

*Emergent compounds fate and removal in
MAR systems under different conditions.
DEMEAU and DEMOWARE project*

Under which conditions organic
micropollutants can be removed?

Algarve (portugal), june 2015

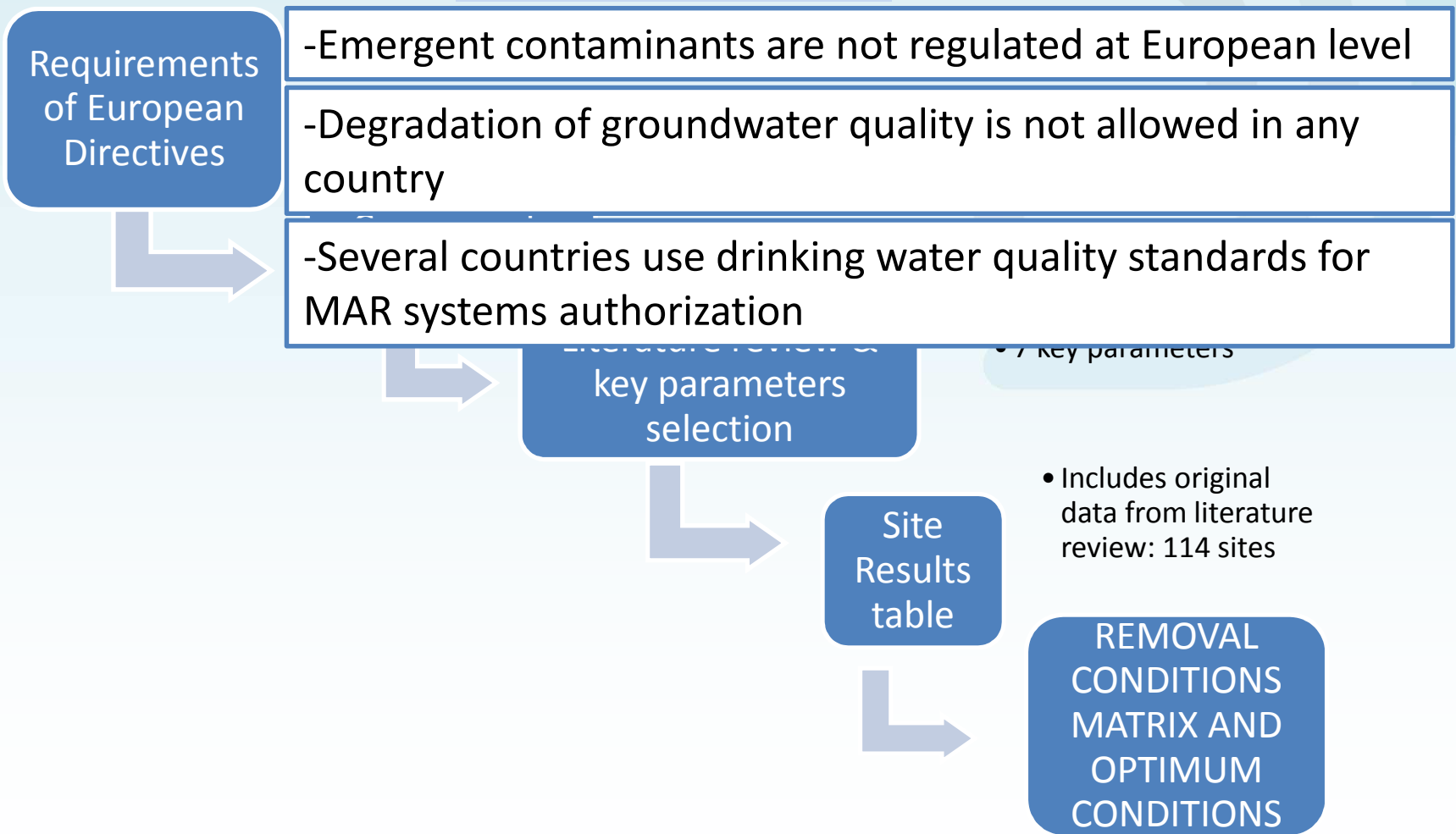
OBJECTIVES

DEMEAU: 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.

Additional specific objectives related to MAR:

