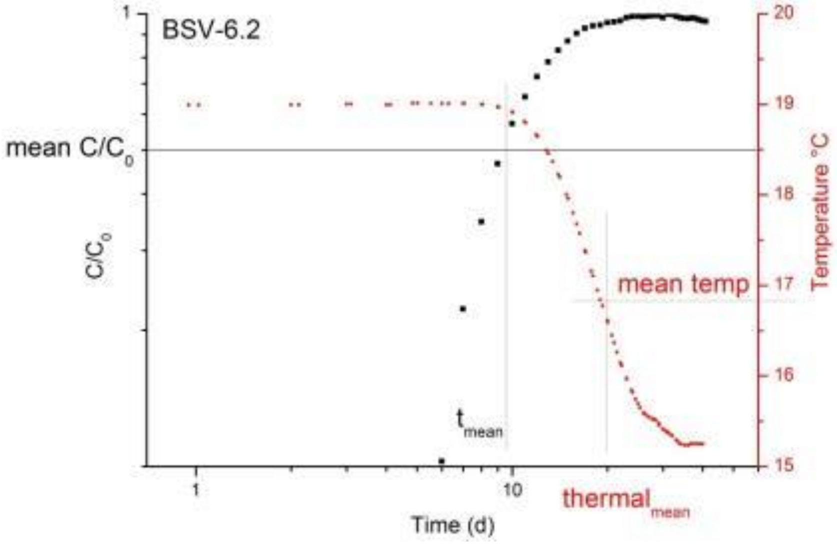


Figure 6-11: Resulting breakthrough curves of conservative transport (black curve) and retarded temperature (red curve) shown for the observation well BSV-6.2

6.3.2 Hydrochemistry

The complete results of all bulk chemistry parameter are shown in annex D. Figure 6-12 shows Piper diagrams (Piper 1944) for data sampled during dry conditions (left) and wet recharge conditions (right). Water chemistry in the observation wells is more similar to source water during recharge (wet conditions) than under dry conditions.

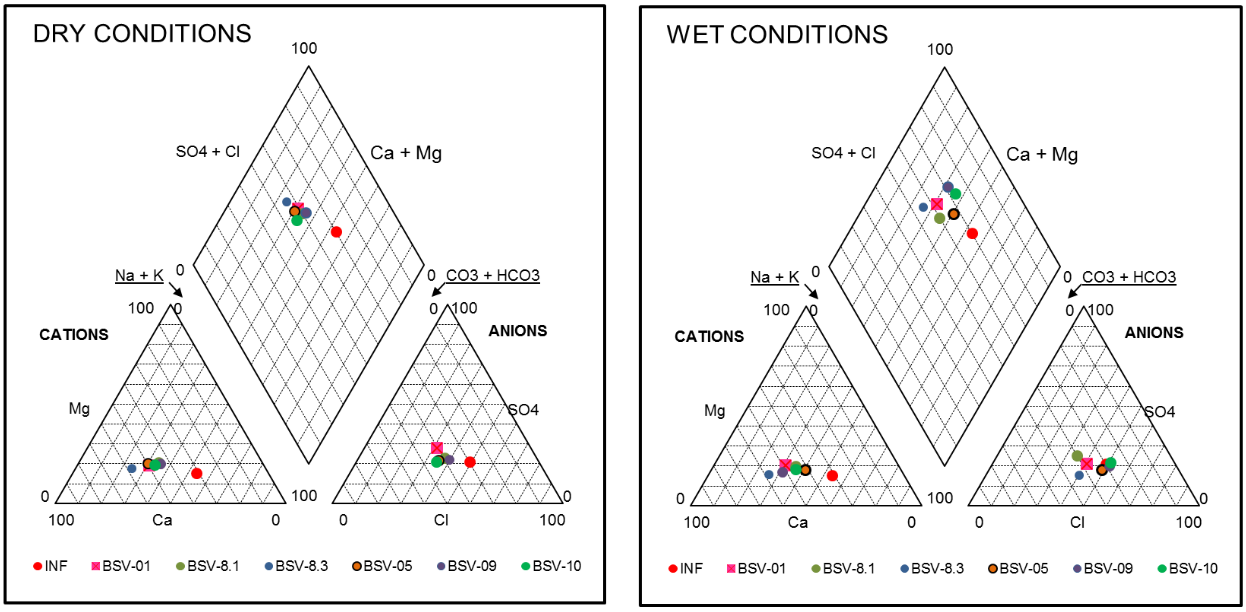


Figure 6-12: Piper diagram of dry and wet conditions, NOTE: infiltration values under dry conditions represents Llobregat River quality (there are no significant changes between Llobregat water and infiltration water)

Figure 6-13 shows slightly higher values of Ammonium and Total Organic Carbon (TOC) in source water (River), while the concentration of both parameters are found in decreased concentrations in the groundwater. Ammonium is not detected in the observations wells (below detection limit) and average concentration of TOC is mostly below 3 mg/L in the observation wells. The decrease of TOC values from BSV-8.3 to BSV-8.1, measured during wet conditions, is indicative of organic carbon consumption along the flow path.

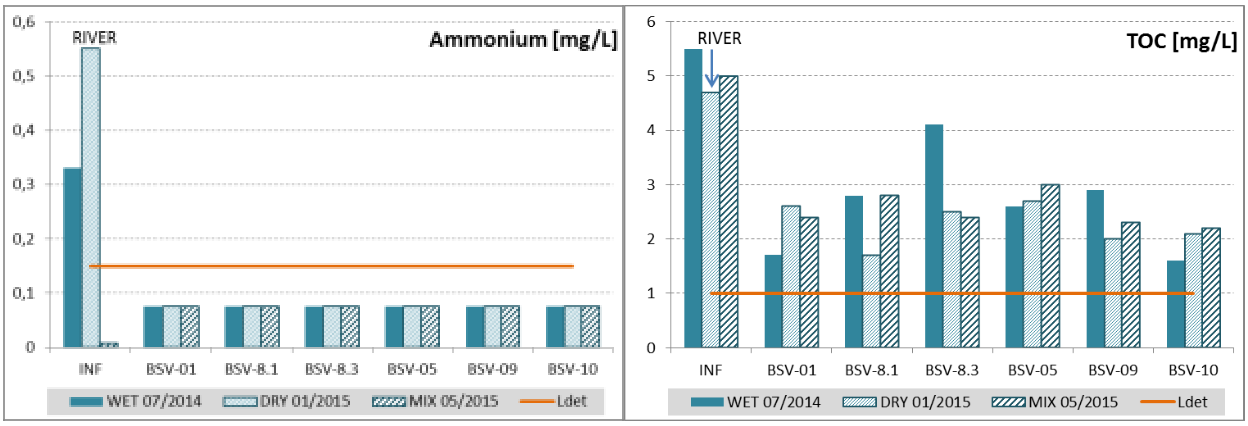


Figure 6-13: Ammonium and TOC concentrations in SVH sampling campaigns NOTE: “Ldet”= Limit of detection

Iron and manganese are found in elevated concentrations in some observation wells (BSV-8.3 and BSV-9) compared to source water concentration (Figure 6-14). This may be explained by dissolution of Fe-/Mn-bearing minerals from the aquifer material. This dissolution may be triggered by recharge periods since high peaks of both metals occur only during wet and mixed conditions, while during dry conditions the concentration of iron and manganese is lowered.

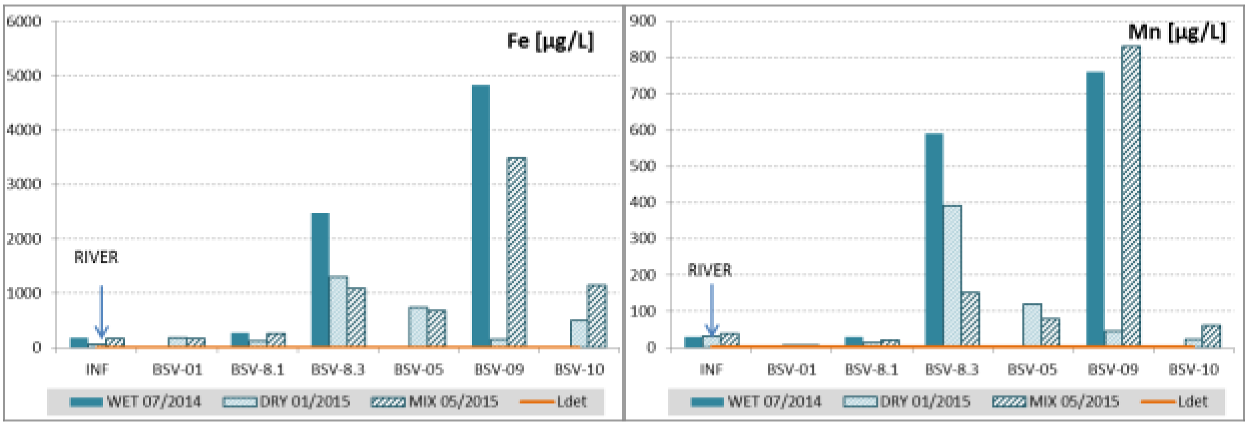


Figure 6-14: Iron and manganese concentrations in SVH sampling campaigns NOTE: “Ldet”= Limit of detection.

6.3.3 Emerging pollutants

6.3.3.1 Source water and native groundwater

Dry condition and BSV-01 samples are used to calculate the native background concentration. From the 53 analysed parameters 5 compounds have been detected equal or above limit of quantification (LOQ). Averaged concentration of emerging pollutants in native groundwater and source water are shown in Figure 6-15.

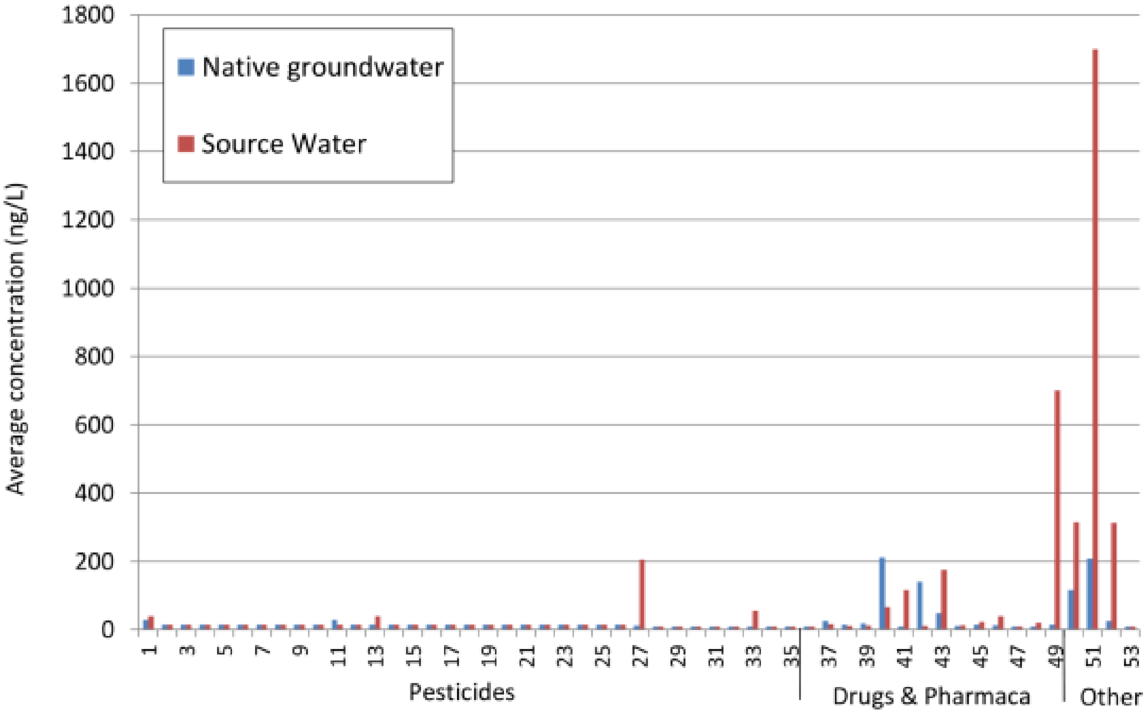


Figure 6-15: **Comparison of emerging pollutants in source water and native groundwater (numbers correspond to compounds as shown in annex E).**

Out of 35 analysed pesticides 4 compounds (PBSM, Diuron, FAA, MCPA) have been detected equal or above LOQ in source water samples (measured in pond- or river water samples). FAA and MCPA show the highest concentration with 220 and 100 ng/L, respectively.

From the group of drugs and pharmaceuticals most compounds have been detected equal or above LOQ. Out of 14 measured drugs and pharmaceuticals 6 compounds have been detected equal or above LOQ in source water samples. Dihydroxydihydrocarbamazepine and Gabapentine show the highest concentration of 175 ng/L and 700 ng/L in average, respectively. Gabapentin is used to treat some types of seizures and for post-herpetic neuralgia (nerve pain caused by shingles).

In the group of stimulants/sweeteners/corrosion inhibitors, acesulfame is present in high concentration of about 1700 ng/L in average. Acesulfame is a calorie-free sugar substitute (artificial sweetener). In the European Union, it is known under the E number (additive code) E950. This compound is not metabolized by the body. It passes through the gastrointestinal tract unchanged.

6.3.3.2 Fate of micropollutants during MAR

Four categories have been established to classify its fate during subsurface passage for each emerging pollutant:

- **Compound in source water below LOQ:** only compounds which are detected ≥ LOQ in source water samples are subject of removal approximation.

- **Compound not removed:** removal < 10% of concentration measured in source water (C_0)

- **Removal approximation:** low removal = 10-50% of C_0, high removal > 50 % of C_0

- **Increase during MAR:** apparent increase of concentration during MAR

The raw data from the laboratories can be found in annex E of this document. Three examples of removal behaviour are shown in the following. A good example of removal during MAR is shown in Figure 6-16. Only wet and mixed conditions samples are shown for groundwater monitoring wells downstream of the infiltration pond. Source water sampled in the pond or in the river and the not influenced monitoring well (BSV-01) upstream of the pond are shown by all available samples.

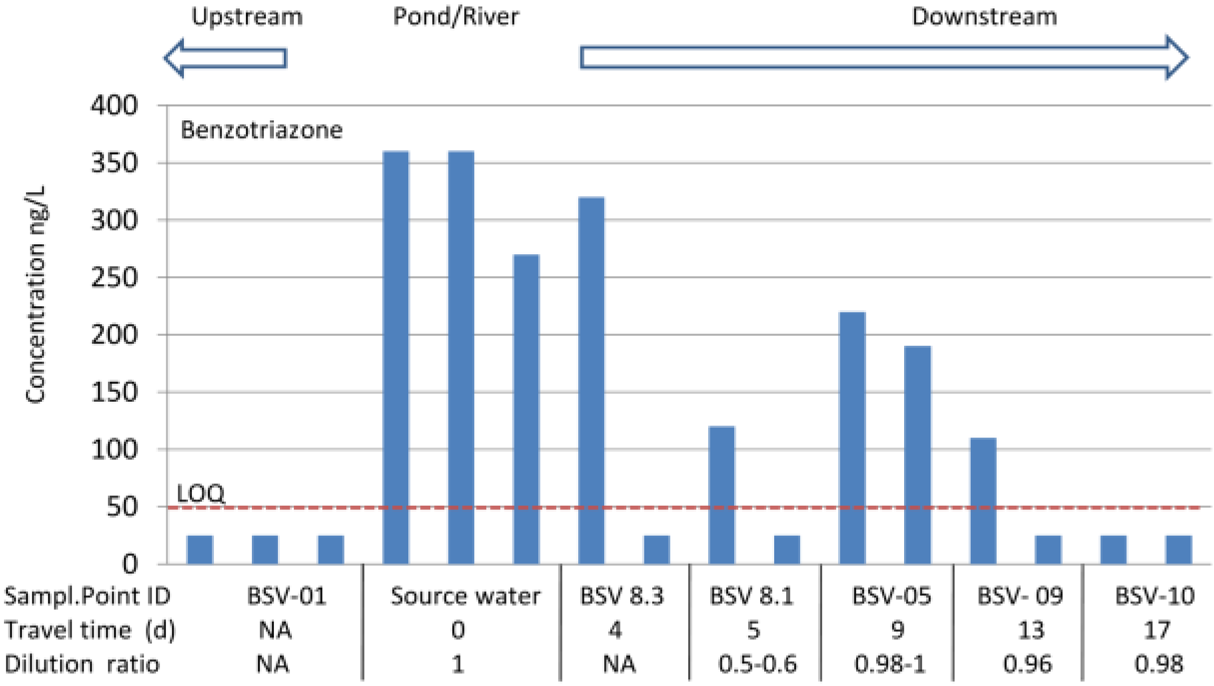


Figure 6-16: Fate of Benzotriazole at Sant Vicenç dels Horts (NA = not applicable, LOQ = limit of quantification).

Benzotriazole in native groundwater is below detection limit (see BSV-01). Source water concentration may reach up to 360 ng/L. After approximately 4 days of travel time in the subsurface concentration in BSV8.3 is decreased to 320 ng/L. This attenuation can be attributed to removal. The dilution factor is not determined for BSV8.3 but can be assumed according to filter screen position and modal distance from infiltration pond to be 1. Further downstream in BSV8.1 large proportion of attenuation must be attributed to dilution. In BSV05 dilution is again minimal and the removal of Benzotriazole to 220 ng/L can be observed. This trend continues in BSV09 until in BSV10 native background concentration is measured. Total removal measured in BSV-10 is therefore calculated with 92%.

Another example of removal is shown in

Figure 6-17. Iopromide is measured in source water with 80-90 ng/L and in all groundwater samples below LOQ even after few days of travel time.

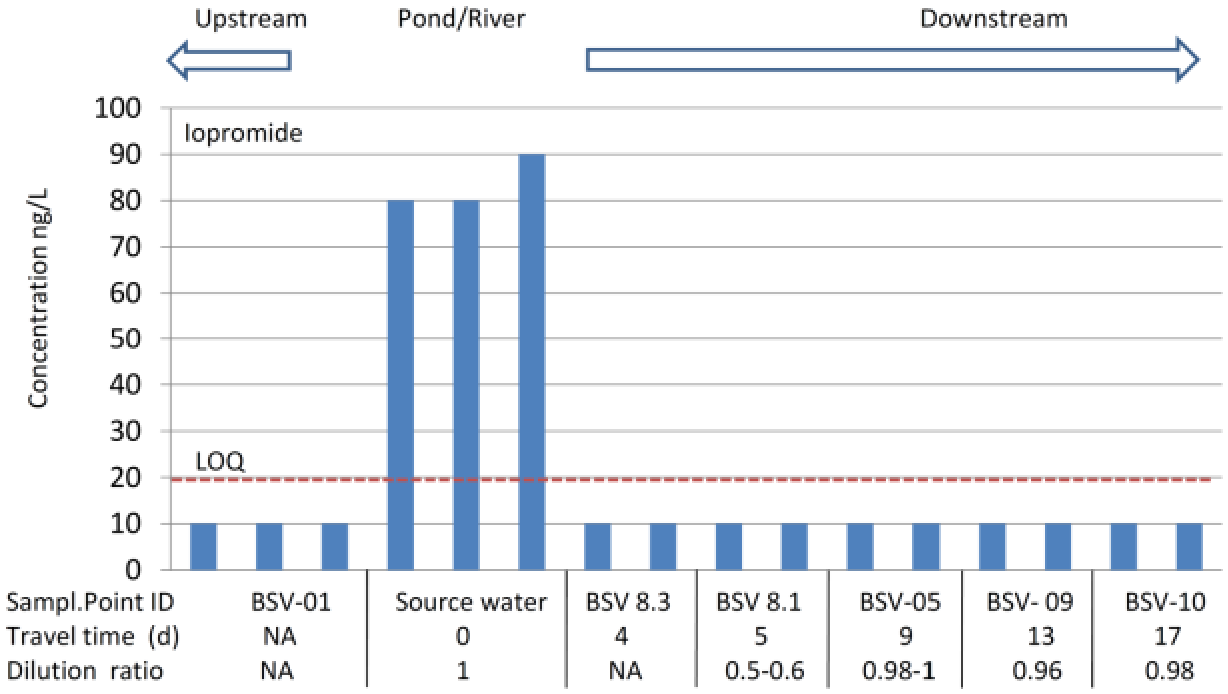


Figure 6-17: Fate of Iopromide at Sant Vicenç dels Horts (NA = not applicable, LOQ = limit of quantification).

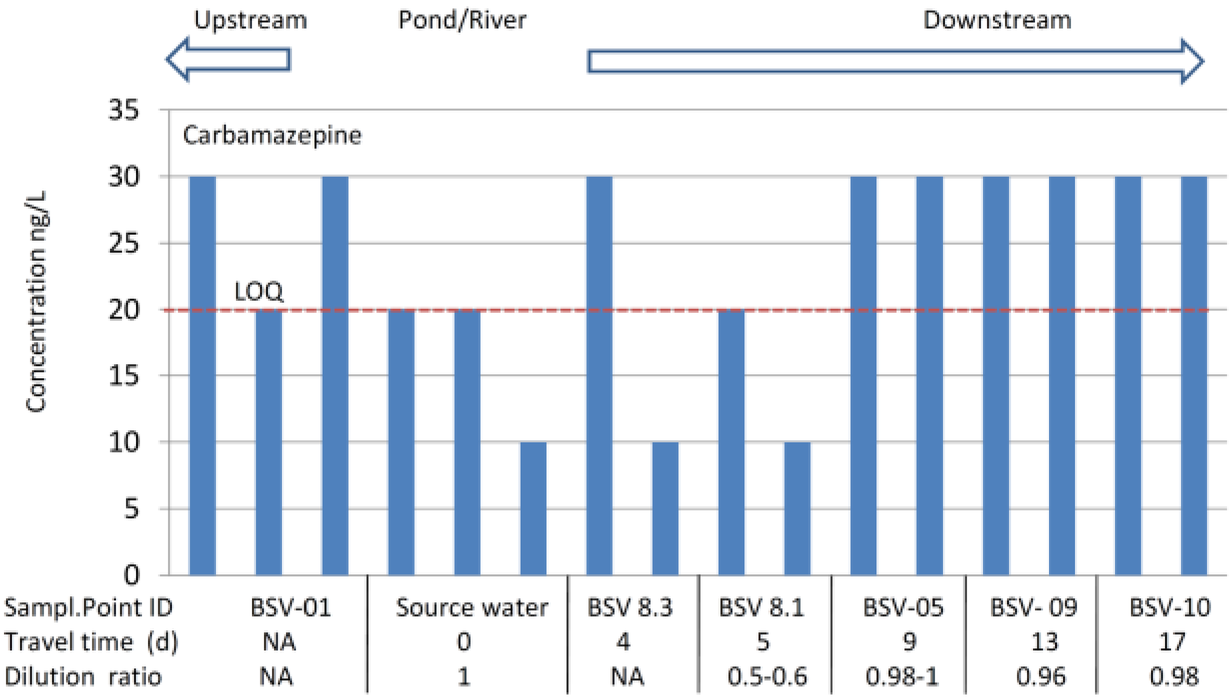


Figure 6-18: **Carbamazepine at Sant Vicenç dels Horts (NA = not applicable, LOQ = limit of quantification).**

In native groundwater Carbamazepine occurs in concentration of 20-30 ng/L (see BSV-01). Source water concentrations are at or below LOQ (20 ng/L). The fate of carbamazepine is difficult to assess, because concentrations are closely around LOQ. It seems that source water concentrations are below native groundwater. Therefore, infiltration of source water should result in concentrations below that of native groundwater. This effect is observed only in BSV8.3 and BSV8.1, but not in observation wells further downstream. Carbamazepine is characterized by strong retardation (R=1.7 – 2.3) and long half-life times (t_{50}=125-233 d). Due to the rather strong substance specific retardation and high stability it seems plausible that Carbamazepine is retarded compared to advective groundwater flow. The measured concentrations may reflect therefore artefacts from recharge periods some time ago, where concentration in source water was higher.

Removal (R) is calculated by $\mathrm{R_{abs}} = \mathrm{C_{SW}} - \mathrm{C_{BSV10}}$ where C stands for average concentration in SW = source water and BSV-10, when average $\mathrm{C_{SW}} \geq \mathrm{LOQ}$. Measurements below LOQ are calculated to $\mathrm{LOQ}/2$, and do not allow for removal evaluation. Substance specific results for all measured pesticides are show in Table 6-9.

Table 6-9: Fate of pesticides during MAR at Sant Vicenç dels Horts.

Compound	Concentration below LOQ or not measured	Not removed	Percentage removal*	Increasing / Accumulating in MAR (MAR conc. > infiltration water
PBSM			25	
Alachlor	X			
Atrazine	X			
Boscalid	X			
Bromacil	X			
Chlorfenvinphos	X			
Chloridazon	X			
Chlortoluron	X			
Desethylatrazine	X			
Desethylterbutylazine	X			
Desisopropylatrazine				X
2,6-Dichloro Benzamide	X			
Diuron			62	
Ethofumesate	X			
Isoproturon	X			
Lenacil	X			
Metalaxyl	X			
Metamitron	X			
Metazachlor	X			
Chloridazon-Methyl-Desphenyl	X			
Metolachlor	X			
Metribuzin	X			
Quinoxyphen	X			
Simazine	X			
Terbuthylazine	X			
Quinmerac	X			
FAA			95	

Compound	Concentration below LOQ or not measured	Not removed	Percentage removal*	Increasing / Accumulating in MAR (MAR conc. > infiltration water
2,4,5-Trichlorophenoxyacetic acid (2,4,5-T)	X			
2,4-Dichlorophenoxyacetic acid (2,4-D)	X			
Bentazon	X			
Bromoxynil	X			
Dichlorprop	X			
2-methyl-4-chlorophenoxyaceticacid (MCPA)			82	
Mecoprop	X			
Chlofibric acid	X			

*removal after approx. 17 days of subsurface travel time measured in BSV10 under wet/mixed conditions, dilution ratio of 1

Table 6-10: Fate of pharmaceuticals during MAR at Sant Vicenç dels Horts.

Compound	Concentration below LOQ or not measured	Not removed	Percentage removal*	Increasing / Accumulating in MAR (MAR conc. > infiltration water
Phenazone (*)	X			
Carbamazepine (*)				X
Metoprolol (*)	X			
Phenylethylmalonamide	X			
Diclofenac (*)			85	
Iopromide (*)			91	
Ibuprofen (*)				X
Dihydroxydihydrocarbamazepine			71	
Primidone (*)	X			
Trimethoprim (*)	X			
Sulfamethoxazole (*)			75	
Bezafibrate (*)	X			

Compound	Concentration below LOQ or not measured	Not removed	Percentage removal*	Increasing / Accumulating in MAR (MAR conc. > infiltration water
N-Acetyl-sulfamethoxazole			50	
Gabapentine			97	

*DEMEAU listed compound; **Removal after approx. 17 days of subsurface travel time measured in BSV10 under wet/mixed conditions, dilution ratio of 1

Table 6-11: Fate of other substances during MAR at Sant Vicenç dels Horts.

Compound	Concentration below LOQ or not measured	Not removed	Percentage removal*	Increasing / Accumulating in MAR (MAR conc. > infiltration water
Coffeine			84	
Acesulfame			77	
Benzotriazole*			92	
Phenylsulfonylsarcosin	X			

*DEMEAU listed compound; **Removal after approx. 17 days of subsurface travel time measured in BSV10 under wet/mixed conditions, dilution ratio of 1

6.3.3.3 Column vs field results

The observations under field conditions are then compared to observations made under lab conditions in column studies. Table 6-12 shows the comparison between observed removal in Sant Vicenç dels Horts and in soil column experiments. A detailed description of the methodology and results of the soil experiments can be found in the project deliverable D12.3 (Hernandez and Gibert (2014)) and in Schaffer *et al. (*2015).

Table 6-12: Qualitative comparison of behaviour in field site and column experiments for DEMEAU compounds

Compound	Soil column results (Schaffer et al. 2015)*	Field site results**
Benzotriazole	Slight removal	High removal
Diclofenac	Slight removal	High removal

Compound	Soil column results (Schaffer et al. 2015)*	Field site results**
Sulfamethoxazole	High removal	High removal
Carbamazepine	Not removed	difficult to assess

*after approx. 7.5 days of travel time in column; **after approx. 17 days of subsurface travel time measured in BSV10

There is a clear correlation in the trends observed at laboratory scale and at field scale. Trimethoprim, iopromide, bezafibrate and benzotriazole show elimination evidences in MAR system, while diclofenac, primidone and carbamazepine concentrations remain almost constant in both experiments. Due to the limited number of samples from the field site and the changing conditions in the MAR system (wet, dry and mix) it is not possible go further with the quantification of the removal at field scale.

6.3.4 Leaching test

The supernatant samples from the reactive layer installed in the field show a DOC similar to river water, whereas the fresh compost provides DOC almost 8 times more than the river water (**Table 3-6**). Analyses were performed in duplicated in the lab to assure the replicability of the experiment.

Table 6-13: DOC release from leaching tests

Samples code	Sample type	Dissolved Organic Carbon (DOC) mg/L
RIVER - A	River water	5.0
RIVER - B		5.1
LAYER - 1A	Sample 1 (4 year compost layer)	4.8
LAYER - 1B		4.9
LAYER - 2A	Sample 2 (4 year compost layer)	4.9
LAYER - 2B		4.9
Compost - A*	Fresh compost layer	39
Compost - B*		39

* These samples were previously diluted to calculate the TOC. Samples A and B are duplicated analysis.

The similarities between river water and samples 1 and 2 indicate no effect of additional DOC release of the 4-year old compost layer. This is a valuable data for operation and maintenance tasks of the infiltration pond in terms of replacement of the reactive layer once the release of DOC is exhausted.

6.3.5 Bioassays: toxicity assessment

6.3.5.1 Quality controls

All samples were tested in the bioassays together with the

- procedure blank,
- bioassay solvent blank (DMSO, EtOH),
- and corresponding reference compound of the assay.

Neither the procedure blank nor the bioassay solvent blank (data not shown) showed activity in the assays. The corresponding reference compound showed in each assay the maximum response in agreement with the historical positive control/reference compound data.

The limit of detection (LOD) - denoting the minimum amount of activity reliably detected – greatly depends on the amount of sample extracted, the concentration factor achieved during sample preparation, and the dilution factor required when testing an extract dissolved in a solvent (e.g. DMSO or ethanol) in the bioassay. Assay LOD and LOQ (limit of quantification, which is triple LOD) values are clearly indicated in the results tables (annex F).

6.3.5.2 Measured activities and toxicity profiles

The activity of the tested extract was expressed as reference compound-equivalent concentration per sample unit and summarized in annex F. The activities were then classified according to the activity significance (

Figure 6-19).

The obtained activity profiles of the MAR samples (left part in

Figure 6-19) were then evaluated and modified according to the available preliminary Algae test EQS (environmental quality standard proposals) and CALUX trigger values (van der Oost et al. 2015) (right part in

Figure 6-19). Trigger values for the other endpoints, are currently being established. Preliminary trigger values currently available for bioassays are shown in Table 6-14.

Table 6-14: Currently available preliminary trigger values for ecosystem health (van der Oost et al. 2015)

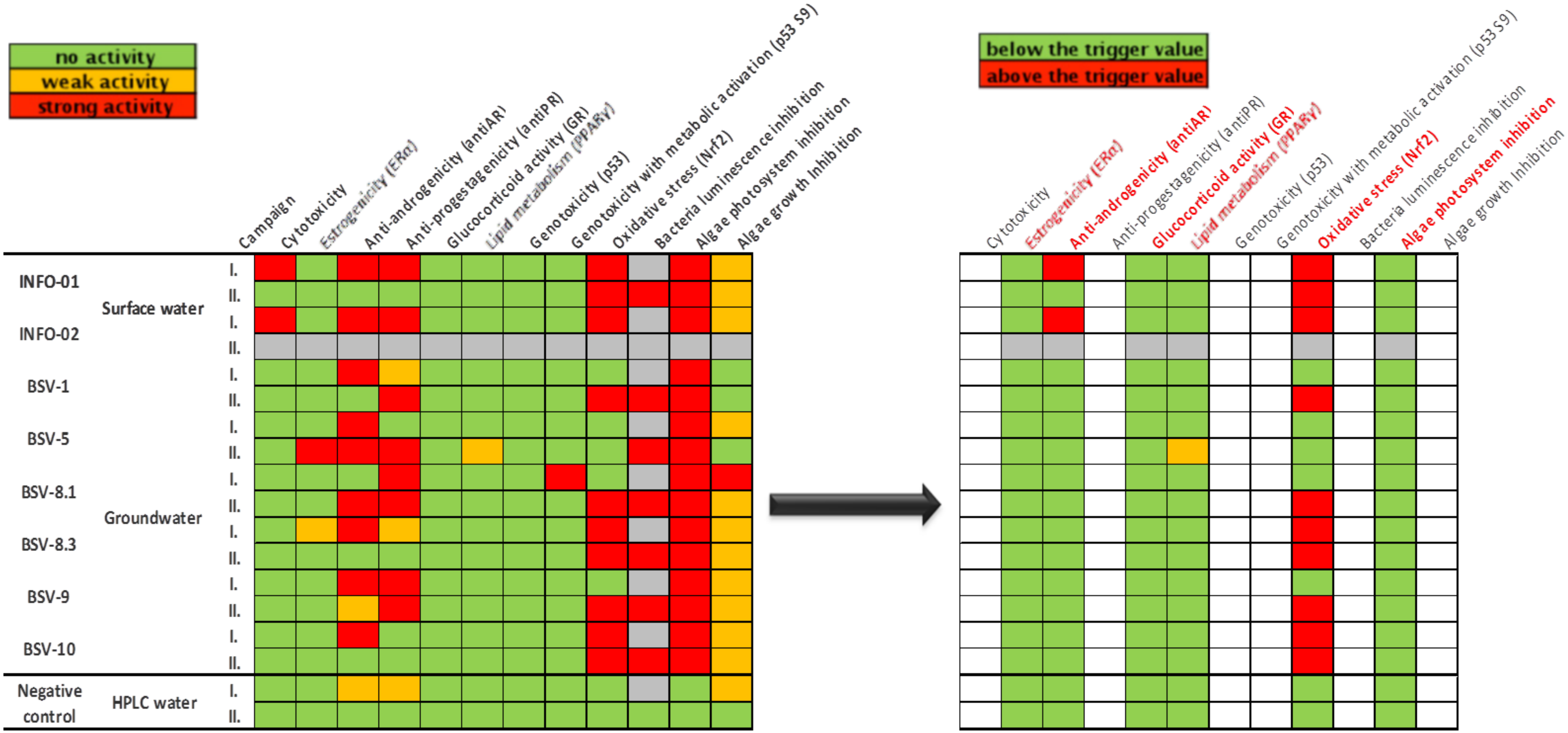
Bioassay	Trigger value	Unit
ERα-CALUX	1	ng 17β-Estradiol-Eq / L
Anti-AR-CALUX	40	µg Flutamide-Eq / L
GR-CALUX	30	ng Dexamethasone-Eq / L

Bioassay	Trigger value	Unit
PPARγ-CALUX	20	ng Rosiglitazone-Eq / L
Nrf2-CALUX	10	µg Curcumin-Eq / L
Combined Algae Test (Photosystem II Inhibition)*	20 (EQS proposal CH), 200 (EQS EU)	ng Diuron-Eq / L

(*)For the "high/low risk evaluation" of the measured activities in the combined algae assay the trigger value based on the EU EQS proposal was used and not based on the Swiss value.

Figure **6-19** summarises activity profile of the tested MAR water samples from Sant Vicenç dels Horts sampling site collected at two time points: I) July 2014 (wet conditions) and II) May 2015 (mixed conditions) in the in vitro bioassay panel (on the left). Detected activities are classified following the criteria showed on the upper part of the figure. The activity profile was then modified (on the right) considering available, preliminary trigger values (for estrogenic, anti-androgenic, glucocorticoid activity, oxidative stress and lipid metabolism). Samples that showed lower activity than the pertinent trigger value became "green" in the table on the right indicating low risk despite of the measured (quantifiable) activity.

The application of effect-based methods (bioassays) enabled to measure the combined effects of emerging pollutants (see results presented in
Figure 6-19). The broad range *in vitro* screening of the MAR water samples revealed the importance of ENDOCRINE - (particularly the activation of the ERα-, anti-AR, anti-PR receptors), OXIDATIVE STRESS (Nrf2-CALUX) and PHOTOSYNTHESIS INHIBITION (Combined algae test) pathways, and showed differences between the samples collected within two different time points (two sampling campaigns). The application of trigger values (thresholds) demonstrated the possibility for estimation of potential environmental risks with *in vitro* bioassay responses.



