Understand Phosphorus dissolution in sewage sludge by Bio-acidification.

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  - P recovery by bioacidification
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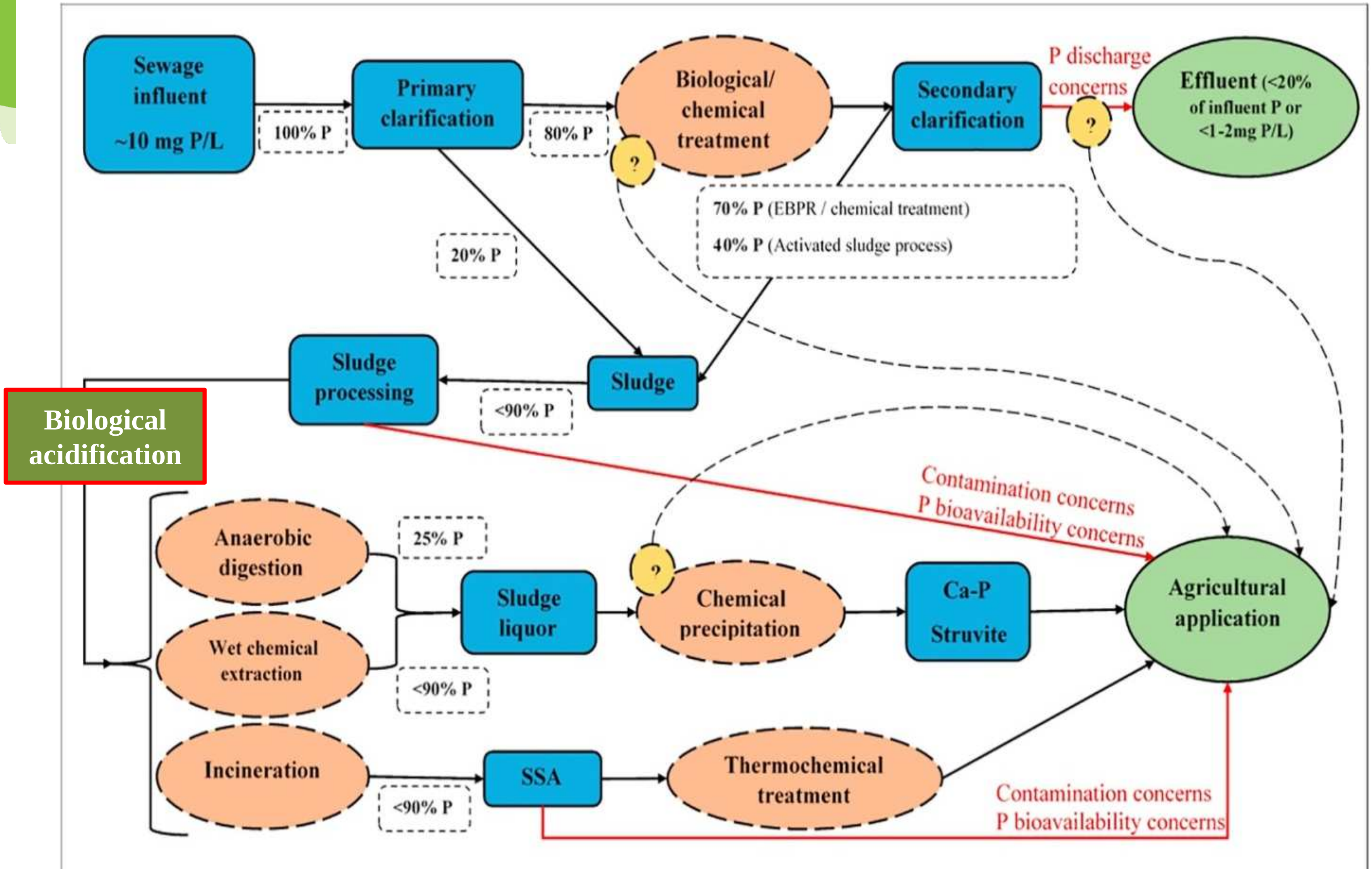
Overview of P removal and Recovery

