Séminaire 2019 de l'OHM Bassin Minier de Provence
Fuveau, 15 novembre 2019

Modified bauxite residue as filter material to upgrade phosphorus removal in small wastewater treatment plants

Cristian Barca*, Dario Scanu, Nicola Podda, Laurent Poizat, Pierre Hennebert
*cristian.barca@univ-amu.fr

Context: phosphorus pollution

Phosphorus (P) is an essential nutrient for biomass growth in aquatic ecosystems.

Excessive intake of P in water bodies may lead:

- **Abnormal growth of algae and aquatic plants (algal bloom);**
- **Degradation of water quality (eutrophication).**

Maine-et-Loire (France)

Lake Winnipeg (Canada)

Images from Internet

Context: phosphorus pollution

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- **Degradation of water quality (eutrophication).**

Treatment requirements for small and medium (10000-100000 P.E.) wastewater treatment plants (WWTP) in sensitive areas (directives 91/271/EEC and 2000/60/EC):

- **Total phosphorus concentration (TP): 2 mg P/L;**
- **Minimum percentage of reduction: 80%;**
- ➢ **National and local requirements are often stricter (even < 0.5 mg P/L)!**

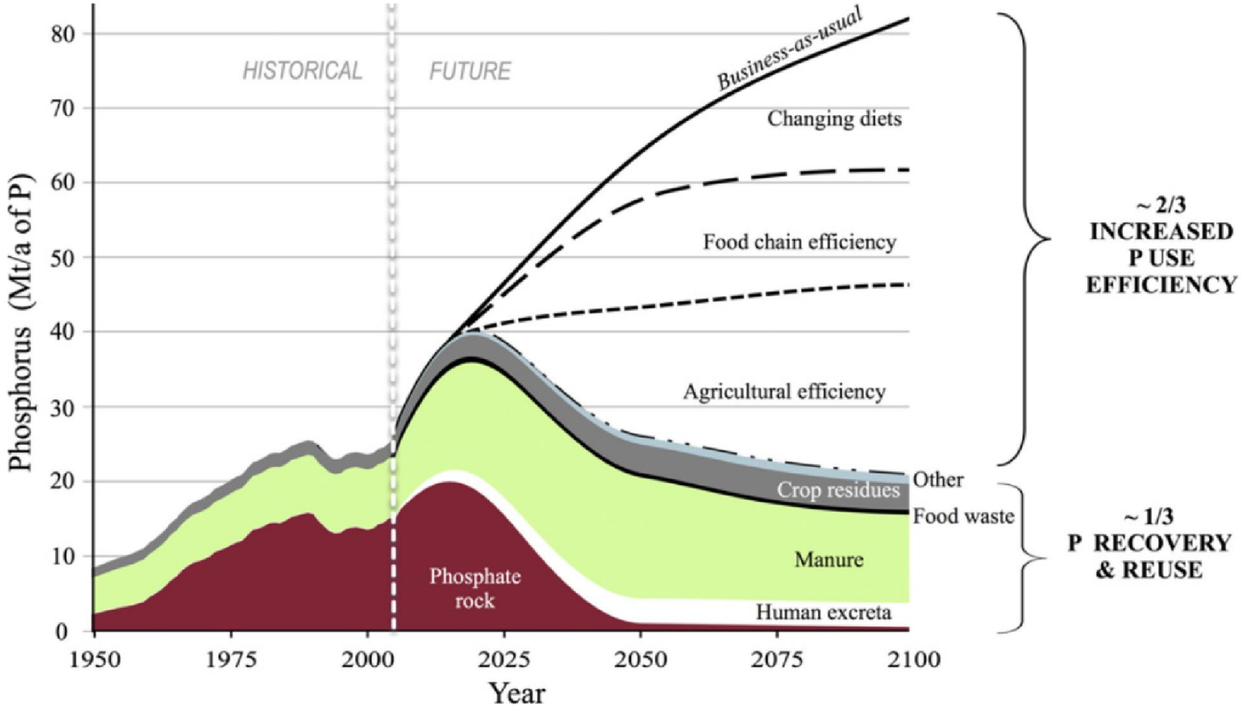
Domestic wastewater in Western Europe (Comber *et al.*, 2013; Boutin *et* Eme, 2017):

- ***Per capita* loadings of P: 2.0-2.6 g P *per capita per* day;**
- **TP concentration (fresh wastewater): 10-18 mg P/L ;**
- ➢ **The need to develop low cost techniques to treat P, especially for small WWTPs.**

Context: shortage of natural resources

Nowadays fertilizer production industry strongly depends on natural deposits of P such as apatite rocks. Prospective studies indicate that (Cordell *et al.*, 2011):

- **The peak of P production from phosphate rocks will occur around 2020;**
- **P is very likely to become a critical resource by 2050;**
- ➢ **There is an urgent need to identify alternative renewable P resources.**



Scenario of long term phosphorus demand (Cordell *et al.*, 2011)

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Nowadays fertilizer production industry strongly depends on natural deposits of P such as apatite rocks. Prospective studies indicate that (Cordell *et al.*, 2011):

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➢ **There is an urgent need to identify alternative renewable P resources.**

P retention and recovery from domestic wastewater represents a promising strategy to (Tarayre et al., 2016; Cieślik and Konieczka, 2017):

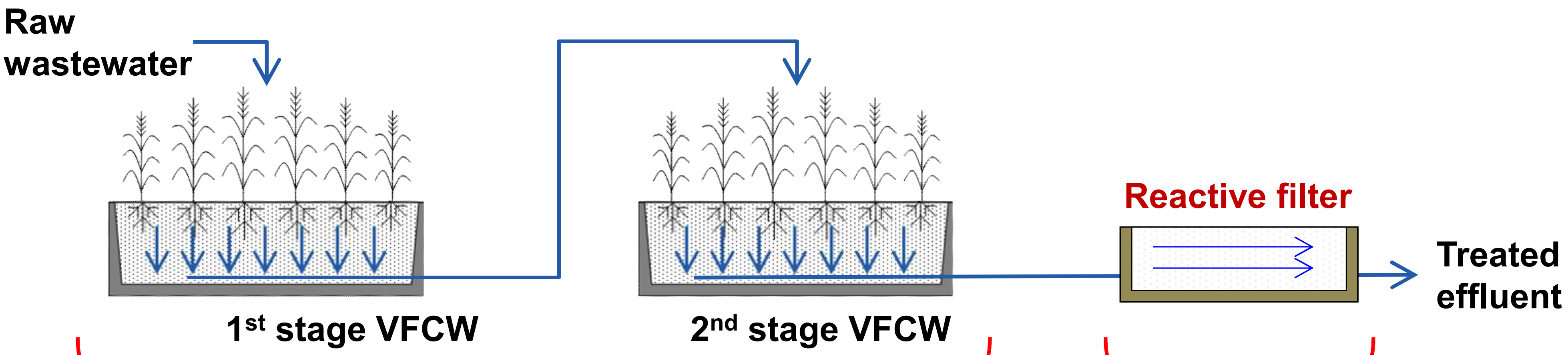
- **Reduce P supply to sensitive ecosystems (risk of eutrophication);**
- **Overcome the shortage of natural deposits of P (*e.g.* apatite rocks);**

➢ **Maximum potential of P recovery: 0.7-0.9 kg P *per capita per* year.**

Context: P treatment in small WWTP

Most common treatment systems for small communities in France (< 2000 P.E.):

- **Two stage vertical flow reed planted constructed wetland (VFCW):**



Biological uptake, vegetal sorption, adsorption, precipitation

Adsorption, precipitation

Two stage VFCWs in France provide (Molle *et al.*, 2005 and 2008):

- **High removal (> 80%): COD, suspended solid (TSS), and Kjeldahl nitrogen (TKN);**
- **Poor removal (< 30%): nitrate ($N\text{-}NO_3$) and total phosphorus (TP);**
- **Addition of separate filter units containing materials with high affinity for P binding.**