🟩 no activity
🟨 weak activity
🟥 strong activity

		Campaign	Cytotoxicity	Estrogenicity (ERα)	Anti-androgenicity (antiAR)	Anti-progestagenicity (antiPR)	Glucocorticoid activity (GR)	Lipid metabolism (PPARγ)	Genotoxicity (p53)	Genotoxicity with metabolic activation (p53 S9)	Oxidative stress (Nrf2)	Bacteria luminescence inhibition	Algae photosystem inhibition	Algae growth Inhibition
INFO-01	Surface water	I.	🟥	🟩	🟥	🟥	🟩	🟩	🟩	🟩	🟥	▨	🟥	🟨
		II.	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟥	🟥	🟥	🟨
INFO-02		I.	🟥	🟩	🟥	🟥	🟩	🟩	🟩	🟩	🟥	▨	🟥	🟨
		II.	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨
BSV-1	Groundwater	I.	🟩	🟩	🟥	🟨	🟩	🟩	🟩	🟩	🟩	▨	🟥	🟩
		II.	🟩	🟩	🟩	🟥	🟩	🟩	🟩	🟩	🟥	🟥	🟥	🟩
BSV-5		I.	🟩	🟩	🟥	🟩	🟩	🟩	🟩	🟩	🟩	▨	🟥	🟨
		II.	🟩	🟥	🟥	🟥	🟩	🟨	🟩	🟩	🟩	🟥	🟥	🟩
BSV-8.1		I.	🟩	🟩	🟩	🟥	🟩	🟩	🟩	🟥	🟩	▨	🟥	🟥
		II.	🟩	🟩	🟥	🟥	🟩	🟩	🟩	🟩	🟥	🟥	🟥	🟨
BSV-8.3		I.	🟩	🟨	🟥	🟨	🟩	🟩	🟩	🟩	🟥	▨	🟥	🟨
		II.	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟥	🟥	🟥	🟨
BSV-9		I.	🟩	🟩	🟥	🟥	🟩	🟩	🟩	🟩	🟩	▨	🟥	🟨
		II.	🟩	🟩	🟨	🟥	🟩	🟩	🟩	🟩	🟥	🟥	🟥	🟨
BSV-10		I.	🟩	🟩	🟥	🟩	🟩	🟩	🟩	🟩	🟥	▨	🟥	🟨
		II.	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟥	🟥	🟥	🟨
Negative control	HPLC water	I.	🟩	🟩	🟨	🟨	🟩	🟩	🟩	🟩	🟩	▨	🟩	🟨
		II.	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩

🟩 below the trigger value
🟥 above the trigger value

Cytotoxicity	Estrogenicity (ERα)	Anti-androgenicity (antiAR)	Anti-progestagenicity (antiPR)	Glucocorticoid activity (GR)	Lipid metabolism (PPARγ)	Genotoxicity (p53)	Genotoxicity with metabolic activation (p53 S9)	Oxidative stress (Nrf2)	Bacteria luminescence inhibition	Algae photosystem inhibition	Algae growth Inhibition
	🟩	🟥		🟩	🟩			🟥		🟩	
	🟩	🟩		🟩	🟩			🟥		🟩	
	🟩	🟥		🟩	🟩			🟥		🟩	
	▨	▨		▨	▨			▨		▨	
	🟩	🟩		🟩	🟩			🟩		🟩	
	🟩	🟩		🟩	🟩			🟥		🟩	
	🟩	🟩		🟩	🟩			🟩		🟩	
	🟩	🟩		🟩	🟨			🟩		🟩	
	🟩	🟩		🟩	🟩			🟩		🟩	
	🟩	🟩		🟩	🟩			🟥		🟩	
	🟩	🟩		🟩	🟩			🟥		🟩	
	🟩	🟩		🟩	🟩			🟥		🟩	
	🟩	🟩		🟩	🟩			🟩		🟩	
	🟩	🟩		🟩	🟩			🟥		🟩	
	🟩	🟩		🟩	🟩			🟥		🟩	
	🟩	🟩		🟩	🟩			🟥		🟩	
	🟩	🟩		🟩	🟩			🟩		🟩	
	🟩	🟩		🟩	🟩			🟩		🟩	

Figure 6-19: Activity profile determined in the bioassays (colours in right matrix: green = activity below trigger value, yellow = coinciding with trigger value, red = activity above trigger value, I = July 2014 sampling (wet conditions); II = May 2015 sampling (mixed conditions)).

Activities that fell under the defined trigger value of the certain bioassay are considered as low risk and suggested no need for further in-depth investigation (effect-directed analysis [EDA] or chemical analysis) to identify the source of the activity, the responsible compound(s). On the contrary, activities above the pertinent trigger values suggest the need for further investigations and imply the possibility of adverse (ecological) health effects. In the case of the Sant Vicenç dels Horts samples, the infiltration water (Llobregat River raw water) could suppose some adverse effects listed below:

- Anti-androgenic activity
- Oxidative stress

This approach – screening samples first with bioassays, followed by low/high risk evaluation with trigger values and chemical analysis if reasonable/justifiable is favoured by WA4 (Bioassays team in DEMEAU project). In this study applied trigger values are preliminary values, thus it is recommend to consider this exercise as an exemplification for the application of such threshold values and discriminating therefore between low and high risk sites.

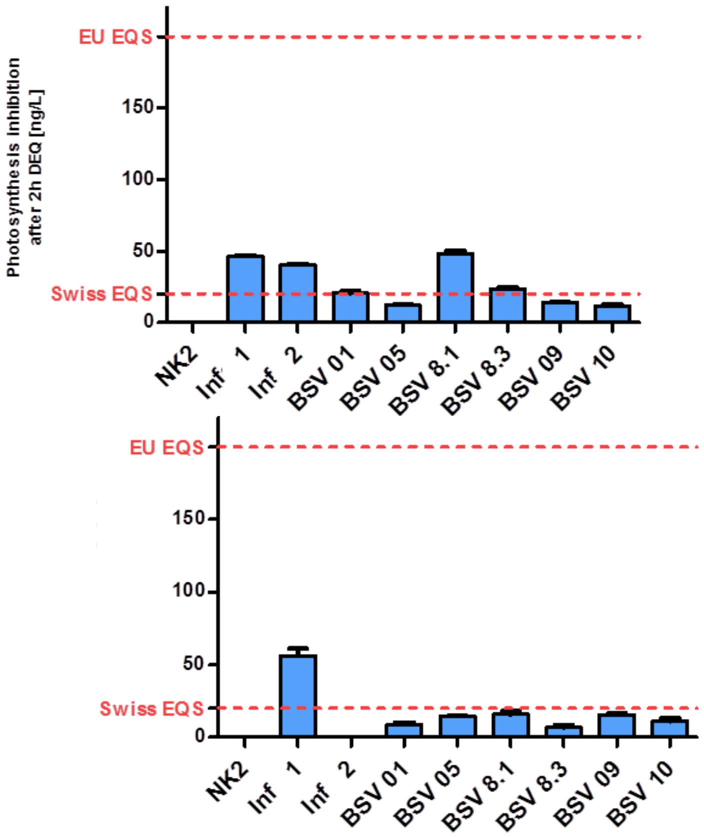


Figure 6-20: Photosynthesis (after 2 hours of exposure) of the MAR samples from SVH – 1st sampling campaign (left) and 2nd sampling campaign (right) - expressed as ng Diuron Eq./L water. NK refers to negative control (HPLC water) went through on extraction and bioanalysis just as the samples.

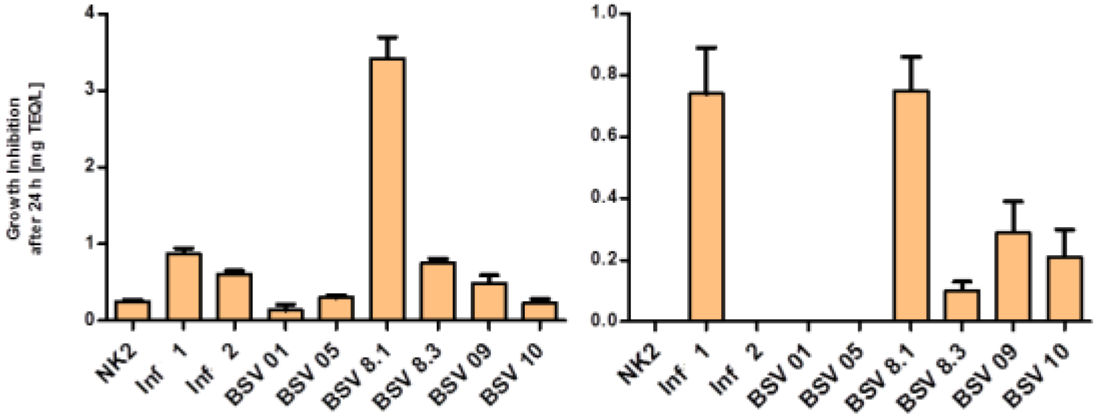
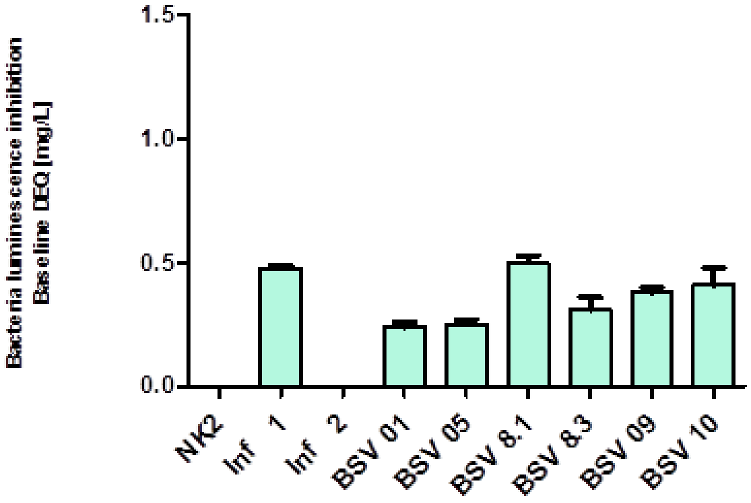


Figure 6-21: **Growth (after 24 hours of exposure) inhibition of the MAR samples from SVH – 1st sampling campaign (left) and 2nd sampling campaign (right) - expressed as ng Diuron Eq./L water. NK refers to negative control (HPLC water) went through on extraction and bioanalysis just as the samples.**

Figure 6-20, Figure 6-21 and represent the response of water samples to the inhibition of photosynthesis and the growth inhibition. The comparison between the two sampling campaigns performed as a duplicated of the experiments is presented. There are no evidences of the same responses in same samples. There are no clear conclusions.



(*) Campaign expressed as ng Diuron Eq./L water

Figure 6-22: **Bacteria luminescence inhibition of the MAR samples from SVH – 2nd sampling. NK refers to negative control (HPLC water) went through on extraction and bioanalysis just as the samples.**

Regarding Figure 6-22, it shows the inhibition of bacteria luminescence, with similar response in all the samples. Trigger values (see Table 6-14) are far above measured activity.

6.4 Summary

DEMEAU project has continued field investigations at the groundwater replenishment site in Sant Vicenç dels Horts. This report presents an interdisciplinary work including the quantification of emerging pollutants and the qualitative assessment of their behaviour in the MAR system, the application of the temperature as a tracer, leaching tests to assess the reactivity of the organic layer and the use of bioassays to determine the toxicity of infiltration water and groundwater.

The hydraulic characterisations by temperature breakthrough curves showed that this approach is feasible and contributes to an improved understand of the infiltration system. Through the application of temperature as a tracer it is possible to achieve a reasonable good understanding of spatial and temporal dynamics in MAR systems.

Three sampling campaigns have been carried out under different recharge conditions: i) full operation in July 2014, ii) dry conditions in January 2015 where the infiltration pond was dry and iii) mixed conditions in May 2015 where the pond was partially filled with water.A brief hydrochemical overview based on bulk water chemistry indicates organic carbon consumption along the flow path.

Leaching tests have been made with fresh compost and four year-old compost samples. The objective of the leaching tests was the evaluation of the long-term (purification) performance of the reactive organic layer installed at the bottom of the infiltration pond. The leaching tests showed that there are no evidences of additional organic carbon release after four years of operation. This finding is crucial for the interpretation of the bulk chemistry and the emerging pollutants, because it is very likely that no additional contaminant removal can be expected from the compost layer anymore.

In total 53 organic micropollutants have been measured during the sampling campaigns. The substances are divided in three groups: i) pesticides, ii) pharmaceuticals and iii) stimulants/sweeteners/corrosion inhibitors, including those identified by the DEMEAU project as target substances. The behaviour of organic micropollutants during subsurface passage was evaluated based on the hydraulic understanding of the recharge system. Most substances have been measured below LOQ and do not allow for removal approximation.

Field results are compared to results obtained from column experiments which were carried out previously within DEMEAU. The comparison between laboratory results and field results found similar removal trends of emerging pollutants. Removal was found to be higher under field conditions, which may be attributed to longer travel times.

The application of effect-based methods (bioassays) enabled to measure the combined effects of emerging pollutants. The broad range in vitro screening of the MAR water samples revealed the importance of endocrine - (particularly the activation of the ERα-, anti-AR, anti-PR receptors), oxidative stress (Nrf2-CALUX) and photosynthesis inhibition (Combined algae test) pathways, and showed differences between the samples collected within two different time points (two sampling campaigns).

Despite the lack of toxicological data for a number of the selected target compounds and the lower relevance of the selected compounds for (eco)toxicological risk assessment, this study greatly demonstrate as well the usefulness of combined analyses of environmental samples. Sampling sites, water sources can this way cost-efficiently pre-screened and characterized for low/high risk even without extensive measurement of a priori selected target chemicals. Not to mention that the targeted chemical analysis might overlook certain chemicals exerting specific effects. Effect-based methods, therefore, could complement conventional chemical analysis in water quality monitoring as pre-screening techniques by (i) identifying toxic “hotspots” for further investigation, (ii) assessing the effect of the entire mixture of compounds present in waters and therefore, (iii) reduce uncertainty in safety evaluation.

6.5 Recommendations for future studies

Operators of MAR system in Sant Vicenç dels Horts are now evaluating the possibility of replacing the vegetal compost layer, as there are no evidences of reactivity after four years of operation. Moreover, the infiltration rate decreased from $1m^3/m^2/d$ to $0.15\ m^3/m^2/d$. This reduction of the infiltration rate has resulted in the temporal inactivity of the MAR system. Future operational practice of the infiltration pond should also include regular maintenance and the DEMEAU project contributed with cost analysis for different maintenance strategies (see report D51.1 available at http://demeau-fp7.eu).

Despite there are hot topics in the research of MAR as the behaviour of emerging pollutants or the dependence of removal rates of hydrogeochemical conditions of the system. Also there is only basic knowledge about the hydraulics of the MAR systems that are still unknown. Elemental knowledge about preferential pathways, residence time or differentiation of infiltration areas of the infiltration pond is an essential request to go deeper in the understanding of the behaviour of emerging pollutants. Continuous temperature measurements are recommended to allow detailed assessment of hydraulic dynamics of the MAR scheme and improved understanding of contaminant behaviour.

Regarding emerging pollutants and MAR systems, future research should be focus in the identification of the hazards in infiltration water. Lot of studies and publications have listed and quantified the emerging substances present in Llobregat River and infiltration water (pharmaceuticals, pesticides, hormones, personal care products, detergents). In this sense, bioassays are a powerful tool to determine the toxic effects of the cocktail of substances present in infiltration water and could help to determine which of them are principally responsible of the undesired effects in organisms.

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7 Summary of field investigations (incl. application of risk assessment) in La Vall d'Uixó (Castellón, Spain)

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7.1 Introduction

In Vall d'Uixó near Castellón (Spain) a new Managed Aquifer Recharge (MAR) site based on Aquifer Storage Transfer and Recovery (ASTR) is currently under development. The framework of the work is the collaboration between the DEMEAU project, looking for demonstrating the feasibility of MAR to eliminate emerging micropollutants and the Water Recovery project, carried out in the area to promote the implementation of a new MAR site in the Mediterranean Spanish coast. DEMEAU has contributed to the Water Recovery project by doing additional sampling campaigns to assess the potential impact of the use of reclaimed water in the system. This report presents the results obtained in La Vall d'Uixó consisting mainly in the following investigations:

- Bulk chemistry: characterisation of source- and groundwater
- Assessment of emerging pollutants and their qualitative behaviour during MAR
- Entry level assessment (based on Australian Guidelines)
- Maximal risk assessment (based on Australian Guidelines)
- Bioassays of MAR samples

A risk assessment has been performed to evaluate the hazards of the injection of reclaimed water coming from the secondary effluent of the local Waste Water Treatment Plant (WWTP). To this end, Australian Guidelines (NRMMC-EPHC-NHMRC 2009) have been applied, following the entry level assessment and the maximal risk evaluation. Three sampling campaigns (2014 to 2015) have been carried out to characterise effluent, river- and groundwater. Bulk chemistry has been analysed in local laboratories, while emerging pollutants have been analysed in two specialised laboratories: University of Castellón (Spain), Göttingen University (Germany). Moreover, there has been an interdisciplinary collaboration with other partners of the DEMEAU project consortium related to assess water toxicity caused by emerging pollutants through bioassays. Samples from Vall d'Uixó were collected, shipped and analysed at BDS (The Netherlands) and EAWAG (Switzerland) using different bioassays. Bioassays have been carried out to assess water toxicity in different steps of the system (surface water, effluent of WWTP and groundwater). The bioassays results are also presented in this report and give information about the toxicity of water samples in the Castellón MAR site: injection water (surface water and reclaimed water) and the initial levels of toxicity in groundwater.

The essential idea of the Water Recovery project is to establish an appropriate implementing methodology for a pilot artificial recharge system with reclaimed wastewater to counteract salinity ingress and thereby contribute to the rehabilitation of coastal aquifers in the Castellón plain. The Water Recovery project has four phases. Phase I (September 2011-October 2012) focused on the selection of the pilot area, its hydrogeological characterisation, the design of the recharge system and establishment of the monitoring network and control program. Phase II (2013) included the construction of the injection wells and new piezometers to complement the existing monitoring network. Phase III (2013-2014) consisted in the injection of about 300,000 m^3 of surface water in the two injection wells. During this phase source water came from a reservoir, which accumulated freshwater in rainy season from the Belcaire River. Water Recovery project has currently finished the third phase. The fourth phase was planned to consist in the injection of effluent from the local Waste Water Treatment Plant (WWTP) in La Vall d'Uixó (Figure 1-1). This last phase is currently in stand-by due to financial constraints.

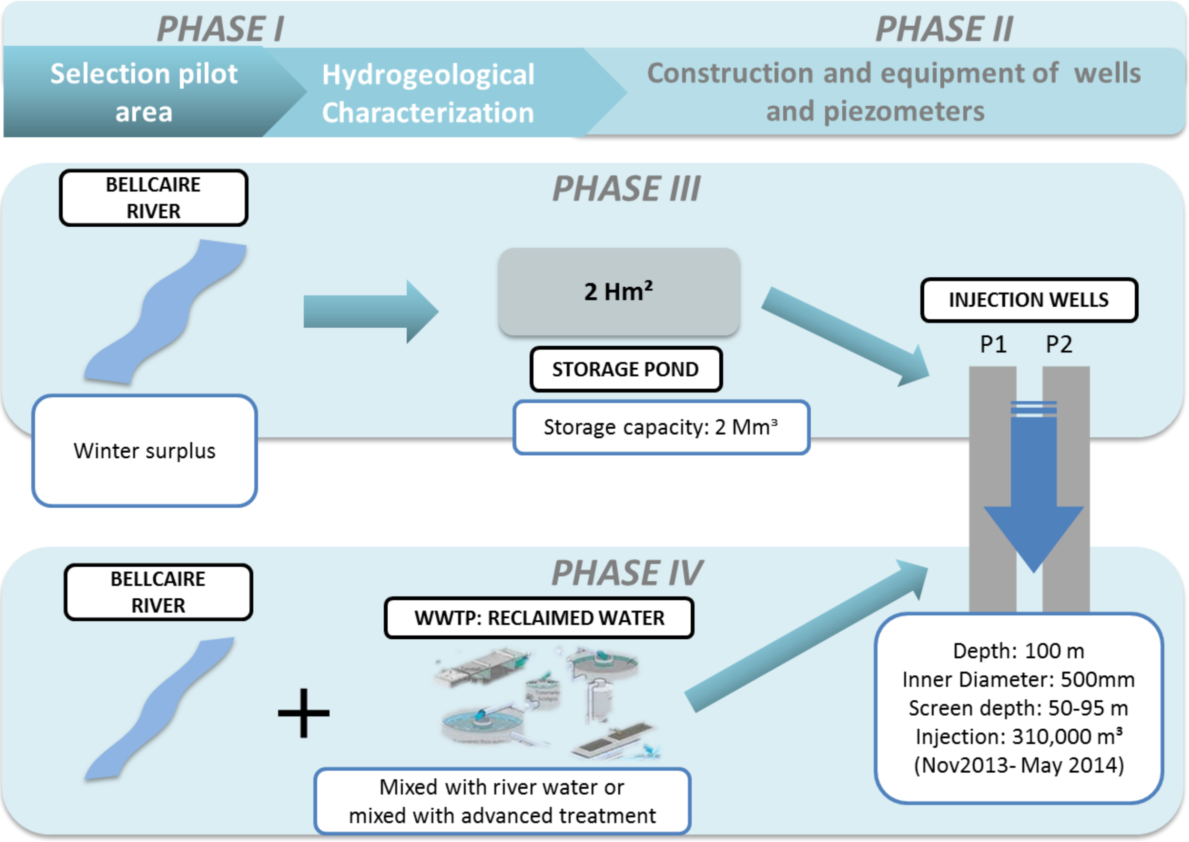


Figure 7-1: **The Water Recovery Project scheme**

7.2 General site description

La Vall d'Uixó is a municipality of approximately 33,000 inhabitants and 67.1 Km^2 of surface, located on the coastline of the province of Castellón (administrative regional district of Spain). The coastal area has an intense agricultural and industrial activity and also supports the main urban centers that attract a growing number of tourists. Almost half of the water demand from these activities is satisfied by groundwater from coastal aquifers.

These aquifers have suffered problems of overexploitation and salinization caused by seawater intrusion. Seawater intrusion is a significant threat to the sustainability of coastal water resources. Therefore, the essential idea of the Water Recovery project was to establish an appropriate implementation methodology to conduct a pilot study of artificial recharge with reclaimed wastewater to combat saltwater intrusion and contribute to the recovery of coastal aquifers.

The study area is located in the natural region called Plana de Castellón (Spain), specifically in the area of La Vall d'Uixó - Rambleta. It consists of a floodplain roughly triangular in shape with an area of 464 km^2 and an altitude between 0 and 130 above sea level.

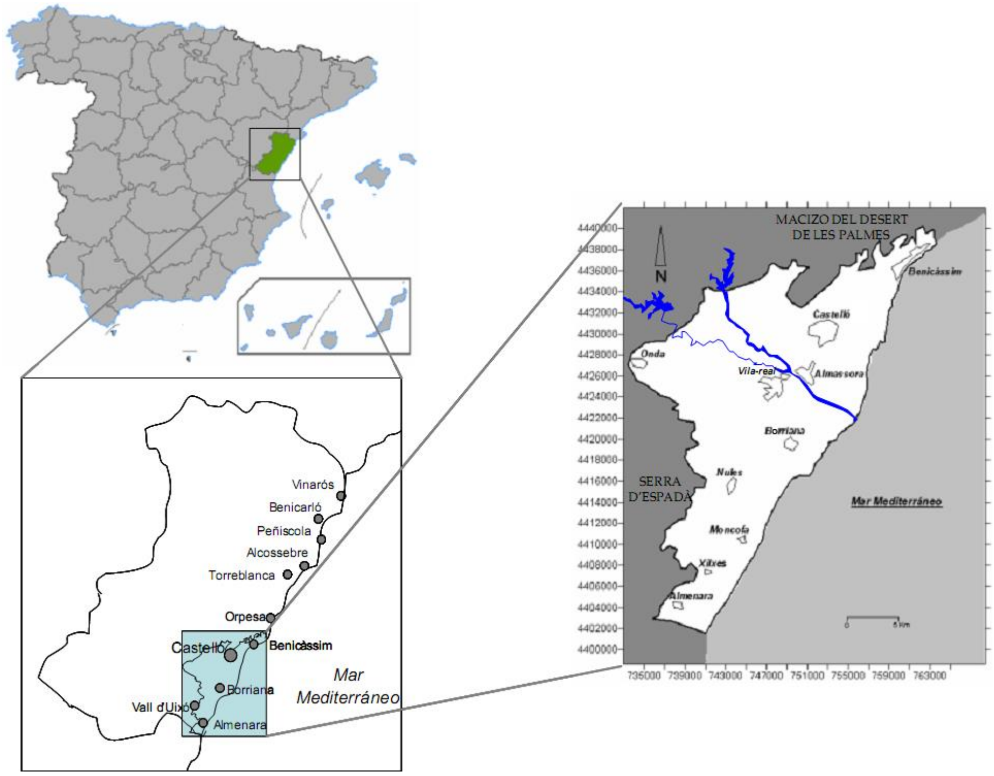


Figure 7-2: Map of location of La Vall d'Uixó (Morell *et al.* 2012)

The historical development of salinity ingress in the aquifer is illustrated in Figure 7-3. Seawater intrusion is known to have occurred in this area since the 1960s, and so the area is characteristic for salinization in Spain. In order to mitigate the seawater intrusion, a variety of organizations and institutions have undertaken studies in this area, including the Júcar Hydrographic Confederation (JHC), the Spanish Geological and Mining Institute (IGME), the Generalitat Valenciana (the Valencia Regional Government), the University Jaume I de Castelló and the Polytechnic University of Valencia. As a result, there is abundant hydrogeological, hydrogeochemical and hydrochemical data for the concerned groundwater body in this area.

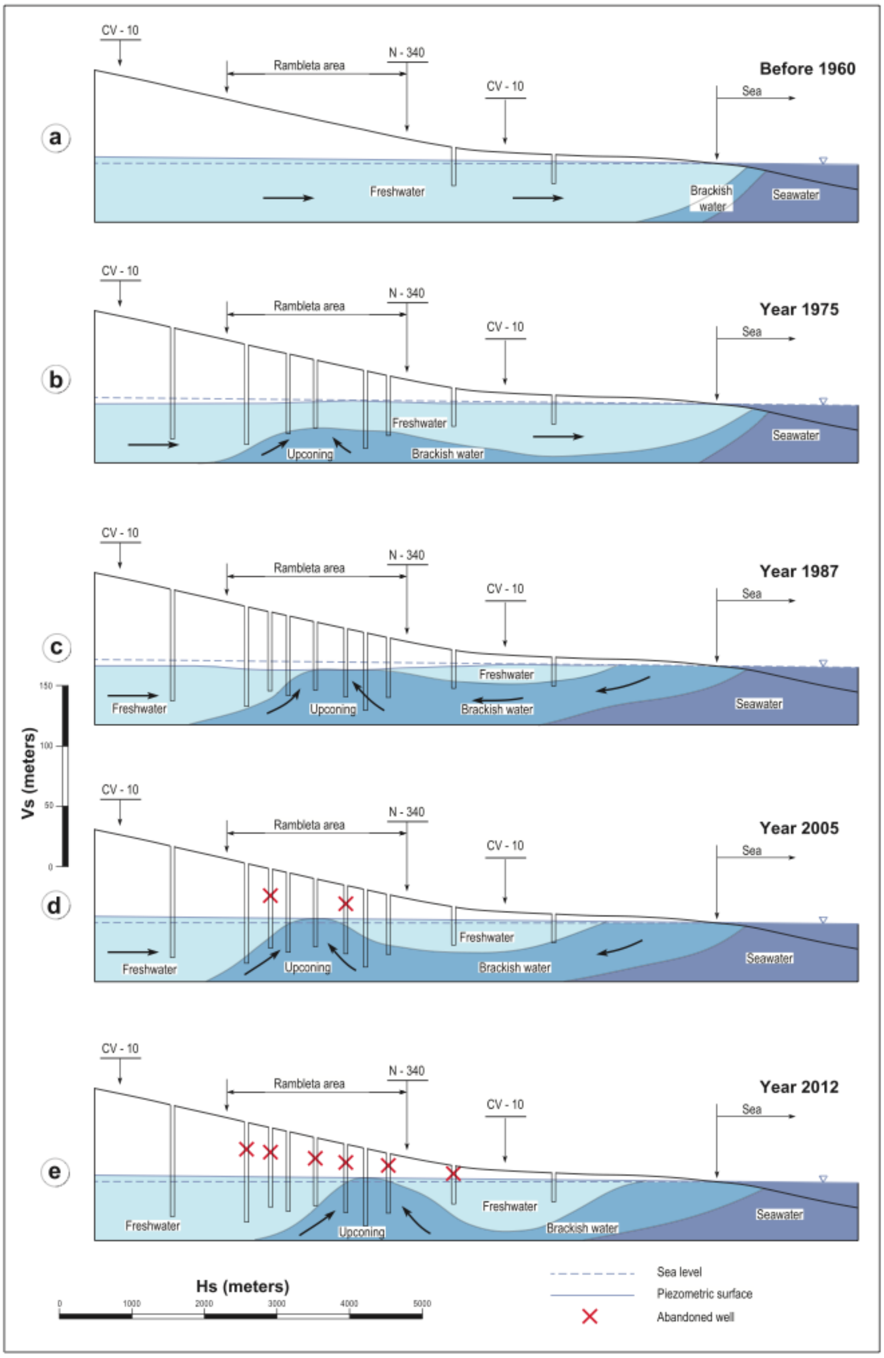


Figure 7-3: Sketch of historical development of salinity ingress in the La Vall d'Uixó aquifer (Morell *et al.* 2012)

The salinization process that affects the Rambleta area is peculiar, since it originates not only from the lateral advance of the so-called saline wedge, but also from the up-coning of saline water generated by the hydrodynamic effect of local concentrations of pumped groundwater abstractions. Considering these two origins of salinization is crucial in the design of the MAR system aiming at not only acting as a hydraulic barrier to repulse the saline front, but also exercising a hydrodynamic effect capable of reducing the saline up-coning.

7.2.1 MAR profile and hydrogeological characterisation of the pilot area

Along the coast of Valencia Community there are a number of coastal plains that accommodate a series of essentially detrital aquifers of great hydrogeological interest. They all feature an extremely flat morphology extending from sea level to maximum elevations of between 100 and 130 m. These geomorphological elements, known by the generic name of "planas" or plains, tend to be distributed longitudinally along the coastline. There is wide variability in their spatial development, both in area and the thickness of the deposits that they comprise. All are limited to the East by the Mediterranean Sea. The Castellón Plain, like other Mediterranean coastal plains, is a tectonic basin that formed during the Tertiary as a result of the Neogene distension. This distension determined the current structure of the entire coastal strip, generating a complex of horsts and grabens that continue beneath the sea. The fill of the basin, including the Castellón Plain aquifer, comprise Neogene and Quaternary sediments of polygenic, continental, littoral and mixed type, capped by a gently sloping glacis that extends to the present-day coastline.

The aquifer formation consists of layers and lenses of conglomerates, sands and gravels, intercalated and contained within a silty-clay series, making up a single Plioquaternary aquifer unit. Nevertheless, two formations are recognized: an upper one and a lower one. The upper one comprises conglomerates, sands and gravels with a significant proportion of fines. The lower one accommodates a higher proportion of clays. Permeability of the upper formation is quite high, while the lower one has much lower permeability. The series overlies either Mesozoic strata of variable permeability (which may form a second aquifer), or impermeable Tertiary or even other Mesozoic sediments.

The thickness of the detrital formation is highly variable, as a result of the morphology of the underlying substratum; it is generally thicker towards the coast. Most commonly it is between 50 and 200 m thick, with a mean of 70 m. The hydrodynamic parameters of the system are extraordinarily variable: transmissivity falls in the range of less than 500 m^2/day to 6,000 m^2/day, peaking near the coast. Storage coefficients are between 5 and 15 %, values characteristic of a free detrital aquifer. Specific flows oscillate between 1 and 20 L/s/m, though it is normally between 5 and 10 L/s/m; meanwhile hydraulic permeability varies from 30-50 to 100-120 m/day.

The area of Rambleta in La Vall d’Uixó is situated in the far southwest of the geographical district known as the Plana de Castellón. This occupies the southern part of Castellón province on the eastern seaboard of the Iberian Peninsula and comprises a more or less triangular alluvial plain covering 464 km^2, with elevations of between 0 and 130 m a.s.l. The hydrographical network consists of a single permanent watercourse - the River Mijares, which bisects the plain. All other surface watercourses are by nature intermittent and sporadic. The administrative code for the identification of this groundwater body is MASub 080.127.

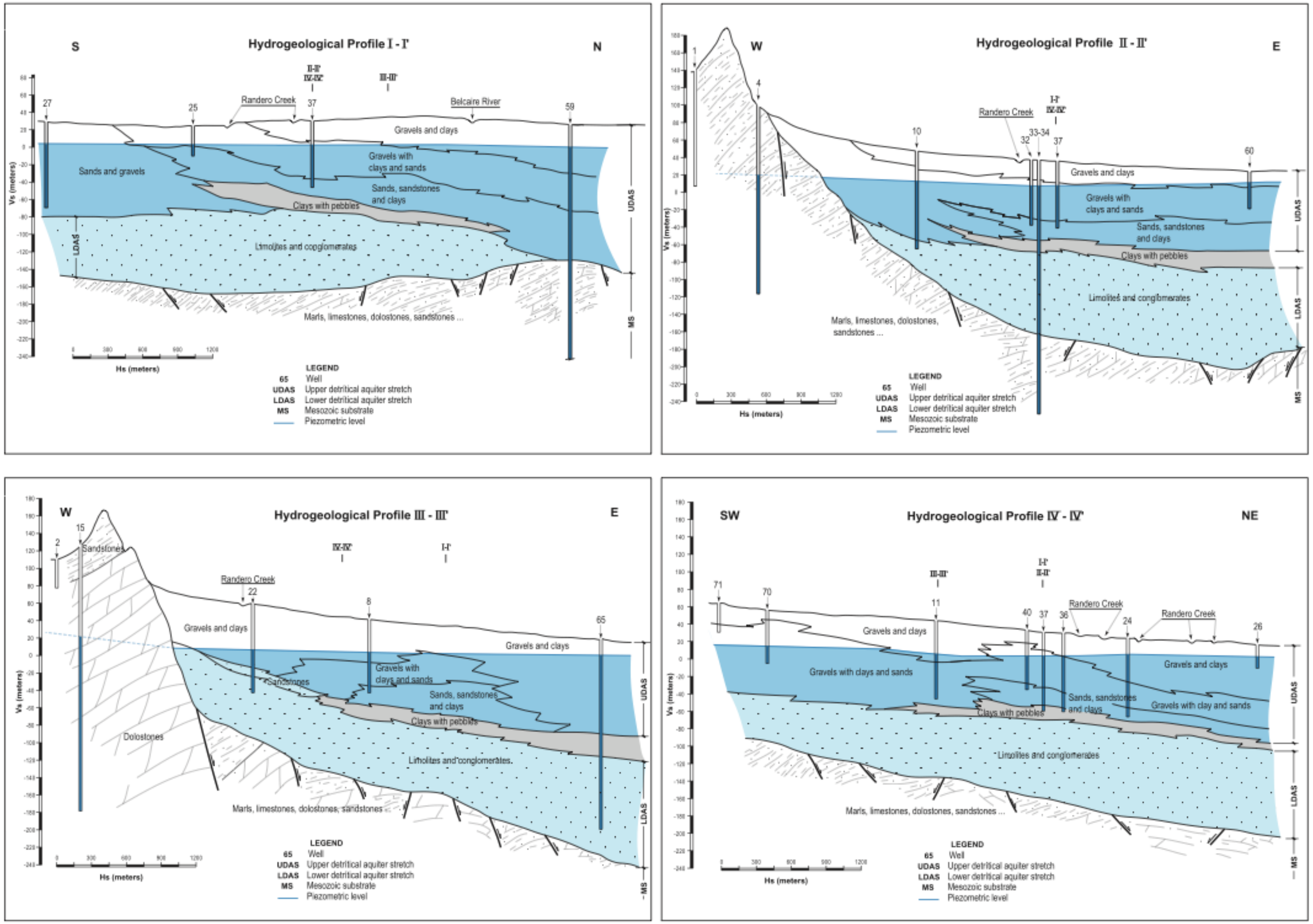


Figure 7-4: Hydrogeological cross-sections (Morell *et al.* 2012)

As a summary, the geologic section presents the following hydrogeological units:

- **Upper detritic aquifer (UDAS):** Sands and gravels (80-90 m). The aquifer exploited by the most of the wells.
- **Lower detritic aquifer (LDAS):** Siltstones, clays, sandstones and conglomerates (50-100 m).
- **Mesozoic substratum:** Triassic limestones, marls and dolomites (Muschelkalk facies), orthoquarzite sandstones (Buntsandstein facies), marl with gypsums (Keuper facies).