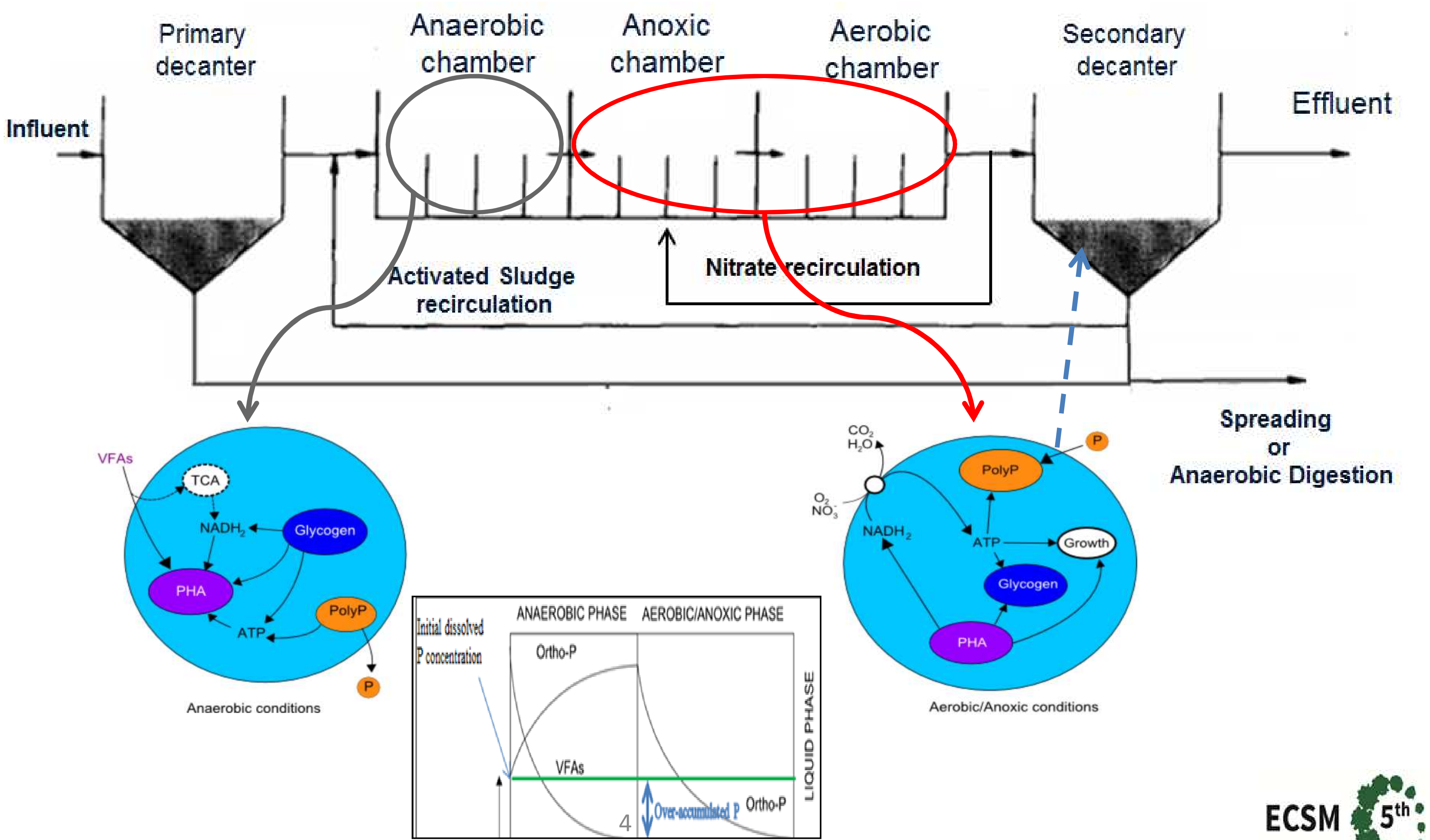


(Melia et al., 2017)