Context: reactive materials

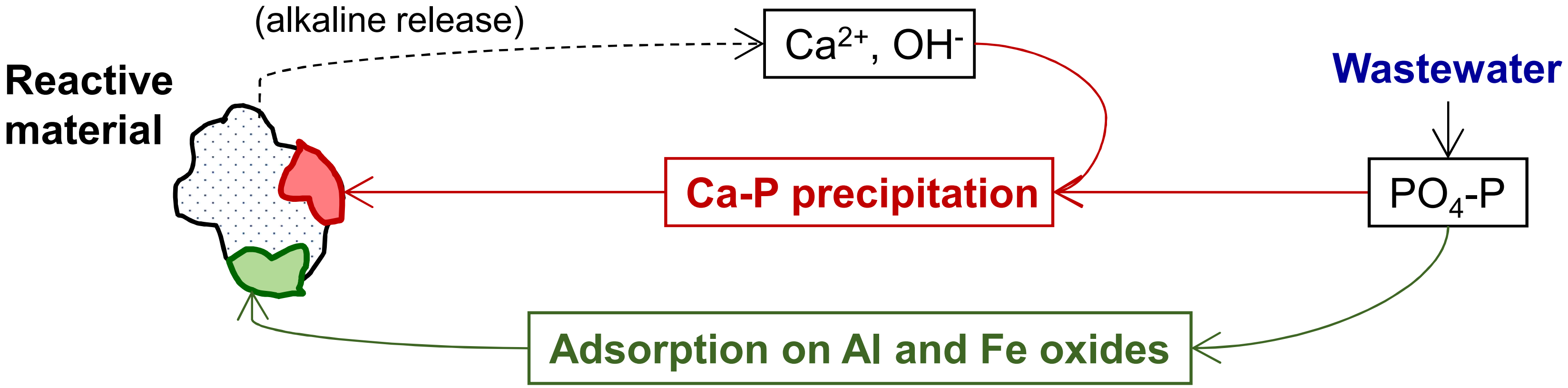
Reactive materials tested for P binding (Johansson Westholm, 2006; Vohla *et al.*, 2011):

- Natural materials: limestone, zeolite, iron rich sand, etc.;
- Man made: Filtralite®, Phosphorite®, Polonite®, etc.;
- Industrial byproducts and waste: steel slag, fly ash, bauxite residue, etc.

Most of these materials present high Ca, Al and/or Fe content.

Main mechanisms of P binding (Chazarenc *et al.*, 2009; Barca *et al.*, 2012):

- Precipitation of Ca-P complexes followed by crystallization on mineral surface;
- Adsorption on Al and Fe oxides and hydroxides.



Modified bauxite residues as filter material

Project BAUXFILTER (ALTEO, LabEx DRIIHM OHM-BMP, 2018-2019):

- **Laboratory M2P2, group Waste and Wastewater Treatment, Aix-en-Provence;**
- **INERIS-ARDEVIE, Aix-en-Provence;**
- **Company ALTEO, Gardanne (Provence, France).**

Bauxite residue: waste of aluminum industry (also known as red mud):

- **Worldwide production (Prajapati *et al.*, 2016): 90 million tons per year;**
- **Chemical composition (ALTEO): Fe_2O_3 (50%), Al_2O_3 (14%), CaO (5,5%), Na_2O (3,5%);**
- **High content of NaOH: high pH leachates;**
- ➢ **Modified bauxite residue (MBR): treated by addition of gypsum to reduce pH < 8.5.**

Bauxite residue storage area of Gardanne with Sainte-Victoire Mountain (Provence, France)

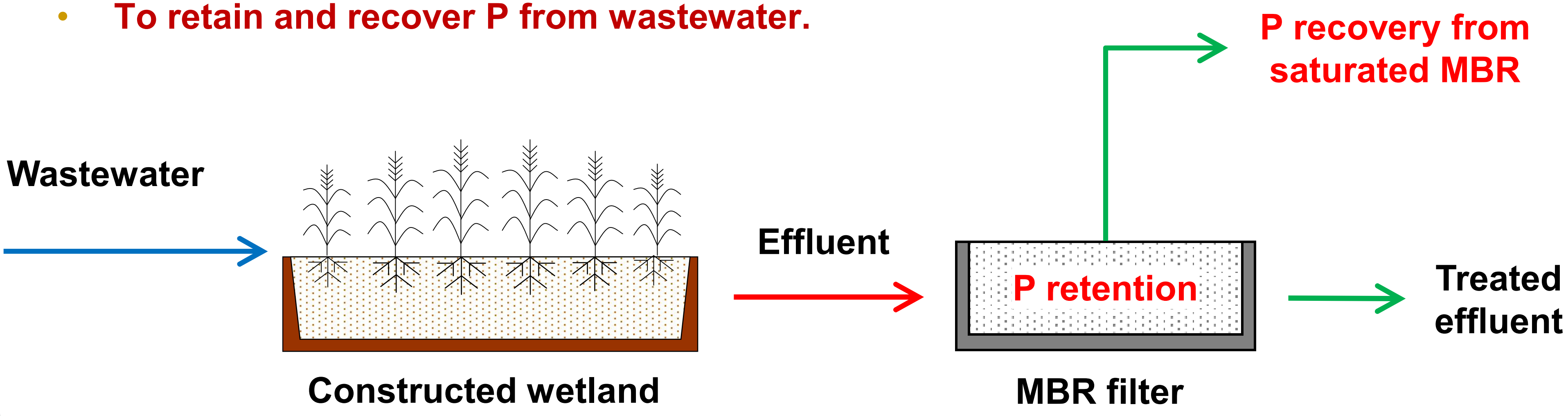
Saint-Victoire Mountain, Paul Cézanne (1839-1906)

The project BAUXFILTER

Aim of the project: developing the use of filters filled with MBR (MBR filters) to retain P from the effluents of small WWTPs.

Main challenges:

- **To reduce P supply to receiving waters;**
- **To valorize an industrial waste as filter material;**
- **To retain and recover P from wastewater.**



Main objectives and approach

Systemic approach involving experiments at different scales of investigation:

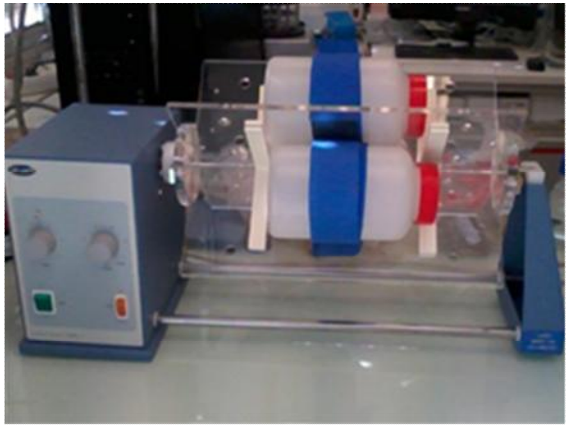
I. **Batch experiments: kinetics and equilibrium capacities of P sorption;**

II. **Lab-scale column experiments: P removal performances under dynamic conditions;**

III. **Lab-scale filter experiments: long term hydraulic and treatment performances.**

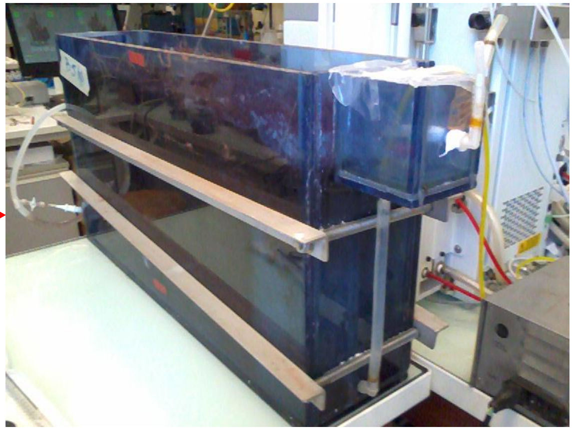
- ➢ **Integration of results and development of a systemic model.**