7.2.2 Role of groundwater in the pilot area

The whole district is underlined by the detrital Castellón Plain Aquifer. The area occupied by this hydrogeological system is economically vigorous, with thriving agriculture, ceramics and chemical industries coexisting. The agriculture is mainly citrus fruit cultivation; industry is dominated by the ceramics industry, which produces 85 % of Spain's total (Spain is the second largest world producer). There is also a significant chemical industry producing essential oils, and factories manufacturing chemical, organic and phyto-sanitary products and fertilizers.

These three economic activities are complemented by an agro-food industry and a well-developed service sector, the tourism. The economic scheme described needs he availability of groundwater resources, which are essential for sustaining these industries. Thus, the pumped abstractions were quantified nearly 201 Mm^3/y over the 1980s, of which 32 Mm^3/y was destined for urban water supply, 11 Mm^3/y for industrial usage, 158 Mm^3/y for irrigation and 0.44 Mm^3/y for livestock. Figure 7-5 shows typical pictures of the area, with the presence of citrus crops close to the wells.

Figure 7-5: Selection of pictures of the pilot area

7.2.3 Groundwater management and reclamation scheme: Water Recovery Project

Figure 7-6 represents the scheme of the MAR established along the Water Recovery Project. Two injection wells were constructed with the aim of injecting water coming from the storage dam. The storage dam can receive surplus water of the Belcaire River (Phase III) and reclaimed water from the WWTP of La Vall d'Uixó (Phase IV, not executed yet). There is a recharge pipe connecting the dam outflow with the injection wells. Figure 7-6 shows an aerial view of the MAR scheme.

Along the Phase III of Water Recovery project, the impact of surface water in the aquifer has been assessed (results available in Water Recovery project final report). The aim of the additional campaigns performed in DEMEAU project is to assess the impact of reclaimed water to/for groundwater. To this end, water quality of the secondary effluent of the WWTP has been considered as injection water. It is the most pessimistic scenario, taking into account that there could be an advanced treatment plant installed or a mix with river water.

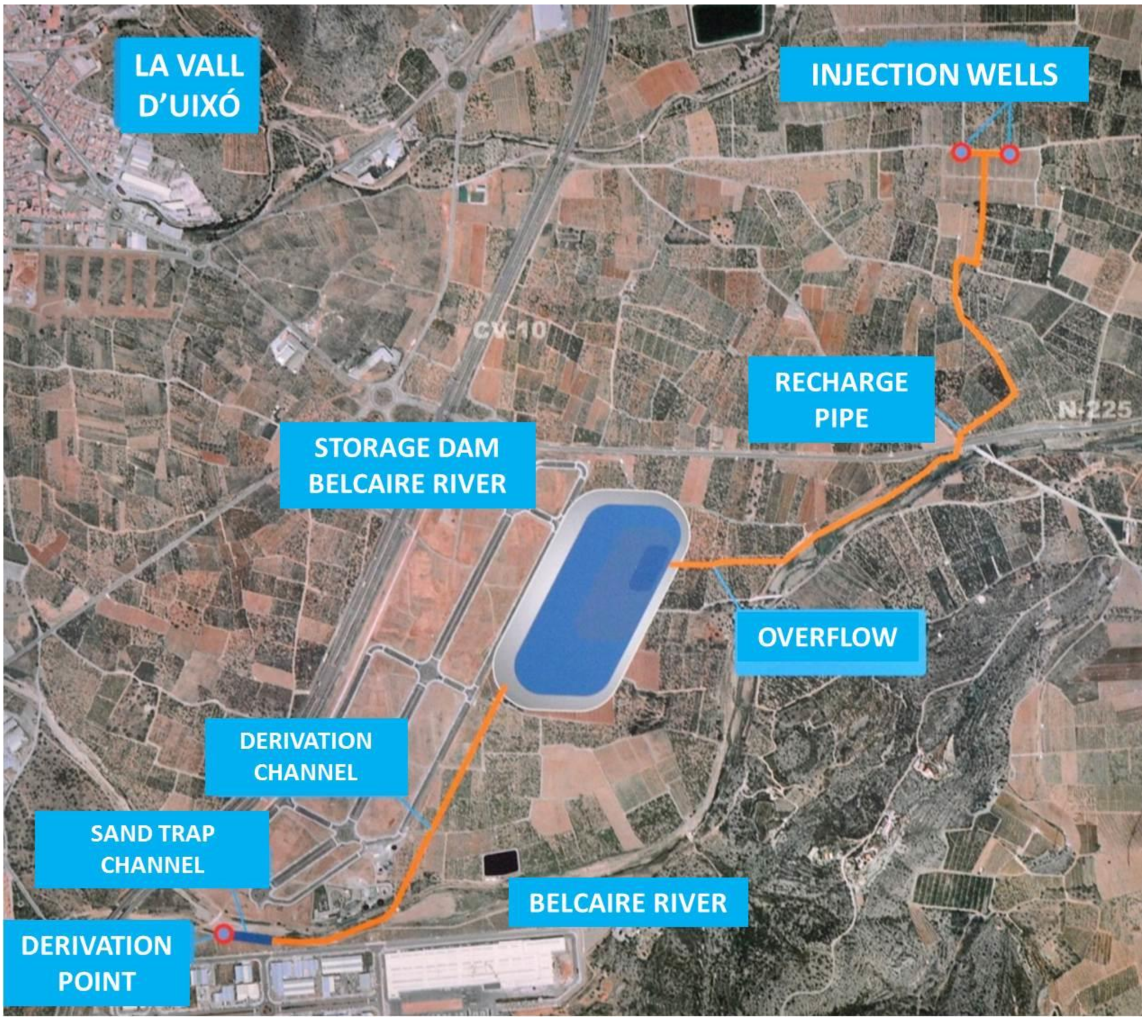


Figure 7-6: MAR scheme in La Vall d'Uixó

7.2.4 Monitoring network

Seven of the sampling points of Water Recovery project have been selected for the additional sampling campaigns carried out within the DEMEAU project. Because the objectives of both projects was to assess the feasibility of a new scheme using reclaimed water, WWTP effluent has been also included in the sampling campaigns, as well as storage dam water for further comparison. A total sum of 13 different types of sampling locations was sampled in the three campaigns. Table 7-1 summarises the main properties of the sampling points and Figure 7-7 shows their geographical distribution.

Table 7-1: Identification of the DEMEAU sampling points

Code	Type of water	Total Depth (m)	Coordinate (X) ETRS 89	Coordinate (Y) ETRS 89
CAS-01 EDAR	Effluent WWTP Working day sample	-	738565	4410127
CAS-02 EDAR	Effluent WWTP Working day sample	-	739120	4410826
CAS-03 EDAR	Effluent WWTP Weekend sample	-	741831	4411429
CAS-04 EDAR	Effluent WWTP Weekend sample	-	741873	4411860
CAS-05 BALSA	Surface Water Storage Dam	-	739584	4412176
CAS-06 SAN VICENTE	Groundwater Agricultural well	52	741067	4412526
CAS-07 LA PAZ	Groundwater Agricultural well	51	740485	4411955
CAS-08 RANDERO	Groundwater Agricultural well	100	740583	4412081
CAS-09 RAMBLETA 2	Groundwater Agricultural well	42	740047	4412030

Code	Type of water	Total Depth (m)	Coordinate (X) ETRS 89	Coordinate (Y) ETRS 89
CAS-10 PRIMITIVA	Groundwater Agricultural well	100	740235	4411950
CAS-11 GARROFERA	Groundwater Agricultural well	N.A.	740105	4411936
CAS-12 PIEZOMETRO 2	Groundwater Borehole near injection wells	59	738565	4410127
CAS-13 PIEZOMETRO 1	Groundwater Borehole near injection wells	60	739120	4410826

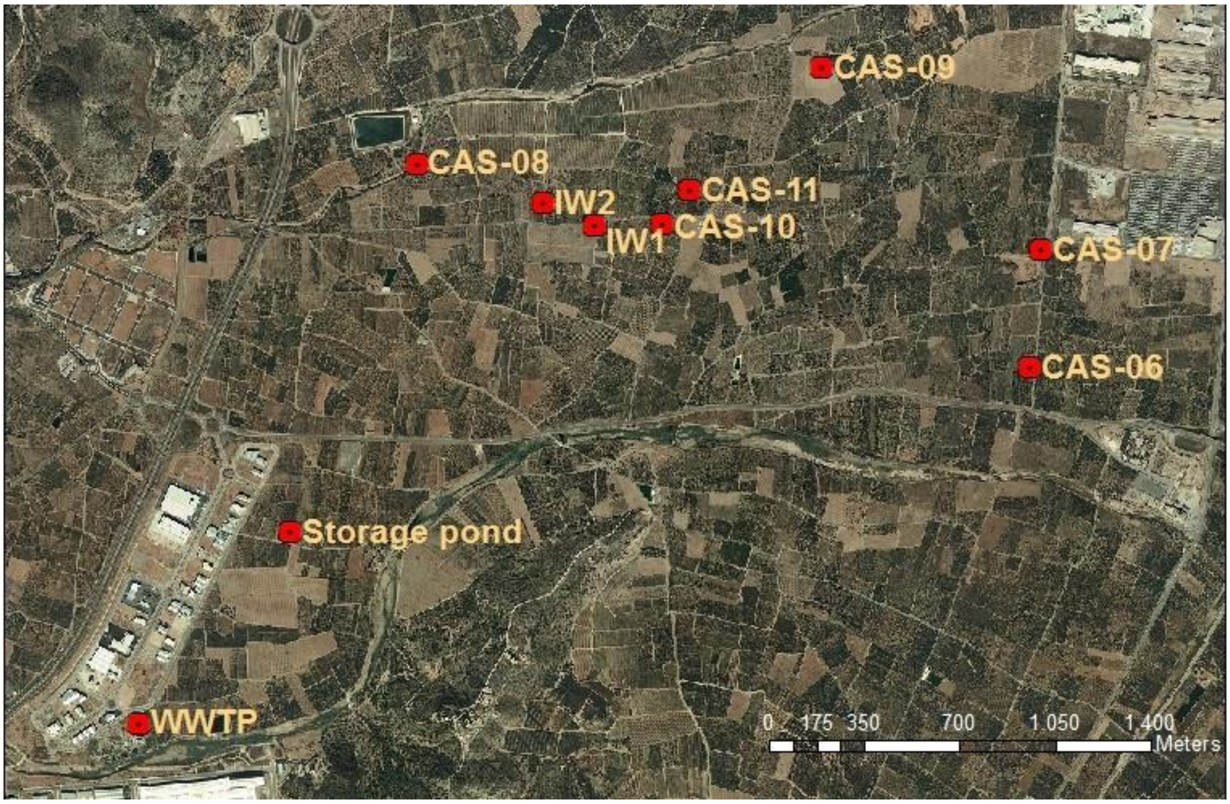


Figure 7-7: Aerial view of sampling points locations

7.3 Materials and Methods

7.3.1 Sampling campaigns

Sampling campaigns have been performed in La Vall d'Uixó three times along the last phase of DEMEAU project in 2014 and 2015. Each laboratory applied validated and certified analytical procedures. Taking advantage of the sampling campaign, samples for bioassays tests were collected. Bioassays tests were performed by BDS (The Netherlands) and Oekotoxzentrum (Switzerland) simultaneously (Table 7-2).

Table 7-2: Summary of sampling campaigns and laboratories involved

Sampling campaign	Micropollutants laboratory	Bulk chemistry laboratory	Bioassays Survey
May 2014	University of Göttingen 250 mL (WWTP effluent; 500 mL groundwater). Glass amber bottles	Instituto Geológico y Minero de España IGME	YES (2 L frozen) Glass amber bottles
January 2015	University of Castellón (Jaume I, IUPA institute) 1L plastic bottle	Instituto Geológico y Minero de España IGME	NO
April 2015	University of Castellón (Jaume I, IUPA institute) 1L plastic bottle	Instituto Geológico y Minero de España IGME	YES (500 mL refrigerated) Glass amber bottles

7.3.2 Hydrochemistry

Hydrochemistry and calculated ion balance ($\mathrm{ion balance}(\%) = \sum \mathrm{cations} - \sum \mathrm{anions} / (\sum \mathrm{cations} + \sum \mathrm{anions} / 2) \times 100$) are shown in annex J. Only samples with ion balance ≤10% were used. All measured and calculated hydrochemical parameters are found in annex J.

7.3.3 Organic micro pollutants analysis

The analysis of micropollutants has been done in two different laboratories, applying the same limit of quantification. DEMEAU's list of pharmaceuticals have been kept in both laboratories, and each of them have added additional emerging compounds and priority substances in the list (see annex K). Samples were taken with bailers, submerged approximately five meters below groundwater level previously measured. Monitoring wells were not purged before sampling. Specific bottles types and volumes were used according laboratories requirements.

7.3.3.1 University of Göttingen (Geoscience Centre)

Samples from May 2014 where analysed by University of Göttingen. Samples were conserved at 4 °C during the transport and storage in Barcelona. Samples were shipped to Göttingen University in cold conditions. Once the bottles arrived to the laboratory, 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).

7.3.3.2 University of Castellón (UIPA Institute)

Samples collected in January and April 2015 were analysed in Castellón in the IUPA Institute. Samples were conserved at 4ºC during the transport (few hours) and directly frozen in Castellón until the analysis. The analytical procedure is fully described in Boix *et al.* (2015) and consists in the direct injection of the sample after a simple centrifugation (2 mL of sample centrifuged at 12,000 rpm for 10 minutes) and then 100 μL of volume was injected into the chromatographic system (liquid chromatography–tandem mass spectrometry UHPLC-MS/MS). Pantoprazole, iopromide and bezafibrate were quantified by absolute areas. However, in most cases it was necessary to correct the matrix effect, for which isotopically labelled internal standards were used. The correction was performed using the labelled analyte itself when this was available (11 of 21 compounds). For other compounds (gemfibrozil, desethyl atrazine, atrazine desisopropil, phenazone, simazine, primidone, and metoprolol) a labelled analogue was used, whose election was a function of retention time and based on preliminary studies. Bulk chemistry was analysed in IGME Laboratory (Valencia) using standard methods.

7.3.4 Bioassays

Bioassays allow the identification of the observed biological effects caused by environmental chemicals and the mixtures that contain them. Recent technological developments have provided powerful quantitative in vitro bioassays to effectively measure a wide range of major classes of toxicants (i.e. acutely toxic compounds, endocrine disrupting substances and genotoxic agents) in the water cycle. As part of the DEMEAU project, scientists recently developed the CALUX cell panel, a type of bioassay panel with the ability to run in an efficient and automated way (Van der Linden et al., 2008). In order to show the potential of these integrated techniques in the field of MAR, collaboration was done between La Vall d'Uixó test site and the laboratories developing and testing these techniques.

MAR water samples from two sampling campaigns conducted in May 2014 and April 2015 were subjected to sample preparation (i.e. extraction) and screening with selected bioassays to characterize their toxicity profile and investigate the impact of micropollutants. Table 7-2 summarises the sampling conditions in La Vall d'Uixó. The aim of this duplicated experiment was to compare results obtained in the same season to assess the replicability of the bioassays. Techniques applied are listed below:

- **CALUX®-panel** consisting of 9 assays (covering toxic endpoints found to be relevant for water quality benchmarking indicated by the toxicity profiling of the DEMEAU compounds and other case studies (van der Linden 2014; Leusch *et al.* 2014 and Escher *et al.* 2014).
- **Combined algae assay** assessing both photosystem II-inhibition and effects on algae growth
- **Bacteria luminescence inhibition** evaluating acute toxicity of the samples.

Prior to the bioassay analyses samples were concentrated by various extraction methods allowing for enriched pollutant concentrations in the extracts and thereby enabling their better detection in the bioassays. It also limits the impact of the matrix components and metals, which are partially separated during the extraction (Macova *et al.* 2010).

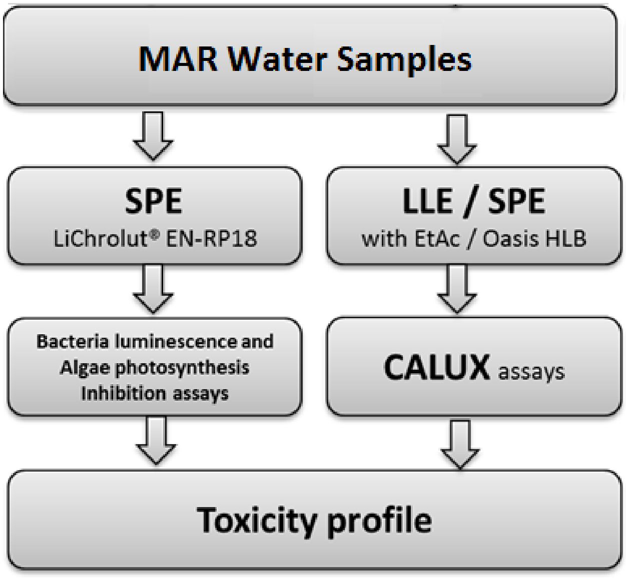


Figure 7-8: Schematic study design of bio screening

Table 6-6 lists the sampling points in La Vall d'Uixó for the performance of bioassays. Additional information as the total depth of the wells or geographical coordinates can be found in Table 7-1, and aerial view for their location is shown in Figure 7-7.

Table 7-3: Selected sampling points for the bioassays

Code	Type of water
CAS-01- EDAR	Effluent WWTP (Working day sample)
CAS-05 - BALSA	Surface Water (Storage Dam)
CAS-06- SAN VICENTE	Groundwater (Agricultural well)
CAS-07- LA PAZ	Groundwater (Agricultural well)
CAS-08- RANDERO	Groundwater (Agricultural well)
CAS-09- RAMBLETA 2	Groundwater (Agricultural well)
CAS-11- GARROFERA	Groundwater (Agricultural well)
CAS-12- PIEZOMETRO 2	Groundwater (Borehole near injection wells)

7.3.4.1 Sample workup

Samples were transported to the partners (BDS, Amsterdam and Oecotox Centre – EAWAG, Dübendorf) for bioassay analyses either frozen (1st campaign done in May 2014) and refrigerated (2nd campaign done in April 2015) and subjected to extraction as soon as possible.

Prior to the combined algae and bacteria luminescence inhibition (Ecotox Centre-EAWAG, Dübendorf) the sample enrichment was done by solid phase extraction (SPE), which allows for increased pollutant concentrations in the extracts and thereby enables a better detection in the bioassays. Briefly, 500 mL was enriched 500 times using LiChrolut® EN-RP18 cartridges (Merck, Germany) after filtration and pH adjustment (pH=3) of the samples. For each SPE a blank is prepared and treated in the same way as the samples, including filtration and pH adjustment. The volume of the SPE blank (ultrapure water) corresponded to the highest sample volume (i.e. 500 mL). Extracts were then stored in 1 ml of a solvent mixture (~50% ethanol, ~50% acetone and methanol) at −20 °C until analysis following the method described by Escher *et al.* (2008b).

Prior to CALUX analysis (BDS, Amsterdam) samples of the 1st sampling campaign (06/2014) were liquid-liquid extracted (LLE) following the in-house standard operation protocol (SOP) of BDS (p-BDS-053). Briefly, from each sample 250 mL was extracted three times with ethyl acetate (200, 50 and 50 mL). All three ethyl acetate fractions were collected, combined and evaporated under a gentle stream of nitrogen till almost dryness and taken up in a final volume of 100 µL of dimethyl sulfoxide

(DMSO). DMSO is a suitable solvent for the CALUX screening. All extracts were stored at -18 ⁰C until analysis.

From the samples of the second campaign in April 2015 somewhat different volumes were worked up due to the various sample volume availability. 350 mL from the Castellón samples were extracted by SPE using Oasis HLB cartridges. During the time between the two sampling campaigns BDS modified his in-house extraction method and stepped over from LLE to SPE with Oasis HLB cartridges. The two methods were fully compared and evaluated and resulted in no changes in extraction efficiency. Similarly to the sample handling in the 1st campaign, extracts were dissolved in 100 µL of DMSO and stored at -18 ⁰C until analysis.

Taking into account all the sample manipulation steps (concentration during extraction and then dilution in the bioassay) during the analysis, 25 times (samples from the first campaign) and 35 times (samples from the second campaign enriched samples were tested in the CALUX bioassays.

7.3.4.2 Method for combined Algae Assay methodology

The Combined Algae Assay on the green algae *Pseudokirchneriella subcapitata* was conducted as described earlier (Escher *et al.* 2008a). The photosynthesis inhibition was measured by means of effective quantum yield (after 2 h of exposure) and the inhibition of the algae growth by means of absorbance at 685 nm (after 24 h of exposure). The herbicide diuron served as the reference substance and ethanol as the solvent control (30 and 80 µl/well, respectively with a setup of 8wells/plate). The reference substance in duplicate and the extracts of the water samples in triplicate were tested in a 1:2 dilution series, with the highest concentration of diuron being 3 × 10−7 M (69.9 µg l−1, in ethanol). Maximum enrichment factors of the water samples in the assay were 133 times. The toxicity of the water samples was expressed as diuron-equivalent concentrations (DEQs) for the endpoint “inhibition of Photosystem II” and toxic equivalent concentrations (TEQs, virtual baseline toxicant) for growth inhibition.

7.3.4.3 Method for bacteria luminescence inhibition assay

The inhibition of the luminescence of the bacterium *Aliivibrio fischeri* (bacteria luminescence inhibition assay) is a commonly used bioassay for screening of surface waters to detect non-specific effects of toxicants. The extracts were added in microtiter plate wells, a geometric dilutions series in ethanol was done and the solvent left to evaporate to dryness. The residues were redissolved in a NaCl buffer solution and added to the reconstituted freeze-dried bacteria (Dr Lange, Düsseldorf, Germany) in another microtiter plate. The bacteria luminescence output was measured prior to addition of sample and after 30 min incubation and the inhibition of bioluminescence was reported as toxic equivalent concentrations for baseline toxicity (baseline-TEQ) (Escher *et al.*, 2008b).

7.3.4.4 Method for CALIX reporter assays

All CALUX reporter assays used for this screening are stable cell lines based on the human osteosarcoma U2OS cells with a luciferase gene under the transcriptional control of responsive elements for activated hormone receptors. These cell lines allow sensitive and specific measurements of hormone receptor action by complex mixtures of compounds. In short, cells were seeded in 384-well plates and cultured for 24 h, after which they were exposed to a dilution series of 13 dilutions with 0.5 log unit increments of the compound or extract in DMSO. The final concentration in the well was 1 %. Along with the test samples, a concentration series of a reference compound was included on the same well plate. After 24 h of exposure cells were lysed and luciferase activity was quantified using a luminometer (Berthold Technologies, Bad Wildbad, Germany) that adds substrate to each well and subsequently measures luminescence for 1 s per well. Only dilutions that were negative in the cytotoxicity test were used for quantification of the response (Pieterse *et al.* 2015, van der Linden *et al.* 2008).

7.3.4.5 Methodology for data analysis

7.3.4.5.1 Hormone assays, PPARγ-CALUX assays, bacteria luminescence inhibition assay and combined algae assay

For assays showing and S-shaped dose-response curves, the measured activity is expressed as being equivalent to a reference compound concentration in the sample, which is determined by interpolating the response of the extract into the concentration-response curve of the reference compound - generally at 50% effect level - and further back-calculation taking all previous dilution and concentration factors into account. Equivalent concentrations are expressed ng or µg reference compound-Eq/L water.

7.3.4.5.2 P53 (+/-S9)-CALUX and Nrf2-CALUX

For these assays (showing other type of dose-response relationship, i.e. no S-shaped curve) induction factors (IF) were calculated by dividing the level of response (relative light units [RLU]) in the assay by the average RLU level of the solvent control wells (DMSO only). Samples were considered to be positive in the assays when the response of at least one concentration showed an increase of at least 50% (i.e., a 1.5-fold induction compared to the negative control). This effect level of the sample was then interpolated from the reference dose-response curve and back-calculated taking all previous dilution and concentration factors into account. Equivalent concentrations are expressed ng or µg reference compound-Eq/L water. Table 7-4 summarises the ecotoxicological effects detected by the in vitro bioassays performed.

Table 7-4: **In vitro bioassay panel used for the characterisation of the activity profile of the MAR samples received from two sampling campaigns**

Toxic pathway	Pertinent in vitro bioassay	Possible adverse health/ecotoxicological effects
Cell viability	Cytotox-CALUX	General (non-specific) toxicity

Toxic pathway	**Pertinent in vitro bioassay**	**Possible adverse health/ecotoxicological effects**
Hormone mediated mode of action (MoA)	ERα-CALUX, (anti)AR-CALUX, (anti)PR-CALUX, GR-CALUX	Tumor development, Birth defects, (Sexual) developmental disorders
Lipid metabolism	PPARγ-CALUX	Obesity and inflammatory diseases
Reactive MoA	P53-CALUX, P53 S9-CALUX	Tumor development
(Oxidative) stress response	Nrf2-CALUX	Inflammation, sensitisation and neurodegenerative diseases
Inhibition of the luminescence of the bacterium	Bacteria luminescence inhibition assay	General (non-specific) toxicity
Inhibition of the photosystem II	Combined algae assay	Photosynthesis inhibition linked to reduced algae/plant survival and growth

7.3.4.5.3 Quality controls

All samples were tested in the bioassays together with the

- procedure blank,
- bioassay solvent blank (DMSO, EtOH),
- and the corresponding reference compound of the assay.

Neither the procedure blank nor the bioassay solvent blank (data not illustrated) showed activity in the assays. The corresponding reference compound showed in each assay the maximum response in agreement with the historical positive control/reference compound data.

The limit of detection (LOD) - denoting the minimum amount of activity reliably detected – mostly depends on the amount of sample extracted, the concentration factor achieved during sample preparation, and the dilution factor required when testing an extract dissolved in a solvent (e.g.

DMSO or ethanol) in the bioassay. Assay LOD and LOQ (limit of quantification, which is triple LOD values are clearly indicated in the results tables.

7.4 Results

7.4.1 Hydrochemistry

Native groundwater is characterized by elevated salinity caused by anthropogenic induced salinity ingression that has affected the area for decades as a consequence of overexploitation of the aquifer. Annex J shows all hydrochemical results obtained from the three sampling campaigns plus an additional campaign that was carried out in 2012 in the framework of the Water Recovery project. Native groundwater hydrochemistry has been previously described in the reports of the Water Recovery Project and in publications (Morell *et al.,* 2014; García *et al.* 2014). According to information reported in these studies native groundwater has a chloride facies with chloride concentrations between 200 and 750 mg/L, originating from the mixing of fresh water and seawater. However, the facies are also sulphate type, with sulphate concentrations of 250 - 700 mg/L, which is much higher that would be expected if the sulphate is coming only from seawater. Magnesium concentrations are also very elevated, between 100 and 230 mg/L. Another notable hydrochemical feature of groundwater in this sector is the presence of very high nitrate concentrations between 190 and 520 mg/L, caused from the intensive agricultural activity.

Ion exchange is a common process during re-freshening or salinization of coastal aquifers (Appelo and Postma 2005). The displacement chromatography under re-freshening conditions, when fresh water flushes a salty or brackish water aquifer, follows:

$$\frac{1}{2}Ca^{2+} + Na\text{-}X \rightarrow \frac{1}{2}Ca\text{-}X2 + Na^{+} \qquad \text{(eq. 1)}$$

Where Ca^{2+} is transferred from the water to the binding sites of the exchanger and Na^{+} is dissolved in return $NaHCO_3$ water type results. When seawater intrudes in a fresh water aquifer ion exchange process can be described as:

$$Na^{+} + \frac{1}{2}Ca\text{-}X2 \rightarrow Na\text{-}X + \frac{1}{2}Ca^{2+} \qquad \text{(eq. 2)}$$

Where Na is taken up by the binding sites of the exchanger and Ca is released to the water in return. The water type changes here from NaCl to $CaCl_2$. These ion exchange processes are illustrated by displaying the alkaline elements (Na + K) substracted by the binding partner chloride against the earth alkaline elements (Ca + Mg) substracted by sulphate and bicarbonate (Figure 7-9). Samples are plotted in units of meq/l. Plausible samples must plot on the 1:1 line and ground water which is not altered by ion exchange would plot in the centre (± 5 meq/L), because the alkaline cations (Na + K) would be balanced by halogen anions (Cl) and the earth alkaline cations (Ca + Mg) would be balanced by sulphate and bicarbonate. If ion exchange takes place according to eq. 1 (re-freshening conditions) sodium would be in excess and Ca would be depleted. Samples displaying a re-freshening effect lie in the lower right corner of **Figure 7-9**. Samples that underwent ion exchange due to salinization (eq.2) of the aquifer are plotting in the upper left corner.

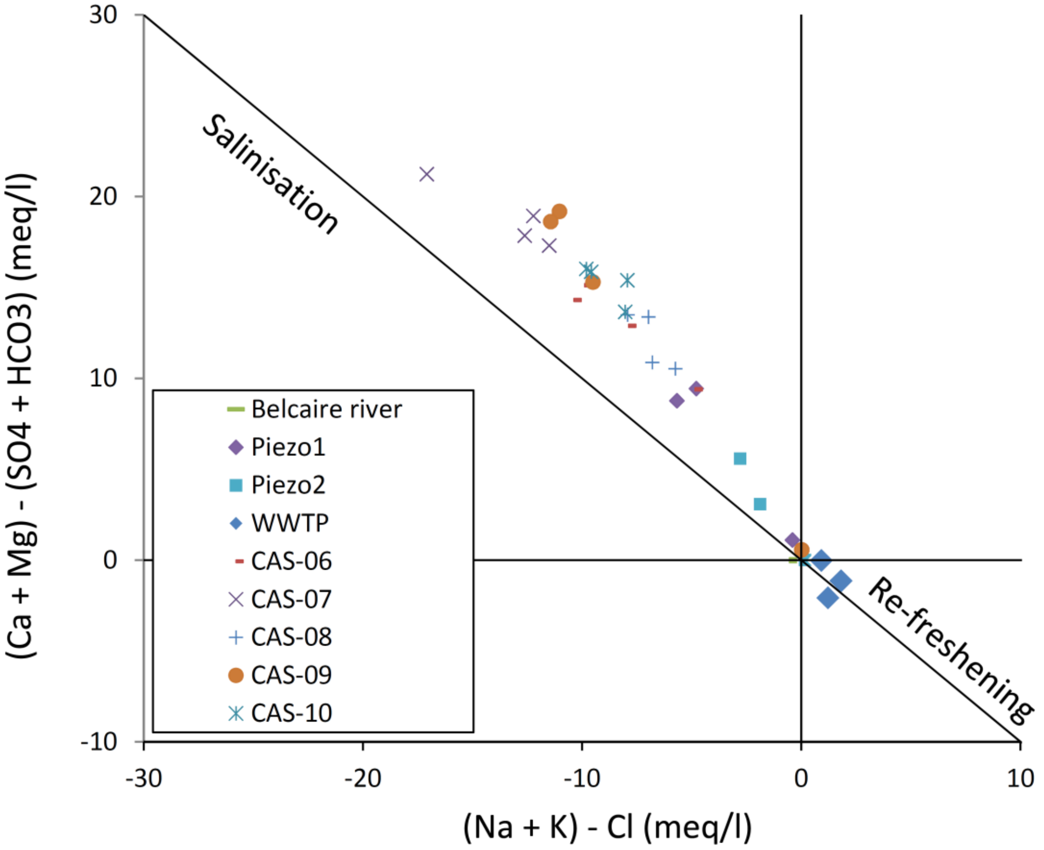


Figure 7-9: **Ion exchange due to salinity ingress**

Ion exchange due to salinization can be observed in most of the wells. The WWTP and Belcaire River samples, as expected, do not indicate ion exchange. In CAS-07 salinization is pronounced as it plots in the very upper left corner of. CAS-09 is also under the influence of on-going salinization, but the sample taken in April 2015 shows a fresh water signature as it plots in the centre. CAS-08 and CAS-10 are deep wells (~ 100 m total depth) and also influenced by on-going salinization. Figure 7-9 clearly indicates on-going salinization and documents minor effects of the injected water on CAS-09 in April 2015 only.

The Cl/Br mass ratio can be used as a tracer of groundwater flow since both ions are chemically inert except in the presence of high amounts of organic matter (Davis et al., 1998). Standard mean ocean water (SMOW) carries a Cl/Br weight ratio of ~288 (Cl_{SMOW} = 19 352 mg/l, Br_{SMOW} = 67.3 mg/l). The Cl/Br ratio in seawater does not change during evaporation until halite starts to precipitate (Alcala and Custodio, 2008). Bromide is less compatible in precipitating halite and enriches disproportionately high compared to chloride in the residual water. The resulting halite is therefore depleted in bromide (rCl/Br ~ 9000), and water which dissolves halite carries high Cl/Br ratios between 1000 - 10 000, while rainfall at coastal areas carries the Cl/Br mass ratio similar to the sea (Davis et al., 1998). The measured Cl/Br mass ratios show a wide range from low ratios ~ 200 to ratios around the standard mean seawater (SMOW) ~300. Most of the samples from the coastal aquifer in Castellón plot above the SMOW Cl/Br mass ratio with increasing Cl concentration (Figure 7-10).

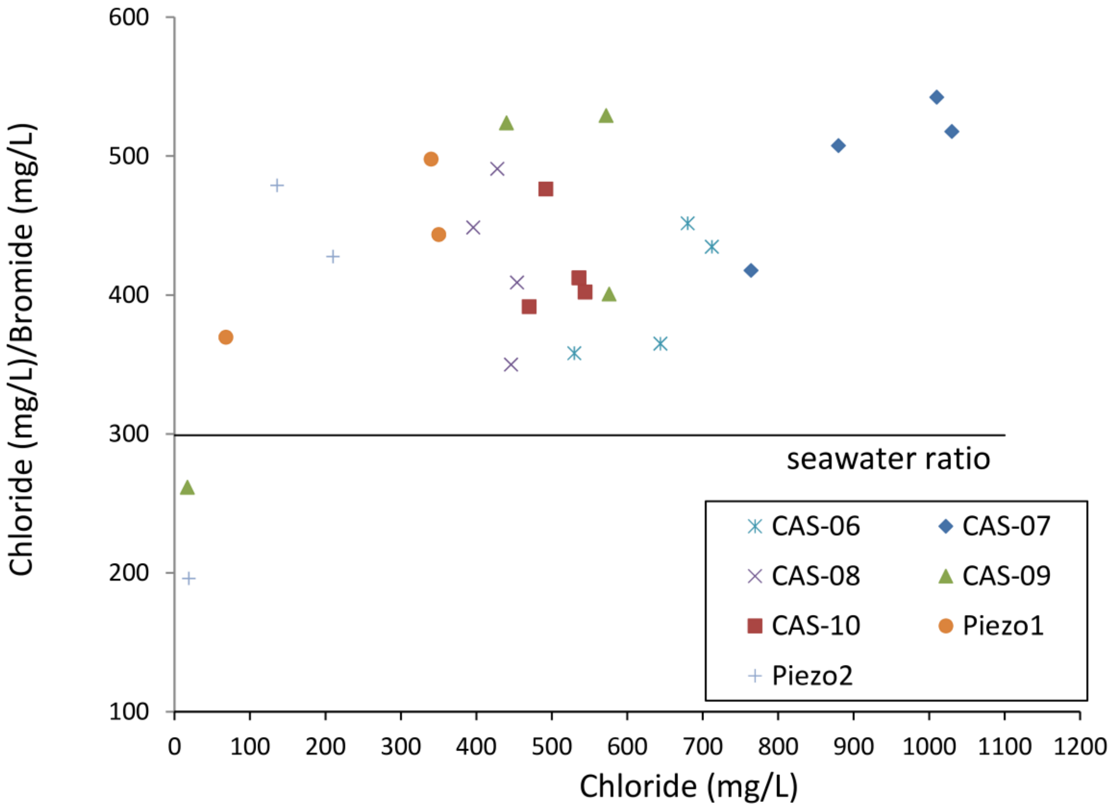


Figure 7-10: Cl/Br weight ratio against Cl (mg/L)

As already indicated by the ion displacement diagram (Figure 7-9) only CAS-09 sampled in April 2015 is influenced by recharge water, because of Cl/Br weight ratio <300 and Cl concentration <200 mg/L. The fact that most other groundwater samples plot above the SMOW ratio indicates additional sources of chloride apart from seawater. Considering the local geology with underlying Keuper formations (Triassic), it is possible that these low lying formations contribute to salinity ingress to some extent. However, since Keuper signature is unknown it is not possible to clearly attribute the elevated Cl/Br ratios to deep groundwater circulation. Moreover, other Cl sources may contribute, e.g. waste water infiltration. Waste water typically carries Cl/Br mass ratios up to 900 (Katz et al. 2011)) and may have contributed to elevated Cl/Br ratios. Bromide measurements from the Belcaire River are not available, but it seems plausible that the river carries Cl/Br weight ratios below that of SMOW. The spring of the Belcaire River lies in the Alfondeguilla Mountains where the rain is most likely depleted in chloride, resulting in Cl/Br ratios below SMOW.