Some 1.01 P removal in WWTP

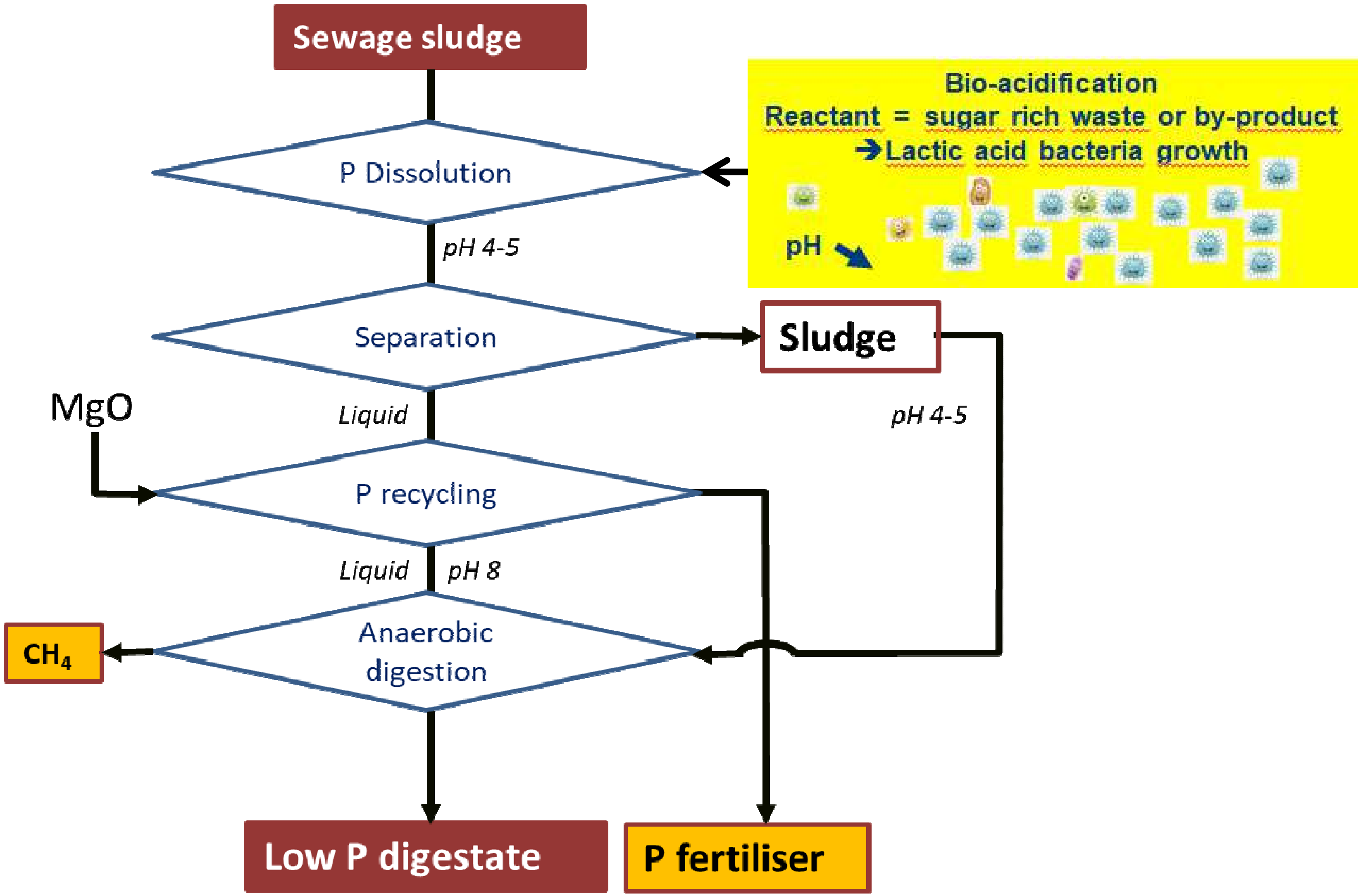
P removal from WWTP

- Biological P removal (EBPR)