Batch experiments



Column experiments

Filter experiments

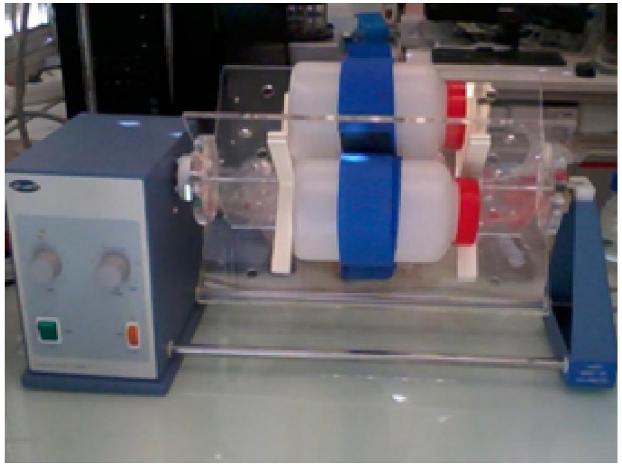


Integration of results

Material & methods: batch experiments

Batch kinetic experiments: to determine the effect of different wastewater composition on equilibrium capacities and rate constants of P sorption:

- **Ratio liquid to solid (ASTM D 4646): 20 L/kg;**
- **Initial volume of solutions: 0.7 L;**
- **Agitation mode: rotary agitation at 2.5 rpm;**
- **Room temperature: 20 ± 2 ° C;**
- **Water samples taken at: 0.5, 1, 2, 4, 6, and 24 h.**

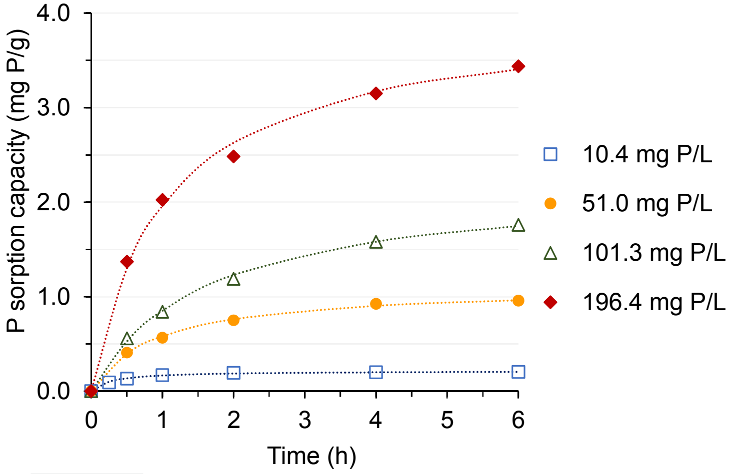


Solutions: 3 different water matrix at 4 different initial P:

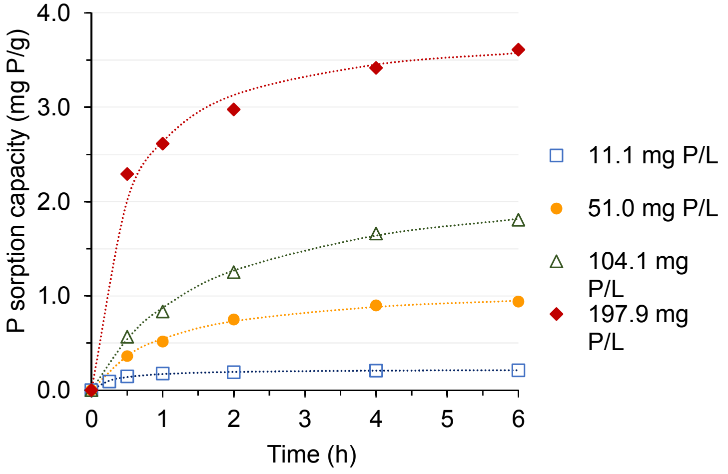
- **Deionized water plus P: 10, 50, 100, and 200 mg P/L;**
- **Tap water plus P: 10, 50, 100, and 200 mg P/L;**
- **Tap water plus 40 mg N-NO_3/L plus P: 10, 50, 100, and 200 mg P/L.**

Results & discussion: batch experiments

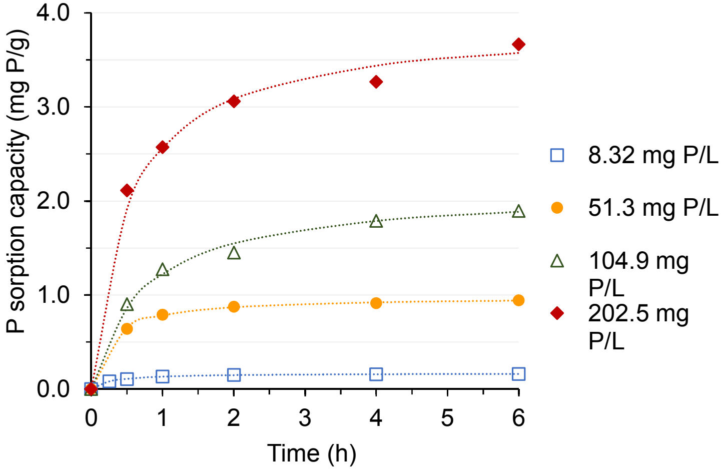
Deionized water + P



Tap water + P



Tap water + N-NO_3 + P



Pseudo 2nd order model (Ho and McKay, 1998):

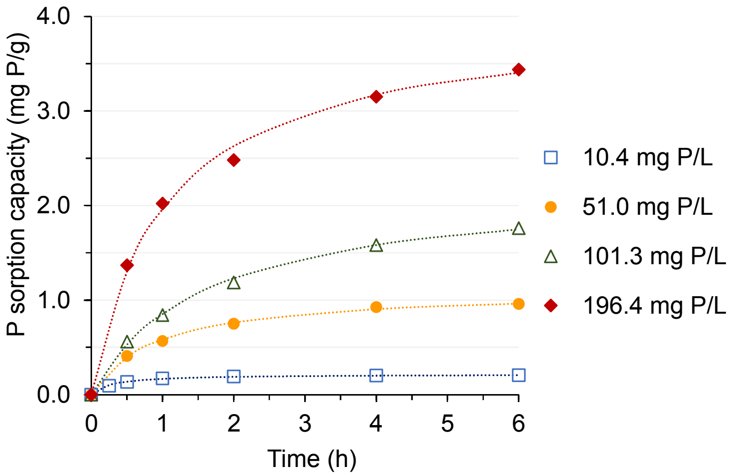
$$\frac{dq_t}{dt} = k_2 \cdot (q_e - q_t)^2 \quad \Rightarrow \quad \frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t$$

- q_e: equilibrium sorption capacity (mg P/g MBR);
- q_t : sorption capacity at time t (mg P/g MBR);
- k_2: rate constant of pseudo-second order (g mg^{-1} h^{-1}).

One or more reactants become limiting: process controlled by the reaction.