The redox conditions in native groundwater are oxic to suboxic, because N occurs only in the form of nitrate. Other redox sensitive compounds (e.g. Fe) do not occur in elevated concentrations (average 0.5 mg/L). As a summary, Figure 7-11 shows the Piper diagrams (Piper 1944) for the five selected wells representing native groundwater. Presentation in the diagram bases on the equivalent concentrations of the main cations and anions in groundwater

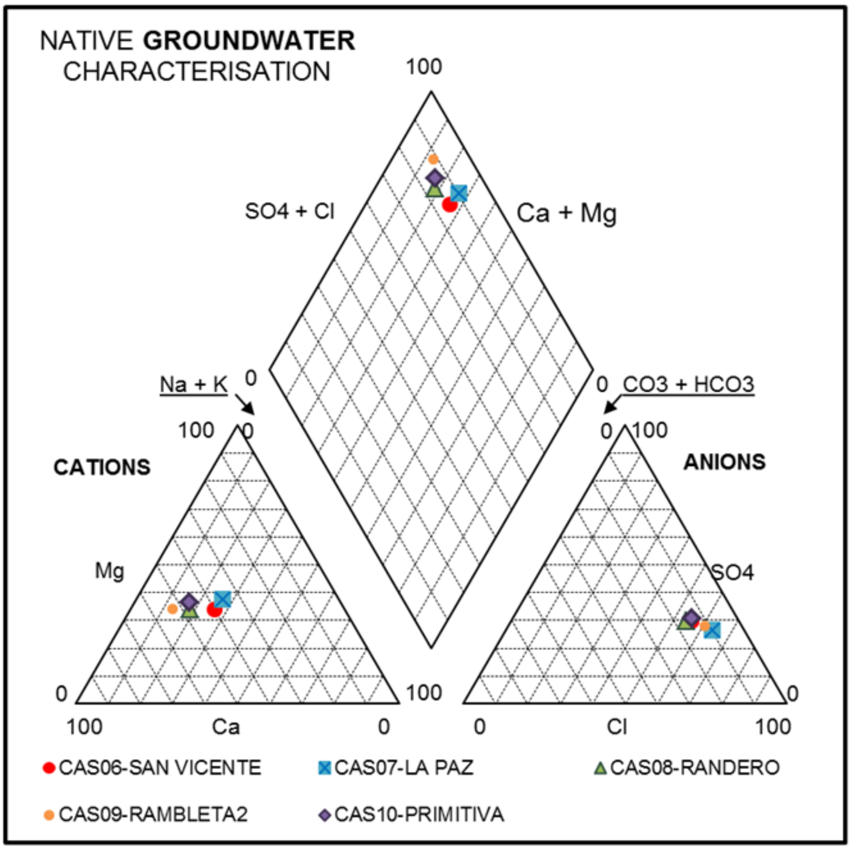


Figure 7-11: Piper diagram of native groundwater (average values)

7.4.2 Bioassays - measured activities and toxicity profiles

The activity of the tested extract was expressed as reference compound-equivalent concentration per sample unit and summarized in annex L. The activities had been classified according to the activity significance Table 7-5. The obtained activity profiles of the MAR samples (left part in Figure 7-12) were then evaluated and modified according to the available preliminary Algae test EQS (environmental quality standard proposals) and CALUX trigger values (van der Oost *et al.* 2015, see right part in Figure 7-12). Trigger values for the other endpoints are currently being established.

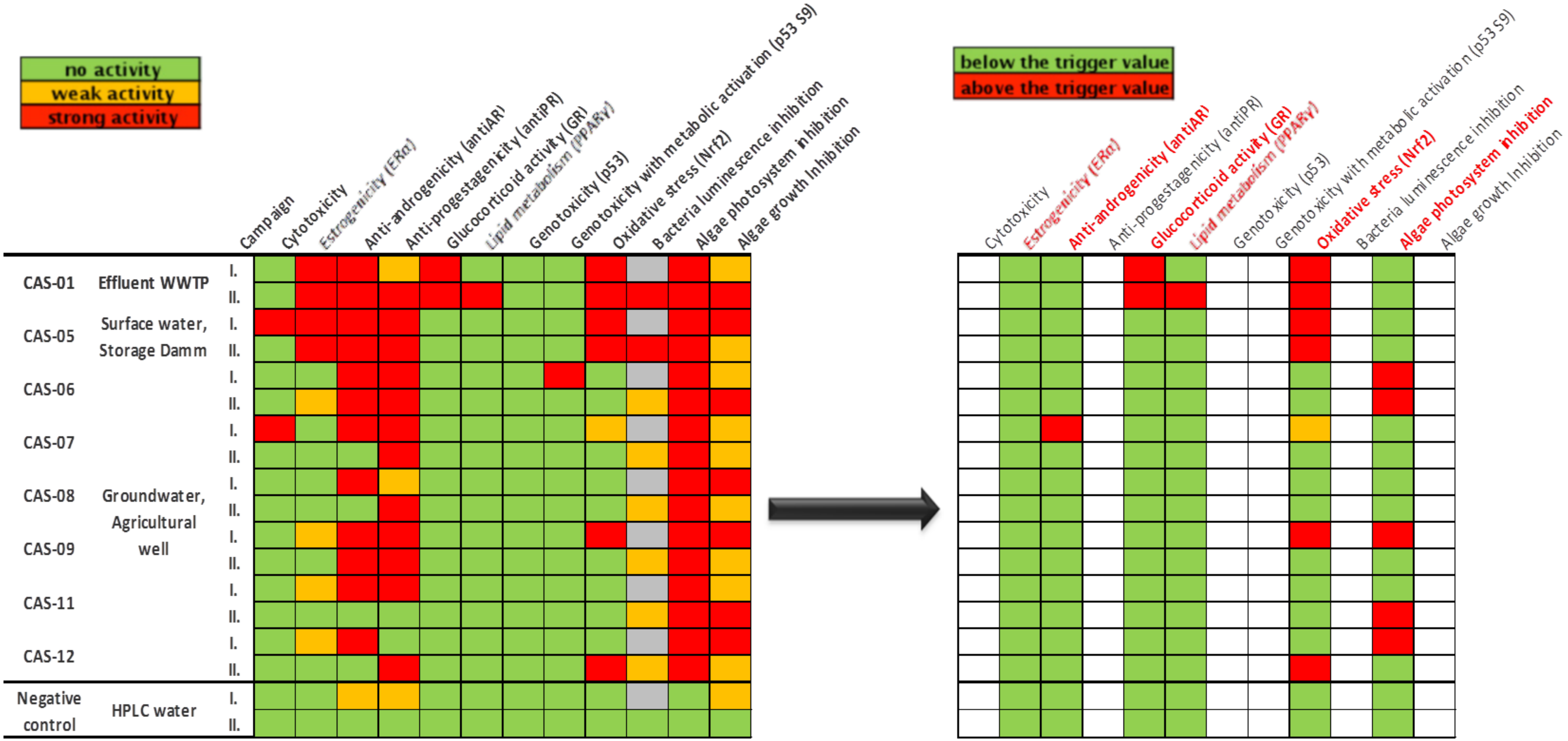
Table 7-5: **Currently available preliminary trigger values for ecosystem health (van der Oost et al. 2015)**

Bioassay	Trigger value	Unit
ERα-CALUX	1	ng 17β-Estradiol-Eq / L
Anti-AR-CALUX	40	µg Flutamide-Eq / L
GR-CALUX	30	ng Dexamethasone-Eq / L
PPARγ-CALUX	20	ng Rosiglitazone-Eq / L
Nrf2-CALUX	10	µg Curcumin-Eq / L
Combined Algae Test (Photosystem II Inhibition)*	20 (EQS proposal CH), 200 (EQS EU)	ng Diuron-Eq / L

(*)For the “high/low risk evaluation” of the measured activities in the combined algae assay the trigger value based on the EU EQS proposal was used and not based on the Swiss value.

Complete results are listed in annex L. Figure 7-12 summarises activity profile of the tested MAR water samples from the La Vall d’Uixó sampling site collected at two time points: 06/2014 (Campaign I) and 04/2015 (Campaign II) in the in vitro bioassay panel (on the left). Detected activities are classified following the criteria showed on the upper part of the figure. The activity profile was then modified (on the right) considering available, preliminary trigger values (for estrogenic, anti-androgenic, glucocorticoid activity, oxidative stress and lipid metabolism). Samples that showed lower activity than the pertinent trigger value became “green” in the table on the right indicating low risk despite of the measured, quantifiable) activity.

The application of effect-based methods (bioassays) enabled to measure the combined effects of emerging pollutants. The broad range *in vitro* screening of the MAR water samples revealed the importance of ENDOCRINE - (particularly the activation of the ERα-, anti-AR, anti-PR receptors), OXIDATIVE STRESS (Nrf2-CALUX) and PHOTOSYNTHESIS INHIBITION (Combined algae test) pathways, and showed differences between the samples collected within two different time points at two sampling campaigns.



🟩	no activity
🟨	weak activity
🟥	strong activity

		Campaign	Cytotoxicity	Estrogenicity (ERα)	Anti-androgenicity (antiAR)	Anti-progestagenicity (antiPR)	Glucocorticoid activity (GR)	Lipid metabolism (PPARγ)	Genotoxicity (p53)	Genotoxicity with metabolic activation (p53 S9)	Oxidative stress (Nrf2)	Bacteria luminescence inhibition	Algae photosystem inhibition	Algae growth Inhibition
CAS-01	Effluent WWTP	I.	🟩	🟥	🟥	🟨	🟥	🟩	🟩	🟩	🟥	▨	🟥	🟨
		II.	🟩	🟥	🟥	🟥	🟥	🟥	🟩	🟩	🟥	🟥	🟥	🟥
CAS-05	Surface water, Storage Damm	I.	🟥	🟥	🟥	🟥	🟩	🟩	🟩	🟩	🟥	▨	🟥	🟥
		II.	🟩	🟥	🟥	🟥	🟩	🟩	🟩	🟩	🟥	🟥	🟥	🟨
CAS-06	Groundwater, Agricultural well	I.	🟩	🟩	🟥	🟥	🟩	🟩	🟩	🟥	🟩	▨	🟥	🟨
		II.	🟩	🟨	🟥	🟥	🟩	🟩	🟩	🟩	🟩	🟨	🟥	🟥
CAS-07		I.	🟥	🟩	🟥	🟥	🟩	🟩	🟩	🟩	🟨	▨	🟥	🟨
		II.	🟩	🟩	🟩	🟥	🟩	🟩	🟩	🟩	🟩	🟨	🟥	🟨
CAS-08		I.	🟩	🟩	🟥	🟨	🟩	🟩	🟩	🟩	🟩	▨	🟥	🟥
		II.	🟩	🟩	🟩	🟥	🟩	🟩	🟩	🟩	🟩	🟨	🟥	🟨
CAS-09		I.	🟩	🟨	🟥	🟥	🟩	🟩	🟩	🟩	🟥	▨	🟥	🟥
		II.	🟩	🟩	🟥	🟥	🟩	🟩	🟩	🟩	🟩	🟨	🟥	🟨
CAS-11		I.	🟩	🟨	🟥	🟥	🟩	🟩	🟩	🟩	🟩	▨	🟥	🟨
		II.	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟨	🟥	🟥
CAS-12		I.	🟩	🟨	🟥	🟩	🟩	🟩	🟩	🟩	🟩	▨	🟥	🟥
		II.	🟩	🟩	🟩	🟥	🟩	🟩	🟩	🟩	🟥	🟨	🟥	🟨
Negative control	HPLC water	I.	🟩	🟩	🟨	🟨	🟩	🟩	🟩	🟩	🟩	▨	🟩	🟨
		II.	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩

🟩	below the trigger value
🟥	above the trigger value

Cytotoxicity	Estrogenicity (ERα)	Anti-androgenicity (antiAR)	Anti-progestagenicity (antiPR)	Glucocorticoid activity (GR)	Lipid metabolism (PPARγ)	Genotoxicity (p53)	Genotoxicity with metabolic activation (p53 S9)	Oxidative stress (Nrf2)	Bacteria luminescence inhibition	Algae photosystem inhibition	Algae growth Inhibition
	🟩	🟩		🟥	🟩			🟥		🟩	
	🟩	🟩		🟥	🟥			🟥		🟩	
	🟩	🟩		🟩	🟩			🟥		🟩	
	🟩	🟩		🟩	🟩			🟥		🟩	
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	🟩	🟩		🟩	🟩			🟩		🟩	

Figure 7-12: Activity profile determined in the bioassays (colours in right matrix: green = activity below trigger value, yellow = coinciding with trigger value, red = activity above trigger value).

Activities that fell under the defined trigger value of the certain bioassay are considered as low risk and suggested no need for further in-depth investigation (effect-directed analysis [EDA] or chemical analysis) to identify the source of the activity, the responsible compound(s). On the contrary, activities above the pertinent trigger values suggest the need for further investigations and imply the possibility of adverse (ecological) health effects. In the case of the Castellón samples, the use of the effluent of WWTP as injection water could suppose some adverse effects listed below:

- Glucocorticoid activity
- Lipid metabolism
- Oxidative stress
- Algae metabolism inhibition

This approach – screening samples first with bioassays, followed by low/high risk evaluation with trigger values and chemical analysis if reasonable/justifiable) is favoured by WA4 (Bioassays team in DEMEAU project). In this study applied trigger values are preliminary values, thus it is recommend to consider this exercise as an exemplification for the application of such threshold values and discriminating therefore between low and high risk sites.

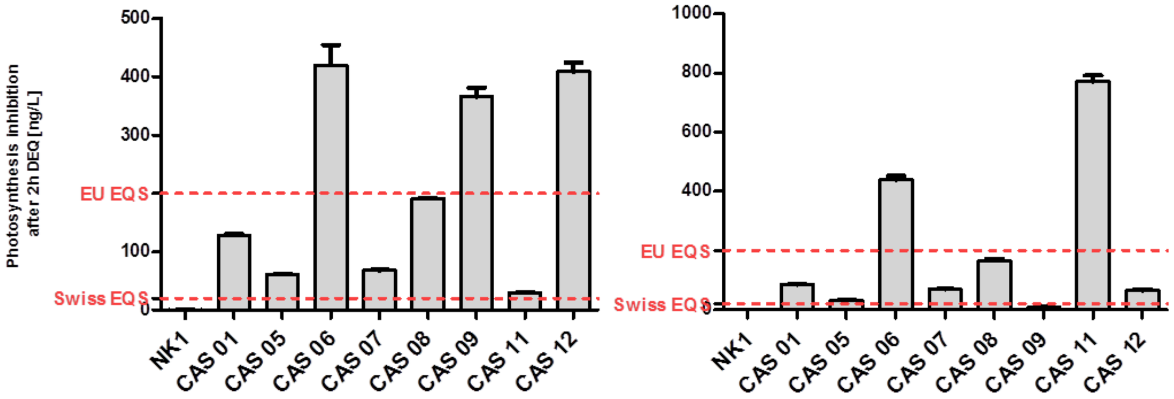


Figure 7-13: Photosynthesis inhibition (after 2 hours of exposure) of the MAR samples from Castellón – 1st sampling campaign (left) and 2nd sampling campaign (right) - expressed as ng Diuron Eq./L water. NK refers to negative control (HPLC water) went through on extraction and bioanalysis just as the samples.

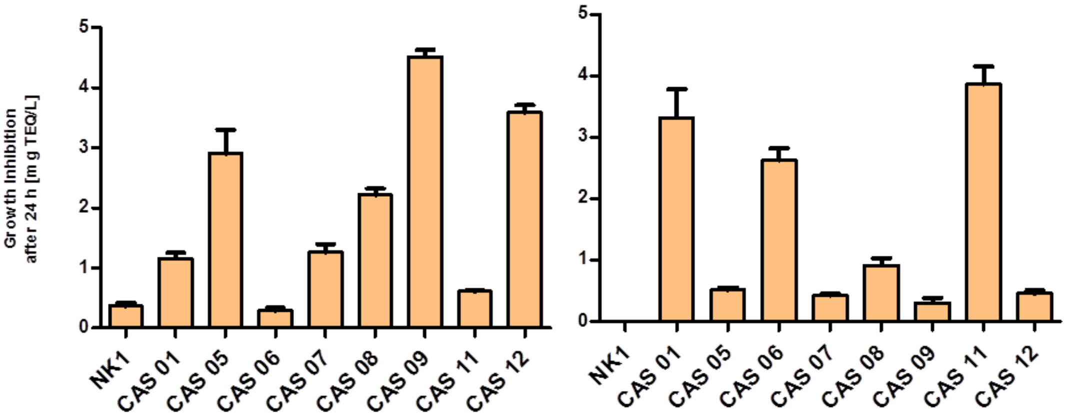
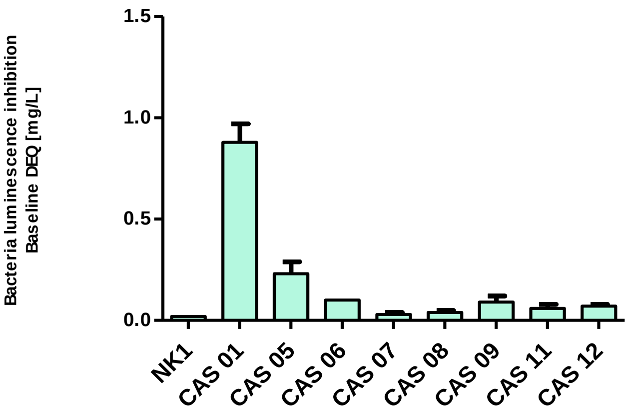


Figure 7-14: **Growth inhibition (after 24 hours of exposure) of the MAR samples from Castellón – 1st sampling campaign (left) and 2nd sampling campaign (right) - expressed as ng Diuron Eq./L water. NK refers to negative control (HPLC water) went through on extraction and bioanalysis just as the samples.**



(*) Campaign expressed as ng Diuron Eq./L water

Figure 7-15: **Bacteria luminescence inhibition of the MAR samples from Castellón – 2nd sampling. NK refers to negative control (HPLC water) went through on extraction and bioanalysis just as the samples.**

Figure 7-13 and Figure 7-14 represent the response of water samples to the inhibition of photosynthesis and the growth inhibition. The comparison between the two sampling campaigns performed as a duplicated of the experiments is presented. There are no evidences of the same responses in same samples. There are no clear conclusions. Regarding Figure 7-15, it shows the inhibition of bacteria luminescence. Effluent of WWTP (code CAS 01) shows a high response in the inhibition of bacteria luminescence, while the rest of samples have a similar response, corresponding to the control values (NK1).

During these investigation the MAR water samples from Castellón were also chemically characterized and analysed for a set of target compounds including the 12 DEMEAU compounds: pharmaceuticals, pesticides, sweeteners, transformation products and various other metabolites, cocaine and nicotine for instance. In order to link analysed chemical concentrations to the observed toxicity in the samples the following exercise was conducted:

- Assay-specific relative potency (REP) factors, which express the estimated toxicity of a test compound compared to the reference compound for a certain mode-of-action (i.e. in a certain bioassay), were gathered for the chemically analyzed compounds or tested in the bioassays (DEMEAU compounds, Table 7-6). REP factors are determined by the effect concentrations (ECx) of the reference compound and of the test compound: REP factor test comp = EC(x) reference compound/ EC(x) test compound. Available REP factors for the chemically analyzed compounds are presented in annex L.
- Chemical concentrations were then transformed into toxicity equivalent concentrations with the aid of the available REP factors.
- To calculate the theoretically expected toxic activities for the chemically analyzed compounds (in terms of equivalent concentrations), the concentration of each compound was multiplied with its REP factor. The expected total biological activity of the sample extract was calculated by summation of the activities calculated for the individual compounds in the mixture.
- Finally, recoveries were determined by comparing the actually measured activity of the sample extracts to the calculated total activity of the chemically analyzed compounds (annex L).

The comparison of chemical and toxicological analyses of the samples taking into account the 12 “DEMEAU compounds” is shown in Table 7-6. This information has to be carefully interpreted due to the following facts:

- Toxicological information was only available for 18 out of the 63 target analysed compounds and limited therefore the prediction of the expected activities.
- The selection of the target analysed compounds do not seem to overlap with compound classes that are known to be present in water samples and exert adverse (ecosystem) health effects.
- Pharmaceuticals were included in the target compound list that have (almost) no activity (based on in-house screening data of a large set of compounds and compound classes at BDS), whereas other compounds often found in environmental waters with relatively high hormonal potency, were not included in the target list, such as personal care products, hormones and hormone-like compounds, chlorinated organic solvents and chemicals.
- A number of pesticides were, however, included in the target analysis and could also be accounted for a greater part of the measured activities in the combined algae assay (sample CAS05 and CAS11 for instance).

🟪
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TOXICITY ↑

▨ Not active
🟦 Not measured

Compound	CAS number	DR	PXR	PPARa	PPARg	LXR	ERa	ERa-anti	ERb	AR	AR-anti	PR	PR-anti	GR	GR-anti	RAR	p53	p53 S9	Nrf2	Hif1a	TCF	AP1	NFkB	ESRE	p21	Cytotox10%	Cytotox50%
E-Carbamazapine	36507-30-9	>-5	>-5	>-5	>-5	>-5	>-5	>-5	>-5	>-5	>-5	>-5	>-5	>-5	>-5	>-5	>-4	>-4	>-5	>-5	>-5	>-5	>-5	>-5	>-5	>-5	>-5
Gemfibrozil	25812-30-0	>-5	>-5	-5.5	>-5	>-5	>-5	>-5	>-5	>-5	>-5	>-5	>-5	>-5	>-5	>-5	>-4	>-4	>-5	>-5	>-5	>-5	>-5	>-5	>-5	>-5	>-5
Iopromide	73334-07-3	>-4	>-4	>-4	>-4	>-4	>-4	>-4	>-4	>-4	>-4	>-4	>-4	>-4	>-4	>-4	>-3	>-3	>-4	>-4	>-4	>-4	>-4	>-4	>-4	>-4	>-4
Primidone	125-33-7	>-4	>-4	>-4	>-4	>-4	>-4	>-4	>-4	>-4	>-4	>-4	>-4	>-4	>-4	>-4	>-3	>-3	>-4	>-4	>-4	>-4	>-4	>-4	>-4	>-4	>-4
Trimethoprim	738-70-5	-4	>-4	>-4	>-4	>-4	>-4	>-4	>-4	>-4	-4.3	>-4	>-4	>-4	>-4	>-4	>-3	>-3	>-4	>-4	>-4	>-4	>-4	>-4	>-4	>-4	>-4
Metoprolol	37350-58-6																										
Bezafibrate	41859-67-0																										
Phenazone	60-80-0	>-4	>-4	>-4	>-4	>-4	-4.1	>-4	>-4	>-4	>-4	>-4	>-4	>-4	>-4	>-4	-3.4	>-3	>-4	>-4	>-4	>-4	>-4	>-4	>-4	>-4	>-4
Diclofenac	15307-79-6	>-4	-4.7	>-4	-4.6	>-4	>-4	>-4	>-4	>-4	-4.9	>-4	-4.5	>-4	-4.2	>-4	-3.6	>-3	>-4	>-4	>-4	>-4	>-4	>-4	>-4	>-4	>-4
Benzotriazole	95-14-7	>-4	>-4	>-4	>-4	>-4	>-4	>-4	>-4	>-4	>-4	>-4	>-4	>-4	>-4	>-4	>-3	>-3	>-4	>-4	>-4	>-4	>-4	>-4	>-4	>-4	>-4
Sulfamethoxazole	723-46-6	>-4	>-4	>-4	>-4	>-4	>-4	>-4	>-4	>-4	>-4	>-4	>-4	>-4	-4	>-4	>-3	>-3	>-4	>-4	>-4	>-4	>-4	>-4	>-4	>-4	>-4
Carbamazepine	298-46-4	>-4	>-4	>-4	>-4	>-4	>-4	>-4	>-4	>-4	-4.7	>-4	-4.5	>-4	>-4	>-4	>-3.4	>-3.4	>-3.4	>-4	>-3.4	>-3.4	>-3.4	>-3.4	>-3.4	-4	-3.4

Table 7-6: Toxicity profile of the 12 “DEMEAU compounds” evaluated in Castellón. NOTE: Values represent logarithmic PC10 (agonistic assays) and PC20 (antagonistic assays) concentrations. PC10 or PC20 refers to a response level induced by a test chemical equals to 10% or 20% of that induced by a maximally inducing concentration of the positive control (PC). NOTE: Metoprolol and Bezafibrate were not tested due to technical issues (i.e. lack of authentic standard and dissolving problem).

7.4.3 Risk assessment of the use of WWTP effluent as source water

7.4.3.1 Stage 1 Entry level risk assessment

MAR guidelines (NRMMC-EPHC-NHMRC, 2009) establish an initial checklist to assess the viability of a potential new MAR site. The key factors for entry-level viability assessment for managed aquifer recharge projects are: demand, source, aquifer, detention storage and management capability. The template for the viability assessment addresses these factors. If the answer to all of the questions given in the table is "Yes", proponents then proceed to determine the degree of difficulty. Table 7-7 shows the viability assessment for La Vall d'Uixó MAR site. The second part of the entry-level assessment is intended to inform stakeholders about the degree of difficulty of the proposed project. The template proposed by Australian guidelines suggests 14 questions related to information needs, and they will determine the scope of further investigations. Following table corresponds to the Part 2 completed for the present case study.

Table 7-7: La Vall d'Uixó entry level assessment part 1 - viability

Attribute	La Vall d'Uixó answer
1. Intended water use	
• Is there an ongoing local demand or clearly defined environmental benefit for recovered water that is compatible with local water management plans?	✓ **Yes.** Economic activity in La Vall d'Uixó is mainly based in citrus crops. There is a local demand of fresh groundwater
2. Source water availability and right of access	
• Is adequate source water available and is harvesting this volume compatible with catchment water management plans?	✓ **Yes.** The storage dam has been constructed to store surplus water in rainy season (volume depending on rainfall annual patterns). WWTP effluent is also potential recharge water (9,000 m^3/day).
3. Hydrogeological assessment	
• Is there at least one aquifer at the proposed manager aquifer recharge site capable of storing additional water?	✓ **Yes**. The quaternary aquifer located in Castellón plain (code MASub 080.127) has storage capacity.
• Is the project compatible with groundwater management plans?	✓ **Yes**. Injection of water in the aquifer is intended to replenish local groundwater resources and improve groundwater quality.

Attribute	La Vall d'Uixó answer
4. Space for water capture and treatment	
- Is there sufficient land available for capture and treatment of the water?	✓ **Yes**. The accumulation dam has 2 Mm^3 of storage capacity. Pre-treatment need has been not yet assessed and is not yet constructed.
5. Capability to design, construct and operate	
- Is there a capability to design, construct and operate a managed aquifer recharge project?	✓ **Yes**. University of Castellón (UJI) and National Geological Survey (IGME) has experience in local hydrogeology, as well as hydrochemistry. IGME has participated actively in the design and construction of several MAR projects on national level. ACUAMED (public national company) is expected to manage the aquifer recharge project or to open a public tender for its operation and maintenance.

Table 7-8: La Vall d'Uixó entry level assessment part 2 – degree of difficulty assessment

NOTE: source water corresponds to the WWTP effluent (secondary treatment)

Question from the Australian Guideline	La Vall d'Uixó answers	Investigations required
1. Source water quality with respect to groundwater environmental values		
- Does source water meet the water quality requirements for the environmental value of ambient groundwater?	**No.** Environmental values of groundwater good quality status are not totally fulfilled by the effluent of WWTP[3]. Require Stage 2 investigations to assess risks. ✓ Yes. Nitrate < 200 mg/L ✓ Yes. Chloride < 650 mg/L ✓ Yes. Sulphate < 525 mg/L × No. Total pesticides > 0.5 µg/L × No. Individual pesticides > 0.1 µg/L ? Not reported: Selenium Good status Se < 0.0207 mg/L	Additional campaigns of pesticides: punctual campaigns reported contradictory values. Quantification of selenium concentration.

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[3] Based on criteria for the chemical status classification in Castellon Plain Groundwater mass. See annex H for further information.

Question from the Australian Guideline	La Vall d'Uixó answers	Investigations required
2. Source water quality with respect to recovered water end use environmental values		
- Does source water meet the water quality requirements for the environmental values of the intended end use of the water on recovery?	**No.** Water quality standards for water reclamation in Spain are regulated by RD1620/2007. Specifically for final use of direct injection (use 5.2 defined in Spanish regulation RD1620/2007): × Yes. Nematodes eggs < 1 egg/10L × Yes. TSS < 10 mg/L × Yes. Turbidity < 2 NTU × No. Total nitrogen > 10 mg N/L × No. Nitrate > 25 mg NO_3/L × Yes. E. coli > 0 UFC/100 mL	Evaluation of the impact of high concentration of nitrate in the aquifer. Comparison with native groundwater Evaluation of the removal of E. coli along soil aquifer treatment.
3. Source water quality with respect to clogging		
- Does source water have low quality; for example: TSS > 10 mg/L; TOC > 10 mg/L; Total nitrogen > 10 mg/L; and is the soil or aquifer free of macropores?	**Low water quality: Yes.** ✓ Yes. TOC > 10 mg/L ✓ Yes. Total nitrogen < 10 mg N/L × No. TSS < 10 mg/L **Presence of macropores: unknown**	Evaluation of the impact of high concentration of nitrate in the aquifer. Comparison with native groundwater. Evaluation of impact of high TOC in the aquifer and potential natural biodegradation.
4. Groundwater quality with respect to recovered water end use environmental values		
- Does ambient groundwater meet the water quality requirements for the environmental values of intended end uses of water on recovery?	**Yes:** Target aquifer is use for agriculture. Farmers use ambient groundwater for direct irrigation without any pre-treatment. Note: salinized wells are abandoned.	None
5. Groundwater and drinking water quality		
- Is either drinking water supply, or protection of aquatic ecosystems with high conservation or ecological values, an environmental value of the target aquifer?	**No**. Castellón Plain aquifer is not intended to produce drinking water. There are no aquatic ecosystems directly related to groundwater due to higher seasonal fluctuations of groundwater level.	None
6. Groundwater salinity and recovery efficiency		

Question from the Australian Guideline	La Vall d'Uixó answers	Investigations required
• Does the salinity of native groundwater exceed either of the following: (a) 10,000 mg/L; (b) the salinity criterion for uses of recovered water?	**Yes (b)**. Some groundwater wells have been abandoned due to salinity values above crops requirements (1,100 µS/cm is the tolerance value, while 3,200 µS/cm causes 50% of yield)[4]	Analysis of the impact of aquifer recharge in the reduction of salinity (already done in Phase III Water Recovery Project). The numerical model developed for conservative transport could be used for the simulation and assessment of WWTP effluent injection
7. Reactions between source water and aquifer		
• Is redox status, pH, temperature, nutrient status and ionic strength of groundwater similar to that of source water?	**No**. Different water quality has the potential of change chemical equilibrium, especially redox status (WWTP effluent is in contact with the atmosphere, while groundwater is anoxic.	Geochemical evaluation
8. Proximity of nearest existing groundwater users, connected ecosystems and property boundaries		
• Are there other groundwater users, groundwater connected ecosystems or a property boundary within 100-1.000m of the MAR site?	**No**. Castellón Plain aquifer is not intended to produce drinking water. There are no aquatic ecosystems directly related to groundwater.	None
9. Aquifer capacity and groundwater levels		
• Is the aquifer: (a) confined and not artesian?; (b) unconfined, with a water table deeper than 4 m in rural areas or 8 m in urban areas?	**Yes (b)**. Unconfined and with water table around 40 – 50 meters below surface level.	None
10. Protection of water quality in unconfined aquifers		
• If the aquifer unconfined, with an intended use of recovered water being drinking water supplies?	**No**	None
11. Fractured rock, karstic or reactive aquifers		
• Is the aquifer composed of fractured rock or karstic media, or known to contain reactive minerals?	**No**. there is no evidences of reactive minerals in the aquifer. Phase III of Water Recovery Project (injection of surface water) has not revealed any undesired mobilization.	None

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[4] Irrigation Water Quality Standards and Salinity Management Strategies, Texas Agicultural Extension Service, The Texas A&M University System, 1996.
Cited in: http://www.fcca.es/static_media/file_uploads/Salinidad_del_agua_de_riego1.pdf

Question from the Australian Guideline	La Vall d'Uixó answers	Investigations required
12. Similarity to successful project		
- Has another project in the same aquifer with similar source water been operating successfully for at least 12 months?	**No**. this will be the first controlled experience. Nevertheless pharmaceuticals have been identified in groundwater, meaning that uncontrolled irrigation with WWTP effluent has been done.	None
13. Management capability		
- Does the proponent have experience with operating managed aquifer recharge sites with the same or higher degree of difficulty, or with water treatment or water supply operations involving a structured approach to water quality risk management?	**Yes**. IGME has experience in previous MAR experiences in Spain. UJI has experience in groundwater hydrochemistry and hydrogeological studies.	None
14. Planning and related requirements		
- Does the proposed project require development approval? Is it in built up area; built on public, flood-prone or steep land; or close to a property boundary? Does it contain open water storage or engineering structures; or is it likely to cause public health or safety issues, nuisance from noise, dust, odour or insects, or adverse environmental impacts?	**No**. The most costly infrastructure is already constructed (accumulation dam and injection wells). Additional pipes for WWTP and dam connection will be necessary, as well as potential pre-treatment and control points for reclaimed water monitoring.	None

7.4.3.2 Maximal risk assessment

Key hazards and acceptance criteria given by Australian guidelines have been applied. In this section 12 key hazards have been evaluated using a semi-quantitative risk assessment, for human health and environmental endpoints. Table 7-9 classifies the risk in low (green), uncertain (orange) and high (red) levels.

Table 7-9: Maximal risk assessment for La Vall d'Uixó

MAR hazards		Human endpoint - agricultural threshold values for citrus irrigation	Environmental endpoint-aquifer WFD targets
1. Pathogens – present in high levels		H	L
2. Inorganic chemicals	Electric conductivity	H	L
	pH	L	L
	Sodium	L	L
	Chloride	H	L
	Boron	L	L
	Bicarbonate	H	L
3. Salinity and sodicity		H	L
4. Nutrients	Nitrate	H	L
	Total Nitrogen	H	L
	Total phosphorous	U	U
	Organic Carbon	U	U
5. Organic chemicals	Pesticides	H	H
	Pharmaceuticals and others	H	H
6. Turbidity and particulates		U	U
7. Radionuclides		L	L
8. Pressure, flow rates, volumes and groundwater levels		L	L
9. Contaminant migration in fractured rocks and karstic aquifers		NA	NA
10. Aquifer dissolution and stability of well and aquitard – pumping wells observed to be stable after 30 years		U	U
11. Aquifer and groundwater – dependent ecosystems		NA	NA
12. Energy and greenhouse gas considerations		L	L

L = Low risk; U = Uncertain risk; H = High risk; NA = Not applicable

7.4.3.2.1.1 Pathogens

Little information is available on the microbial impact of Castellón well injection systems on the environment. This section focuses on the impact of pathogens that affect humans only. Main source of pathogens in the Castellón Plain aquifer would be the injection of WWTP effluent without disinfection pre-treatment. RD1620/2007 identifies Intestinal nematodes eggs (maximum 1 egg/10 L) and *E. coli* (maximum 0 UFC/100 mL). According to the controls done in the effluent of WWTP, only E. *coli* has been detected with an average of 19,700 UFC/100 mL and a maximum of 31,000 UFC/100 mL (see weekly results in Figure 7-16). Intestinal nematodes eggs is also analysed in routine analysis, with no positive samples.

