

# Task 1.2.1

## Pharmaceuticals fate and removal in MAR systems under different conditions

REMOVAL CONDITIONS MATRIX  
(Barcelona, 2 october 2014)



## OBJECTIVES

**DEMEAU** is focused to demonstrate MAR benefits and limitations with a special focus on emerging pollutants and to draw recommendations for its optimal design and operation with minimum environmental impact and in compliance with European directives.

Specific objectives addressed in this work:

- the identification of key parameters that control environmental impacts related to emerging pollutants and their respective attenuation during subsurface passage.
- The identification of optimum conditions for the removal of trace contaminants.

## METHODOLOGY

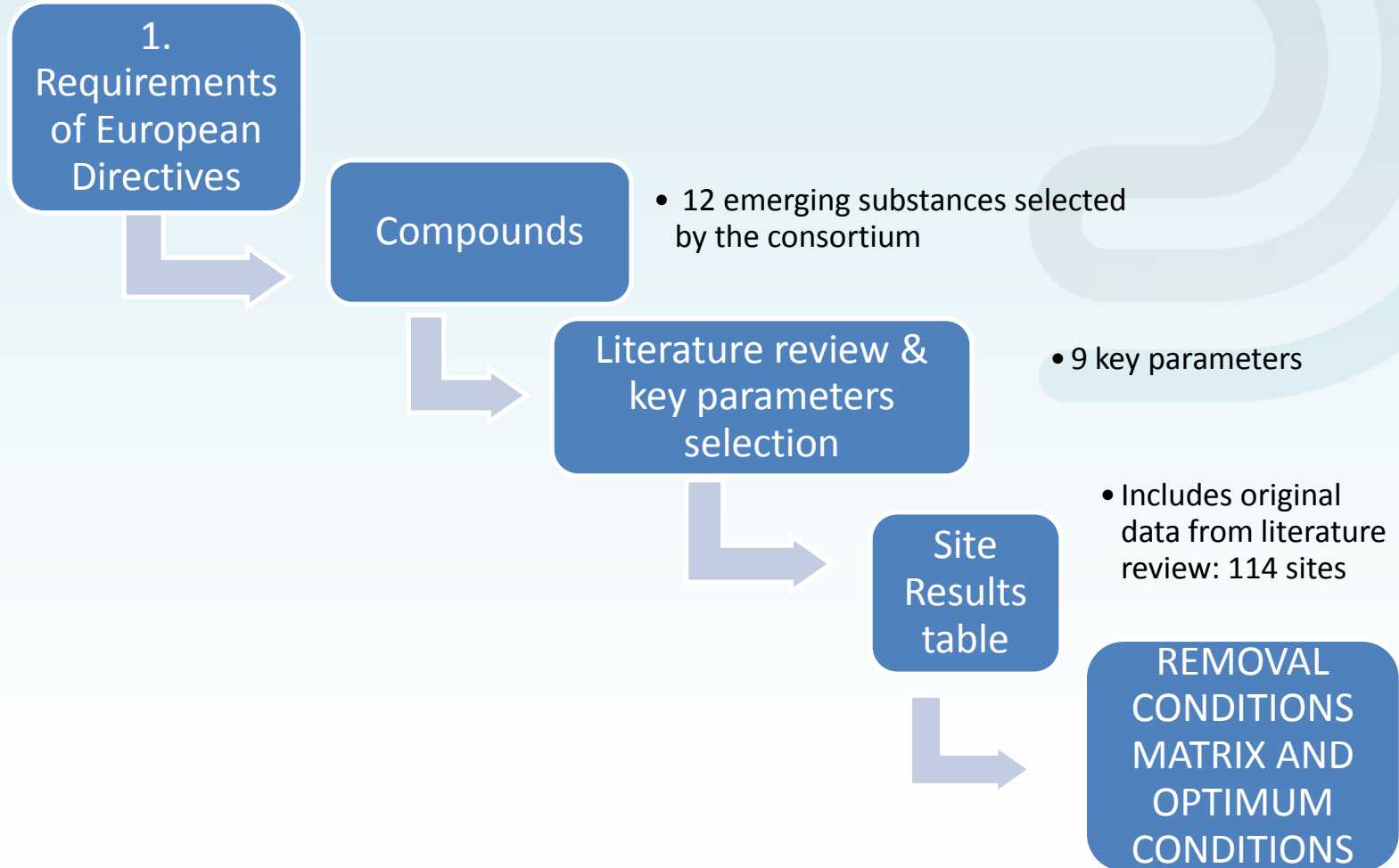
We have compiled information related to trace organic removal rates of 12 selected emerging pollutants in different Managed Aquifer Recharge (MAR) sites.