Overview of P removal and Recovery

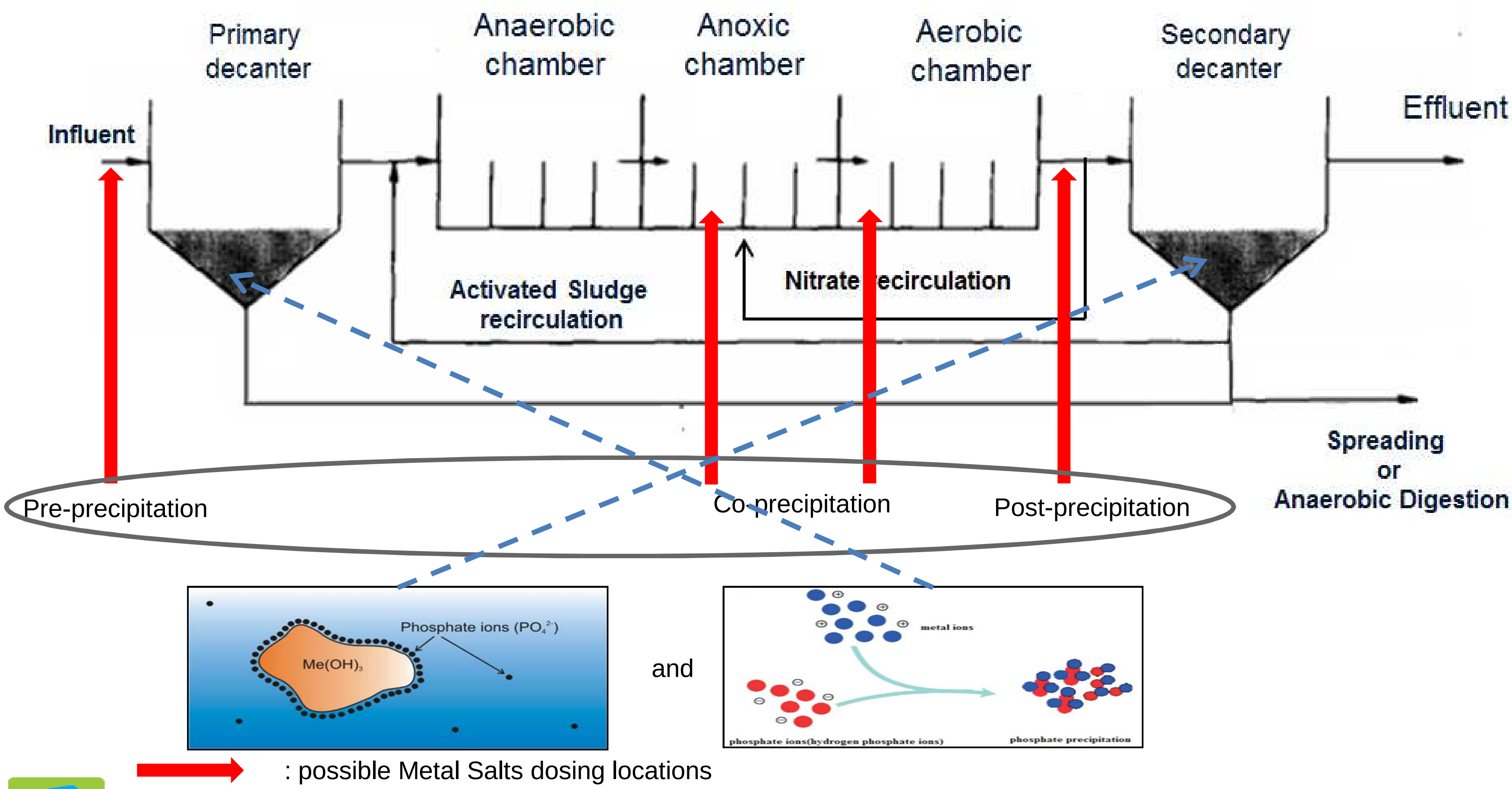
P recovery by bioacidification



Some 1.01 P removal in WWTP

P removal from WWTP

- Chemical P removal (CPR) and CPR +EBPR



Some 1.01 P removal in WWTP

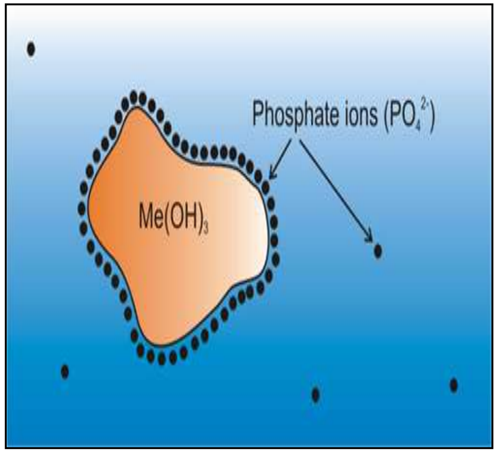
P removal from WWTP using Iron slats

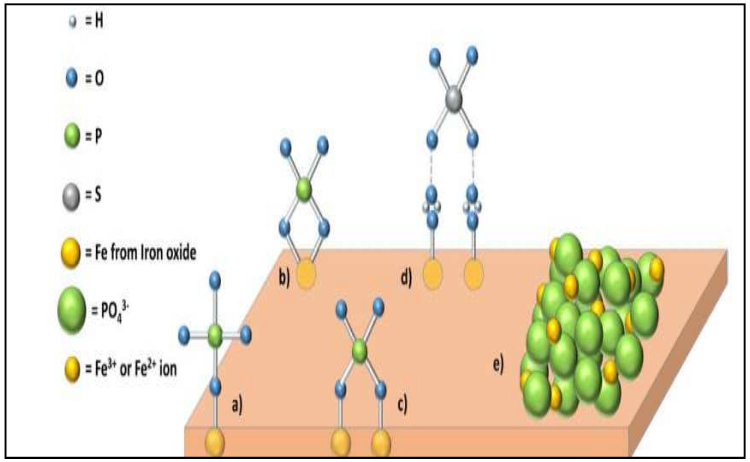
- Most used iron salt: **Ferric-slats ($FeCl_3$)** and **Ferrous-Salts ($FeSO_4$)**