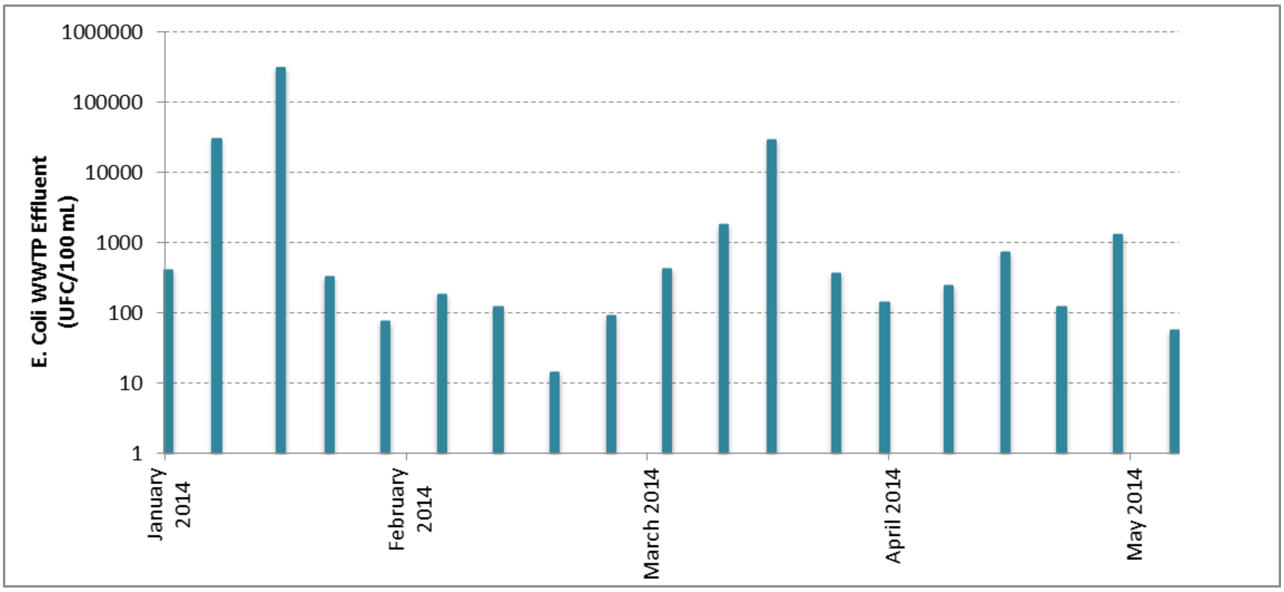

Figure 7-16: E. coli concentration in WWTP Effluent (2014)

E. coli survival has been included in multiple studies to evaluate its decay rate in groundwater along MAR. Banning *et al.* (2005) determined that *E. coli* was dramatically reduced in no sterilized microcosms compared to the sterilized ones, suggesting that indigenous microorganisms play an important role in the die-off of *E.coli* in the environment. Same conclusion was achieved by RECLAIM WATER[5] project in their results of pathogens decay studies carried out in Adelaide (Australia). They found a decay rate of *E. coli* in non-filtered groundwater of -10 log·day^{-1}, while the decay rate in filtered groundwater[6] was -5 log·day^{-1} (Tandoi *et al*. 2012).

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[5] http://cordis.europa.eu/result/rcn/46853_en.html

[6] Achieved by passing the groundwater sample twice thorough sterile 0.2 µm nitrocellulose filters.

Table 7-10 summarises maximum inactivation times reported in literature. Considering the high levels of *E. coli* found in WWTP effluent, this MAR hazard has been considered as high risk, despite there are no evidences at test site of the potential elimination or/and reduction of pathogens concentration.

Table 7-10: Minimum die-off of *E. coli*, in days observed during MAR

Parameter	days	Reference	Comments
T_{90}[7]	3	NRMMC-EPHC-NHMRC, 2009	In situ Australian aerobic and anoxic aquifers (20ºC)
T_{90}	0.1	Tandoi *et al.* (2012)	Diffusion chamber experiments performed in Adelaide (Australia)
T_{90}	1	Gordon and Toze (2003)	Aerobic conditions. Study on pathogen decay in groundwater not necessarily relating to specific MAR schemes. Same result at 18ºC and 25ºC
T_{90}	3	Toze et al (2002)	Aerobic conditions. Study undertaken as part of specific MAR scheme (22ºC)
T_{90}	1	Toze and Hanna (2002)	Aerobic conditions. Study undertaken as part of specific MAR scheme (27ºC)

A preliminary calculation has been done to estimate the residence time in the aquifer. Australian Guidelines suggest the “Dual-well system” for ASTR systems considering equal abstraction and injection rates. At this stage of pre-evaluation in La Vall d’Uixó site this is unpredictable, as the pumping regime of each well depends on the abstraction strategy, energy costs, alternative source of water availability, crops seasonality and rainfall regime among others.

Regarding the distance between injection and recovery locations, travel time has been calculated under the less favourable condition, taking into account the closest wells: CAS08 (located at 550 meters of injection well 1) and CAS11 (located at 445 meters of injection well nº2). Following formula has been applied:

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[7] T_{90} = The time taken for 90% die-off

$$t_{\min} = \frac{\pi D n_e L^2}{3Q}$$

Where,

t_{min} = minimum travel time

L = distance between injection and recovery wells (m)

D= aquifer thickness (m)

n_e = porosity of the aquifer

Q = rate of steady-state pumping (in and out) (m^3/d)

Assuming steady-state conditions and equal abstraction and injection rates (D = 85-100 m; n_e = 0.02-0.08; Q=8640 m^3/d) and minimum distance from injection well to the nearest farmer well (L=445 m) the estimated travel time distribution is shown in Figure 7-17.

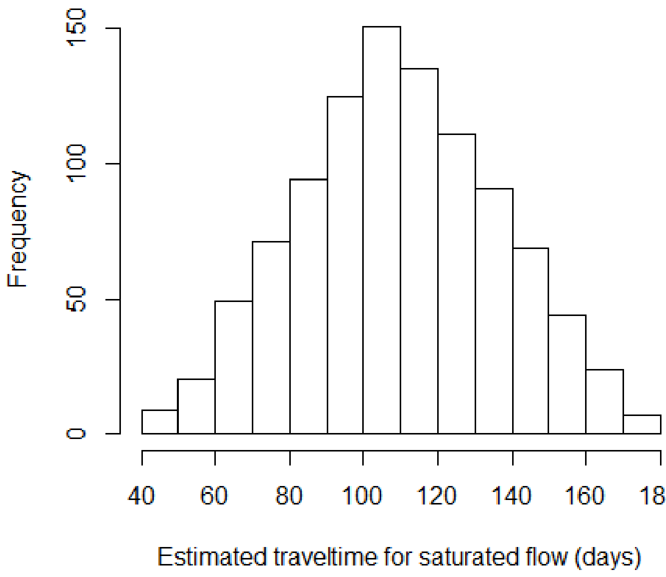

Figure 7-17: Estimated travel time distribution from injection well to nearest farmer well

Travel time was calculated by a very simple stochastic approach in order to account for hydrogeological variations, fluctuations in pathogen concentration and resulting variations in pathogen removal during subsurface passage. Minimum travel time is about 40 d assuming a low removal rate of T90 = 6d accounting only for die-off, it is reasonable to conclude that most of pathogens injected in the aquifer will not reach the extraction point of groundwater.

Anyway, some preventive measures can be applied to reduce the risk of pathogenic hazards and achieve performance targets can be classified in source control, process control and end point control:

- Source control: removing pathogens using technical pre-treatment processes.
- Process control: Enlarge residence time in the aquifer before recovery.
- End-point control: reducing exposure through preventive measures on-site, e.g. providing individual protection equipment (gloves and masks) to the farmers during irrigation with recovered water.

The concept of tolerable risk is central to the management of enteric pathogens via MAR. Australian guidelines adopt a tolerable risk of 10^{-6} disability adjusted life years (DALYs) per person and year, which is the same value that WHO adopted in 2006. Pathogen decay should be assessed at each specific site where reliance is placed on the aquifer for pathogen inactivation. An in situ assessment of pathogen survival is described in Pavelic et al. (1998). If residual risk of pathogens remains unacceptable, then additional forms of disinfection should be considered along with their consequences, e.g. trihalomethanes risks.

7.4.3.2.2 Inorganic chemicals

This section is applicable to the major ions (calcium, magnesium, sodium, potassium, chloride, sulphate, bicarbonate, bromide and fluoride), metals (aluminium, cadmium. chromium, cooper, iron, manganese, nickel, lead, strontium and zinc), metalloids (arsenic, boron and silicon) and gases (hydrogen, sulphide and methane).

Despite monitoring programme along DEMEAU sampling included a large list of inorganic chemicals (see annex J of the document), these key inorganic compounds for citrus irrigation and environmental standards of WFD have been selected. Figure 7-18 and Table 7-11 show mean values measured in WWTP effluent, native groundwater and Belcaire River and the comparison to citrus irrigation recommendations.

Regarding irrigation requirements, salinity has been determined as the limiting factor for local groundwater and WWTP effluent direct utilisation. In fact, historical aquifer salinization has been the driver for the execution of the Water Recovery project in La Vall d'Uixó area, as it is the most common problem for the agricultural areas near the coast. A table published in 1976 about agricultural water quality criteria for irrigation is nowadays applied in La Vall d'Uixó as a guideline for water classification and fertilisation plans according to the water suitability for crops irrigation (Ayers and Westcott 1976). Table 7-11 shows the citrus irrigation recommendations in La Vall d'Uixó compared to mean values found in native groundwater, Belcaire river water and WWTP effluent. Red coloured values indicate concentrations above citrus irrigation recommendations. Electrical conductivity, chloride, nitrate and bicarbonate are the critical parameters exceeding irrigation recommendations. Specifically four WWTP effluent components (electric conductivity, chloride, nitrate and bicarbonate) have high risk of pollute groundwater if their initial concentrations are not reduced along aquifer passage. All these compounds have been identified with high risk in the summary table of MAR hazards (Table 7-11). If source water for the MAR scheme is a 1:1 blend of WWTP effluent with Belcaire River these critical substances can be reduced to nitrate and bicarbonate only. As there is a specific section for the risk evaluation of nutrients, including nitrate, it has been included separately in the following section.

Table 7-11: Inorganic quality standards for citrus irrigation

Parameter	Native GW	Belcaire River	WWTP effluent	1:1 Blend of WWTP effluent with Belcaire water	Citrus irrigation recommendations
Electric conductivity [µS/cm]	*3225*	310	*1329*	820	1100 (a)
pH-value	7.4	6.7	7.5	7	6.5 – 8.4 (b)
Sodium [SAR index]	2.0	0.6	2.4	1.5	3 (b)
Chloride [mg/L]	*581*	19.0	*143.25*	81	142 (b)
Boron [mg/L]	*1.0*	-	0.16	-	0.7 (b)
Nitrate [mg/L]	*287*	0.0	*61*	*30*	5 (b)
Bicarbonate HCO_3- [mg/L]	*229*	*110.0*	*353*	*231.5*	91.5 (b)

NOTE: Red cursive values indicate values above citrus irrigation recommendations

(a) http://www.fcca.es/static_media/file_uploads/Salinidad_del_agua_de_riego1.pdf

(b) FAO recommendations: Ayres and Westcott (1976)

Regarding the environmental fate of WWTP effluent as recharge water, there is the list of compounds established as control indicators for the good status of groundwater bodies in Spain. The quality standards are specific for each aquifer. Table 7-12 lists the quality standards for inorganic substances in the Castellón aquifer plain. Concentrations above the standards are marked in red colour. Only nitrate concentration in native groundwater exceeds the good quality status standards. None of the inorganic parameters in WWTP effluent is above quality standards for the aquifer, so in this case, risk of MAR using this water has been classified as low in Table 7-9.

Table 7-12: Inorganic quality standards for WFD accomplishment in Castellón plain aquifer

(NOTE: Red cursive values indicate values above threshold values established in the Castellón plain aquifer)

Parameter	Native GW	Belcaire River	WWTP effluent	Threshold values stabilised (transposition of WFD in the Castellón plain aquifer)
Nitrate [mg/L]	288	0	61.5	< 200
Chloride [mg/L]	581.1	19.0	143.25	< 650
Sulphate [mg/L]	387.0	44.0	189.25	< 525
Selenium [mg/L]	N.A.	N.A.	N.A.	< 0.0207

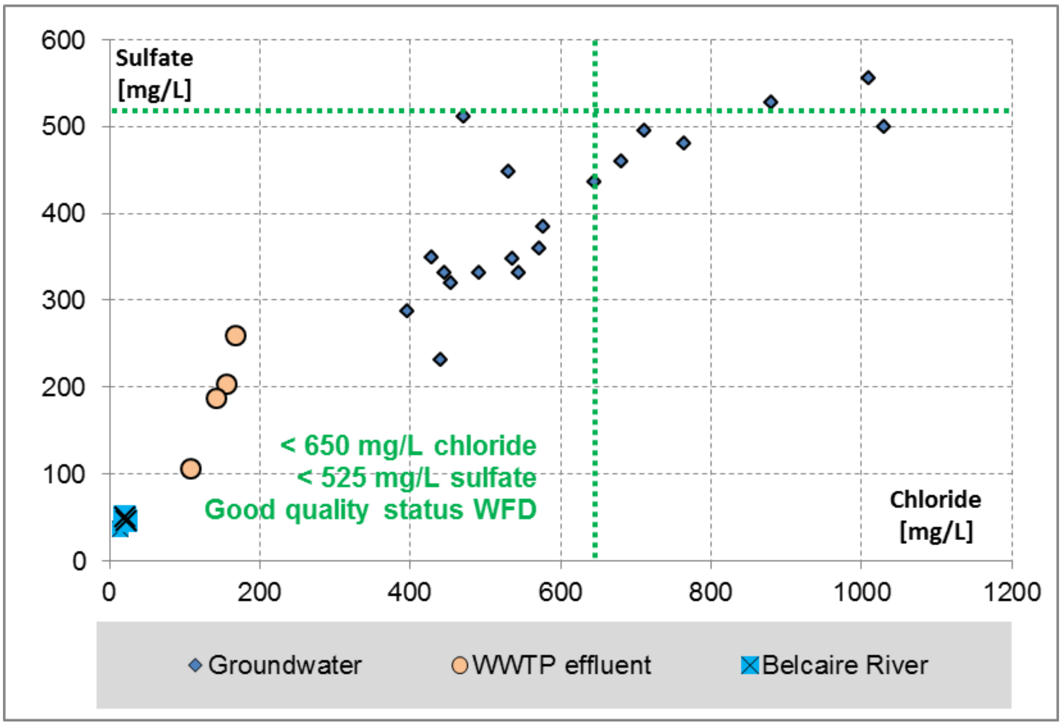

Figure 7-18: Sulphate and chloride in recharge water compared to Environmental standards WFD in Castellón plain aquifer

7.4.3.2.3 Salinity and sodicity

The mixing of recharge water and ambient groundwater in MAR will cause the salinity of recovered water to differ from that of the recharge water. In general, the salinity of ambient groundwater within aquifer targeted for MAR should be similar to or higher than the source water. Therefore, native groundwater will represent an additional source of salinity (and sodicity) in recovered water. Levels reported of salinity in La Vall d'Uixó groundwater wells are around 3,000 – 4,000 µS/cm. Due to the dilution effect, high salinity values are not expected in recovered water. In fact, phase III of Water Recovery project demonstrated a quick response of the aquifer in the reduction of groundwater salinity.

7.4.3.2.4 Nutrients: nitrogen, phosphorous and organic carbon

Nitrogen and phosphorous are identified as key environmental hazards in the Australian guidelines. This is due to their potential to cause nutrient imbalance in irrigation water, soil eutrophication, and toxic effects on terrestrial biota. While subsurface storage is likely to reduce nutrient concentration, the overall nutrient balance of the recovered water still needs to be considered in relation to its beneficial use. The dominant nitrogen species in recycled water are organic nitrogen, ammonium and nitrate.

Figure 7-19 represents values of nitrate in WWTP effluent compared to groundwater nitrate concentrations. Direct injection of WWTP effluent would represent the introduction in the aquifer of nitrate levels below the standard value assigned for nitrate in the Castellón plain aquifer (200 mg/L).

Risk related to nitrate has been classified as high risk in Table 7-9 for the agricultural endpoint. In contrast, total organic carbon (TOC) in WWTP effluent is much higher than present in the aquifer (17 mg/L in the WWTP effluent versus 1 mg/L in groundwater). The risk of injecting WWTP effluent has been classified as high, as the consequences of high TOC in WWTP effluent.

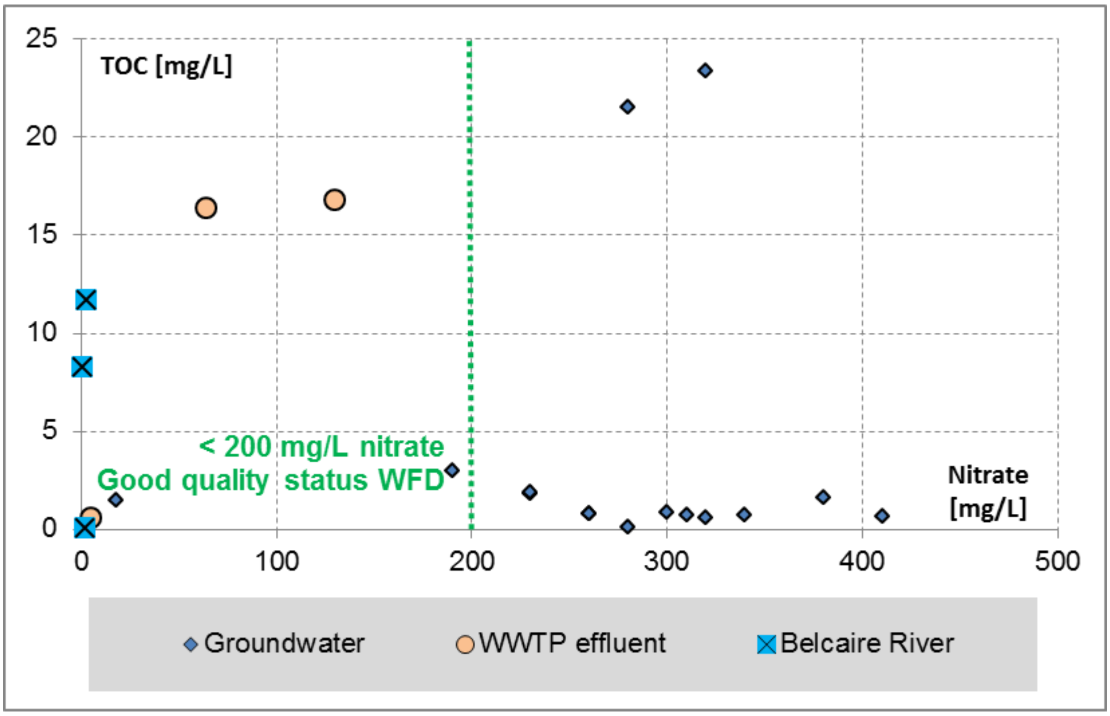

Figure 7-19: TOC and nitrate in recharge water compared groundwater in La Vall d'Uixó

Regarding the risk assessment of nitrogen for crops irrigation, it has been classified as high risk, as the quality standards for agriculture establishes a maximum of 5 mg/L of nitrogen, while in WWTP effluent the average concentration of nitrate is 61 mg/L and ammonium concentration mean value is 17 mg/L.

Phosphorous has not been monitored in the project. Only total phosphorous concentration was analysed in the WWTP effluent in a punctual sample in 2012 that was quantified 3.7 mg/L. The risk assessment of phosphorous in La Vall d'Uixó has thus been classified as unknown (uncertain risk).

7.4.3.2.5 Organic chemicals

Determining the presence of organic chemicals in WWTP effluent and carrying out the associated risk assessment can be difficult, due to intermittent loadings. This study has taken advantage of the outputs generated in DEMEAU project. Six sampling campaigns have been performed during 2014 – 2015 in the effluent of the WWTP Vall d'Uixó. Three sampling campaigns were carried out in weekends (Sunday afternoon) and three sampling campaigns were done in weekdays (Monday or Wednesday morning). All results can be found in the annex K.

During maximal risk assessment the maximum concentrations of organic micro pollutants is compared to native groundwater assuming no removal at all during subsurface passage. This shows the maximum risks if no preventive measures or natural attenuation occurs.

The maximal concentration measured in WWTP effluent, storage pond (Belcaire River) and groundwater shows large differences (

Figure 7-20). WWTP effluent shows elevated concentrations in almost all groups of organic micro pollutants compared to storage pond or groundwater. Only pesticides are found in higher concentrations in groundwater compared to the effluent. The Belcaire River shows the lowest concentrations for all groups of micro pollutants. The Vall d'Uixó aquifer is contaminated by various organic micro pollutants and does not reflect a near natural aquifer condition. The aquifer chemistry reflects the usage of effluent for irrigation over years.

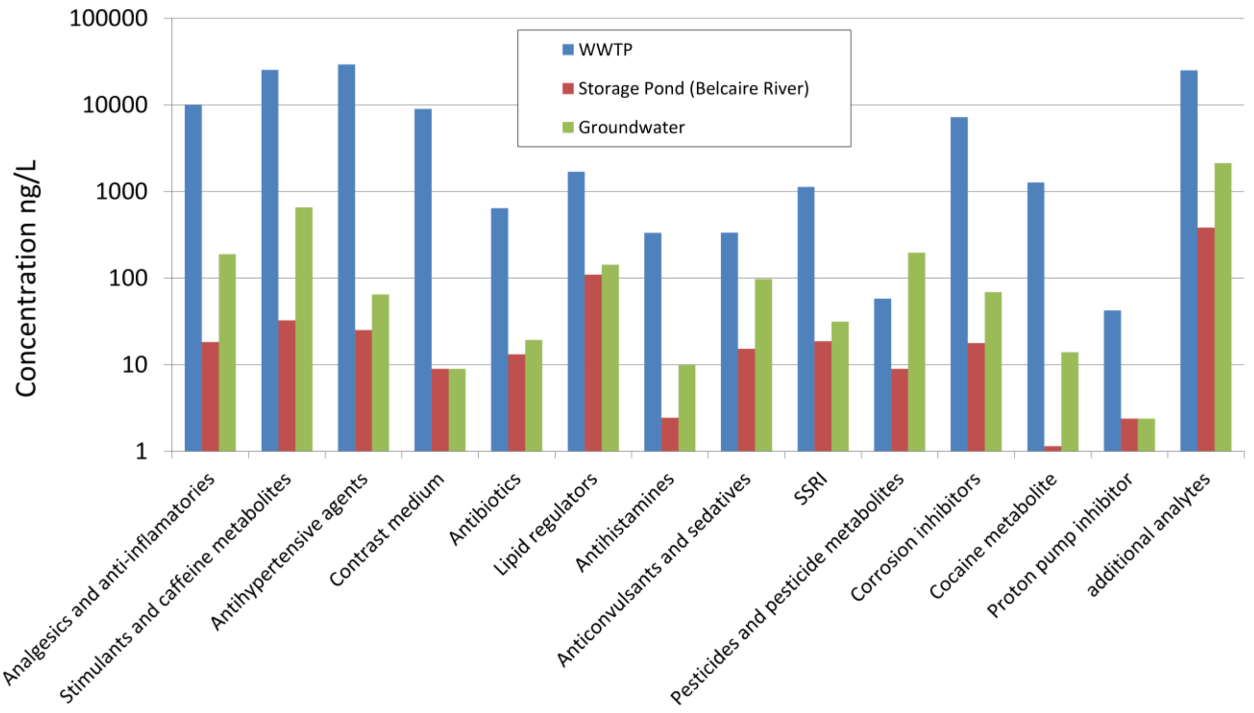

Figure 7-20: Maximal sum concentration found in WWTP effluent, storage dam and groundwater for the different groups of organic compounds (SSRI = selective serotonin and norepinephrine re-uptake inhibitors).

WFD application in Castellón plain aquifer indicates a maximum of 0.1 µg/L of individual concentration of active substances in pesticides and a maximum of 0.5 µg/L of total pesticides (CHJ, 2014). The analysis included seven pesticides (atrazine, DEA, DIA, diuron, isoproturon, mecoprop and metazchlor) as well as two herbicides (simazine and terbuthylazine, shown in additional analytes). The most abundant substance was terbuthylazine, with a maximum concentration of 155 ng/L. Nevertheless, maximal risk associated to pesticides is classified high, due the loading of pesticides in effluent. For all other groups risks associated to OMP´s are considered high.

Figure 7-21 shows the mean concentration of types of chemical compounds in the effluent of the WWTP La Vall d'Uixó. Number in brackets in the legend means the number of different compounds considered in in the study. Mean values have been calculated separating samples of working days and samples of weekend (Sunday afternoon). Some classes of compounds as artificial sweeteners (cyclamate and acesufame), stimulants, caffeine metabolites and cocaine metabolites (benzoylecgonine) were found in high concentration in the weekend compared to concentration along the weekdays. Contrast media (iopromide) was found more abundant in weekdays than in the weekend samples. This phenomenon highlights the importance of population habits in the compounds found in the WWTP effluent. As sampling campaigns performed were limited due to analytic costs, these results can be used as first estimation values and not as reference values.

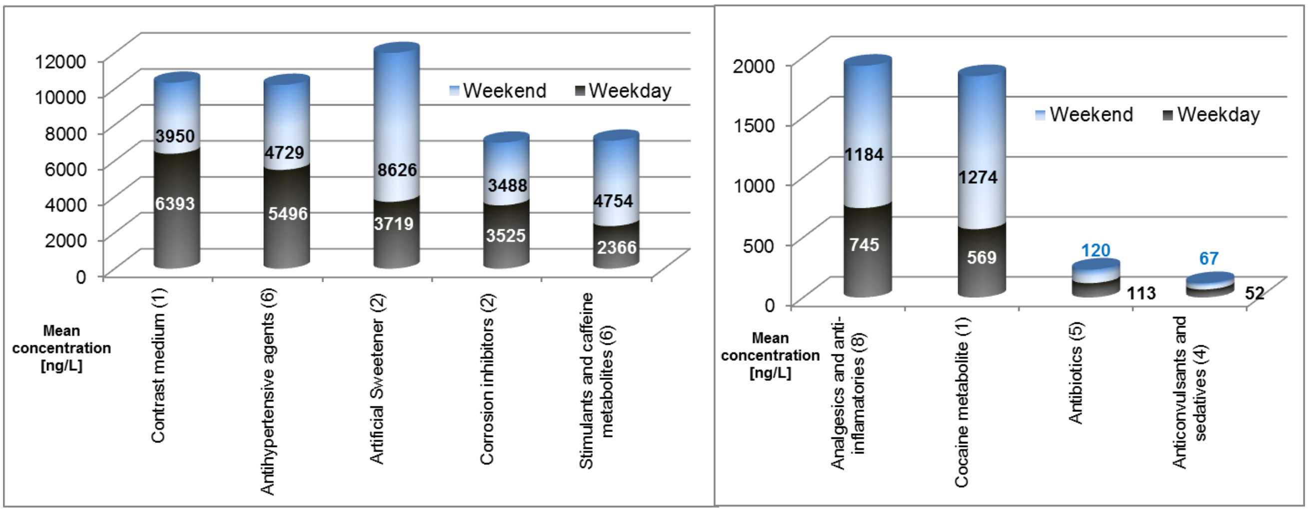

Figure 7-21: Mean concentrations of organic compounds in WWTP effluent (Number in brackets correspond to total number of compounds for each class)

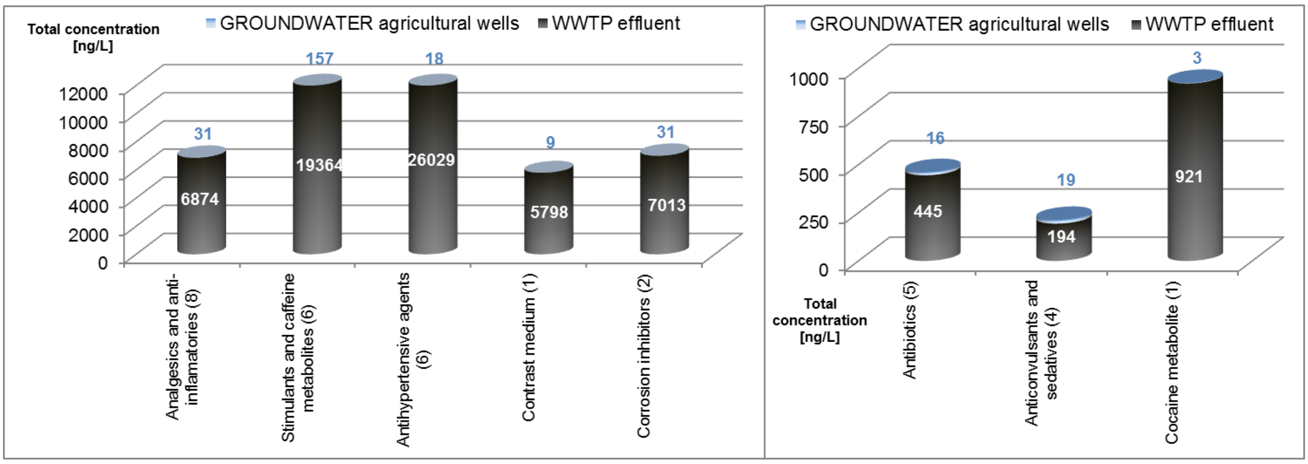

Figure 7-22: Pharmaceuticals and drugs in WWTP effluent and native groundwater (Number in brackets correspond to total number of compounds for each class)

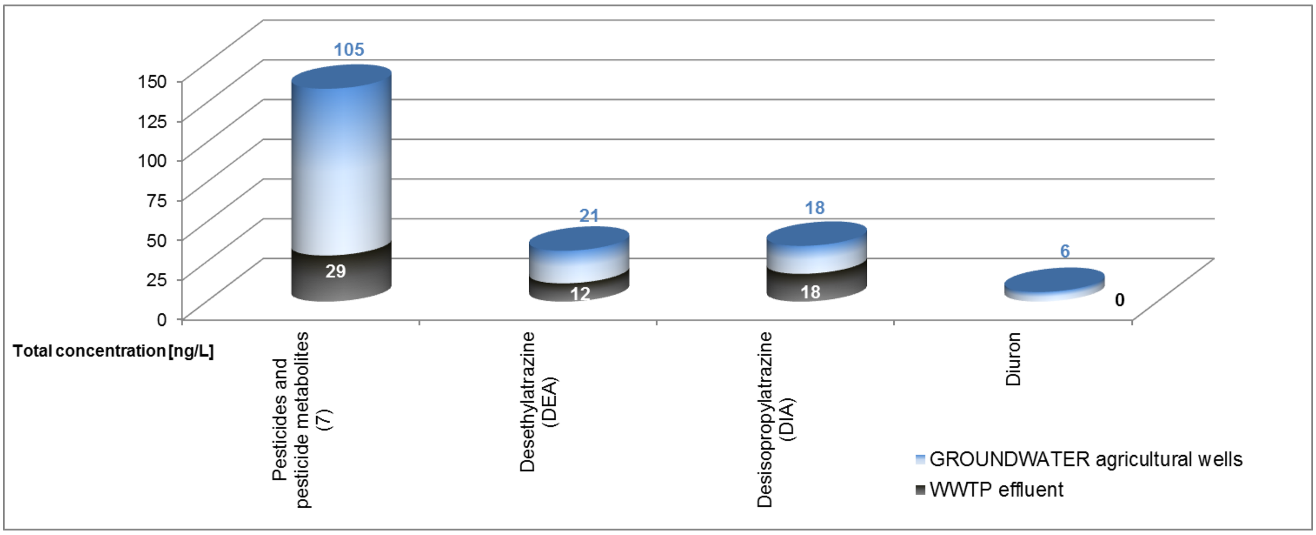

Figure 7-23: **Pesticides in WWTP effluent and native groundwater (Number in brackets correspond to total number of compounds for each class)**

Figure 7-22 and Figure 7-23 represents total concentration of drugs and pesticides found in WWTP effluent and in native groundwater. There is a clear relation in the type of pollutant and the source of water. As expected, antibiotics or analgesics are present in the effluent of WWTP.

Regarding undesirable substances as pharmaceuticals, contrast media, artificial sweeteners and illicit drugs metabolites found in WWTP effluent, there are no trigger values already established to determine level of risk. Individual quantification of contaminants had been complemented with the toxicity assessment of water samples. Results of toxicity of WWTP effluent of Vall d'Uixó are presented in this report in the bioassays section.

Due to the toxic character of the water, and according to the prevention principle, the risk assessment of organic pollution had been classified as "high" in Table 7-9.

Once established the threshold values in the aquifer or in the recovery water in irrigation wells, preventive measures to reduce the amount of organic pharmaceuticals and undesirable substances in recharge water can be:

- **Controlling source of pollutants:** avoid the inflow from hospitals and nursing homes to canalisation. This is an emerging trend of separating concentrate effluents containing pharmaceuticals. Finally, the effluent of the WWTP municipal plant will contain less concentration of these undesirable compounds.
- **Installing pre-treatment:** install a technical pre-treatment at the WWTP (e.g. advanced oxidation processes) to reduce the input of micro pollutants in the environment.
- **Ensuring enough residence time in soil-aquifer:** study the fate of degradable compounds and ensure sufficient residence time in the aquifer for removal below threshold values (residual risk assessment).

7.4.3.2.6 Turbidity and particulates

Turbidity has not been monitored in the project. Only turbidity in the WWTP effluent in a punctual sample in 2012 was determined and quantified 1.77 NTU. The risk assessment of turbidity and particulates in La Vall d'Uixó has been classified as unknown (uncertain risk) and requires further investigations.

7.4.3.2.7 Radionuclides

Radionuclides are radioactive isotopes or unstable forms of elements. There are no evidences of radium or radon in the groundwater of the area. Conglomerates, sands and clays constitute the Castellón plain aquifer. Sedimentary deposits are usually not related to radioactive activity. Volcanic and metamorphic rocks are correlated to potential release of radionuclides in groundwater, but they are not present in the study area. Therefore, this risk is considered to be low.

7.4.3.2.8 Pressure, flow rates, volumes and groundwater levels

Excessive pressure can cause failure of poorly completed injection or other wells, allowing water to escape to other aquifer or the ground surface. Castellón plain aquifer is a free aquifer, so aquitard rupture cannot happen. During phase III of Water Recovery Project, 100 L/s have been injected in the aquifer, without any negative consequence in the injection well nor in the farmers' recovery wells. The risk evaluation for these aspects is considered to be low..

7.4.3.2.9 Contaminant migration in fractured rocks and karstic aquifers

The intended MAR scheme is located in Castellón plain aquifer which is neither karstic nor fractured aquifer. Hence, this category does not apply to the Castellón plain aquifer.

7.4.3.2.10 Aquifer dissolution and stability of well and aquitard

Recharge water may react with the aquifer matrix material, resulting in dissolution of mineral or reduction in the aquifers bulk volume or strength. To assess this point a hydrochemical reactive numerical model should be carried out. PRHEEQC software is recommended to perform the numerical model, as it can include dissolution and precipitation equations, as well as reactive transport. This evaluation is out of the scope of this work, so the risk assessment of the hydrochemical stability has been classified as unknown (uncertain risk).

7.4.3.2.11 Aquifer and groundwater-dependent ecosystems

Castellón plain aquifer has no related wetlands, streams, lakes, estuaries or other aquatic ecosystems in La Vall d'Uixó. Neither indigenous microorganisms nor stygofauna have been clearly identified in the aquifer. This section does not apply to La Vall d'Uixó MAR scheme.

7.4.3.2.12 Energy and greenhouse gas considerations

Decisions to establish a MAR project need to take into account energy requirements in relation to alternative supply systems. In that sense, a local project of injection of WWTP effluent to improve groundwater levels and reduce salinity in the aquifer is more energy saving than the installation of a desalination of a reverse osmosis plant to reclaim WWTP effluent. Moreover, the most costly infrastructures (accumulation dam and injection wells) have been already constructed, so future investment will be focused on pre-treatment, operation, and maintenance and monitoring of the MAR scheme.

7.4.3.3 Residual risk assessment

Table 7-9 summarises the maximal risk assessment carried out assuming the injection of effluent from the WWTP directly into the Castellón plain aquifer. This is an important step to identify main hazards for the environment and the end use of reclaimed water: irrigation of citrus in La Vall d’Uixó. According to the Australian Guidelines, next step in risk assessment development will be to refill the table with the valuation of risk (High or Low) after the inclusion of some improvements in the MAR scheme.