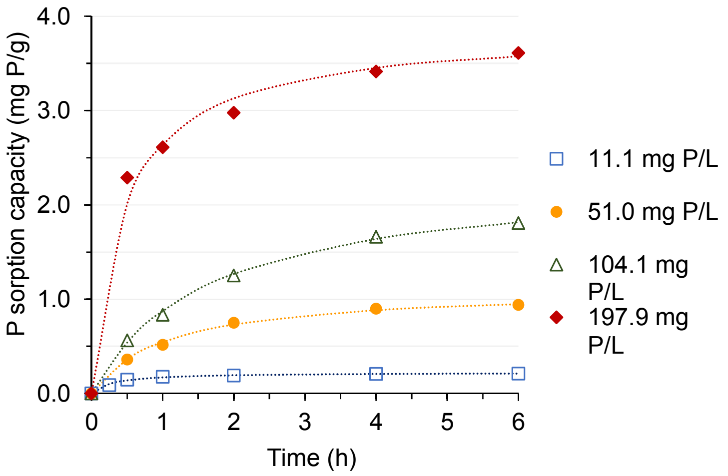
Results & discussion: batch experiments

Deionized water + P



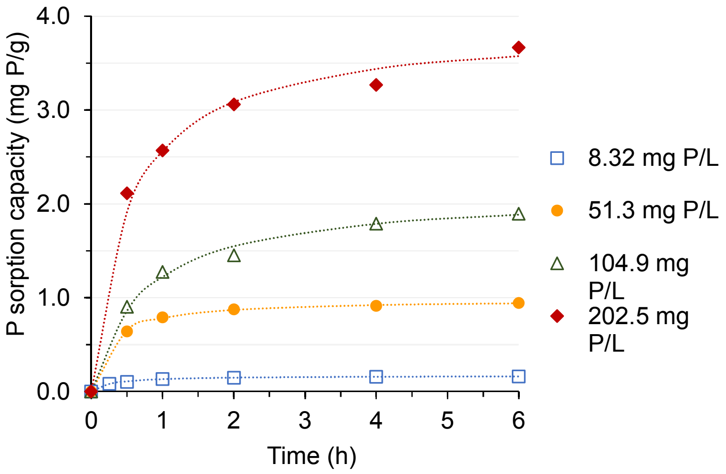
Initial P (mg P/L)	**K_2 (g/(mg*h))**	**q_e (mg/g)**	**R^2 (-)**
10.4	16.087	0.215	0.999
51.0	0.989	1.115	0.999
101.3	0.281	2.217	0.998
196.4	0.240	3.997	0.997

Tap water + P



Initial P (mg P/L)	**K_2 (g/(mg*h))**	**q_e (mg/g)**	**R^2 (-)**
11.1	14.484	0.224	0.999
51.0	0.854	1.116	0.998
104.1	0.261	2.316	0.998
197.9	0.564	3.849	0.998

Tap water + N-NO_3 + P



Initial P (mg P/L)	**K_2 (g/(mg*h))**	**q_e (mg/g)**	**R^2 (-)**
8.32	21.482	0.168	0.999
51.3	4.010	0.981	0.999
104.9	0.646	2.115	0.997
202.5	0.498	3.884	0.995

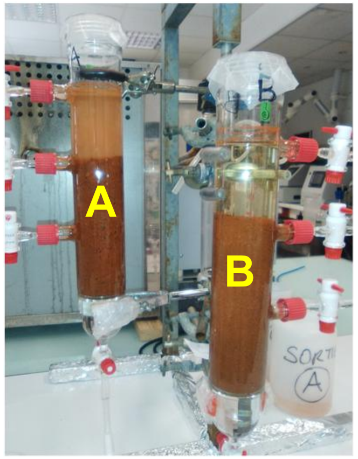
- **K_2 decreases and q_e increases with increasing initial P: saturation capacity not achieved;**
- **Different water matrix did not appear to affect P sorption kinetic.**

Material & methods: column experiments

Main objectives: to determine and describe the effect of aerobic and anoxic conditions on:

- P removal performances;
- P removal mechanisms.

Glass columns (0.5 L)

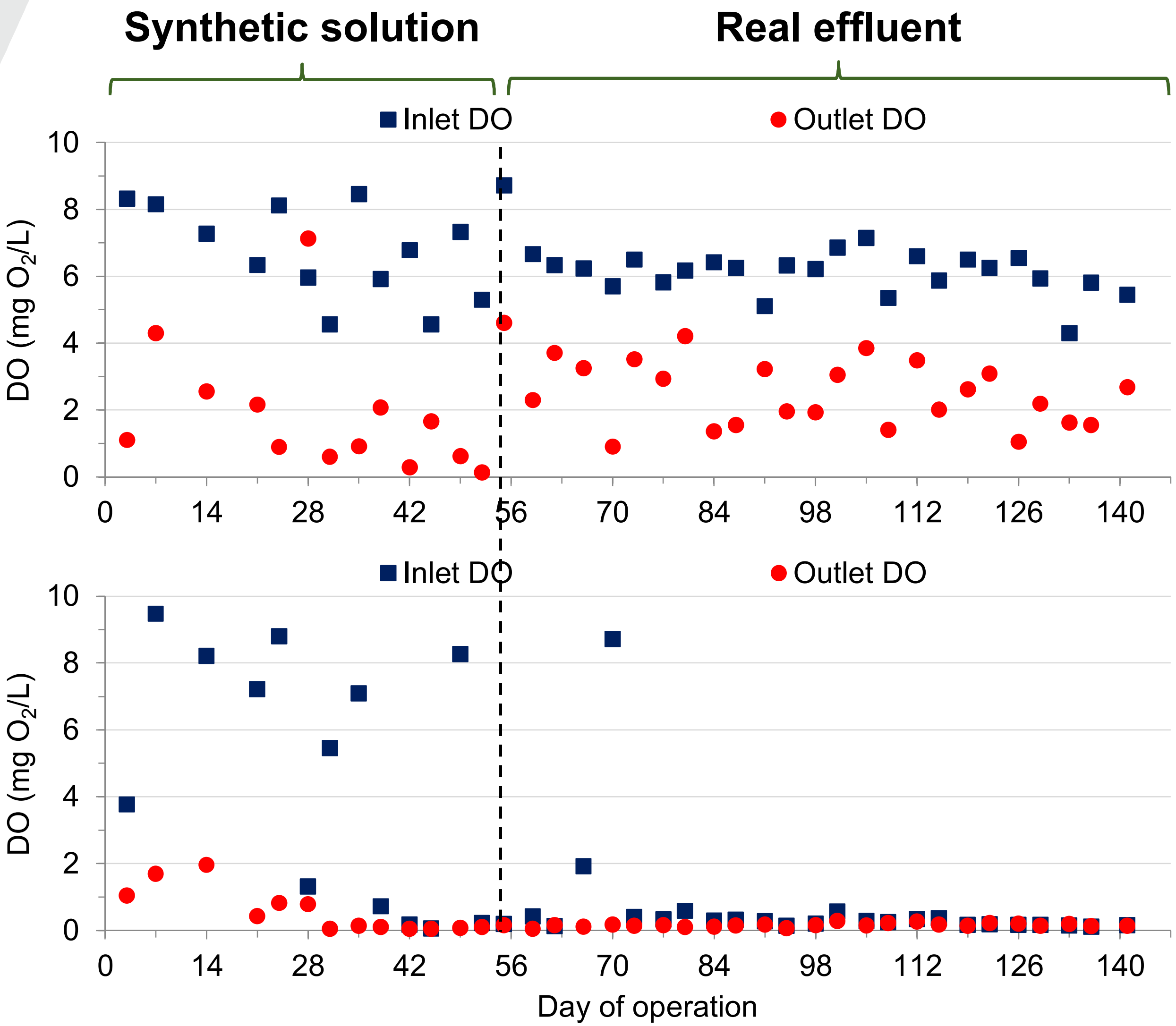


Two MBR columns were continuously fed according to a HRTv of 1 day for the full period of 5 months of operation:

- Day 1 to 54: synthetic solution:
  - Column A: tap water + 10 mg P/L + 40 mg N/L (KNO_3);
  - Column B: tap water + 10 mg P/L + 40 mg N/L (KNO_3) + 500 mg COD/L (glucose);
- Day 55 to 140: real effluent from a small WWTP*:
  - Column A: raw real effluent;
  - Column B: real effluent + 500 mg COD/L.

*Effluent from the two stage VFCW of Rougiers (Var, France), 1500 P.E..