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

Methodology



2. SELECTION of COMPOUNDS

12 emerging substances

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

These compounds were 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

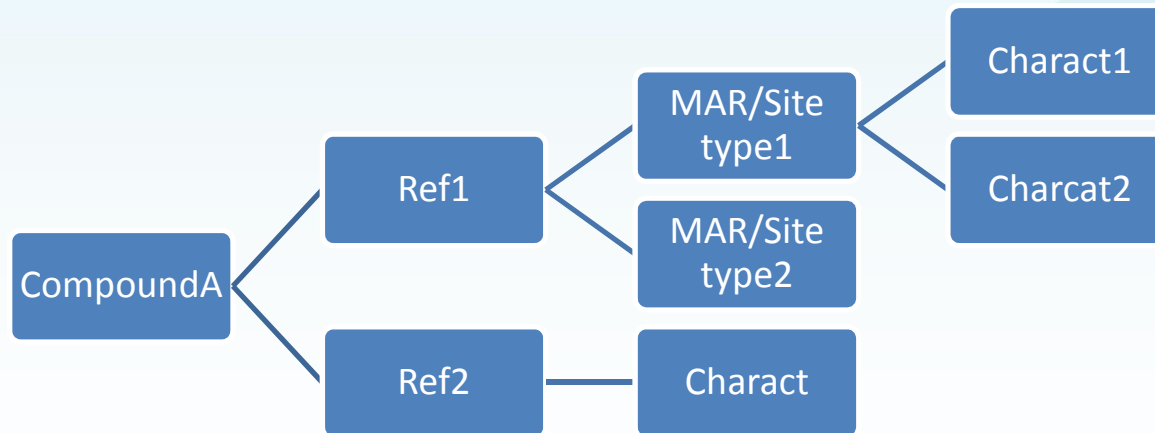
4. KEY PARAMETERS EVALUATION

In each of these compiled investigation sites, the most determinant key parameters that are of relevance for MAR impacts with treated waste were 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 (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

Removal conditions matrix was 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:

Not removed: 0-20%

Partially removed: 20-50%

Significantly removed: 50-90%

Removed: 90-100%

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

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 ₃ and Mn and Fe reduction	7	150-300	Not removed	[8], [21]	
		15 - 50 days	Porous shallow	<u>Oxic</u> and NO ₃ -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 ₃ and Mn 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	Bezafibrate			
< 6 months				
< 1 year				
> 1 year				

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

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

Summary of findings

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

	Reduction conditions			
	Oxic	NO3	Fe-Mn	SO4
< 7 days				
< 1 month	Trimethoprim			
< 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		Benzotriazole		
< 1 year				
> 1 year				

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

	Reduction conditions			
	Oxic	NO3	Fe-Mn	SO4
< 7 days	Sulfamethoxazole			
< 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	Primidone			
< 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



Port de la Selva Site: Hydrological modeling for optimal SAT design

Martí Bayer y Ester Vilanova

THE PROJECT



- Seasonal infiltration of tertiary effluent of wastewater treatment plant
- Goals:
 - Augment water level in aquifer
 - Prevent seawater intrusion

TASK

Modelling of groundwater recharge to determine the seasonal dynamics and fate of recharged water in the ambient aquifer with the aim to optimize operation with respect to treatment (travel times, redox conditions) and quantity.