7.5 Summary

The La Vall d'Uixó (Spain) pilot site has been selected by DEMEAU because it is a new Aquifer Storage Transfer and Recovery (ASTR) site consisting of two injection wells surrounded by farmer wells for irrigation in a water scarce area. Potential water source for this MAR site is the effluent of the local WWTP, which is a quite constant water source in terms of availability, but gives concerns in terms of water quality. The investigations carried out within DEMEAU supports the work previously done by the Water Recovery Project (2011 – 2014), coordinated by IGME (Instituto Geológico y Minero de España) and UJI (Universitat Jaume I). The Water Recovery Project consists of different implementation phases and aimed to establish an appropriate MAR scheme with reclaimed wastewater to counteract salinity ingress in the coastal aquifer. In the third phase of the project two injection wells have recharged 310,000 m^3 with water from the Belcaire River. To foster the implementation of the fourth and final phase of the Water Recovery Project, DEMEAU focused on the evaluation of the effluent of the local WWTP as source water for the ASTR system. This has been done by three sampling campaigns to analyse bulk chemistry, emerging pollutants and bioassays in native groundwater (six agricultural wells), Belcaire River (the current source water of the MAR scheme) and WWTP effluent (potential future source water). Risk assessment based on Australian MAR guidelines have been applied to evaluate risks related to the usage of WWTP effluent as source water. The Australian guidelines have been applied in two steps: entry level assessment and maximal risk assessment. Entry level assessment concluded that La Vall d'Uixó is suitable for a MAR scheme using reclaimed water, while maximal risk assessment identified hazards associated to reclaimed water as source water. As La Vall d'Uixó is an agricultural area of citrus crops, the use of reclaimed water for the injection in the MAR system must be compatible with the use of recovered water for irrigation. The risk assessment done in this report considered this end use of water, as there are no drinking water wells in the area. High risks have been identified for inorganic chemicals (conductivity, chloride and bicarbonate) and nutrients (nitrate). Risks associated to inorganics can be minimized by mixing effluent and Belcaire River water 1:1.

Bulk chemistry coincided mainly with the description carried out in Water Recovery project, identifying two main quality problems in native groundwater: (1) salinity ingress (2) high nitrate concentration due to the intensive agricultural practices in the area. Ion displacement pattern in groundwater samples clearly indicates on-going salinization and documents minor effects of the injected water on few wells only. Cl/Br ratios indicate additional sources of chloride apart from seawater. It seems plausible that the underlying Keuper formations (Triassic) contribute to salinity ingress and SO4 excess in groundwater to some extent.

Chlorides and nitrate are regulated by the implementation in Spain of the EU Water Framework Directive for the Castellón aquifer. The threshold value for nitrate is 200 mg/L, while the threshold value for chloride is 650 mg/L. WWTP effluent has nitrate and chlorides below the threshold concentrations (60 mg/L and 140 mg/L respectively) and, therefore, the MAR with reclaimed water would suppose a reduction of groundwater pollution and a step towards a qualitative good status in the aquifer.

In total 63 organic micro pollutants have been analysed in groundwater, surface water and WWTP effluent. WWTP effluent shows elevated concentrations in almost all groups of organic micro pollutants compared to river- or groundwater. Only pesticides are found in higher concentrations in groundwater compared to the effluent. The Belcaire River shows the lowest concentrations for all groups of micro pollutants. It was shown that the Vall d'Uixó aquifer is contaminated by various organic micro pollutants and does not reflect a near natural aquifer condition. The aquifer chemistry in terms of organic micro pollutants reflects the usage of (untreated) effluent for direct irrigation over years. Elevated concentration of artificial sweeteners, analgesics, stimulants, caffeine metabolites and cocaine metabolites were found in WWTP samples taken during weekends compared to workday samples. In contrast, iopromide has been quantified in higher concentrations in the effluent of WWTP in work days than in the weekend, as this contrast media is used in hospitals for diagnostic tests normally carried out from Monday to Friday. These patterns of the effluent of WWTP during the week of weekend could be determinant for the selection of the working days as most suitable days to store treated waste water.

In order to link analysed chemical concentrations to the observed toxicity in the samples a procedure based on bioassay-specific relative potency (REP) factors was applied. REP factors are determined by the effect concentrations of the reference compound and of the test compound.

Despite the lack of toxicological data for a number of the selected target compounds and the lower relevance of the selected compounds for (eco)toxicological risk assessment, this study greatly demonstrate the usefulness of combined analyses of environmental samples. Effect-based methods could complement conventional chemical analysis in water quality monitoring as pre-screening techniques by (1) identifying toxic "hotspots" for further investigation, (2) assessing the effect of the entire mixture of compounds present in waters and therefore and (3) reduce uncertainty in safety evaluation.

7.6 Recommendations for future studies

Some information gaps have been identified during the risk assessment for the MAR scheme in Castellón. Specifically the following aspects should be analysed in future studies before using the WWTP effluent as source water:

- **Pathogens**: residence time within the aquifer has been calculated theoretically. Preferential flow paths or high abstraction pumping rates have been not considered in the preliminary assessment in this report. It is recommended to assess the hydraulic performance by tracer tests under real conditions.

- **Hydrogeochemical changes in the aquifer:** changes in redox state and pH value can cause variations in precipitation-dissolution reactions. A mineralogical analysis is recommended to know if there are arsenic bearing minerals that could possibly mobilise.

- **Physical clogging:** During the study there were no data of turbidity values and suspended solids in WWTP effluent. This is a topic very well studied in ASR and ASTR schemes that should be addressed in future studies.

The aim of Water Recovery Project was to check the feasibility of reclaimed water as source water for MAR. Phase IV of the project was intended to test effluent and to design additional pre-treatment or mixing ratios of river water with treated effluent. Unfortunately, phase IV of the Water Recovery Project has been cancelled due to lack of funding. Hopefully this work will help in future to support the implementation of the MAR reuse scheme.

Apart from of the scientific work carried out, it was noticed that it was a fluent collaboration between technicians and local farmers. This is a result of a strong interest of farmers for having an improvement on water quantity and quality. An important recommendation for following studies is to maintain this good cooperation and present information in an open manner.

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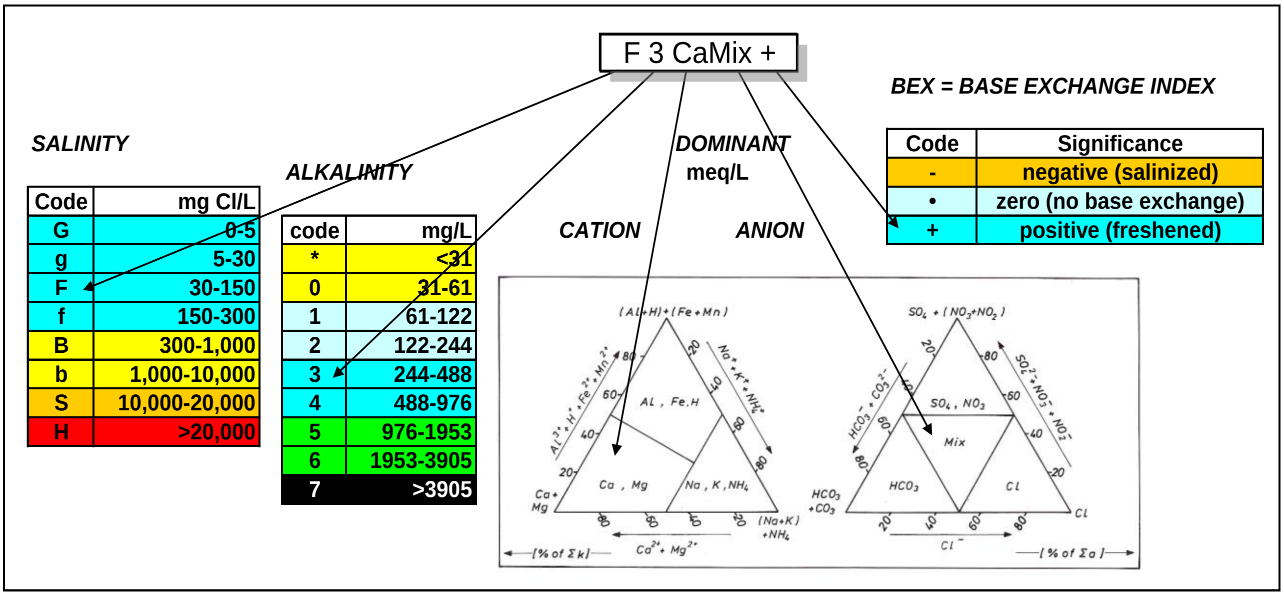
Annex A Hydrochemical water type classification following Stuyfzand (1993)



SALINITY

Code	mg Cl/L
G	0-5
g	5-30
F	30-150
f	150-300
B	300-1,000
b	1,000-10,000
S	10,000-20,000
H	>20,000

ALKALINITY

code	mg/L
*	<31
0	31-61
1	61-122
2	122-244
3	244-488
4	488-976
5	976-1953
6	1953-3905
7	>3905

BEX = BASE EXCHANGE INDEX

Code	Significance
-	negative (salinized)
•	zero (no base exchange)
+	positive (freshened)

Level	Environment	Criteria [mg/L]						
		O_2	NO_3^-	Mn^{2+}	Fe^{2+}	SO_4^{2-}	H_2S #	CH_4
0	Oxic	$O_2 \geq 0.9\ (O_2)_{SAT}$		< 0.1	< 0.1	≥ 0.9 $(SO_4)_O$	no	< 0.1
1	O2-reducing (Penoxic)	$1 \leq O_2 < 0.9\ (O_2)_{SAT}$		< 0.1	< 0.1	≥ 0.9 $(SO_4)_O$	no	< 0.1
2	NO_3-reducing (Suboxic)	< 1	≥ 1	< 0.1	< 0.1	≥ 0.9 $(SO_4)_O$	no	< 0.1
3	Transition (Mn-reducing)	< 0.5	< 1	≥ 0.1	< 0.1	≥ 0.9 $(SO_4)_O$	no	< 0.1
4	Iron reducing	< 0.5	< 0.5		≥ 0.1	≥ 0.9 $(SO_4)_O$	no	< 0.1
5	Sulphate reducing	< 0.5	< 0.5			A	yes	< 1
6	Methanogenic	< 0.5	< 0.5			B		≥ 1
Redox clusters:		O_2	NO_3^-	Mn^{2+}	Fe^{2+}	SO_4^{2-}	H_2S #	CH_4
0-2	(sub)oxic	≥ 1 or	≥ 1	< 0.1	< 0.1		no	< 0.1
3-4	anoxic	< 0.5	< 0.5		≥ 0.1	≥ 0.9 $(SO_4)_O$	no	< 0.25
5-6	deeply anoxic	< 0.5	< 0.5			C	yes or	≥0.5
M	mixed @	≥ 1 or	≥ 1	≥ 0.15 or ≥ 0.15			or	>0.1

#: yes/no = yes/no clear H_2S-smell in field $(SO_4)_O$ = original SO_4 concentration in mg/L.

A: if Cl ≤ 300 mg/L then $0.1(SO_4)_O < SO4 < 0.9(SO_4)_O$; if Cl > 300 mg/L then $0.5(SO_4)_O < SO4 < 0.9(SO_4)_O$

B: if Cl ≤ 300 mg/L then $SO_4 < 0.1(SO_4)_O$ or SO_4 <1 mg/L ; if Cl > 300 mg/L then $SO_4 < 0.5(SO_4)_O$

C: $SO_4 < 0.9(SO_4)_O$ or, if Cl < 300 mg/L , SO_4 < 1 mg/L

$(O_2)_{SAT} = 14.594 - 0.4\,t + 0.0085\,t^2 - 97\ 10^{-6}\,t^3 - 10^{-5}\,(16.35 + 0.008\,t^2 - 5.32/t)\ Cl$, with t = temp. in °C, Cl in mg/L.

@: sample composed of a mix of water from different redox environments

Annex B Emerging organic substances in the river Meuse source water:

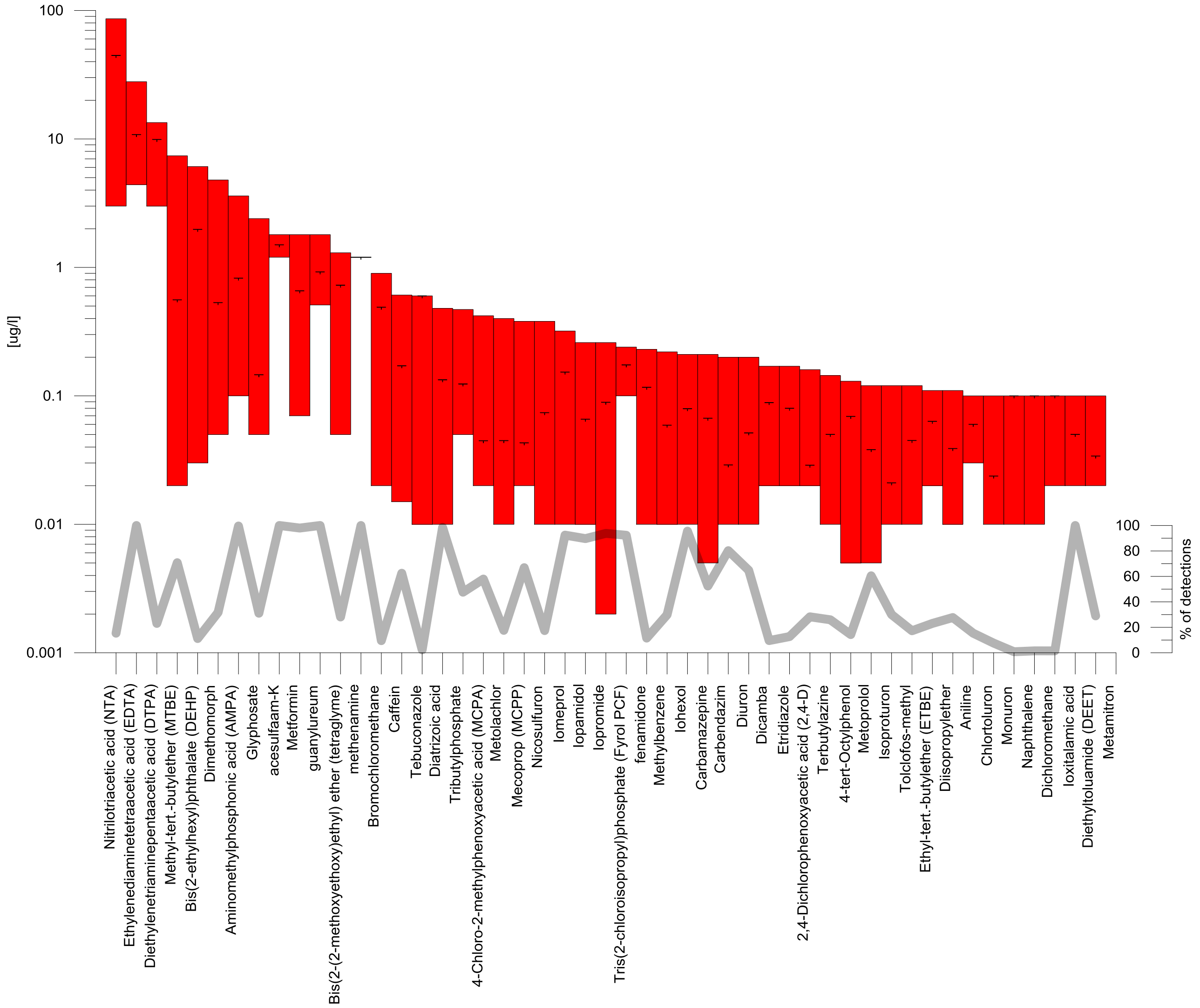


Figure B-0-1: First fifty emerging organic substances identified in Brakel since January 2003 until December 2013, ordered by size. The bars go from the lowest detection limit to the highest concentration measured. The small black horizontal lines in the bars represent the average of the data measured above detection limit and the thick grey line the percentage of detections over the limit of quantification (LOQ).

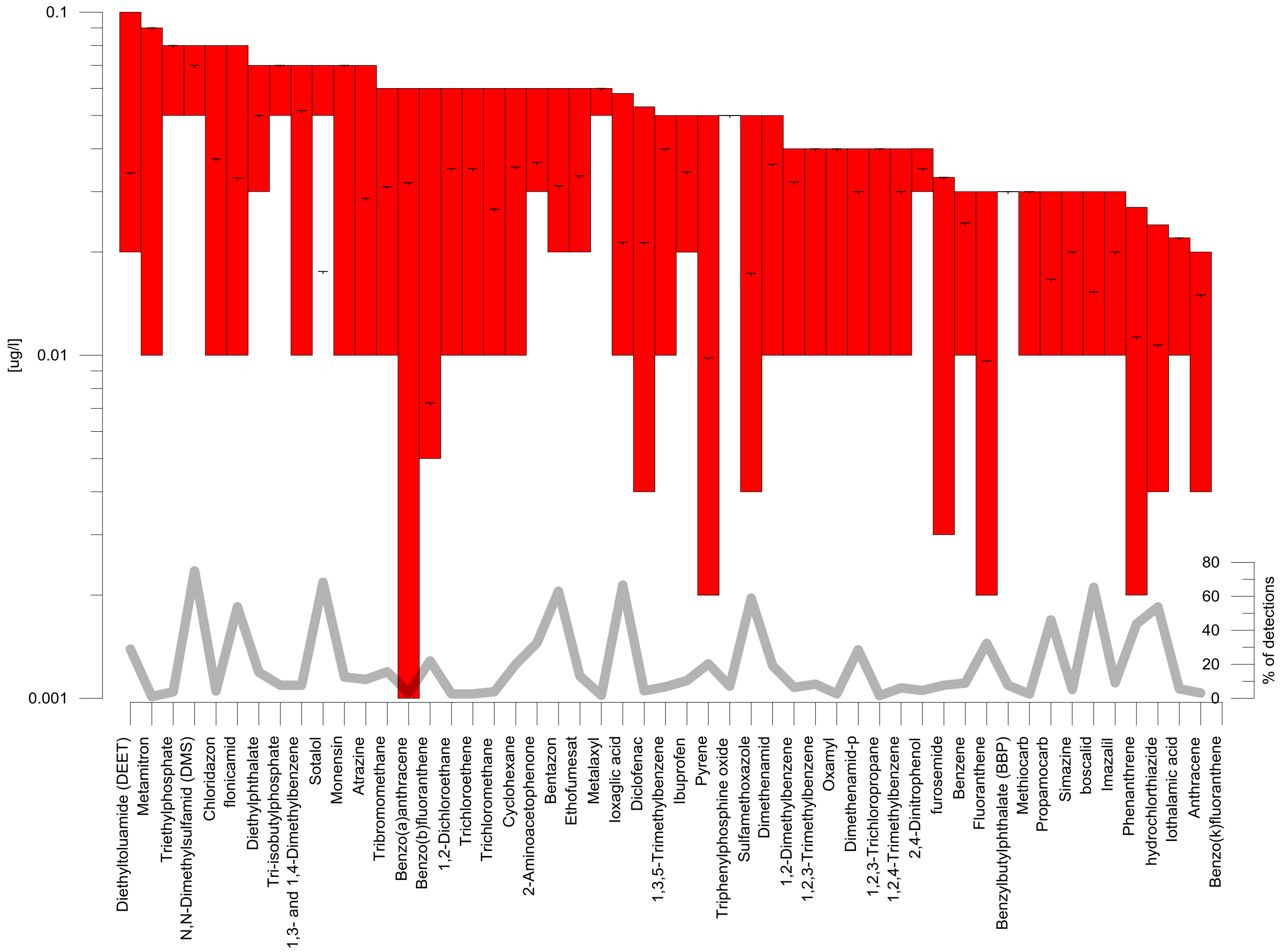


Figure B-0-2: Second fifty (50-100) emerging organic substances identified in Brakel since January 2003 until December 2013, ordered by size. The bars go from the lowest detection limit to the highest concentration measured. The small black horizontal lines in the bars represent the average of the data measured above detection limit and the thick grey line the percentage of detections over the limit of quantification (LOQ).

Table B-0-1: **Parameters measured in the Rhine intake (Brakel) that were detected above the detection limit in more than 60% of the analysis performed from January 2003 to December 2013. The table shows the maximum concentrations measured, the number of analysis done for each parameter, the number of results under detection limit (DL) and the percentage of samples with the compound detected above the DL in the period 2003-2013.**

Parameter	max value	units	Nr. analysis	under DL	% over DL
Ethylenediaminetetraacetic acid (EDTA)	27.9	µg/l	60	0	100
Methyl-tert.-butylether (MTBE)	7.4	µg/l	291	85	71
Aminomethylphosphonic acid (AMPA)	3.6	µg/l	244	1	100
acesulfaam-K	1.8	µg/l	4	0	100
guanylureum	1.8	µg/l	6	0	100
Metformin	1.8	µg/l	50	1	98
methenamine	1.2	µg/l	1	0	100
Caffein	0.61	µg/l	32	12	63
Diatrizoic acid	0.48	µg/l	68	1	99
Mecoprop (MCPP)	0.38	µg/l	465	154	67
Iomeprol	0.32	µg/l	66	5	92
Iopromide	0.26	µg/l	113	7	94
Iopamidol	0.26	µg/l	68	7	90
Tris(2-chloroisopropyl)phosphate (Fyrol PCF)	0.24	µg/l	13	1	92
Iohexol	0.21	µg/l	68	3	96
Carbendazim	0.2	µg/l	329	65	80
Diuron	0.2	µg/l	628	221	65
Metoprolol	0.12	µg/l	124	49	60
Ioxitalamic acid	0.1	µg/l	18	0	100
N,N-Dimethylsulfamid (DMS)	0.08	µg/l	8	2	75
Sotalol	0.07	µg/l	82	26	68
Bentazon	0.06	µg/l	184	68	63
Ioxaglic acid	0.058	µg/l	18	6	67
boscalid	0.03	µg/l	52	18	65
losartan	0.016	µg/l	13	4	69
oxazepam	0.015	µg/l	13	0	100
Bisoprolol	0.014	µg/l	13	0	100
Lidocaine	0.014	µg/l	18	2	89
temazepam	0.012	µg/l	13	0	100
Atenolol	0.011	µg/l	13	0	100
heptadecafluorooctane-1-sulphonic acid	0.0094	µg/l	26	0	100
Primidone	0.008	µg/l	20	7	65
Perfluoroctanoate (PFOA)	0.0073	µg/l	26	0	100
perfluoro-1-butanesulfonate linear (L_PFBS)	0.0065	µg/l	26	0	100
undecafluorohexanoic acid	0.0037	µg/l	26	6	77
Perfluorohexane sulfonate (PFHxS)	0.0013	µg/l	26	2	92

Annex C Average concentration of EOS in source and recovered water at Scheveningen BAR system.

Table C-0-1: Micro pollutants in the infiltrating and recovered water in Scheveningen MAR system. The substances are ordered from highest to lowest average concentrations, the amount of samples from the infiltrating water and the lowest detection limit per parameter are indicated. Also the number of different detection limits is included and the percentage of samples over detection limit. The mean recovered concentration is also included together with the percentage of removal regarding the initial average concentration.

Parameter	Type of contaminant	Source water					Recovered water					Removal (%)
		Mean conc. (µg/l)	Nr samples	lowest DL (µg/l)	Nr DL	Samples >DL (%)	Mean conc. (µg/l)	Nr samples	lowest DL (µg/l)	Nr DL	Samples >DL (%)	
hexa(methoxymethyl) melamine	solvent	0.215	44	0.03	1	98	0.21					2
triisobutylphosphate	solvent	0.147	15	0.05	1	40	0.05	38	0.03	2	4	66
Tributylphosphate	solvent	0.105	18	0.05	2	33	0.101	39	38	1	1	3
chlorobenzene	solvent	0.088	133	0.02	2	1	0.02	105	105	2	0	77
Triethylphosphate	solvent	0.066	18	0.05	2	11	0.05	39	39	1	0	24
methylbenzene	solvent	0.065	132	0.02	2	2	0.03	104	100	2	4	54
dichloromethane	solvent	0.029	123	0.02	1	1	0.023	72	71	1	1	23
Tetraglyme	solvent	0.024	4	0.01	1	75		39	39	1	0	
ethylbenzene	solvent	0.021	133	0.02	2	1	0.02	73	36	1	37	4
1,3,5-trimethylbenzene	solvent	0.02	123	0.02	1	2	0.02	39	39	1	0	1
diglyme	solvent	0.018	4	0.0136	0	100						
Carbamazepine	Pharmac.	0.081	164	0.05	2	34		31	0.2	1	3	
bromodichloromethane	Pharmac.	0.036	133	0.02	2	1	0.02	117	117	3	0	44
tribromomethane	Pharmac.	0.03	132	0.02	2	7	0.02	117	117	3	0	33
ortho-phthalic acid	Pharmac.	0.025	111	0.02	1	1	0.02	63	60	1	3	20
p-isopropylmethylbenzene	Pharmac.	0.024	106	0.02	1	3	0.025	73	0.01	1	37	-3
Diclofenac	Pharmac.	0.023	109	0.02	1	6		65	65	2	0	
metsulfuron-methyl	Pharmac.	0.02	43	0.02	1	2	0.02	39	39	1	0	0
phenanthrene	Pharmac.	0.013	69	0.005	3	4	0.019	39	38	3	1	-46
naphtalene	Pesticide	0.037	170	0.02	3	1	0.043	106	104	4	2	-18
dimethomorph	Pesticide	1.182	64	0.05	2	8	0.07	39	38	1	1	94
AMPA	Pesticide	0.777	77	0.2	0	100	0.557	3	0	0	3	28
flumioxazine	Pesticide	0.26	36	0.05	1	3	0.05	26	26	1	0	81
fenamidone	Pesticide	0.2	45	0.01	1	4	0.01	33	33	1	0	95
aldicarb-sulphoxide	Pesticide	0.176	82	0.01	4	2	0.01	67	67	3	0	94
folpet	Pesticide	0.16	51	0.06	1	2	0.06	39	39	1	0	63

Parameter	Type of contaminant	Source water					Recovered water					Removal (%)
		Mean conc. (µg/l)	Nr samples	DL lowest (µg/l)	Nr DL	Samples >DL (%)	Mean conc. (µg/l)	Nr samples	DL lowest (µg/l)	Nr DL	Samples >DL (%)	
butoxycarboxim	Pesticide	0.12	68	0.01	3	1	0.01	39	39	1	0	92
glyphosate	Pesticide	0.082	77	0.05	1	9	0.05	66	63	1	3	39
dicamba	Pesticide	0.066	111	0.02	1	3	0.02	219	219	2	0	70
diisopropylether	Pesticide	0.065	132	0.02	2	8	0.02	105	105	2	0	69
Sum 2,4 en 2,5-dichlorophenol	Pesticide	0.06	63	0.02	1	2	0.02	24	24	1	0	67
methiocarb	Pesticide	0.055	81	0.01	4	4	0.01	68	68	3	0	82
3,4-Dichlorophenyl urea (DCPU)	Pesticide	0.055	13	0.01	1	8	0.012	42	0.03	1	3	78
metazachloro	Pesticide	0.053	164	0.02	3	1	0.02	212	212	3	0	62
desethylterbutylazine	Pesticide	0.052	106	0.05	2	1	0.05	39	0.01	1	1	4
metalaxyl	Pesticide	0.05	51	0.05	1	2	0.05	39	39	1	0	0
nicosulfuron	Pesticide	0.047	54	0.01	2	19	0.05	39	39	1	0	-6
2,4-D	Pesticide	0.047	110	0.02	1	2	0.02	221	221	2	0	57
atrazine	Pesticide	0.043	252	0.01	5	1	0.012	312	311	3	1	72
methabenzthiazuron	Pesticide	0.043	108	0.01	3	2	0.01	129	129	2	0	76
3-(3,4-dichlorofenyl)-1-methylurea	Pesticide	0.036	68	0.03	1	3	0.03	98	98	1	0	17
tolclofos-methyl	Pesticide	0.034	164	0.01	3	14	0.01	208	208	2	0	71
diuron	Pesticide	0.033	154	0.01	4	41	0.021	169	146	3	23	37
bentazone	Pesticide	0.032	110	0.02	1	54	0.024	221	185	2	36	26
2,4,5-TP	Pesticide	0.032	111	0.02	1	1	0.02	222	222	2	0	38
DNOC (2-methyl-4,6-dinitrophenol)	Pesticide	0.031	70	0.03	1	1	0.03	38	0.03	1	2	4
dinoterb (2-tert.butyl-4,6-dinitrophenol)	Pesticide	0.031	70	0.03	1	1	0.03	104	0.02	2	4	3
terbuthylazine	Pesticide	0.031	35	0.01	1	66	0.01	25	24	1	1	68
fluopicolide	Pesticide	0.03	36	0.01	1	3	0.01	26	26	1	0	67
metolachlor	Pesticide	0.029	275	0.01	4	12	0.01	414	414	4	0	66
pyrazon	Pesticide	0.029	41	0.01	2	24	0.02	42	42	2	0	31
simazine	Pesticide	0.028	252	0.01	5	0	0.01	117	0.02	3	2	64
MCPP (mecoprop)	Pesticide	0.026	111	0.02	1	7	0.021	217	0.02	2	1	19
ethofumesate	Pesticide	0.023	51	0.02	1	6	0.02	33	0.01	1	1	14
dimethenamid	Pesticide	0.023	87	0.01	2	11	0.01	33	32	1	1	57
flonicamid	Pesticide	0.023	43	0.01	1	49	0.02	221	221	2	0	13
MCPA	Pesticide	0.023	111	0.02	1	5	0.02	39	39	1	0	12
diethyltoluamide (DEET)	Pesticide	0.023	51	0.02	1	8	0.02	39	37	1	2	11
thiabendazole	pesticide	0.021	43	0.01	1	21	0.085	105	105	2	0	-303
carbendazim	Pesticide	0.021	87	0.01	2	90	0.012	117	115	3	2	42
thiophanate-methyl	Pesticide	0.02	43	0.02	1	2	0.02	71	0.02	2	0	0

Parameter	Type of contaminant	Source water					Recovered water					Removal (%)
		Mean conc. (µg/l)	Nr samples	lowest DL (µg/l)	Nr DL	Samples >DL (%)	Mean conc. (µg/l)	Nr samples	lowest DL (µg/l)	Nr DL	Samples >DL (%)	
BAM (2,6-dichlorobenzamide)	Pesticide	0.018	15	0.01	1	93		117	0.02	3	0	
isoproturon	Pesticide	0.017	155	0.01	4	16	0.01	172	171	3	1	43
chlorotoluron	Pesticide	0.017	155	0.01	4	1	0.01					41
thiametoxam	pesticide	0.017	43	0.01	1	56	0.01	39	39	1	0	40
boscalid	Pesticide	0.016	45	0.01	1	69	0.01	33	32	1	1	39
N,N-Diethyl-m-toluamide (DEET)	Pesticide	0.015	13	0.01	1	54		105	0.02	2	0	
linuron	Pesticide	0.014	151	0.01	3	9	0.018	166	165	2	1	- 29
imidacloprid	Pesticide	0.014	43	0.01	1	30	0.01	39	39	2	0	28
dichlobenil	Pesticide	0.013	165	0.01	2	5	0.01	78	78	2	0	25
propamocarb	Pesticide	0.013	43	0.01	1	37	0.01	38	38	1	0	20
paclobutrazol	pesticide	0.013	43	0.01	1	9	0.01	39	39	1	0	20
oxamyl	Pesticide	0.012	80	0.01	4	1	0.01	68	68	3	0	17
carbetamide	Pesticide	0.01	43	0.01	1	2	0.01	39	39	1	0	0
chlorpyrifos	Pesticide	0.01	51	0.01	2	2	0.01	39	39	2	0	0
primicarb	Pesticide	0.01	43	0.01	1	2	0.01	39	39	1	0	0
Sum PAH	Others	0.043	37	0.02	4	5	0.025	39	0.05	1	1	41
MTBE	Others	0.333	53	0.03	1	96	0.117	61	0	0	61	65
triphenylphosfine oxide (TPP)	Others	0.173	44	0.03	2	16	0.103	44	43	2	1	40
Som trihalomethanes	Others	0.065	124	0.02	4	19	0.065	66	0.05	1	3	0
trichloromethane	Others	0.062	133	0.02	3	12	0.037	117	105	4	12	40
ethyl-tertiair-butylether (ETBE)	Others	0.039	122	0.02	1	9	0.02	71	71	1	0	49
2,6-dichlorobenzoic acid	Others	0.035	111	0.02	1	1	0.02	189	189	1	0	43
benzene	Others	0.032	133	0.02	2	1	0.02	105	105	2	0	38
PAH	Others	0.031	57	0.01	3	2	0.01	35	35	5	0	68
1,2-dichloroethane	Others	0.02	133	0.02	2	2	0.021	72	72	1	0	-4
fluorantheen	Others	0.018	70	0.005	3	1	0.005	39	39	3	0	72
anthracene	Others	0.015	70	0.005	3	3	0.005	36	36	3	0	66

Annex D Bulk chemistry SVH

Table D-0-2: List of parameters and detection methods of bulk chemistry.

Parameters	Parameters	Units of determination	Methodology	Limit of detection (LDet)
General parameters	pH	Units of pH	Portable probe	4 - 14
	Electrical Conductivity	µS/cm	Portable probe	15-15000
	TOC	mg C/L	UV-VIS spectrophotometer	> 1
	Total hardness	mg HCO_3/L	Potentiometric titration	--
Major compounds	Nitrate	mg/L	Ionic chromatography	>0.5
	Ammonium	mg/L	Colorimetric (method indophenol)	>0.15
	Chloride	mg/L	Volumetric titration	>30
	Total Phosphorous	mg/L	UV-VIS spectrophotometer	>0.1
	Sulphate	mg/L	Ionic chromatography	>5
Metals	Sodium	mg/L	Spectroscopy inductively coupled plasma (ICP / AES)	>5
	Potassium	mg/L		>5
	Calcium	mg/L		>5
	Magnesium	mg/L		>2
	Aluminium	µg/L		>25
	Manganese	µg/L		>2
	Iron	µg/L		>5

Table D-0-3: Analytical results of bulk chemistry for the infiltration basin (INF) and monitoring well BSV-01

	INF1	INF2	INF			BSV-01		
	July 2014	July 2014	July 2014	January 2015	May 2015	July 2014	January 2015	May 2015
NO2-(mg/L)	< 0.03	< 0.03	0.015	0.31	0.25	0.015	0.015	0.015
NO3- (mg/L)	0.713	0.616	0.6645	19.2	5.53	6.2	17.5	12.3
Ni (µg/L)	12	5	8.5	7	8	2.5	2.5	2.5
Ammonium (mg/L)	0.43	0.23	0.33	0.55	0.0075	0.075	0.075	0.075
Cl (mg/L)	239	227	233	275	283	233	150	232
EC. (20°C) µS/cm	1141	1131	1136	1525	1426	1371	1145	1488
TOC (mg/L)	5.7	5.3	5.5	4.7	5	1.7	2.6	2.4
pH	8.1	8.2	8.15	8.4	8.3	7.4	7.7	7.6
SO42-(mg/L)	139	126	132.5	205	158	159	178	200
Fe (µg/L)	227	154	190.5	62	158	9	176	166
Mn (µg/L)	40	18	29	31	38	1	6.4	7
Al (µg/L)	122	99	110.5	55	226	12.5	258	204
Na (µg/L)	-	-	-	156	-	-	89	-
HCO_3^-(mg/L)	-	-	-	275	239	-	327	367
CO_3^{-2} (mg/L)	-	-	-	11.5	7.1	-	0	0
P (µg/L)	111	74	92.5	146	184	44	10	25
K(mg/L)	26	26	26	32	33	16	20	23
Ca (mg/L)	81	75	78	133	101	121	122	151
Mg (mg/L)	24	23	23.5	45	31	30	28	38

Table D-0-4: Analytical results of bulk chemistry for BSV-8.1 & BSV-8.3

	BSV8.1	BSV8.1	BSV8.1	BSV8.3	BSV8.3	BSV8.3
	July 2014	January 2015	May 2015	July 2014	January 2015	May 2015
NO2-(mg/L)	0.041	0.015	0.073	0.015	0.015	0.015
NO3- (mg/L)	12.7	11.2	21.4	2.75	8.93	19.3
Ni (µg/L)	5	5	2.5	8	9	2.5
Ammonium (mg/L)	0.075	0.075	0.075	0.075	0.075	0.075
Cl (mg/L)	214	199	198	226	168	201
EC. (20°C) µS/cm	1448	1333	1475	1248	1211	1470
TOC (mg/L)	2.8	1.7	2.8	4.1	2.5	2.4
pH	7.6	7.6	7.7	7.8	8	7.9
SO42-(mg/L)	209	164	212	113	142	200
Fe (µg/L)	276	121	256	2472	1297	1079
Mn (µg/L)	29	12	19	590	390	150
Al (µg/L)	133	172	266	1547	1602	1615
Na (µg/L)	-	117	-	-	101	-
HCO_3^-(mg/L)	-	362	422	-	362	423
CO_3^{-2} (mg/L)	-	0	0	-	0	0
P (µg/L)	71	23	59	441	376	165
K(mg/L)	25	18	22	25	23	26
Ca (mg/L)	127	132	150	196	204	184
Mg (mg/L)	34	37	41	32	37	43

Table D-0-5: Analytical results of bulk chemistry for BSV-05, BSV-09 & BSV10.