What are the mechanisms of P removal by iron salts ?

- **P-Adsorption on iron oxide (hydroxide or oxyhydroxide)**

$$Fe^{3+} + 3\ OH^{-} \longrightarrow Fe(OH)_3 \xrightarrow[\text{Dissolved P}]{} Fe(OH)_3{\sim}P$$





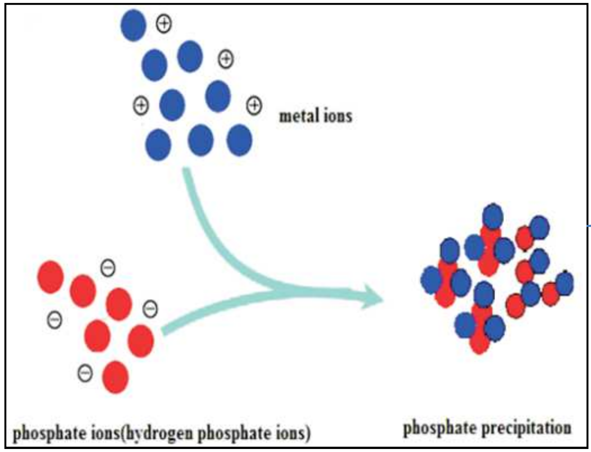
Wilfert et al. 2015

Some 1.01 P removal in WWTP

P removal from WWTP using Iron slats

What are the mechanisms of P removal by iron salts?