METHODOLOGY



El Port de la Selva Basin: 10.5 Km²

Sub-Basin La Selva 2.9 Km²

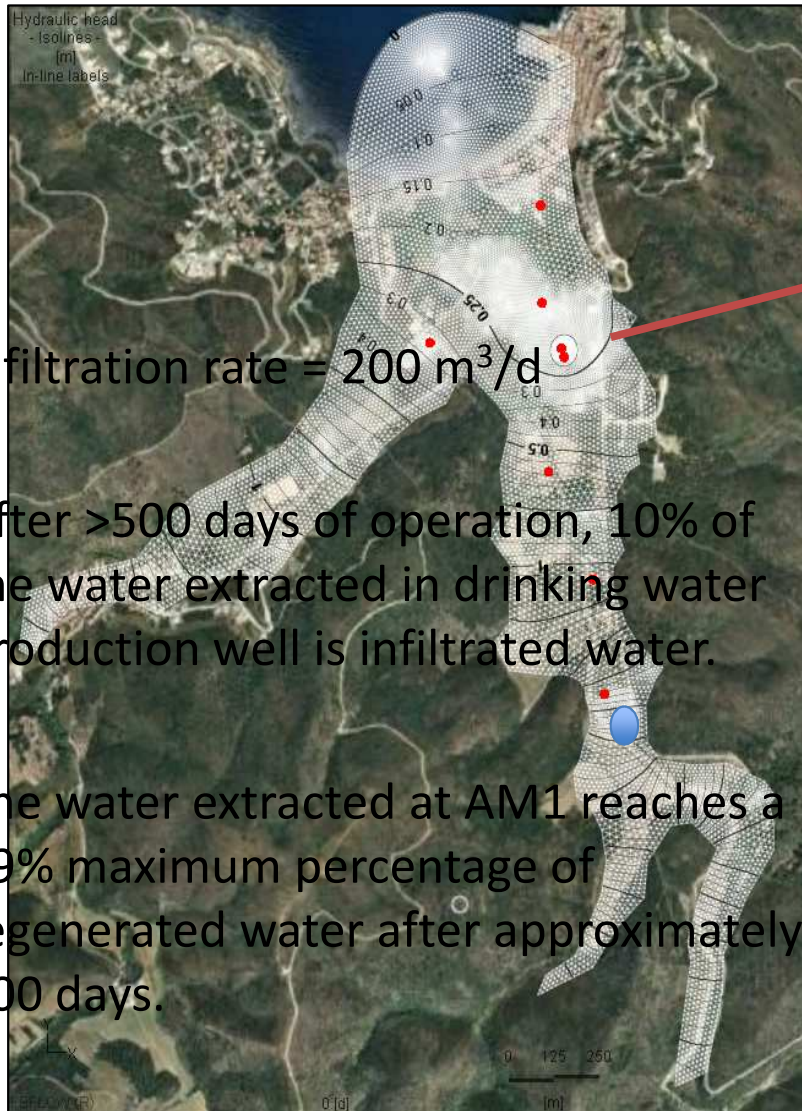
Sub-Basin Riera de Romanyac 7.6 Km²

Alluvial aquifer: 0.66 Km²

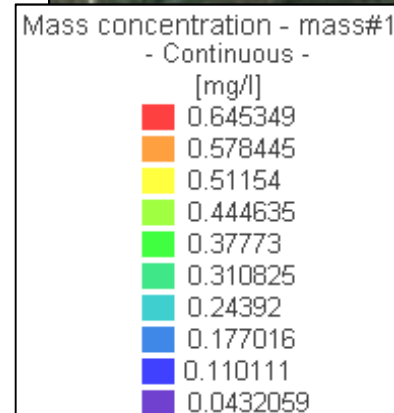
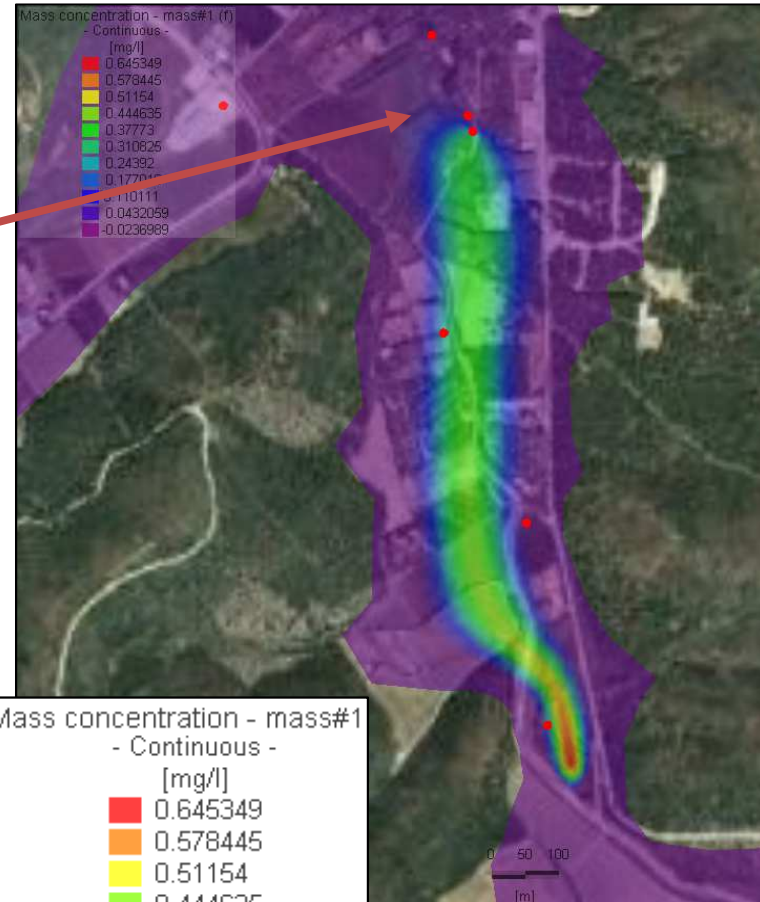
In order to estimate travel times from the infiltration basins to the water supply wells, a Finite Element numerical model was developed using the code FEFLOW. The model will be capable to analyze different scenarios accounting for the seasonal trends and future increase in water demand to optimize the capacity of the SAT system ensuring safe conditions in terms of water quality.

Numerical model: results

- Infiltration rate = $200 \text{ m}^3/\text{d}$
- After >500 days of operation, 10% of the water extracted in drinking water production well is infiltrated water.
- The water extracted at AM1 reaches a 19% maximum percentage of regenerated water after approximately 800 days.



Dilution plume for long-term conditions.



Dilution plume
("concentration" indicates % of infiltrated water)

El Port de la Selva: Results of first trace organic screening (50 compounds in total)

Trace organics	Unit	Secondary effluent	Tertiary effluent	Guideline value for drinking water (Germany)
Benzotriazole	ng/L	n.a.	135	3000
Carbamazepine	ng/L	190	190	300
Diclofenac	ng/L	< 10	4	300
X-ray contrast m.	ng/L	n.d.	n.d.	
Metoprolol	ng/L	n.a.	55	
Sulfamethoxazole	ng/L	840	100	
Trimethoprin	ng/L	n.a.	33	
Gabapetin	ng/L	1600	< 15	None yet
Diuron	ng/L	2300	60	
Acesulfame	ng/L	870	530	>3000

- ✓ Discharge of secondary effluent highly variable along a year.
- ✓ Tertiary treatment (capacity of 25 m³/h) consisting of coagulation, flocculation, filtration and combined UV-chlorine disinfection

Thanks for your attention !

Any questions?

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