	BSV05	BSV05	BSV05	BSV09	BSV09	BSV09	BSV10	BSV10	BSV10
	July 2014	January 2015	May 2015	July 2014	January 2015	May 2015	July 2014	January 2015	May 2015
NO2-(mg/L)	0.015	0.015	0.015	0.015	0.015	0.015	0.015	0.015	0.015
NO3- (mg/L)	3.43	11.3	12.8	4.42	9.78	17	5.63	13.9	13.1
Ni (µg/L)	2.5	5	2.5	8	6	2.5	6	2.5	2.5
Ammonium (mg/L)	0.075	0.075	0.075	0.075	0.075	0.075	0.075	0.075	0.075
Cl (mg/L)	237	169	279	254	204	206	269	168	252
EC. (20°C) µS/cm	1287	1205	1478	1402	1295	1363	1473	1215	1500
TOC (mg/L)	2.6	2.7	3	2.9	2	2.3	1.6	2.1	2.2
pH	7.6	8	7.9	7.8	7.6	8	7.6	7.7	7.9
SO42-(mg/L)	120	141	169	132	152	177	156	137	176
Fe (µg/L)	13	738	676	4832	150	3478	10	498	1140
Mn (µg/L)	1	120	78	760	45	830	1	23	61
Al (µg/L)	104	377	367	802	69	1835	12.5	374	1086
Na (µg/L)	-	106	-	-	119	-	-	110	-
HCO_3^-(mg/L)	-	351	277	-	333	344	-	365	347
CO_3^{-2} (mg/L)	-	0	0	-	0	0	-	0	0
P (µg/L)	50	189	152	178	22	368	10	31	63
K(mg/L)	27	27	31	26	25	27	23	24	26
Ca (mg/L)	95	150	132	171	128	311	119	133	148
Mg (mg/L)	25	37	36	34	35	56	29	33	38

Annex E Emerging pollutants SVH

Table E-0-6: Overview of micropollutants for each sampling campaign.

Name	Chemical formula	Molecular Weight (gr/mol)	Substance class	07/2014-WET	01/2015 - DRY	05/2015-MIX
Alachlor	$C_{14}H_{20}ClNO_2$	269.78	Herbicide		X	
Atrazine	$C_8H_{14}ClN_5$	215.68	Herbicide		X	X
Boscalid	$C_{18}H_{12}Cl_2N_2O$	343.2	Pesticide/ fungicide		X	X
Bromacil	$C_9H_{13}BrN_2O_2$	261.11	Pesticide/ herbicide		X	X
Chlorfenvinphos	$C_{12}H_{14}Cl_3O_4P$	359.56	Insecticide		X	
Chloridazon	$C_{10}H_8ClN_3O$	22.66	Herbicide		X	X
Chlortoluron	$C_{10}H_{13}ClN_2O$	212.68	Herbicide		X	X
Desethylatrazine	$C_6H_{10}ClN_5$	187.63	Herbicide		X	X
Desethylterbutylazine	$C_7H_{12}ClN_5$	201.65	Herbicide		X	X
Desisopropylatrazin	$C_5H_8ClN_5$	173.6	Herbicide		X	X
2,6-Dichloro Benzamide	$Cl_2C_6H_3CONH_2$	190.03	Fungicide		X	X
Diuron	$C_9H_{10}Cl_2N_2O$	233.1	Herbicide		X	X
Ethofumesate	$C_{13}H_{18}O_5S$	286.34	Herbicide		X	X
Isoproturon	$C_{12}H_{18}N_2O$	206.28	Pesticide/ herbicide		X	X
Lenacil	$C_{13}H_{18}N_2O_2$	234.3	Herbicide		X	
Metalaxyl	$C_{15}H_{21}NO_4$	27933	Fungicide		X	
Metamitron	$C_{10}H_{10}N_4O$	202.22	Herbicide		X	X
Metazachlor	$C_{14}H_{16}ClN_3O$	277.75	Herbicide		X	X
Chloridazon-Methyl-Desphenyl	$C_5H_6ClN_3O$	159.57	Pesticide		X	X
Metolachlor	$C_{15}H_{22}ClNO_2$	283.80	Herbicide		X	X
Metribuzin	$C_8H_{14}N_4OS$	214.28	Pesticide/ fungicide		X	X
Quinoxyphen	$C_{15}H_8Cl_2FNO$	308.13	Fungicide		X	
Simazine	$C_7H_{12}ClN_5$	201.66	Herbicide		X	X
Terbuthylazine	$C_9H_{16}ClN_5$	229.71	Herbicide		X	X
Quinmerac	$C_{11}H_8ClNO_2$	221.64	Herbicide		X	X

Name	Chemical formula	Molecular Weight (gr/mol)	Substance class	07/2014-WET	01/2015 - DRY	05/2015-MIX
2,4,5-Trichlorophenoxyacetic acid (2,4,5-T)	$C_8H_3Cl_3O_3$	255.48	Pesticide		X	
2,4-Dichlorophenoxyacetic acid (2,4-D)	$C_8H_6Cl_2O_3$	221.04	Herbicide		X	X
Bentazon	$C_{10}H_{12}N_2O_3S$	240.28	Herbicide		X	X
Bromoxynil	$C_7H_3Br_2NO$	276.92	Herbicide		X	
Dichlorprop	$C_9H_8Cl_2O_3$	235.06	Herbicide		X	X
MCPA	$C_9H_9ClO_3$	200.62	Herbicide		X	X
Mecoprop	$C_{10}H_{11}ClO_3$	214.65	Herbicide	X	X	X
Chlofibric acid	$C_{10}H_{11}ClO_3$	214.645	Herbicide		X	X
Phenazone (*)	$C_{11}H_{12}N_2O$	188.22	Analgesic	X	X	X
Carbamazepine (*)	$C_{15}H_{12}N_2O$	236.27	Anticonvulsant	X	X	X
Metoprolol (*)	$C_{15}H_{25}NO_3$	267.36	Blocker	X	X	X
Diclofenac (*)	$C_{14}H_{11}NCl_2O_2$	296.15	Analgesic	X	X	X
Iopromide (*)	$C_{18}H_{24}I_3N_3O_8$	791.11	Contrast medium	X	X	X
Ibuprofen (*)	$C_{13}H_{18}O_2$	206.29	Antiinflammatory			X
Dihydroxydihydrocarbamazepine	$C_{15}H_{14}N_2O_2$	254.28	Metabolite of Carbamazepine		X	X
Primidone (*)	$C_{12}H_{14}N_2O_2$	218.25	Anticonvulsant	X	X	X
Phenylethylmalonamide	$C_{11}H_{14}N_2O_2$	206,24	Metabolite of Primidone		X	X
Trimethoprim (*)	$C_{14}H_{18}N_4O_3$	290.32	Antibiotic	X	X	
Sulfamethoxazole (*)	$C_{10}H_{11}N_3O_3S$	253.27	Antibiotic	X	X	X
4-formylaminoantipyrin (FAA)	$C_{12}H_{13}N_3O_2$	231.25	Antiinflamatory		X	X
Bezafibrate (*)	$C_{19}H_{20}ClNO_4$	361.82	Fibrate drug	X	X	X
N-Acetyl-sulfamethoxazole	$C_{12}H_{13}N_3O_4S$	295.31	Antibiotic		X	X
Gabapentine	C=9	171.23	Analgesic		X	X
Phenylethylmalonamide	$C_{11}H_{14}N_2O_2$	206.24	Anticolvulsant		X	X
Caffeine	$C_8H_{10}N_4O_2$	194,19	Stimulant		X	X
Acesulfame	$C_4H_4KNO_4S$	201,24	Artificial sweetener		X	X
Benzotriazole (*)	$C_6H_5N_3$	119,13	Corrosion Inhibitor	X	X	X

Name	Chemical formula	Molecular Weight (gr/mol)	Substance class	07/2014-WET	01/2015 - DRY	05/2015-MIX
Phenylsulfonylsarcosin	$C_{11}H_{14}N_2O_2$	206,24	Metabolite of corrosion inhibitor		X	X

(*) indicates DEMEAU listed compound

Table E-0-7: Analytical results of pesticides.

No	Compound	LOQ [ng/l]	INF1 - 07/2014 -WET	INF2 - 07/2014-WET	INF - 01/2015 - DRY	INF-05/2015-MIX	BSV-01 - 07/2014-WET	BSV-01 - 01/2015 - DRY	BSV-01-05/2015-MIX	BSV-8.1 - 07/2014-WET	BSV-8.1 - 01/2015 - DRY	BSV-8.1-05/2015-MIX	BSV-8.3 - 07/2014-WET	BSV-8.3 - 01/2015 - DRY	BSV-8.3-05/2015-MIX	BSV-05 - 07/2014-WET	BSV-05 - 01/2015 - DRY	BSV-05-05/2015-MIX	BSV-09 - 07/2014-WET	BSV-09 - 01/2015 - DRY	BSV-09-05/2015-MIX	BSV-10 - 07/2014-WET	BSV-10 - 01/2015 - DRY	BSV-10-05/2015-MIX
1	PBSM	30			30	50		15	30		40	15		30	30		15	30		30	70		40	30
2	Alachlor	30			15	n.a.		15	n.a.		15	n.a.		15	n.a.		15	n.a.		15	n.a.		15	n.a.
3	Atrazine	30			15	15		15	15		15	15		15	15		15	15		15	15		15	15
4	Boscalid	30			15	15		15	15		15	15		15	15		15	15		15	15		15	15
5	Bromacil	30			15	15		15	15		15	15		15	15		15	15		15	15		15	15
6	Chlorfenvinphos	30			15	n.a.		15	n.a.		15	n.a.		15	n.a.		15	n.a.		15	n.a.		15	n.a.
7	Chloridazon	30			15	15		15	15		15	15		15	15		15	15		15	15		15	15
8	Chlortoluron	30			15	15		15	15		15	15		15	15		15	15		15	15		15	15
9	Desethylatrazin	30			15	15		15	15		15	15		15	15		15	15		15	15		15	15
10	Desethylterbutylazin	30			15	15		15	15		15	15		15	15		15	15		15	15		15	15

No	Compound	LOQ [ng/l]	INF1 - 07/2014 -WET	INF2 - 07/2014-WET	INF - 01/2015 - DRY	INF-05/2015-MIX	BSV-01 - 07/2014-WET	BSV-01 - 01/2015 - DRY	BSV-01-05/2015-MIX	BSV-8.1 - 07/2014-WET	BSV-8.1 - 01/2015 - DRY	BSV-8.1-05/2015-MIX	BSV-8.3 - 07/2014-WET	BSV-8.3 - 01/2015 - DRY	BSV-8.3-05/2015-MIX	BSV-05 - 07/2014-WET	BSV-05 - 01/2015 - DRY	BSV-05-05/2015-MIX	BSV-09 - 07/2014-WET	BSV-09 - 01/2015 - DRY	BSV-09-05/2015-MIX	BSV-10 - 07/2014-WET	BSV-10 - 01/2015 - DRY	BSV-10-05/2015-MIX
11	Desisopropylatrazin	30			15	15		15	30		40	15		30	30		15	30		30	70		40	30
12	2,6-Dichlorbenzamid	30			15	15		15	15		15	15		15	15		15	15		15	15		15	15
13	Diuron	30			30	50		15	15		15	15		15	15		15	15		15	15		15	15
14	Ethofumesate	30			15	15		15	15		15	15		15	15		15	15		15	15		15	15
15	Isoproturon	30			15	15		15	15		15	15		15	15		15	15		15	15		15	15
16	Lenacil	30			15	n.a.		15	n.a.		15	n.a.		15	n.a.		15	n.a.		15	n.a.		15	n.a.
17	Metalaxyl	30			15	n.a.		15	n.a.		15	n.a.		15	n.a.		15	n.a.		15	n.a.		15	n.a.
18	Metamitron	30			15	15		15	15		15	15		15	15		15	15		15	15		15	15
19	Metazachlor	30			15	15		15	15		15	15		15	15		15	15		15	15		15	15
20	Methyldesphenylchloridazon	30			15	15		15	15		15	15		15	15		15	15		15	15		15	15

No	Compound	LOQ [ng/l]	INF1 - 07/2014 -WET	INF2 - 07/2014-WET	INF - 01/2015 - DRY	INF-05/2015-MIX	BSV-01 - 07/2014-WET	BSV-01 - 01/2015 - DRY	BSV-01-05/2015-MIX	BSV-8.1 - 07/2014-WET	BSV-8.1 - 01/2015 - DRY	BSV-8.1-05/2015-MIX	BSV-8.3 - 07/2014-WET	BSV-8.3 - 01/2015 - DRY	BSV-8.3-05/2015-MIX	BSV-05 - 07/2014-WET	BSV-05 - 01/2015 - DRY	BSV-05-05/2015-MIX	BSV-09 - 07/2014-WET	BSV-09 - 01/2015 - DRY	BSV-09-05/2015-MIX	BSV-10 - 07/2014-WET	BSV-10 - 01/2015 - DRY	BSV-10-05/2015-MIX
21	Metolachlor	30			15	15		15	15		15	15		15	15		15	15		15	15		15	15
22	Metribuzin	30			15	15		15	15		15	15		15	15		15	15		15	15		15	15
23	Quinoxyphen	30			15	n.a.		15	n.a.		15	n.a.		15	n.a.		15	n.a.		15	n.a.		15	n.a.
24	Simazine	30			15	15		15	15		15	15		15	15		15	15		15	15		15	15
25	Terbuthylazine	30			15	15		15	15		15	15		15	15		15	15		15	15		15	15
26	Quinmerac	30			15	15		15	15		15	15		15	15		15	15		15	15		15	15
27	FAA	20			220	190		10	20		10	10		10	10		10	70		10	10		10	10
28	2,4,5-T	20			10	n.a.		10	n.a.		10	n.a.		10	n.a.		10	n.a.			n.a.		10	n.a.
29	2,4-D	20			10	10		10	10		10	10		10	10		10	10		10	10		10	10
30	Bentazon	20			10	10		10	10		10	10		10	10		10	10		10	10		10	10
31	Bromoxynil	20			10	n.a.		10	n.a.		10	n.a.		10	n.a.		10	n.a.			n.a.		10	n.a.

No	Compound	LOQ [ng/l]	INF1 - 07/2014 -WET	INF2 - 07/2014-WET	INF - 01/2015 - DRY	INF-05/2015-MIX	BSV-01 - 07/2014-WET	BSV-01 - 01/2015 - DRY	BSV-01-05/2015-MIX	BSV-8.1 - 07/2014-WET	BSV-8.1 - 01/2015 - DRY	BSV-8.1-05/2015-MIX	BSV-8.3 - 07/2014-WET	BSV-8.3 - 01/2015 - DRY	BSV-8.3-05/2015-MIX	BSV-05 - 07/2014-WET	BSV-05 - 01/2015 - DRY	BSV-05-05/2015-MIX	BSV-09 - 07/2014-WET	BSV-09 - 01/2015 - DRY	BSV-09-05/2015-MIX	BSV-10 - 07/2014-WET	BSV-10 - 01/2015 - DRY	BSV-10-05/2015-MIX
32	Dichlorprop	20			10	10		10	10		10	10		10	10		10	10		10	10		10	10
33	MCPA	20			10	100		10	10		10	10		10	10		10	10		10	10		10	10
34	Mecoprop	20	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10
35	Chlofibric acid	20			10	10		10	10		10	10		10	10		10	10		10	10		10	10

Table E-0-8: Analytical results of pharmaceuticals & other substances

No	Compound	LOQ [ng/l]	INF1 - 07/2014 -WET	INF2 - 07/2014-WET	INF - 01/2015 - DRY	INF-05/2015-MIX	BSV-01 - 07/2014-WET	BSV-01 - 01/2015 - DRY	BSV-01-05/2015-MIX	BSV-8.1 - 07/2014-WET	BSV-8.1 - 01/2015 - DRY	BSV-8.1-05/2015-MIX	BSV-8.3 - 07/2014-WET	BSV-8.3 - 01/2015 - DRY	BSV-8.3-05/2015-MIX	BSV-05 - 07/2014-WET	BSV-05 - 01/2015 - DRY	BSV-05-05/2015-MIX	BSV-09 - 07/2014-WET	BSV-09 - 01/2015 - DRY	BSV-09-05/2015-MIX	BSV-10 - 07/2014-WET	BSV-10 - 01/2015 - DRY	BSV-10-05/2015-MIX
36	Phenazone	20	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10
37	Carbamazepine	20	30	20	30	20	20	10	30	10	20	10	30	30	30	30	30	30	30	20	30	20	20	10
38	Metoprolol	20	10	10	10	10	15	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	15	10
39	Phenylethylmalonamide	20		10	10		15	10		10		10		10		10		10		10	10		15	10
40	Diclofenac	20	10	970	10	10	180	10	10	10	10	10	10	10	10	10	10	10	10	970	10	10	180	10
41	Iopromide	20	10	10	10	80	180	90	10	10	10	10	10	10	10	10	10	10	10	10	10	80	180	90
42	Ibuprofen	50		n.a.	50		n.a.	11		50		50		50		50		50		n.a.	50		n.a.	11
43	Dihydroxydihydrocarbamazepine	30		40	70		170	180		15		15		130		100		50		40	70		170	180
44	Primidone	20	10	10	20	10	10	20	10	20	10	20	10	20	10	20	10	20	10	10	20	10	10	20
45	Trimethoprim	30	15	15	n.a.	15	30	n.a.	15	n.a.	15	n.a.	15	n.a.	15	n.a.	15	n.a.	15	15	n.a.	15	30	n.a.

No	Compound	LOQ [ng/l]	INF1 - 07/2014 -WET	INF2 - 07/2014-WET	INF - 01/2015 - DRY	INF-05/2015-MIX	BSV-01 - 07/2014-WET	BSV-01 - 01/2015 - DRY	BSV-01-05/2015-MIX	BSV-8.1 - 07/2014-WET	BSV-8.1 - 01/2015 - DRY	BSV-8.1-05/2015-MIX	BSV-8.3 - 07/2014-WET	BSV-8.3 - 01/2015 - DRY	BSV-8.3-05/2015-MIX	BSV-05 - 07/2014-WET	BSV-05 - 01/2015 - DRY	BSV-05-05/2015-MIX	BSV-09 - 07/2014-WET	BSV-09 - 01/2015 - DRY	BSV-09-05/2015-MIX	BSV-10 - 07/2014-WET	BSV-10 - 01/2015 - DRY	BSV-10-05/2015-MIX
46	Sulfamethoxazole	20	10	20	10	20	50	50	10	10	10	10	10	10	10	20	10	20	10	20	10	20	50	50
47	Bezafibrate	20	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10
48	N-Acetyl-sulfamethoxazole	20		10	10		30	10		10		10		10		10		10		10	10		30	10
49	Gabapentine	30		15	15		750	650		15		15		300		100		15		15	15		750	650
50	Caffeine	10		190	150		420	210		150		50		320		50		50		190	150		420	210
51	Acesulfame			290	120		2000	1400		150		210		770		1100		390		290	120		2000	1400
52	Benzotriazole	50	25	25	25	360	310	270	320	25	120	25	220	190	110	25	25	25	25	25	25	360	310	270
53	Phenylsulfonylsarcosin	20		10	10		10	10		10		10		10		10		10		10	10		10	10
36	Phenazone	20	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10
37	Carbamazepine	20	30	20	30	20	20	10	30	10	20	10	30	30	30	30	30	30	30	20	30	20	20	10
38	Metoprolol	20	10	10	10	10	15	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	15	10

No	Compound	LOQ [ng/l]	INF1 - 07/2014 -WET	INF2 - 07/2014-WET	INF - 01/2015 - DRY	INF-05/2015-MIX	BSV-01 - 07/2014-WET	BSV-01 - 01/2015 - DRY	BSV-01-05/2015-MIX	BSV-8.1 - 07/2014-WET	BSV-8.1 - 01/2015 - DRY	BSV-8.1-05/2015-MIX	BSV-8.3 - 07/2014-WET	BSV-8.3 - 01/2015 - DRY	BSV-8.3-05/2015-MIX	BSV-05 - 07/2014-WET	BSV-05 - 01/2015 - DRY	BSV-05-05/2015-MIX	BSV-09 - 07/2014-WET	BSV-09 - 01/2015 - DRY	BSV-09-05/2015-MIX	BSV-10 - 07/2014-WET	BSV-10 - 01/2015 - DRY	BSV-10-05/2015-MIX
39	Phenylethylmalonamide	20		10	10		15	10		10		10		10		10		10		10	10		15	10
40	Diclofenac	20	10	970	10	10	180	10	10	10	10	10	10	10	10	10	10	10	10	970	10	10	180	10
41	Iopromide	20	10	10	10	80	180	90	10	10	10	10	10	10	10	10	10	10	10	10	10	80	180	90
42	Ibuprofen	50		n.a.	50		n.a.	11		50		50		50		50		50		n.a.	50		n.a.	11
43	Dihydroxydihydrocarbamazepine	30		40	70		170	180		15		15		130		100		50		40	70		170	180
44	Primidone	20	10	10	20	10	10	20	10	20	10	20	10	20	10	20	10	20	10	10	20	10	10	20
45	Trimethoprim	30	15	15	n.a.	15	30	n.a.	15	n.a.	15	n.a.	15	n.a.	15	n.a.	15	n.a.	15	15	n.a.	15	30	n.a.
46	Sulfamethoxazole	20	10	20	10	20	50	50	10	10	10	10	10	10	10	20	10	20	10	20	10	20	50	50
47	Bezafibrate	20	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10
48	N-Acetyl-sulfamethoxazole	20		10	10		30	10		10		10		10		10		10		10	10		30	10
49	Gabapentine	30		15	15		750	650		15		15		300		100		15		15	15		750	650

No	Compound	LOQ [ng/l]	INF1 - 07/2014 -WET	INF2 - 07/2014-WET	INF - 01/2015 - DRY	INF-05/2015-MIX	BSV-01 - 07/2014-WET	BSV-01 - 01/2015 - DRY	BSV-01-05/2015-MIX	BSV-8.1 - 07/2014-WET	BSV-8.1 - 01/2015 - DRY	BSV-8.1-05/2015-MIX	BSV-8.3 - 07/2014-WET	BSV-8.3 - 01/2015 - DRY	BSV-8.3-05/2015-MIX	BSV-05 - 07/2014-WET	BSV-05 - 01/2015 - DRY	BSV-05-05/2015-MIX	BSV-09 - 07/2014-WET	BSV-09 - 01/2015 - DRY	BSV-09-05/2015-MIX	BSV-10 - 07/2014-WET	BSV-10 - 01/2015 - DRY	BSV-10-05/2015-MIX
50	Caffeine	10		190	150		420	210		150		50		320		50		50		190	150		420	210
51	Acesulfame			290	120		2000	1400		150		210		770		1100		390		290	120		2000	1400
52	Benzotriazole	50	25	25	25	360	310	270	320	25	120	25	220	190	110	25	25	25	25	25	25	360	310	270
53	Phenylsulfonylsarcosin	20		10	10		10	10		10		10		10		10		10		10	10		10	10

Annex F Bioassays SVH

Table F-0-9: Activities (ng or µg reference compound equivalent concentration/L water sample) detected in the in vitro bioassays for the MAR water samples from the SVH sampling site collected at two time points: 07/2014 (Campaign I) and 05/2015 (Campaign II)

												Combined algae assay	
		Cytotox CALUX	Erα CALUX	antiAR CALUX	antiPR CALUX	GR CALUX	PPARg2 CALUX	p53 CALUX	p53 S9 CALUX	Nrf2 CALUX	Microtox assay	PSII inhibition 2 h	Growth inhibition
Sample name	**Campaign**	-	ng 17ß-estradiol eq./L water	ng Flutamide eq./L water	ng Ru486 eq./L water	ng Dexamethasone eq./L water	ng Rosiglitazone eq./L water	µg Actinomycin D eq./L water	µg Cyclophosphamide eq./L water	µg Curcumine eq./L water	Baseline TEQ mg/L water	ng Diuron eq./L water	mg baseline toxicity eq./L water
INF01	**I.**	+	LOD (<0.03)	85300	1.65	< LOD (0.9)	LOD (<33.7)	LOD (<0.04)	LOD (<2400)	165	-	46.5	0.88
	II.	-	LOD (<0.04)	LOD (<1500)	LOD (<0.06)	< LOD (4.5)	LOD (<45)	LOD (<0.01)	LOD (<290)	40	0.48	56.0	0.74
INF02	**I.**	+	LOD (<0.03)	74700	1.03	< LOD (0.9)	LOD (<33.7)	LOD (<0.04)	LOD (<2400)	57	-	40.5	0.61
	II.	-	-	-	-	-	-	-	-	-	-	-	-
BSV-1	**I.**	-	LOD (<0.01)	6900	<LOQ (0.03)	< LOD (0.9)	LOD (<11.2)	LOD (<0.04)	LOD (<2400)	LOD (<17)		20.6	0.14
	II.	-	LOD	LOD (<1500)	1.5	< LOD (4.5)	LOD (<45)	LOD (<0.01)	LOD (<290)	44	0.24	8.7	0.00

												Combined algae assay	
		Cytotox CALUX	Erα CALUX	antiAR CALUX	antiPR CALUX	GR CALUX	PPARg2 CALUX	p53 CALUX	p53 S9 CALUX	Nrf2 CALUX	Microtox assay	PSII inhibition 2 h	Growth inhibition
Sample name	Campaign	-	ng 17ß-estradiol eq./L water	ng Flutamide eq./L water	ng Ru486 eq./L water	ng Dexamethasone eq./L water	ng Rosiglitazone eq./L water	µg Actinomycin D eq./L water	µg Cyclophosphamide eq./L water	µg Curcumine eq./L water	Baseline TEQ mg/L water	ng Diuron eq./L water	mg baseline toxicity eq./L water
			(<0.04)										
BSV-5	**I.**	-	LOD (<0.01)	2500	LOD (<0.02)	< LOD (0.9)	LOD (<11.2)	LOD (<0.04)	LOD (<2400)	LOD (<17)	-	12.4	0.30
	II.	-	0.23	25000	3.4	< LOD (4.5)	<LOQ (110)	LOD (<0.01)	LOD (<290)	LOD (<15)	0.25	14.5	0.00
BSV-8.1	**I.**	-	LOD (<0.01)	LOD (<1500)	0.10	< LOD (0.9)	LOD (<11.2)	LOD (<0.04)	22700	LOD (<17)	-	48.5	3.42
	II.	-	LOD (<0.04)	4900	2.3	< LOD (4.5)	LOD (<45)	LOD (<0.01)	LOD (<290)	83	0.50	15.8	0.75
BSV-8.3	**I.**	-	< LOQ (0.01)	6200	0.06	< LOD (0.9)	LOD (<11.2)	LOD (<0.04)	LOD (<2400)	19	-	23.8	0.76
	II.	-	LOD (<0.04)	LOD (<1500)	LOD (<0.14)	< LOD (4.5)	LOD (<45)	LOD (<0.01)	LOD (<290)	39	0.31	6.9	0.10
BSV-9	**I.**	-	LOD (<0.01)	8900	0.22	< LOD (0.9)	LOD (<11.2)	LOD (<0.04)	LOD (<2400)	LOD (<17)	-	14.2	0.49
	II.	-	LOD (<0.04)	<LOQ(2600)	1.4	< LOD (4.5)	LOD (<45)	LOD (<0.01)	LOD (<290)	50	0.38	15.6	0.29
BSV-	**I.**	-	LOD	3400	LOD (<0.02)	< LOD (0.9)	LOD (<11.2)	LOD (<0.04)	LOD (<2400)	44	-	11.9	0.23

												Combined algae assay	
		Cytotox CALUX	Erα CALUX	antiAR CALUX	antiPR CALUX	GR CALUX	PPARg2 CALUX	p53 CALUX	p53 S9 CALUX	Nrf2 CALUX	Microtox assay	PSII inhibition 2 h	Growth inhibition
Sample name	Campaign	-	ng 17ß-estradiol eq./L water	ng Flutamide eq./L water	ng Ru486 eq./L water	ng Dexamethasone eq./L water	ng Rosiglitazone eq./L water	µg Actinomycin D eq./L water	µg Cyclophosphamide eq./L water	µg Curcumine eq./L water	Baseline TEQ mg/L water	ng Diuron eq./L water	mg baseline toxicity eq./L water
10			(<0.01)										
	II.	-	LOD (<0.04)	LOD (<1500)	LOD (<0.06)	< LOD (4.5)	LOD (<45)	LOD (<0.01)	LOD (<290)	39	0.41	11.0	0.21
Negative control	**I.**	-	LOD (<0.03)	< LOQ (242)	0.08	< LOD (0.9)	LOD (<11.2)	LOD (<0.04)	LOD (<2400)	LOD (<17)	-	0.6	0.37
	II.	-	LOD (<0.06)	LOD (<2500)	LOD (<0.03)	< LOD (7.6)	LOD (<76)	LOD (<0.01)	LOD (<290)	LOD (<15)	0.0	0.0	0.00

***Samples extracts were also measured in the p53 CALUX assay with metabolitic activation by adding 59 enzyme mix**

****Photosynthesis inhibition was measured 2 hours after exposure**

***** Growth inhibition was measured 24 hours after exposure**

****** Not analysed**

Annex G MAR Profile SVH

Table G-0-10: MAR profile at Sant Vicenç dels Horts.

MAR component	Attribute		Description
General information	Country		Spain
	City		Barcelona
	Site name		Sant Vicenç dels Horts infiltration system
	Operator name		Agència Catalana de l'Aigua
	Type of MAR (e.g. Well injection and recovery, Aquifer transfer and recovery, bank filtration etc.)		Infiltration Ponds
	Year commenced		2008
	Current status		Full operation
	Map coordinates		41.39/ 2.02
	Operational scale (m^3/a)		~ 1.8
	Objective		Environmental
Capture zone	Influent source (Type of water used for recharge)		River water (Reclaimed water in future)
Pre-treatment	Source water treatment before recharge		Settling basin
Recharge	No of recharge facilities		2 ponds (1 recharge, 1 settling)
	Hydraulic loading rate (m^3/m^2 d)		~ 1
	Recharged volume (m^3/a)		~ 1.8
Sub-surface	Residence time (d) of recharged water in the sub-surface until recovery		unknown
	Aquifer properties	Range of hydraulic conductivity representative for the target aquifer (m/s)	1×10^{-2}
		Lithology of target aquifer	porous
		Range of thickness of unsaturated zone (m)	Few m
		Thickness of target aquifer (m)	Up to 10
Recovery	Distance of recovery wells from point of recharge (m)		-
	Recovered volume (m^3/a)		-

MAR component	Attribute	Description
	Recovered infiltrate (%) Average percentage of recovered infiltrate (in case of bank filtration share of bank-filtrate in abstraction wells)	-
	No of recovery facilities (e.g. no. of wells, drains)	-
Post-treatment	Water treatment after recovery	-
End-use	Final use of water recharged by the facility	Environmental (aquifer is used for agriculture, drinking water, industry)

Annex H Environmental quality standards for groundwater bodies CAS

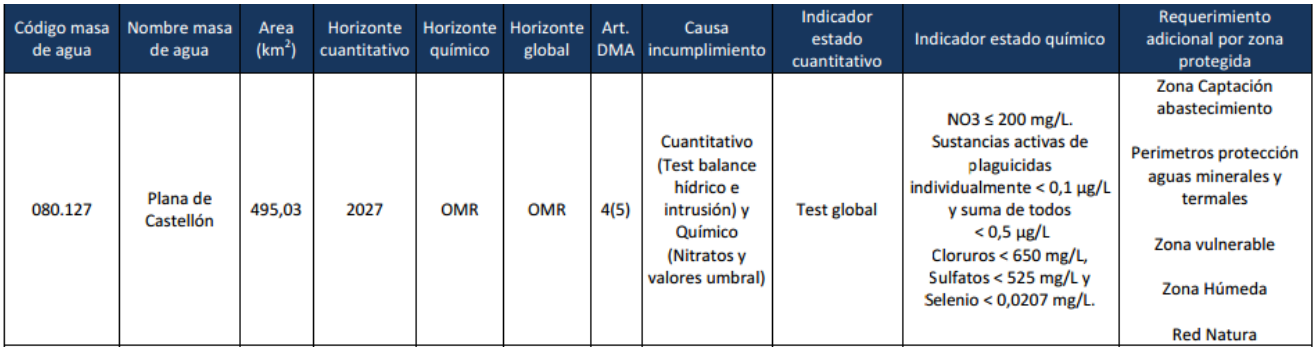
Table H-0-11: Environmental quality standards for groundwater bodies in Castellón

	Nitrate [mg/L]	Pesticides [µg/L]	Chloride [mg/L]	Sulphate [mg/L]	Selenium [mg/L]
Chemical status indicator (*)	< 200	Individual concentration of active substances < 0.1 µg/L Total pesticides < 0.5 µg/L	< 650	< 525	0.0207
WWTP Effluent 10/02/2012 [a]	46.9	Chlorphirifos = 0.6 µg/L Molinate = 2.6 µg/L Terbutilazine = 0.26 µg/L Total pesticides = 3.96 µg/L	156	204	Not reported
WWTP Effluent 20/05/2014	130 [b]	Pesticides < < 0.1 µg/L [c] Total pesticides < 0.5 µg/L [c]	168 [b]	260 [b]	Not reported
WWTP Effluent 20/01/2015	5 [b]	Pesticides < < 0.1 µg/L [d] Total pesticides < 0.5 µg/L [d]	142 [b]	187 [b]	Not reported
WWTP Effluent 15/04/2015	64 [b]	Pesticides < < 0.1 µg/L [d] Total pesticides < 0.5 µg/L [d]	107 [b]	106 [b]	Not reported

(a) Aklabs Laboratory. Source: Water Recovery Project report. Internal report.
(b) IGME Laboratory: Source: sampling campaign DEMEAU (this report)
(c) Göttingen University Laboratory: Source: sampling campaign DEMEAU (this report)
(d) University of Castellón (UJI): Source: sampling campaign DEMEAU (this report)

(*) Source: CHJ, 2014 (Environmental objectives for the accomplishment of WFD):

Table H-0-12: Threshold values established in the adaptation of WFD in Spain (original table):



Código masa de agua	Nombre masa de agua	Area (km^2)	Horizonte cuantitativo	Horizonte químico	Horizonte global	Art. DMA	Causa incumplimiento	Indicador estado cuantitativo	Indicador estado químico	Requerimiento adicional por zona protegida
080.127	Plana de Castellón	495,03	2027	OMR	OMR	4(5)	Cuantitativo (Test balance hídrico e intrusión) y Químico (Nitratos y valores umbral)	Test global	NO3 ≤ 200 mg/L. Sustancias activas de plaguicidas individualmente < 0,1 µg/L y suma de todos < 0,5 µg/L Cloruros < 650 mg/L, Sulfatos < 525 mg/L y Selenio < 0,0207 mg/L.	Zona Captación abastecimiento Perimetros protección aguas minerales y termales Zona vulnerable Zona Húmeda Red Natura

Annex I MAR profile CAS

Table I-0-13: MAR profile at La Vall d'Uixó

MAR component	Attribute		Description
General information	Country		Spain
	City		Vall d'Uixó
	Site name		Aquifer Recharge system of la Vall d'Uixó
	Operator name		AQUAMED
	Type of MAR (e.g. Well injection and recovery, Aquifer transfer and recovery, bank filtration etc.)		Injection wells
	Year commenced		2012
	Current status		Experimental – pilot scale
	Map coordinates		40.018/ -0.15
	Operational scale (m^3/a)		Pilot
	Objective		Irrigation
Capture zone	Influent source (Type of water used for recharge)		River water (Reclaimed water in future)
Pre-treatment	Source water treatment before recharge		Storage pond
Recharge	No of recharge facilities		2 injection wells
	Hydraulic loading rate (m^3/m^2 d)		100 L/s each well
	Recharged volume (m^3/a)		Puntual
Sub-surface	Residence time (d) of recharged water in the sub-surface until recovery		unknown
	Aquifer properties	Range of hydraulic conductivity representative for the target aquifer (m/s)	$1.4x10^{-3}$ - $3.5×10^{-4}$
		Lithology of target aquifer	porous
		Range of thickness of unsaturated zone (m)	Between 10 – 50
		Thickness of target aquifer (m)	100 – 500 m
Recovery	Distance of recovery wells from point of recharge (m)		Unknown (private wells for irrigation)
	Recovered volume (m^3/a)		Unknown (private wells for irrigation)

MAR component	Attribute	Description
	Recovered infiltrate (%) Average percentage of recovered infiltrate (in case of bank filtration share of bank-filtrate in abstraction wells)	More than 20 wells in the area
	No of recovery facilities (e.g. no. of wells, drains)	
Post-treatment	Water treatment after recovery	None
End-use	Final use of water recharged by the facility	Agriculture, Irrigation of citric crops (orange and clementine)