The elimination rates are then classified and evaluated based on previously selected key parameters of MAR systems.

As a result, the optimum conditions that can help to design and operation of infiltration facilities are identified in terms of water quality impacts.

The results of this study provide guidance to the authorities and water suppliers to evaluate the trace organic removal in an existing or a new designed MAR facilities.

## Methodology



## 2. SELECTION of COMPOUNDS

12 emerging substances

Benzotriazole  
Bezafibrate  
Carbamazepine  
Epoxi-carbamazepine  
Diclofenac  
Gemfibrozil  
Iopromide  
Metoprolol  
Phenazone  
Primidone  
Sulfamethoxazole  
Trimethoprim

These compounds have been selected by project consortium based on the following criteria:

- commonly found in wastewater / drinking water supplies,
- environmental relevance,
- broad spectrum of chemical and physical properties,
- covering the range from good to bad elimination by  $O_3$  and/or UV/ $H_2O_2$
- the existence of analytical methods by project partners

### 3. BIBLIOGRAPHIC RESEARCH

Publications where the attenuation of these 12 selected compounds have been analyzed and evaluated during subsurface package:

- ✓ > 25 publications
- ✓ > 100 sites

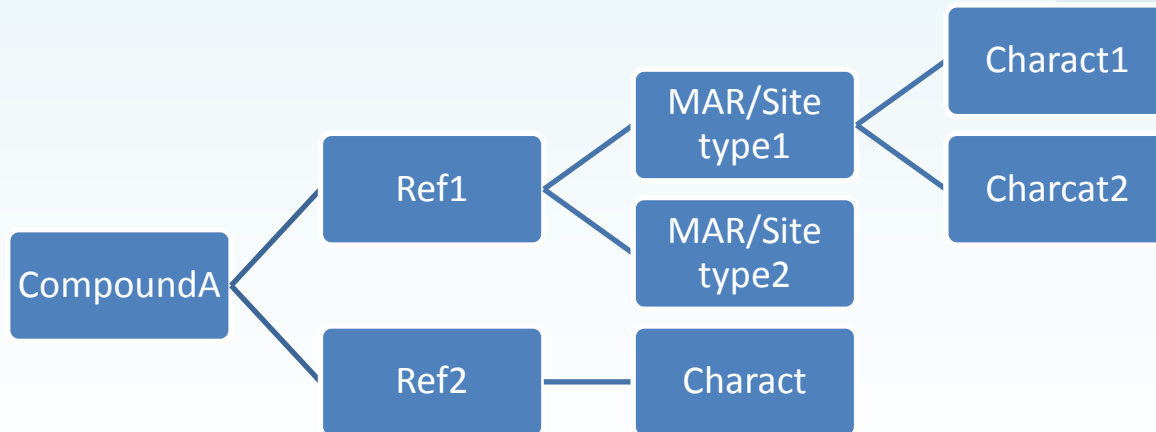
### 4. KEY PARAMETERS EVALUATION

In each of these compiled investigation sites, the most determinant key parameters that are of relevance for MAR impacts with treated waste water have been evaluated:

**MAR type, Aquifer type, Redox conditions, DOC/TOC, Residence time, Concentration of the emerging substance in source water, and Temperature.**

## 5. SITE RESULTS TABLE

For each compound, information from literature review has been structured by reference source, specific site, type of MAR, aquifer characteristics and season when appropriate (114 entries).