Results & discussion: DO concentrations



Column A: aerobic conditions

Synthetic solution (day 1-54):

- **Outlet DO: 1.9 ± 1.9 mg O_2/L**

Real effluent (day 55-140):

- **Outlet DO: 2.6 ± 1.0 mg O_2/L**

Column B: anoxic conditions

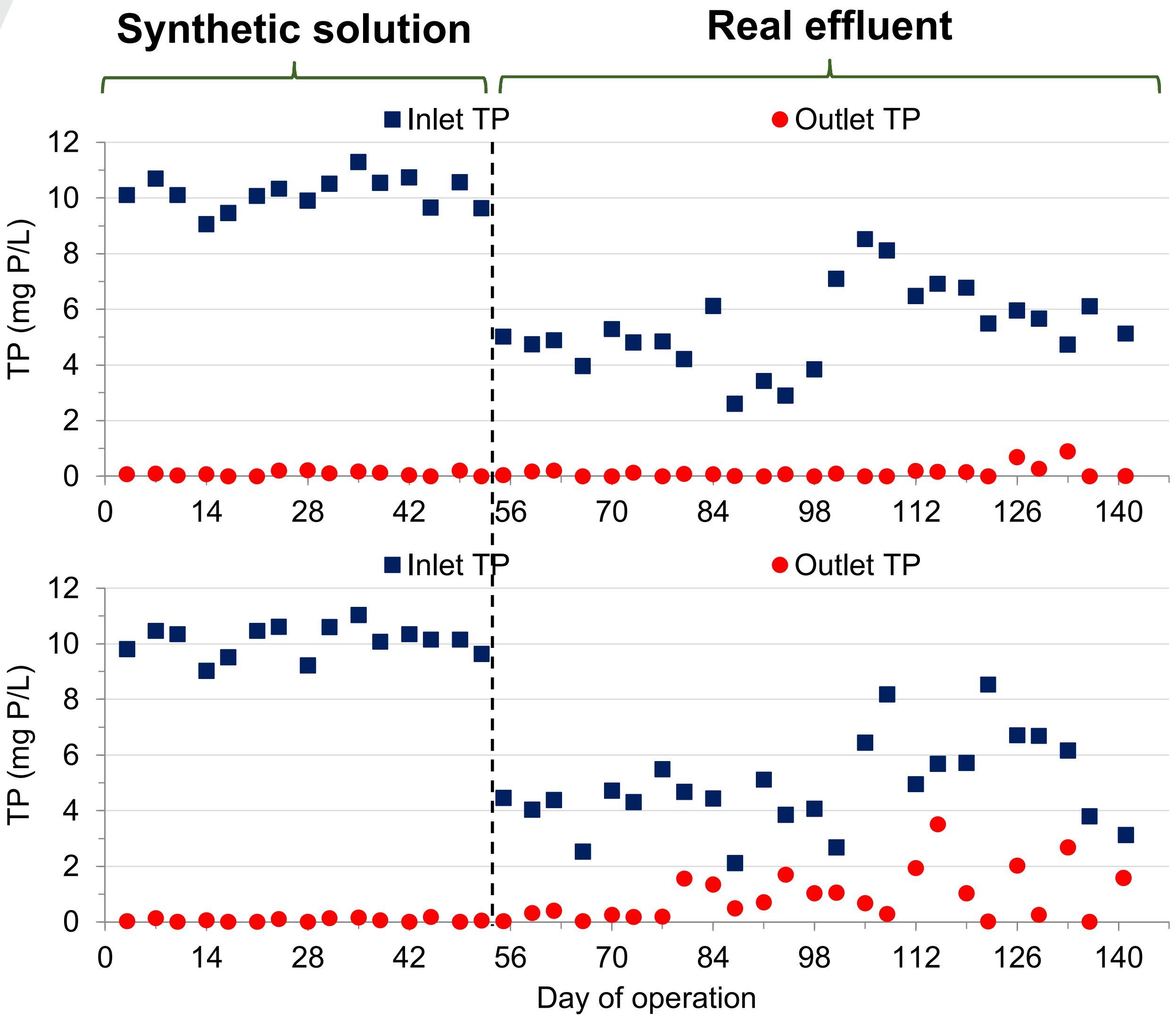
Synthetic solution (day 1-54):

- **Outlet DO: 0.6 ± 0.6 mg O_2/L**

Real effluent (day 55-140):

- **Outlet DO: 0.2 ± 0.1 mg O_2/L**

Results & discussion: TP removal



Column A: aerobic

Synthetic solution (day 1-54):

- **Inlet TP: 10.3 ± 0.5 mg P/L**
- **Outlet TP: 0.1 ± 0.1 mg P/L**

Real effluent (day 55-140):

- **Inlet TP: 5.5 ± 1.5 mg P/L**
- **Outlet TP: 0.1 ± 0.1 mg P/L**

Column B: anoxic

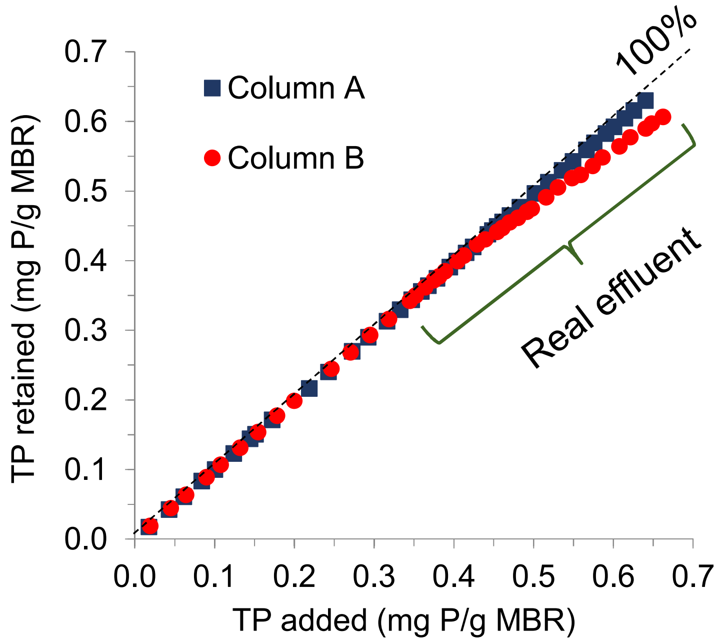
Synthetic solution (day 1-54):

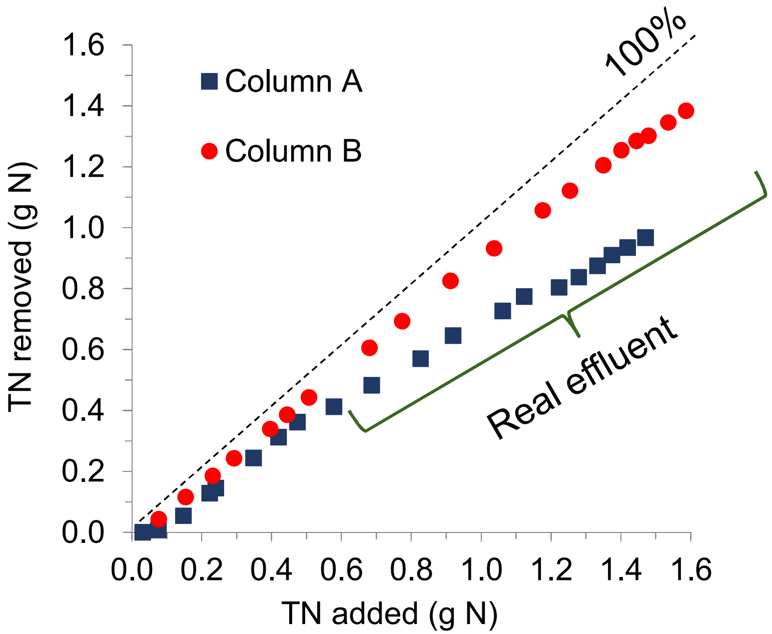
- **Inlet TP: 10.3 ± 0.5 mg P/L**
- **Outlet TP: 0.1 ± 0.1 mg P/L**

Real effluent (day 55-140):

- **Inlet TP: 5.5 ± 1.7 mg P/L**
- **Outlet TP: 0.9 ± 0.9 mg P/L**

Results & discussion: TP retention capacity





TP retention capacities over 140 days:

- **Column A: 0.63 mg P/g MBR**
- **Column B: 0.61 mg P/g MBR**

TP retention efficiency over 140 days:

- **Column A: 98 % → more efficient!**
- **Column B: 91 %**

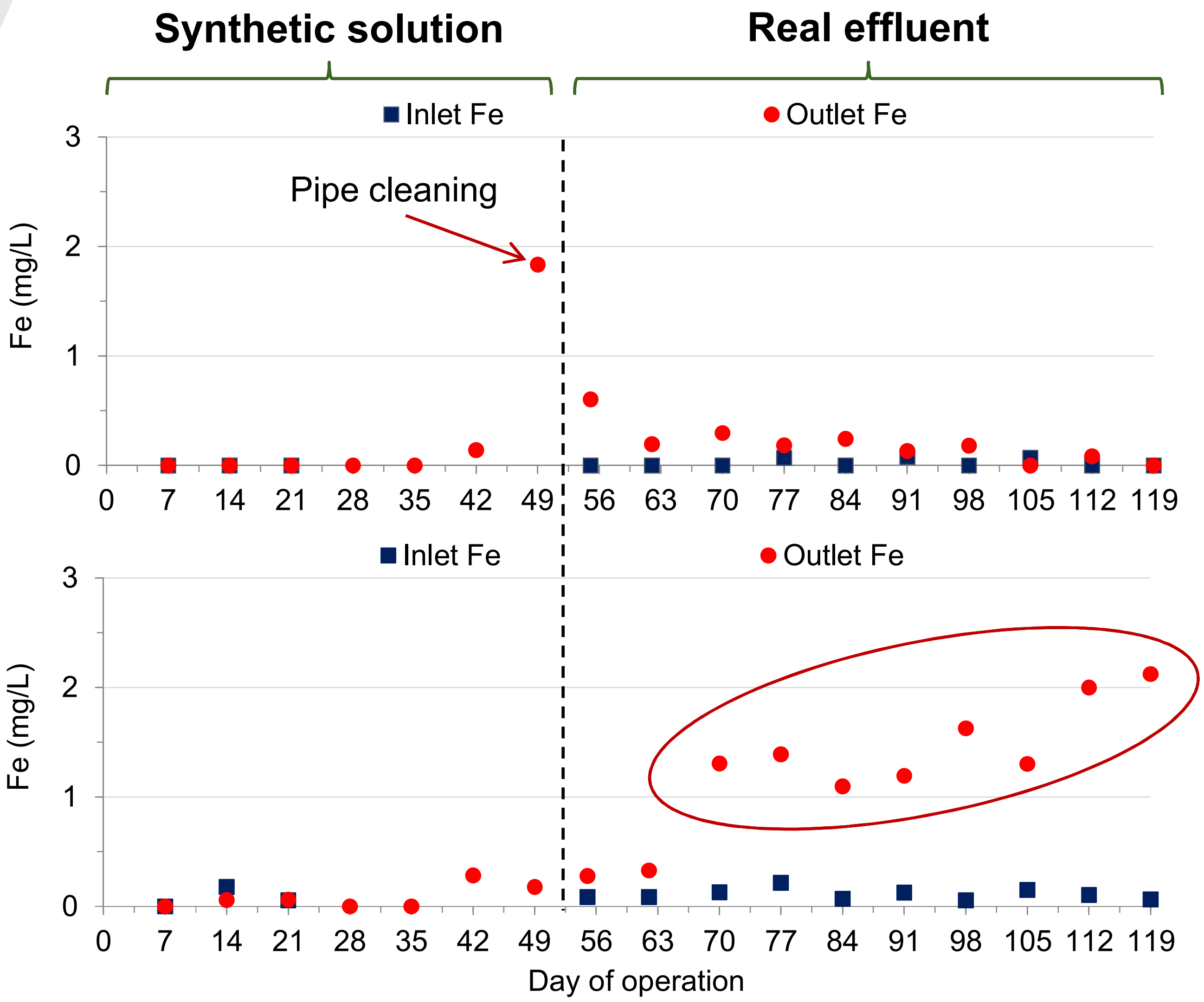
Average outlet TN over 140 days:

- **Column A: 11.9 mg N/L → removal 66 %**
- **Column B: 4.3 mg N/L → removal 87 %**

Column B shows higher TN removal:

- **Heterotrophic denitrification under anoxic conditions**

Results & discussion: Fe concentrations



Column A: aerobic

Synthetic solution (day 1-54):

- **Outlet Fe: 0.28 ± 0.69 mg Fe/L**

Real effluent (day 55-120):

- **Outlet Fe: 0.21 ± 0.17 mg Fe/L**

Column B: anoxic

Synthetic solution (day 1-54):

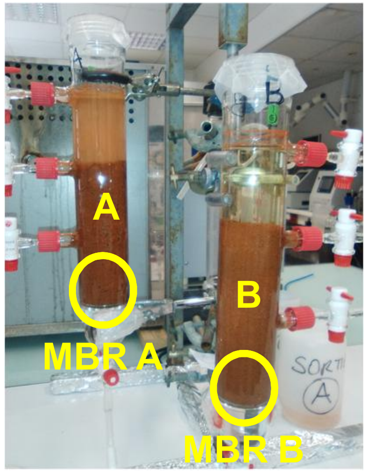
- **Outlet Fe: 0.23 ± 0.07 mg Fe/L**

Real effluent (day 55-120):

- **Outlet Fe: 1.26 ± 0.61 mg Fe/L**

➢ **Fe release from MBR**

Material & methods: chemical extractions



Chemical extractions: to identify main mechanisms of P removal.

Three different samples of MBR:

- **Raw MBR:** MBR before the use to treat water;
- **MBR A:** MBR from the inlet of column A;
- **MBR B:** MBR from the inlet of column B.

After 140 days of column operation

1. *Aqua regia* extractions (EN 13346, 2000): to determine total P content.
2. Sequential extractions (Moir *et al.*, 1993; Barca *et al.*, 2014): to quantify:
   1. Bicarbonate extractable P: weakly bound P;
   2. Hydroxide extractable P: leachable Al and Fe bound P;
   3. Diluted acid extractable P: leachable Ca bound P;
   4. Hot concentrated acid extractable P: P in stable residual compounds*.
3. Amorphous Fe extractions (EN 12782-1, 2009): reactive Fe under amorphous form.

*Mainly attributed to: Ca-P crystals and/or organic P.

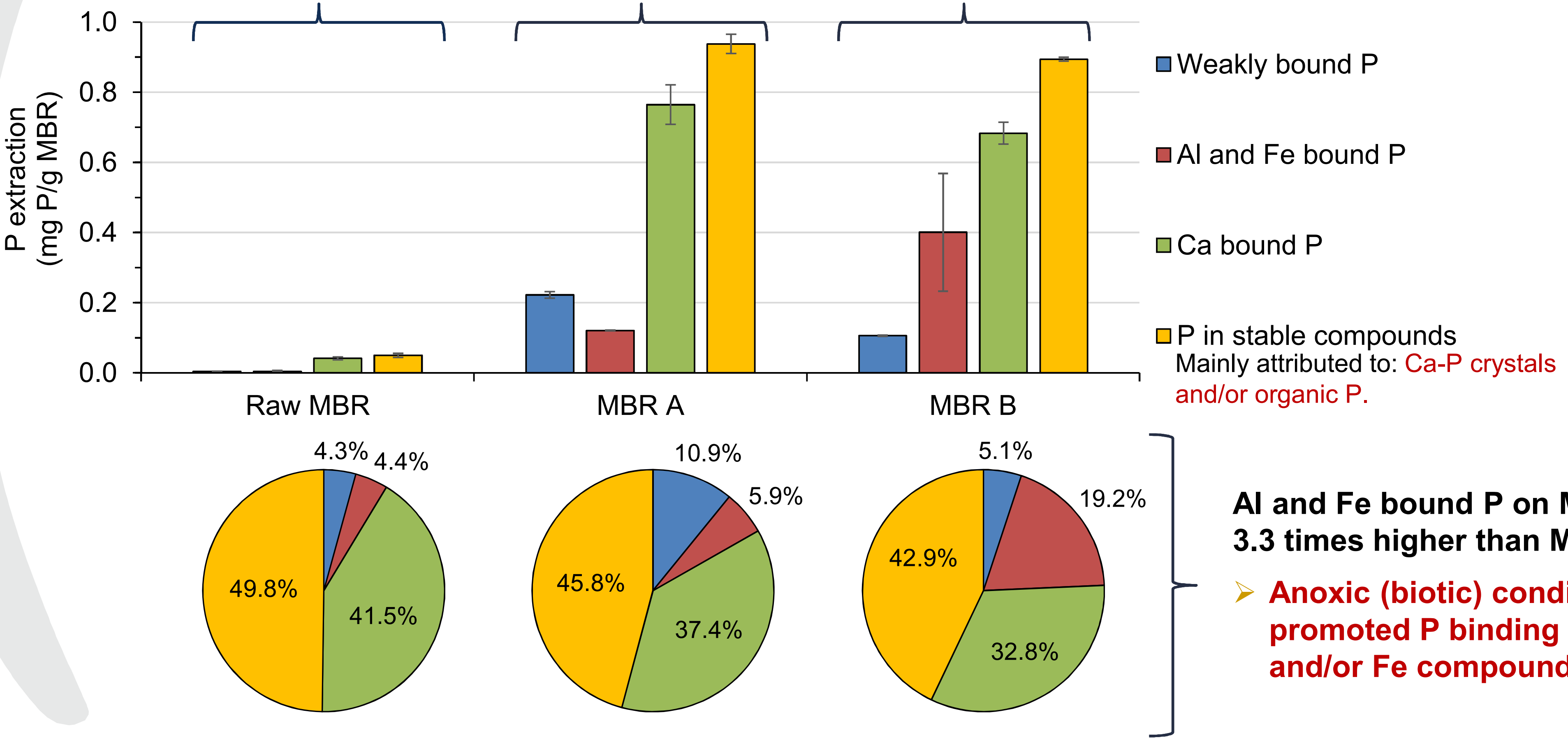
Results & discussion: P removal mechanisms