Annex J Bulk chemistry CAS

Table J-0-14: **List of chemical parameters analysed in sampling campaigns**

Parameters		Unit
General parameters	Temperature	ºC
	Turbidity	NTU
	pH	Units of pH
	Electrical Conductivity	µS/cm
	COD	mg O_2/L
	BOD_5	mg O_2/L
	TOC	mg C/L
	Total hardness	mg HCO_3/L
Major compounds	Nitrate	mg/L
	Total nitrogen	mg/L
	Ammonium	mg/L
	Chloride	mg/L
	Total Phosphorous	mg/L
	Sulphate	mg/L

Parameters		Unit
Metals	Sodium	mg/L
	Potassium	mg/L
	SiO_2	mg/L
	Zinc	mg/L
	Lead	mg/L
	Chromium (VI)	mg/L
	Calcium	mg/L
	Magnesium	mg/L
	Arsenic	mg/L
	Bromine	mg/L
	Aluminum	µg/L
	Barium	µg/L
	Strontium	µg/L
	Manganese	µg/L
	Total Chromium	µg/L
	Iron	µg/L
Aggregated indexes	Ion balance	%
	SAR index	meq

Table J-0-15: **Bulk chemistry of groundwater samples**

	RANDERO 04/2012	RANDERO 05/2014	RANDERO 01/2015	RANDERO 04/2015	RAMBLETA 2 04/2012	RAMBLETA 2 05/2014	RAMBLETA 2 01/2015	RAMBLETA 2 04/2015	PRIMITIVA 04/2012	PRIMITIVA 05/2014	PRIMITIVA 01/2015	PRIMITIVA 04/2015	LA PAZ 04/2012	LA PAZ 05/2014	LA PAZ 01/2015	LA PAZ 04/2015	SAN VICENTE 04/2012	SAN VICENTE 05/2014	SAN VICENTE 01/2015	SAN VICENTE 04/2015
	CAS-08	CAS-08	CAS-08	CAS-08	CAS-09	CAS-09	CAS-09	CAS-09	CAS-10	CAS-10	CAS-10	CAS-10	CAS-07	CAS-07	CAS-07	CAS-07	CAS-06	CAS-06	CAS-06	CAS-06
Turbidity [NTU]																				
pH	7.33	7.24	7.08	7.17	7.62	7.64	7.23	8.12	7.43	7.2	7.13	7.2	7.42	7.66	7.5	7.17	7.57	7.35	7.28	7.48
E. Conductivity	2660	280	2770	2420	2300	3410	3340	454	3360	3930	3090	2720	4340	3930	4370	4540	3090	3460	3780	3740
Suspended																				
COD [mgO2/L]																				
BOD5[mgO2/L]																				
TOC [mgC/L]			0.71	0.02		0.6	1.53	1.43		0.78	23.3	0.52		0.64	21.4	0.75		1.73	2.89	1.82
Nitrate [mg/L]	270	310	260	280	300	410	380	18	400	300	320	320	360	340	280	260	300	230	190	230
Total nitrogen																				
Ammonium		0	0	0		0	0	0		0	0	0		0	0	0		0	0	0
Chloride [mg/L]	454	446	428	396	440	576	572	17	470	544	536	492	1030	764	880	1010	530	644	680	712
Total		0	0	0		0	0	0.32		0.13	0	0		0.13	0	0		0.45	0	0.49
Sulphate [mg/L]	320	332	350	288	232	384	360	46	512	332	348	332	500	480	528	556	448	436	460	496

	RANDERO 04/2012	RANDERO 05/2014	RANDERO 01/2015	RANDERO 04/2015	RAMBLETA 2 04/2012	RAMBLETA 2 05/2014	RAMBLETA 2 01/2015	RAMBLETA 2 04/2015	PRIMITIVA 04/2012	PRIMITIVA 05/2014	PRIMITIVA 01/2015	PRIMITIVA 04/2015	LA PAZ 04/2012	LA PAZ 05/2014	LA PAZ 01/2015	LA PAZ 04/2015	SAN VICENTE 04/2012	SAN VICENTE 05/2014	SAN VICENTE 01/2015	SAN VICENTE 04/2015
	CAS-08	CAS-08	CAS-08	CAS-08	CAS-09	CAS-09	CAS-09	CAS-09	CAS-10	CAS-10	CAS-10	CAS-10	CAS-07	CAS-07	CAS-07	CAS-07	CAS-06	CAS-06	CAS-06	CAS-06
Lead [µg/L]		0.02	1.14	1.93		0.91	1.57	2.11		1.04	1.56	1.79		1.73	180	28.6		10.7	0.04	6.33
Zinc [mg/L]		6.34	23.3	8.26		12.5	64.8	12.3		13.2	13.1	11.9		15.9	259	18.6		24.5	22.5	25.1
Aluminium		5.3	10.6	15.6		13	12.8	39.6		21.4	9.17	17.3		17.2	3507	608		10.7	9.54	69.6
Barium (µg/L)		44.6	40.8	48.9		68.3	63.9	68.3		51.4	44.5	46.7		31.8	100	67.2		50.3	42.8	51.9
Br [mg/L]	0.0011	1.27	0.87	0.88	0.0008	1.43	1.08	0.06	0.0012	1.35	1.3	1.03	0.0019	1.82	1.73	1.86	0.0014	1.76	1.50	1.63
Sodium [mg/L]	107	125	118	122	65	118	107	11	120	125	125	132	273	200	304	371	226	187	199	277
K [mg/L]	9	7	6	5	3	3	2	1	4	4	4	4	4	9	4	5	11	6	6	6
SiO2 [mg/L]	13.3	14.5	15	15	10.1	12.8	13.1	7.8	14.7	15.6	16.4	15.9	13.9	15.2	16.5	16	13.6	24.7	28.3	27.4
Sr [µg/L]	855	109	103	982	624	1241	1104	230	928	1208	1135	1084	732	755	1468	1569	817	1445	1377	1413
Mn [µg/L]		4.35	13.3	5.38		3.72	4.98	6.96		1	1	1		1	263	27.2		595	557	564
Total Chromium	0.1				0.39				0.31				0.31				0.68			
Chromium (VI)																				
Total hardness	178	248	223	243	157	128	189	203	187	236	231	246	176	271	248	253	231	293	320	320
Calcium [mg/L]	268	300	256	228	290	336	368	56	300	326	308	272	316	304	332	358	240	324	320	300
Magnesium	118	114	110	111	100	152	132	25	172	128	140	134	228	208	192	204	128	156	160	164

	RANDERO 04/2012	RANDERO 05/2014	RANDERO 01/2015	RANDERO 04/2015	RAMBLETA 2 04/2012	RAMBLETA 2 05/2014	RAMBLETA 2 01/2015	RAMBLETA 2 04/2015	PRIMITIVA 04/2012	PRIMITIVA 05/2014	PRIMITIVA 01/2015	PRIMITIVA 04/2015	LA PAZ 04/2012	LA PAZ 05/2014	LA PAZ 01/2015	LA PAZ 04/2015	SAN VICENTE 04/2012	SAN VICENTE 05/2014	SAN VICENTE 01/2015	SAN VICENTE 04/2015
	CAS-08	CAS-08	CAS-08	CAS-08	CAS-09	CAS-09	CAS-09	CAS-09	CAS-10	CAS-10	CAS-10	CAS-10	CAS-07	CAS-07	CAS-07	CAS-07	CAS-06	CAS-06	CAS-06	CAS-06
Arsenic [mg/L]	0.00014				0.0002				0.0001				0.0002				0.0008			
Fe (µg/L)		91.2	392	263		194	147	120		30	59.7	132		30	3897	567		64.4	373	377
Calculated values																				
Ion balance [%]	4.47	4.81	-0.36	1.07	3.78	4.53	3.21	5.74	2.98	4.35	3.51	1.52	-3.48	-0.62	3.13	5.09	-0.86	4.12	2.34	3.25
SAR index	1.4	1.6	1.6	1.7	0.8	1.3	1.2	0.3	1.4	1.5	1.5	1.6	2.9	2.2	3.3	3.9	2.9	2.1	2.3	3.2

Table J-0-16: Bulk chemistry of WWTP effluent, Belcaire River and groundwater monitoring Piezo 1+2 wells.

	WWTP				average	Belcaire River			Average	1:1 blend	Piezo 1			Piezo 2		
	Historical 02/02/2012	DEMEAU May 2014	DEMEAU Jan 2015	DEMEAU April 2015		DEMEAU May 2014	DEMEAU Jan 2015	DEMEAU April 2015			DEMEAU May 2014	DEMEAU Jan 2015	DEMEAU April 2015	DEMEAU May 2014	DEMEAU Jan 2015	DEMEAU April 2015
Turbidity [NTU]	1.77				1.77											
pH	7.64	7.36	7.59	7.27	7.465	8.04	7.8	4.29	6.7	7.09	7.43	7.11	7.08	7.45	7.39	7.17
E. Conductivity [µS/cm]	1408	1432	1454	1023	1329	232	352	347	310.3	819.79	583	1970	2100	327	893	1245
Suspended Solids [mg/L]	7.2				7.2											
COD [mgO2/L]	72				72											
BOD5[mgO2/L]	16				16											
TOC [mgC/L]		16.78	0.57	16.4	11.26	8.28	0.03	11.7	6.7	8.95	2.52	0.025	0.7	3.21	0.025	1.32
Nitrate [mg/L]	46.9	130	5	64	61.48	0	-	0	0.0	30.74	27	180	220	4	68	140
Total nitrogen [mg/L]	46				46											
Ammonium [mg/L]	34			0	17			0.44	0.4	8.72	0	0	0	0	0	0
Chloride [mg/L]	156	168	142	107	143.3	14	21	22	19.0	81.13	68	340	350	19	136	210
Total Phosporous[mg/L]	3.7				3.7						0	0	0	0	0	0.16
Sulphate [mg/L]	204	260	187	106	189.3	37	50	45	44.0	116.63	85	252	282	45	121	162
Lead [µg/L]	0.27				0.27						0.38	0.02	1.18	0.23	0.2	0.72

	WWTP				average	Belcaire River			Average	1:1 blend			Piezo 1			Piezo 2
	Historical 02/02/2012	DEMEAU May 2014	DEMEAU Jan 2015	DEMEAU April 2015		DEMEAU May 2014	DEMEAU Jan 2015	DEMEAU April 2015			DEMEAU May 2014	DEMEAU Jan 2015	DEMEAU April 2015	DEMEAU May 2014	DEMEAU Jan 2015	DEMEAU April 2015
Zinc [mg/L]	2.42			12.6	7.51						6.28	10.7	10.4	5.15	6.31	5.06
Aluminium (µg/L)				13.6	13.6			370	370.0	191.80	8.24	13.7	18.8	10.1	7.37	8.41
Barium (µg/L)				11.8	11.8			63.2	63.2	37.50	41.4	95.3	109	38.5	79.3	115
Br [mg/L]	0.16				0.16						0.18	0.683	0.789	0.1	0.284	0.491
Sodium [mg/L]	95	130	120	111	114	12	14	19	15.0	64.50	35	90	117	16	45	72
K [mg/L]											3	6	7	2	4	5
SiO2 [mg/L]											10.7	14	13.8	9.9	11.8	12.6
Sr [µg/L]											298	869	894	170	411	590
Mn [µg/L]											60.8	92.3	185	31.9	81.7	40.4
Total Chromium [µg/L]	25															
Chromium (VI) [mg/L]	0.003															
Total hardness [mg HCO3/L]	439	272	400	304	353.8	74	118	138	110.0	231.88	156	203	233	119	134	149
Calcium [mg/L]	102	120	92	75	97.25	11	28	30	23.0	60.13	61	204	220	35	92	128
Magnessium [mg/L]	45	47	46	28	41.5	17	19	17	17.7	29.58	29	87	99	14	39	61
Arsenic[mg/L]																

	WWTP				average	Belcaire River			Average	1:1 blend			Piezo 1			Piezo 2
	Historical 02/02/2012	DEMEAU May 2014	DEMEAU Jan 2015	DEMEAU April 2015		DEMEAU May 2014	DEMEAU Jan 2015	DEMEAU April 2015			DEMEAU May 2014	DEMEAU Jan 2015	DEMEAU April 2015	DEMEAU May 2014	DEMEAU Jan 2015	DEMEAU April 2015
Fe (µg/L)		156	188	114	152.7	151	127		139.0	145.83	9651	13747	32068	6627	13703	15348
Calculated																
Ion balance [%]	-24.91	-7.44	-6.7	-3.3	-	29.4	0.11	-32.5	-	-	3.99	0.87	4.66	2.99	1.1	3.78
SAR index					2.4				0.6							

Annex K Organic micro pollutants CAS

Table K-0-17: **Results of organic pollutants in the WWTP effluent**

			05.06.2014	05.06.2014	20.01.2015	15.04.2015	08.06.2014	08.06.2014	18.01.2015	12.04.2015
			Work. DAY	Work. DAY	Work. DAY	Work. DAY	Weekend	Weekend	Weekend	Weekend
Application	**Compound**	**LOQ [ng/l]**	**CAS 01**	**CAS 02**	**CAS 01**	**CAS 01**	**CAS 03**	**CAS 04**	**CAS 03**	**CAS 03**
Analgesics and anti-inflamatories	Diclofenac*	10	965	1026	538	769	1084	1128	408	802
	Ibuprofen*	18	na	na	9	-	na	na	9	-
	Naproxen	24	35	54	na	na	95	103	na	na
	Paracetamol	19	8.5	8.5	na	na	8.5	8.5	na	na
	Phenazone*	10	567	614	612	563	468	452	145	607
	Acetaminophen	19	na	na	106	42	na	na	44	36
	Benzoylecgonine	12	na	na	226	898	na	na	585	197
	4-Acetaminoantipyrine (Metamizole metabolite)	15	3018	3386	na	na	6095	7132	na	na
Stimulants and caffeine metabolites	Caffeine	22	1895	2002	na	na	2525	3062	na	na
	Paraxanthine	16	1383	1380	na	na	2247	2306	na	na
	Theobromine	26	1796	1882	na	na	3132	3212	na	na

			05.06.2014	05.06.2014	20.01.2015	15.04.2015	08.06.2014	08.06.2014	18.01.2015	12.04.2015
			Work. DAY	Work. DAY	Work. DAY	Work. DAY	Weekend	Weekend	Weekend	Weekend
Application	**Compound**	**LOQ [ng/l]**	**CAS 01**	**CAS 02**	**CAS 01**	**CAS 01**	**CAS 03**	**CAS 04**	**CAS 03**	**CAS 03**
	Theophylline	17	468	489	na	na	447	582	na	na
	1-Methylxanthine	105	2380	2452	na	na	4901	5381	na	na
	3-Methylxanthine	140	5888	6379	na	na	10413	10856	na	na
Antihypertensive agents	**Atenolol**	18	48	45	na	na	49	49	na	na
	Metoprolol*	21	10.5	10.5	36	30	10.5	10.5	26	21
	Sotalol	24	12	12	na	na	12	12	na	na
	Valsartan	15	24632	25523	23172	23350	23945	25168	13509	24283
	Losartan	10	1144	1164	na	na	1098	1141	na	na
	Irbesartan	10	2550	2527	1547	1147	2434	2351	1123	1246
Contrast medium	**Iopromide***	90	8995	8942	1244	6734	4794	4694	2362	8616
Antibiotics	**Clarithromycin**	38	17	17	na	na	17	17	na	na
	Erythromycin	22	11	11	na	na	11	11	na	na
	Roxithromycin	48	24	24	na	na	24	24	na	na
	Sulfamethoxazole*	13	301	303	140	153	342	328	115	158
	Trimethoprim*	13	241	248	103	145	197	185	81	102
Lipid regulators	**Bezafibrate***	18	9	9	1219	1095	9	9	780	1270

			05.06.2014	05.06.2014	20.01.2015	15.04.2015	08.06.2014	08.06.2014	18.01.2015	12.04.2015
			Work. DAY	Work. DAY	Work. DAY	Work. DAY	Weekend	Weekend	Weekend	Weekend
Application	**Compound**	**LOQ [ng/l]**	**CAS 01**	**CAS 02**	**CAS 01**	**CAS 01**	**CAS 03**	**CAS 04**	**CAS 03**	**CAS 03**
	Clofibric acid	17	8.5	8.5	na	na	8.5	8.5	na	na
	Gemfibrozil*	10	5.0	5.0	327.0	416	19	17	359	322
Antihistamines	**Cetirizine**	11	308	327	na	na	285	299	na	na
	Loratadine	14	7	7	na	na	7	7	na	na
Anticonvulsants and sedatives	**Carbamazepine***	11	148	137	84	73	124	128	97	86
	Diazepam	7.0	27	30	na	na	24	25	na	na
	Primidone*	14	39	44	151	37	28	23	57	28
	Tetrazepam	13	6.5	6.5	na	na	6.5	6.5	na	na
SSRI (selective serotonin and norepinephrine reuptake inhibitors)	**Citalopram**	16	83	86	na	na	70	72	na	na
	Fluoxetine	80	40	40	na	na	40	40	na	na
	Sertraline	80	40	40	na	na	40	40	na	na
	Venlafaxine	5.0	na	na	962	831	na	na	619	801
Pesticides and pesticide metabolites	**Atrazine**	7.0	3.5	3.5	na		3.5	3.5	na	na
	Desethylatrazine (DEA)	8.5	4.3	4.3	11	-	4.3	4.3	12	-
	Desisopropylatrazine	28	14	14	16	-	14	14	19	-
	Diuron	17	8.5	8.5	na		8.5	8.5	na	na

			05.06.2014	05.06.2014	20.01.2015	15.04.2015	08.06.2014	08.06.2014	18.01.2015	12.04.2015
			Work. DAY	Work. DAY	Work. DAY	Work. DAY	Weekend	Weekend	Weekend	Weekend
Application	**Compound**	**LOQ [ng/l]**	**CAS 01**	**CAS 02**	**CAS 01**	**CAS 01**	**CAS 03**	**CAS 04**	**CAS 03**	**CAS 03**
	Isoproturon	15	7.5	7.5	na		7.5	7.5	na	na
	Mecoprop	6.0	3.0	3.0	na		3.0	3.0	na	na
	Metazachlor	9.0	4.5	4.5	na		4.5	4.5	na	na
Corrosion inhibitors	1H-Benzotriazole	24	2152	2222	na		2056	2163	na	na
	Tolyltriazole	25	4729	4996	na		4857	4875	na	na
Cocaine metabolite	Benzoylecgonine	12	550	588	na		1274	1274	na	na
Proton pump	Pantoprazole	24	26	34	12	12	32	42	12	12
Antipsychotic	Haloperidol	20	10	10	na	na	10	10	na	na
Breast cancer	Tamoxifen	30	15	15	na	na	15	15	na	na
Nicotine metabolite	Cotinine	15	7.5	7.5	na	na	7.5	7.5	na	na
Herbicide	Terbuthylazine	10	150	155	15	23	122	125	9	70
	Simazine	-	na	na	2.5	1.1	na	na	2	2.1
Aten./Metopr.	Atenololic acid	20	10	10	na	na	10	10	na	na
SMX-TP	Desamino-SMX	7.5	3.75	3.75	na	na	3.75	3.75	na	na
	4-Nitro-SMX	5.0	2.5	2.5	na	na	2.5	2.5	na	na
Metamizole	4-Acetaminoantipyrine	15	3018	3386	na	na	6095	7132	na	na

			05.06.2014	05.06.2014	20.01.2015	15.04.2015	08.06.2014	08.06.2014	18.01.2015	12.04.2015
			Work. DAY	Work. DAY	Work. DAY	Work. DAY	Weekend	Weekend	Weekend	Weekend
Application	**Compound**	**LOQ [ng/l]**	**CAS 01**	**CAS 02**	**CAS 01**	**CAS 01**	**CAS 03**	**CAS 04**	**CAS 03**	**CAS 03**
(Val-)Sartan TP	**Valsartan acid**	10	256	283	na	na	306	297	na	na
Artif. Sweetener	**Acesulfame**	5.0	6910	6758	na	na	15476	15735	na	na
	Cyclamate	5.0	598	611	na	na	1651	1643	na	na
Biocide	**Irgarol**	5.0	2.5	2.5	na	na	2.5	2.5	na	na

na = not analysed; *DEMEAU listed compound

Annex L Bioassays CAS

Table L-0-18: Activities (ng or µg reference compound equivalent concentration/L water sample) detected in the in vitro bioassays for the MAR water samples from the CASTELLÓN sampling site collected at two time points: 06/2014 (Campaign I) and 04/2015 (Campaign II)

												Combined algae assay	
		Cytotox CALUX	ERα CALUX	antiAR CALUX	antiPR CALUX	GR CALUX	PPARg2 CALUX	p53 CALUX	p53 S9 CALUX*	Nrf2 CALUX	Bacteria luminescence inhibition	PSII inhibition**	Growth inhibition***
Sample name	**Campaign**	-	ng 17ß-estradiol eq./L water	ng Flutamide eq./L water	ng Ru486 eq./L water	ng Dexamethasone eq./L water	ng Rosiglitazone eq./L water	µg Actinomycin D eq./L water	µg Cyclophosphamide eq./L water	µg Curcumine eq./L water	mg baseline toxicity eq./L water	ng Diuron eq./L water	mg baseline toxicity eq./L water
CAS-01 EDAR	I.	-	0.1	10600	<LOQ (0.09)	109.3	LOD (<11.2)	LOD (<0.04)	LOD (<2400)	47	na****	128.8	1.16
	II.	-	3.8	10000	3.4	260.0	450.0	LOD (<0.01)	LOD (<715)	130	0.88	85.0	3.32
CAS-05 BALSA	I.	+	0.1	15700	1.1	< LOD (0.9)	LOD (<11.2)	LOD (<0.04)	LOD (<2400)	25	na	61.8	2.90
	II.	-	1.2	21000	7.0	< LOD (7.6)	LOD (<76)	LOD (<0.01)	LOD (<715)	67	0.23	31.7	0.52
CAS-06 SAN VICENTE	I.	-	LOD (<0.01)	7000	0.2	< LOD (0.9)	LOD (<11.2)	LOD (<0.04)	59500	LOD (<17)	na	420.4	0.29
	II.	-	<LOQ (0.11)	32000	5.3	< LOD (7.6)	LOD (<76)	LOD (<0.01)	LOD (<715)	LOD (<22)	0.10	439.5	2.63
CAS-07 LA PAZ	I.	+	LOD (<0.01)	44400	0.9	< LOD (0.9)	LOD (<11.2)	LOD (<0.04)	LOD (<2400)	<LOQ (13)	na	68.4	1.26
	II.	-	LOD (<0.06)	LOD (<2500)	1.5	< LOD (7.6)	LOD (<76)	LOD (<0.01)	LOD (<715)	LOD (<22)	0.03	69.6	0.43
CAS-08 RANDERO	I.	-	LOD (<0.01)	6500	<LOQ (0.07)	< LOD (0.9)	LOD (<11.2)	LOD (<0.04)	LOD (<2400)	LOD (<17.0)	na	191.5	2.22
	II.	-	LOD (<0.06)	LOD (<2500)	2.9	< LOD (7.6)	LOD (<76)	LOD (<0.01)	LOD (<715)	LOD (<22)	0.04	166.0	0.92
CAS-09 RAMBLETA 2	I.	-	<LOQ (0.01)	13800	0.2	< LOD (0.9)	LOD (<11.2)	LOD (<0.04)	LOD (<2400)	35.4	na	366.5	4.52
	II.	-	LOD (<0.06)	11000	3.0	< LOD (7.6)	LOD (<76)	LOD (<0.01)	LOD (<715)	LOD (<22)	0.09	7.9	0.31
CAS-11 GARROFERA	I.	-	< LOQ (0.02)	4607	0.4	< LOD (0.9)	LOD (<11.2)	LOD (<0.04)	LOD (<2400)	LOD (<17.0)	na	30.7	0.61
	II.	-	LOD (<0.06)	LOD (<2500)	LOD (<0.03)	< LOD (7.6)	LOD (<76)	LOD (<0.01)	LOD (<715)	LOD (<22)	0.06	772.7	3.87
CAS-12 PIEZOMETRO 2	I.	-	<LOQ (0.01)	5200	LOD (<0.03)	< LOD (0.9)	LOD (<11.2)	LOD (<0.04)	LOD (<2400)	LOD (<17.0)	na	408.8	3.59
	II.	-	LOD (<0.06)	LOD (<2500)	2.3	< LOD (7.6)	LOD (<76)	LOD (<0.01)	LOD (<715)	27	0.07	65.5	0.46
Negative Control	I.	-	LOD (<0.01)	< LOQ (242)	0.08	< LOD (0.9)	LOD (<11.2)	LOD (<0.04)	LOD (<2400)	LOD (<17)	na	0.8	0.25
	II.	-	LOD (<0.06)	LOD (<2500)	LOD (<0.03)	< LOD (7.6)	LOD (<76)	LOD (<0.01)	LOD (<715)	LOD (<22)	0.02	0.0	0.00

* Sample extracts were also measured in the p53 CALUX assay with metabolic activation using the S9 enzyme mix

** Photosynthesis inhibition was measured 2 hours after exposure

*** Growth inhibition was measured 24 hours after exposure

**** Not analysed

Table L-0-19: Overview of the individual REP factors available for the target compounds analysed in the MAR water samples from Castellón. REP factors are calculated by the following equation: test comp= EC(x) Reference compound/ EC(x) Test compound

		ERα-CALUX		antiAR-CALUX		antiPR-CALUX		GR-CALUX		PPARγ-CALUX		p53-CALUX		p53 S9-CALUX		Nrf2-CALUX		PS II Inhibition	
		PC10 (M)	REP	PC10 (M)	REP	PC10 (M)	REP	PC10 (M)	REP	PC10 (M)	REP	PC10 (M)	REP	PC10 (M)	REP	PC10 (M)	REP	EC50 (M)	REP
Reference compound		3.2E-12	1.0E+00	3.2E-07	1.0E+00	1.0E-10	1.0E+00	3.2E-10	1.0E+00	1.0E-08	1.0E+00	1.3E-09	1.0E+00	na	na	6.3E-06	1.0E+00	1.8E-08	1.0E+00
DEMEAU	Diclofenac	-	-	1.3E-05	-	3.2E-05	3.2E-06	-	-	2.5E-05	4.0E-04	2.5E-04	5.1E-06	-	-	-	-	na	na
	Phenazone	7.9E-05	4.0E-08	-	-	-	-	-	-	-	-	4.0E-04	3.2E-06	-	-	-	-	na	na
	Metoprolol	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na
	Iopromide	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	na	na
	Sulfamethoxazole	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	na	na
	Trimethoprim	-	-	5.0E-05	6.3E-03	-	-	-	-	-	-	-	-	-	-	-	-	na	na
	Bezafibrate	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na
	Gemfibrozil	-	-	-	-	-		-	-	-	-	-	-	-	-	-	-	na	na
	Carbamezapine	-	-	2.0E-05	1.6E-02	3.2E-05	3.2E-06	-	-	-	-	-	-	-	-	-	-	na	na
	Primidone	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	na	na
OTHERS	Diuron	-	-	2.5E-06	1.3E-01	-	-	-	-	-	-	7.9E-05	1.6E-05	-	-	-	-	1.8E-08	1.0E+00
	Atrazine	3.2E-05	1.0E-07	3.2E-05	1.0E-02	-	-	-	-	-	-	-	-	-	-	-	-	2.3E-07	8.0E-02
	Simazine	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	2.8E-07	6.6E-02
	Irgarol - Cerbutryn	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	1.6E-08	1.2E+00
	Tamoxifen	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	Isoproturon	-	-	-	-	-	-	-	-	-	-	3.2E-04	4.1E-06	-	-	-	-	1.2E-07	1.5E-01
	Mecoprop	-	-	-	-	-	-	-	-	1.0E-04	1.0E-04	1.0E-03	1.3E-06	-	-	-	-	-	-
	Terbuthylazine	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na	5.2E-08	3.5E-01

“na”: not available / not analysed
“-”: not detected

Table L-0-20:A and B. Overview of the theoretically expected and actually measured activities (ng or µg reference compound equivalent concentrations / L water) of the tested MAR water samples from Castellón. Expected activities are calculated based on the REP factors of the individual compounds and their actual concentration in the water samples. The magnitude of activity that could be explained by the chemically measured compounds are indicated as explained activity (%).

		ERα-CALUX			antiAR-CALUX			antiPR-CALUX			GR-CALUX			PPARγ-CALUX		
A		Expected	Measured	Explained	Expected	Measured	Explained	Expected	Measured	Explained	Expected	Measured	Explained	Expected	Measured	Explained
		ng EEQ/L water		%	ng Flu-Eq/L water		%	ng Ru486-Eq/L water		%	ng Dex.-Eq/L water		%	ng Rosigl.-Eq/L water		%
CAS-01 EDAR	I.	2.3E-05	1.3E-01	0.02%	2.9E+01	1.1E+04	0.27%	3.5E-03	1.6E+00	0.21%	0.0E+00	1.1E+02	0.0%	3.8E-01	LOD (<11.2)	-
	II.	2.2E-05	3.8E+00	0.0006%	2.1E+01	1.0E+04	0.21%	2.7E-03	LOD (<0.06)	-	0.0E+00	2.6E+02	0.0%	3.1E-01	4.5E+02	0.07%
CAS-05 BALSA	I.	1.1E-07	1.3E-01	0.00008%	1.6E-01	1.6E+04	0.0010%	6.6E-06	1.0E+00	0.0006%	0.0E+00	< LOD (0.9)	-	4.6E-04	LOD (<11.2)	-
	II.	4.0E-08	1.2E+00	0.000003%	2.2E-01	2.1E+04	0.0011%	4.1E-05	-	-	0.0E+00	< LOD (7.6)	-	4.0E-04	LOD (<76)	-
CAS-06 SAN VICENTE	I.	1.2E-06	LOD (<0.01)	-	1.2E+00	7.0E+03	0.017%	1.5E-04	<LOQ (0.03)	0.52%	0.0E+00	< LOD (0.9)	-	8.4E-03	LOD (<11.2)	-
	II.	9.5E-07	1.1E-01	0%	3.2E-01	3.2E+04	0.0010%	6.0E-05	1.5E+00	0.004%	0.0E+00	< LOD (7.6)	-	4.0E-04	LOD (<76)	-
CAS-07 LA PAZ	I.	1.1E-07	LOD (<0.01)	-	6.2E-01	4.4E+04	0.0014%	6.0E-05	LOD (<0.02)	-	0.0E+00	< LOD (0.9)	-	7.2E-03	LOD (<11.2)	-
	II.	2.8E-08	LOD (<0.06)	-	5.0E-02	LOD (<2500)	-	6.6E-06	3.40	0.0002%	0.0E+00	< LOD (7.6)	-	4.0E-04	LOD (<76)	-
CAS-08 RANDERO	I.	1.1E-07	LOD (<0.01)	-	7.3E-01	6.5E+03	0.011%	7.9E-05	1.0E-01	0.08%	0.0E+00	< LOD (0.9)	-	9.6E-03	LOD (<11.2)	-
	II.	4.0E-08	LOD (<0.06)	-	5.0E-02	LOD (<2500)	-	6.6E-06	2.3E+00	0.0003%	0.0E+00	< LOD (7.6)	-	4.0E-04	LOD (<76)	-
CAS-09 RAMBLETA 2	I.	7.2E-07	1.0E-02	0.007%	1.4E+00	1.4E+04	0.010%	5.1E-05	6.0E-02	0.08%	0.0E+00	< LOD (0.9)	-	7.5E-03	LOD (<11.2)	-
	II.	4.0E-08	LOD (<0.06)	-	5.0E-02	1.1E+04	0.0005%	6.6E-06	LOD (<0.14)	-	0.0E+00	< LOD (7.6)	-	4.0E-04	LOD (<76)	-
CAS-11 GARROFERA	I.	7.2E-07	2.0E-02	0.004%	9.4E-01	4.6E+03	0.02%	6.6E-06	2.2E-01	0.003%	0.0E+00	< LOD (0.9)	-	4.6E-04	LOD (<11.2)	-
	II.	4.0E-08	LOD (<0.06)	-	5.0E-02	LOD (<2500)	-	6.6E-06	1.4E+00	0.0005%	0.0E+00	< LOD (7.6)	-	4.0E-04	LOD (<76)	-
CAS-12 PIEZOMETRO 2	I.	1.1E-07	1.0E-02	0.001%	1.6E-01	5.2E+03	0.003%	6.6E-06	LOD (<0.02)	-	0.0E+00	< LOD (0.9)	-	9.1E-04	LOD (<11.2)	-
	II.	7.9E-08	LOD (<0.06)	-	5.0E-02	LOD (<2500)	-	6.6E-06	LOD (<0.06)	-	0.0E+00	< LOD (7.6)	-	4.0E-04	LOD (<76)	-

"-" not to be calculated

		p53-CALUX			p53 S9-CALUX			Nrf2-CALUX			Bacteria luminescence inhibition			PSII Inhibition		
B		Expected	Measured	Explained*	Expected	Measured	Explained	Expected	Measured	Explained	Expected	Measured	Explained	Expected	Measured	Explained
		µg Act D-Eq/L water		%	µg Cychlop.-Eq/L water		%	µg Curcumin-Eq/L water		%	mg TEQ/L water		%	ng Diuron.-Eq/L water		%
CAS-01 EDAR	I.	6.8E-03	LOD (<0.04)	-	0.0E+00	LOD (<2400)	-	0.0E+00	4.7E+01	0	-	-	-	6.1E+01	1.3E+02	47%
	II.	5.7E-03	LOD (<0.01)	-	0.0E+00	LOD (<715)	-	0.0E+00	1.3E+02	0%	na	8.8E-01	-	0.0E+00	8.5E+01	0%
CAS-05 BALSA	I.	2.7E-05	LOD (<0.04)	-	0.0E+00	LOD (<2400)	-	0.0E+00	25.00	0%	-	-	-	2.8E+01	6.2E+01	45%
	II.	8.3E-06	LOD (<0.01)	-	0.0E+00	LOD (<715)	-	0.0E+00	67.00	0%	na	2.3E-01	-	1.5E+01	3.2E+01	48%
CAS-06 SAN VICENTE	I.	2.2E-04	LOD (<0.04)	-	0.0E+00	6.0E+04	0%	0.0E+00	LOD (<17)	-	-	-	-	7.9E+00	4.2E+02	2%
	II.	8.2E-05	LOD (<0.01)	-	0.0E+00	LOD (<715)	-	0.0E+00	LOD (<22)	-	na	1.0E-01	-	3.8E+00	4.4E+02	1%
CAS-07 LA PAZ	I.	1.1E-04	LOD (<0.04)	-	0.0E+00	LOD (<2400)	-	0.0E+00	<LOQ (13)	0%	-	-	-	8.9E+00	6.8E+01	13%
	II.	8.3E-06	LOD (<0.01)	-	0.0E+00	LOD (<715)	-	0.0E+00	LOD (<22)	-	na	0.03	-	2.1E+00	69.65	3%
CAS-08 RANDERO	I.	1.4E-04	LOD (<0.04)	-	0.0E+00	LOD (<2400)	-	0.0E+00	LOD (<17.0)	-	-	-	-	2.0E+00	1.9E+02	1%
	II.	8.3E-06	LOD (<0.01)	-	0.0E+00	LOD (<715)	-	0.0E+00	LOD (<22)	-	na	3.9E-02	-	9.0E-01	1.7E+02	1%
CAS-09 RAMBLETA 2	I.	2.8E-04	LOD (<0.04)	-	0.0E+00	LOD (<2400)	-	0.0E+00	35.40	0%	-	-	-	1.4E+01	3.7E+02	4%
	II.	8.3E-06	LOD (<0.01)	-	0.0E+00	LOD (<715)	-	0.0E+00	LOD (<22)	-	na	9.3E-02	-	1.5E+00	7.9E+00	19%
CAS-11 GARROFERA	I.	1.3E-04	LOD (<0.04)	-	0.0E+00	LOD (<2400)	-	0.0E+00	LOD (<17.0)	-	-	-	-	1.6E+01	3.1E+01	52%
	II.	8.3E-06	LOD (<0.01)	-	0.0E+00	LOD (<715)	-	0.0E+00	LOD (<22)	-	na	6.4E-02	-	3.1E+00	7.7E+02	0%
CAS-12 PIEZOMETRO 2	I.	4.4E-05	LOD (<0.04)	-	0.0E+00	LOD (<2400)	-	0.0E+00	LOD (<17.0)	-	-	-	-	4.1E+00	4.1E+02	1%
	II.	1.2E-05	LOD (<0.01)	-	0.0E+00	LOD (<715)	-	0.0E+00	27.00	0%	na	7.2E-02	-	1.3E+00	6.6E+01	2%

"-" not to be calculated

*Expected activities here are way below the detection limit (LOD) of the assay; therefore explained activity share is not to be calculated