## 5. SITE RESULTS TABLE (example)

Compound	Ref.	Site location	MAR type	Aquifer type	Redox conditions	Q.m. in recharging water	Q.m. in aquifer during recharge	Residence time	Co (ng/L)	Cf measured (ng/L)	LOQ (ng/L)	Removal (%)	Temp.
Benzotriazole	[9]	Shafdan, Tel Aviv, Israel	Short term: Hybrid SAT: ultrafiltration + dug well	Unconfined. Mainly sand and sandstone 15 m unsaturated zone	Anaerobic NO <sub>3</sub> reduction	DOC=10 mg/L	DOC=2 mg/L (80% removed)	20-60 d	2300	1500	0.1	35% at short term SAT	
	[9]	Shafdan, Tel Aviv, Israel	Long term: conventional by 1 day flooding	Unconfined. Mainly sand and sandstone 15 m unsaturated zone	Anaerobic	DOC=10 mg/L	DOC=1 mg/L (90% removed)	180-365 d	n.a. (at present 2300)	500	0.1	78% at long term SAT	
	[9]	Gaobeidian, Beijing, China	ASTR. Post-wastewater treatment + Injection well	Shallow aquifer (17.5 m) as is injected into a well the non-saturated zone has no effect	The previous ozonation treatment reduced the Btrj concentration and no subsequent changes were observed after ASTR.	n.a.	n.a.	60-90 d (passage of 34 m)	550	350	0.1	21% removed	
	[13]	Lake Tegel, Berlin, Germany	Bank filtration	Sandy	Anoxic to anaerobic	DOC=8 mg/L	DOC= 5-6 mg/L	120 - 150 d	2300	1000	n.a.	56% removal 86% removal at pumping well (considering	



## 5. SITE RESULTS TABLE (analysis)

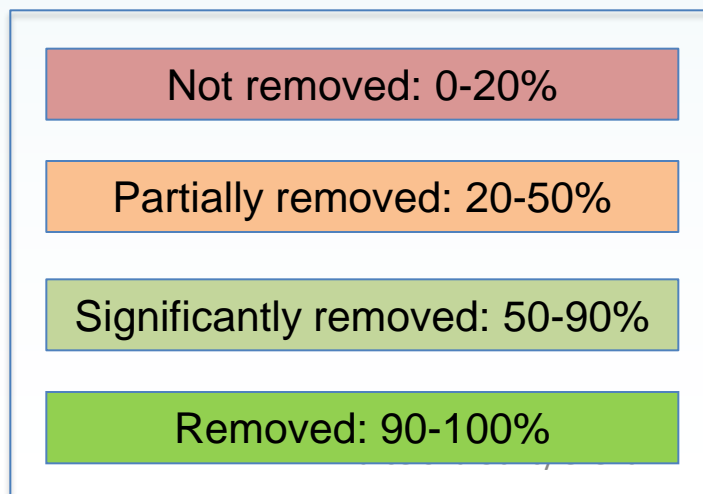
- 91% of the cases are alluvial or sandy aquifers.
- Only half of the sites have analyzed the DOC/TOC of the recharging water. In these sites the DOC content is between 5-8 except in 3 cases.
- Temperature is not always available, and can be related to DOC content.
- 86 % of the cases are infiltration ponds or river bank filtration. There is few data from injection experiments.
- Dilution factor has been taken into account in the interpretation.

Then, organic matter content, type of site and temperature are not relevant or real key parameters of these analyses **with the available information**

## 6. REMOVAL CONDITIONS MATRIX

Compiled information has shown that removal basically depends on a suite of variables or can also be site-dependent and it has been no possible to categorize the role of different key parameters in the compound removal.

**Removal conditions matrix** has been elaborated in order to relate the results with a suite of parameters and values that control these results. It is a tool to identify the optimum conditions to achieve the best removal rates for each compound.



Conditions with similar results are grouped in function of removal rates:

## 6. REMOVAL CONDITIONS MATRIX

	MAR TYPE	Residence time water	AQUIFER	REDOX	DOC (mg/l)	Initial concentration	RESULTS REF	REMOVAL
PHENAZONE	INJECTION						No data	Best results under <u>oxic</u> conditions. Removal can be inexistent in anoxic conditions indeed at long residence times. In some cases not consistent along flow path (high removal at short residence time and worst at long residence time).
	INFILTRATION	30 -120 days	Porous shallow	NO <sub>3</sub> and <u>Mn</u> and Fe reduction	7	150-300	Not removed [8], [21]	
		15 - 50 days	Porous shallow	<u>Oxic</u> and NO <sub>3</sub> -Mn reduction	7	220-770	41%-66% of removal [5], [8], [21]	
		2-120 days	Porous shallow	<u>Oxic</u> conditions	7	300	91% of removal [21]	
PRIMIDONE	INJECTION						No data	Not removed in most of the conditions. Recalcitrant in MAR. Nevertheless in some projects with long <u>Rt</u> and locally confined aquifers, removals of around 30% have been reported.
	INFILTRATION	20 - 60 days	Porous shallow and deep confined aquifers. Karst	<u>Oxic</u> to/and NO <sub>3</sub> and <u>Mn</u> reduction	7-10	50-225	Not removed [3], [6], [7], [9], [12], [15]	
		> 1 year	Porous shallow and deep confined aquifers	no data	5	202	31%-50% of removal [15]	