Sequential P extraction experiments:

Raw MBR: **0.10 mg P/g MBR**

MBR A: **2.04 mg P/g MBR**

MBR B: **2.08 mg P/g MBR**



Mainly attributed to: Ca-P crystals and/or organic P.

***Aqua regia* extraction :**

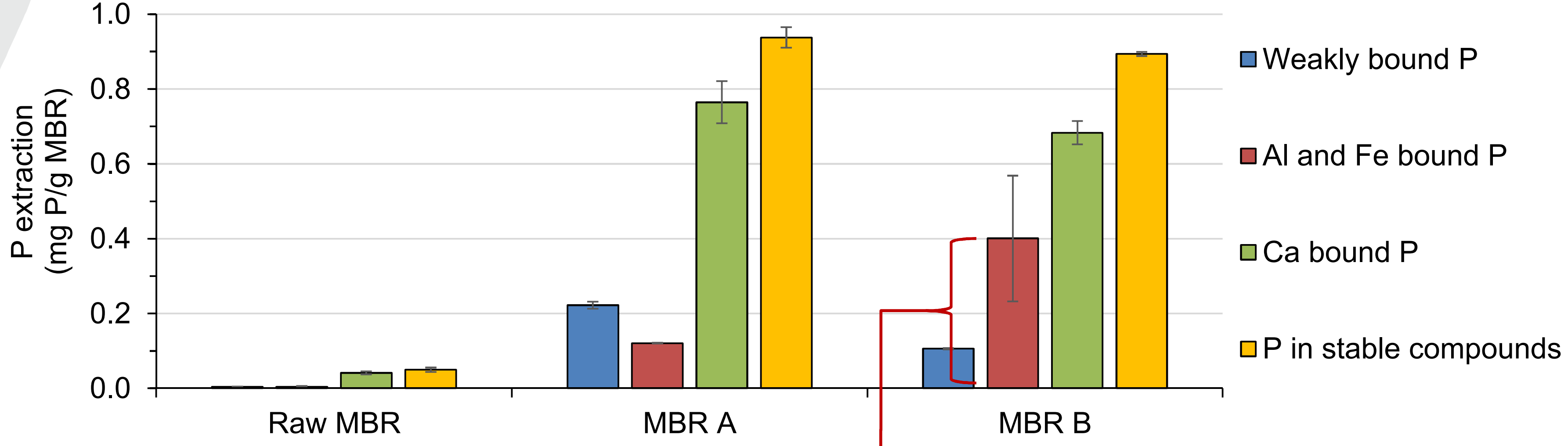
MBR A: 2.3 mg P/g MBR

MBR B: 2.6 mg P/g MBR

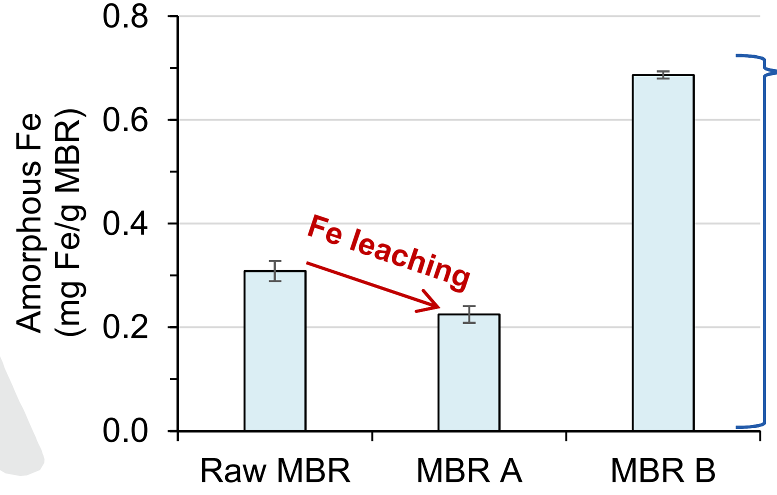
Al and Fe bound P on MBR B 3.3 times higher than MBR A:

- **Anoxic (biotic) conditions promoted P binding to Al and/or Fe compounds**

Results & discussion: P removal mechanisms



Amorphous Fe extraction experiments:



0.40 mg P/g MBR

0.69 mg Fe/g MBR

Molar ratio Fe/P: 0.95 ⇒ **Stoichiometric molar ratio of Fe/P complexes: 1**

Amorphous Fe content of MBR B 3.1 times higher than MBR A:

- **Mobilization of stable Fe under anoxic (biotic) conditions:**
  - **i. More Fe was available for P binding;**
  - **ii. Fe-releases from column B (anoxic).**

Material & methods: pilot filter experiments

Main objectives:

- To evaluate long term P removal performances;
- To investigate long term P removal mechanisms.

Lab-scale filter:

- Total volume: 31.5 L;
- MBR volume: 22.5 L.

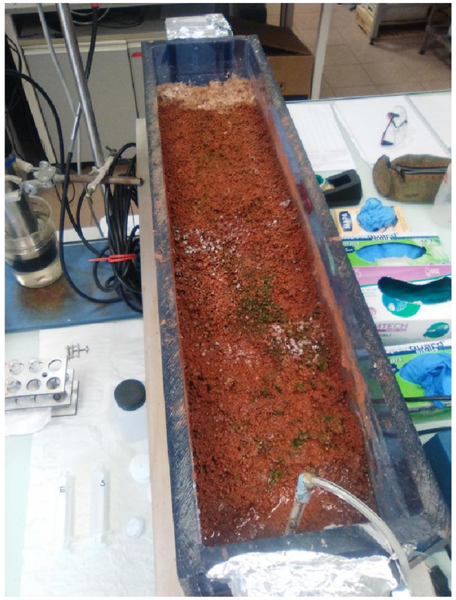
Filter operation:

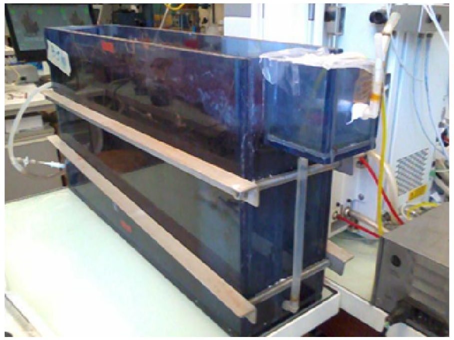
- Feeding mode: continuous sub-horizontal flow;
- Theoretical HRTv: 1 day;
- Feeding solution: tap water + 10 mg P/L + 40 mg N/L (KNO_3).