## Summary of findings

Five of the selected trace organic compounds show high removal rates under both oxic and anoxic/anaerobic redox conditions, any organic matter content and after short and long residence times in MAR infiltration systems: **Bezafibrate**, **Gemfibrozil**, **Diclofenac**, **Iopromide** and **Trimethoprim**. If these substances are present in the source water no specific considerations are needed for ensuring removal of these compounds

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

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

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

## Summary of findings

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

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

The rest of the studied compounds require specific conditions to achieve best removal rates in MAR systems.

## Summary of findings

**Benzotriazole** shows some attenuation in nitrate and iron-manganese reduction conditions when residence time is longer than 6 months. On the other hand **Phenazone** reaches 100% removal rates in oxic to anoxic conditions at short residence times in MAR infiltration systems.

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

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

## Summary of findings

**Carbamazepine** and **Sulfamethoxazole** show very low removal rates with some specific exceptions. Carbamazepine or Sulfamethoxazole needs very long residence time (at least 6 months) and anaerobic conditions or strictly anaerobic conditions (sulfate redox conditions) to be removed.

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

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

## Summary of findings

In all compiled sites, **Primidone** shows no removal in most of the conditions. Only organic matter could have some influence in this compound. Then this compound can be used as a tracer in most MAR systems.

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

There is not enough information on **Epoxi-Carbamazapine** and **Metoprolol** in order to summarize which best MAR characteristics ensure their removal. The TOC content could be also important in **Epoxi-Carbamazepine**



Thanks for your attention !

[Ester.vilanova@amphos21.com](mailto:Ester.vilanova@amphos21.com)

The logo for AMPHOS 21, with 'AMPHOS' in large black letters and '21' in white on an orange rectangular background.

## Summary of findings

Benzotriazole	<ul style="list-style-type: none"> <li>• Only partially removed. Best results in infiltration MAR types and with long residence times (redox conditions Fe-Mn). ASTR with short distances has no removal.</li> </ul>
Bezafibrate	<ul style="list-style-type: none"> <li>• Significant removal in most of the conditions. Best results in infiltration MAR types with reduction conditions; no influence of residence time.</li> </ul>
Carbamazepine	<ul style="list-style-type: none"> <li>• Not removed in most of the conditions, considered recalcitrant in MAR. Nevertheless, in some projects some removals have been reported but groundwater dilution can occur.</li> </ul>
Diclofenac	<ul style="list-style-type: none"> <li>• High removal rates in both oxic and anoxic conditions and short and long residence time. Nevertheless, in some cases low removal rate is obtained.</li> </ul>
Epoxi-carbamazepine	<ul style="list-style-type: none"> <li>• Few data available. Removal depends on DOC at short residence times.</li> </ul>
Gemfibrozil	<ul style="list-style-type: none"> <li>• High removal rates. Quite rapid process, but removals higher than 50% are always expected. DOC is not relevant.</li> </ul>

Iopromide	<ul style="list-style-type: none"><li>Removed in both oxic and anoxic conditions. Best results in infiltration sites rather in injection systems.</li></ul>
Metroprolol	<ul style="list-style-type: none"><li>Few data available. Good removal in long residence time.</li></ul>
Phenazone	<ul style="list-style-type: none"><li>Best results under oxic conditions. Removal can be inexistent in anoxic conditions indeed at long residence times.</li></ul>
Primidone	<ul style="list-style-type: none"><li>Not removed in most of the conditions. Recalcitrant in MAR.</li></ul>
Sulfamethoxazole	<ul style="list-style-type: none"><li>Best results in anoxic conditions (Fe-Mn and PO4 reduction conditions). Low removal rates in oxic conditions.</li></ul>
Trimethoprim	<ul style="list-style-type: none"><li>Best results at long term in both oxic and anoxic conditions.</li></ul>

In most cases, there is consistency on the attenuation conditions of each compound