The filter has been operated for a total period of 30 months over the last 5 years (experiment started at IMT-Atlantique, Nantes)

(alternating periods of 6 months of operation and 6 months of rest)

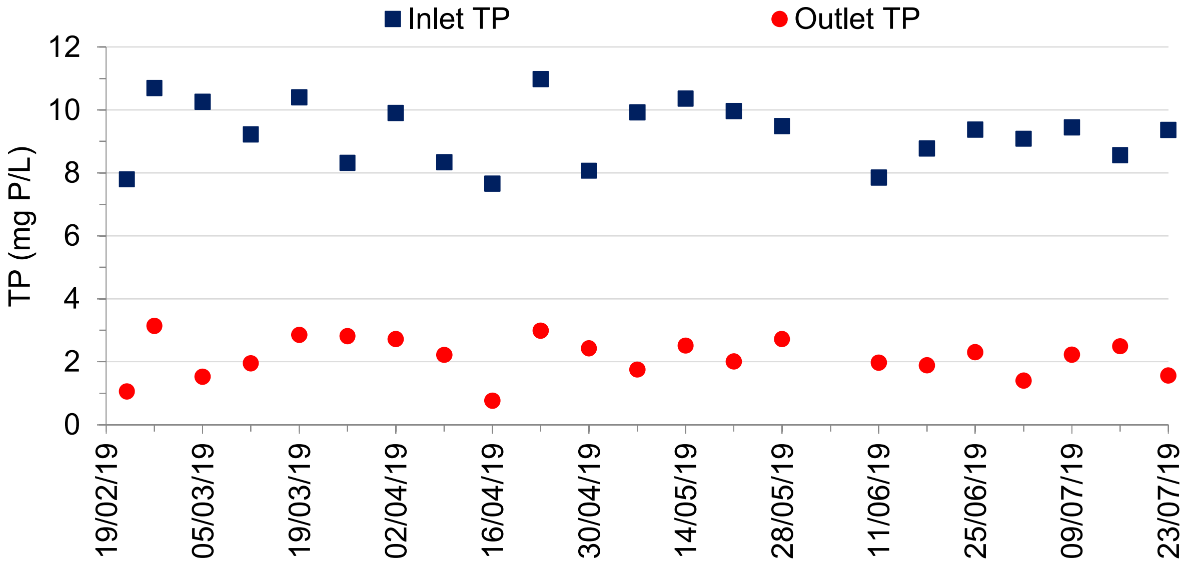
Pilot filter (31.5 L)





Results & discussion: pilot filter experiments

Inlet and outlet TP during the last 6 months of operation (Feb-Jul 2019):



Filter performances (Feb-Jul 2019):

- **TP removal efficiency: 77 ± 6 %;**
- **Outlet TP: 2.1 ± 0.6 mg P/L;**
- **Outlet pH: 8.1 ± 0.2.**

➢ **No clogging during the full period of operation.**

Calculated P retention capacity over the full period of 30 months of operation:

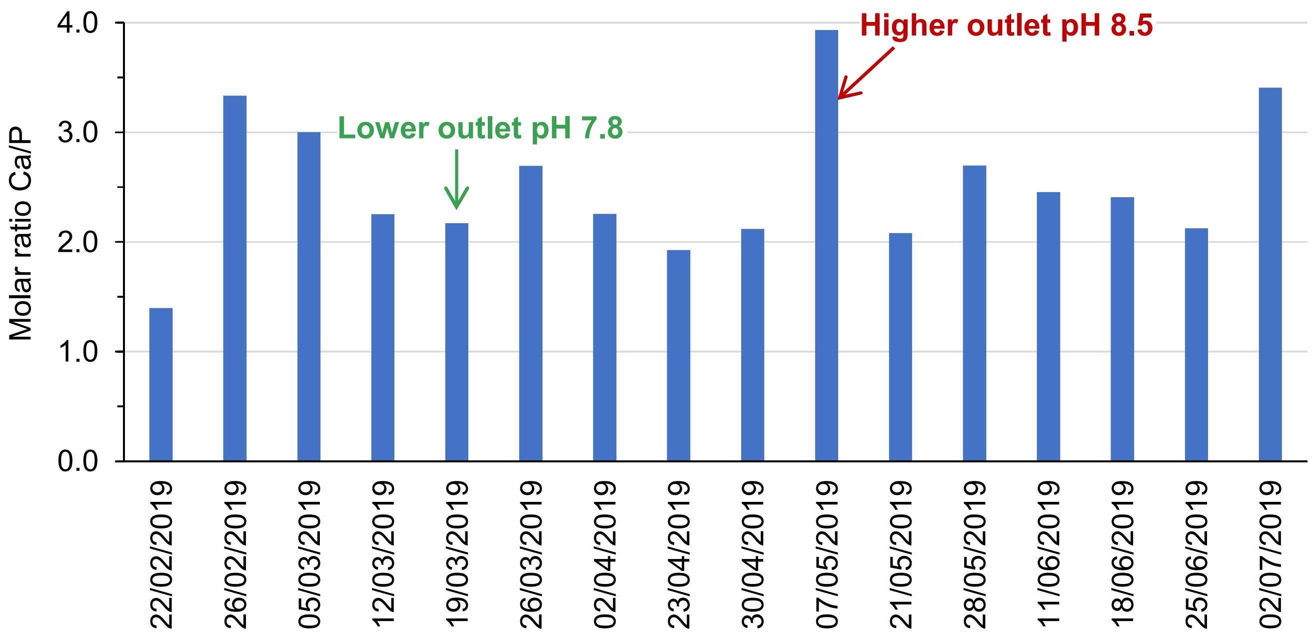
➢ **2.9 g P/kg MBR (< than batch exp.): filter may work several years before saturation.**

Outlet TP stabilized around a value of 2 mg P/L after 24 months of operation:

➢ **P removal controlled by chemical equilibria of ion species in solution.**

Results & discussion: pilot filter experiments

Molar ratio Ca removed / P removed during the last 6 months of operation (Feb-Jul 2019):



Most recurrent Ca-P complexes (Valsami-Jones, 2001)

Name and formula	Molar ratio Ca/P	Solubility product (mol/L)
Brushite $CaHPO_4 \cdot 2H_2O$	1	$2.49 \cdot 10^{-7}$
Monetite $CaHPO_4$	1	$1.26 \cdot 10^{-7}$
Octacalcium phosphate $Ca_4H(PO_4)_3 \cdot 2.5H_2O$	1.33	$1.25 \cdot 10^{-47}$
Tricalcium phosphate $Ca_3(PO_4)_2$	1.5	$1.20 \cdot 10^{-29}$
Hydroxyapatite $Ca_5(PO_4)_3OH$	1.67	$4.7 \cdot 10^{-59}$

Experimental molar ratio Ca removed / P removed: 1.4 - 3.9

Molar ratio Ca/P of most common Ca-P complexes: 1 - 1.67

Co-precipitation of Ca-P and $CaCO_3$ under alkaline conditions (Barca *et al.*, 2014)

Conclusions

MBR is an efficient material to remove P from wastewater:

- High P retention capacity (> 4 g P/kg MBR);
- High long time P removal efficiency (about 80 % after 30 months of filter operation);
- Almost neutral effluent pH (7-8);
- Good hydraulic conductivity.

Main mechanism of P removal:

i. Ca-P precipitation, filtration and crystallization of Ca-P complexes;
ii. P binding to Al and/or Fe compounds.

Anoxic (biotic) conditions can promote mobilization of Fe-compounds, thus:

- Promoting Fe-P binding;
- Leading to Fe releases from the filter.

➢ A strict control of aerobic conditions is recommended.

Perspectives

Field scale experiments: to evaluate long term (5-10 years) hydraulic and P removal performances of MBR filters under real operating conditions.

P recovery experiments: to evaluate the most efficient technique to recover P from MBR filters after saturation of P retention capacity.

Photos: field scale steel slag filters (PhD Barca, 2012), European Project SLASORB