- **Iron-Phosphate precipitation**



Fe(II) or Fe(III) Oxidative conditions:

$FeCl_3 + PO_4^{3-} \rightarrow FePO_4 + 3Cl^-$

Fe(II) Reducing conditions:

$3FeSO_4 + +2PO_4^{3-} \rightarrow Fe_3(PO_4)_2 + 3SO4^{2-}$

Depending on ORP conditions

Some 1.01 P removal in WWTP

P removal from WWTP using Iron slats

Is there an effects of the Iron Salts nature / dosing location in Fe-CPR ?

Wastewater origin	Fe:P molar ratio	Iron salts type	Number and location of salts dosing	Influent P concentration (mg/l)	residual P (mg/l)	P removal (%)	reference
Letchworth	0.89	Ferric Sulphate	2 biol	nd	1.00	80	Strickland, 1998
	1.11			nd	0.51	93	
	1.61			nd	0.36	96	
Sheboygan	0.89	Ferric Chloride	2 clarifier	6.38	0.90	85	EPA, 1987
Letchworth	0.72	Ferrous Sulphate	2 biol	nd	2.30	63	Strickland, 1998
	1.28			nd	0.72	86	
	1.56			nd	0.62	93	
Appleton	0.89	Ferrous Chloride	Plant influent	10.45	0.80	92	EPA, 1987
Port Clinton	1.09		2 biol	5.2	0.50	90	
Port Washington	0.8		1 clarifier	5.9	1.00	83	

Some 1.01 P removal in WWTP

→ 1.02

P removal from WWTP using Iron slats

- No effect of iron salts' nature (ferric or ferrous) was reported for P removal efficiency **(when properly managed**)

BUT → Fe-P precipitate (sludge) →

Iron salt	dosing Location	Fe-P menirals (Sludge quality)
Fe(III)Cl3	Aerobic chamber	*Ferrihydrite 42-45% *Fe(III)Phosphate 46-50% *Lepidorocite 8.5%
Fe(II)SO4	Aerobic chamber	*Ferrihydrite 0-2% *Fe(III)Phosphate 39-42% *Lepidorocite 50-54%
Fe(II)SO4	Anoxic chamber	*Ferrihydrite 6-12% *Fe(III)Phosphate 50% *Lepidorocite 30-32%

Wu et al, 2015 in MBR system and synthetic WW

Objectives

Answer two questions :

- **In which forms P and Fe are present in a selected/specific sewage sludge ?**
- **Which solid P and Fe forms are dissolving after bioacidification?**

Three ways could be used:

- **Direct analysis of the sludge (XRD, XANES, Mössbauer-spectroscopy, …)**
- **Sequential Extraction**
- **Modeling (High-level modeling!!!)**

Materials and methods

The sequential Extraction method (based on the SEDEX method (Ruttenberg, 1992) and Gu et al 2015)

Step	Extractant	T (^0C)	pH	Time (h)	V (ml)	P- fraction	Fe fraction	Reference
1	Centrifugation					Dissolved P	Dissolved Fe	-
2	1M $MgCl_2$					Exchangeable P (Labil, loosely adsorbed)	Exchangeable Fe	SEDEX: Ruttenberg, 1992
3	0.5 wt % 2,2 `-bipyridine + 0.1 M KCl					Fe(II)-P bound (Vivianite-Like)	Fe(II) compounds (Vivianite)	Gu et al.
4	0.1 M NaOH					P-adsorbed to metal hydroxides	-	SMT/SEDEX
5	1M HCl					Ca-P and acid sensitive minerals	Most Iron (hydr)oxides	SMT/SEDEX
6	Total mineralization					Organic and Refractory	Refractory Fe	-

We can distinguish the Fe(II) compounds from the Fe(III) compounds

Materials and methods

Sludge origin and Characteristics

Characteristics	WWTP 1*	WWTP 2*
Sludge type	Thickened	Thickened
Total Solids(TS) (g/kg sludge)	49	42
Mineral matter content (MM) (g/kg sludge)	14	9
Volatile Solids(VS) (g/kg sludge)	35	33
pH	6.7	6.1
Alkalinity (g HCO_3/kgw)	10.1	9.8
Total concentrations of chemical species		
P (mM)	49	37
Fe (mM)	22	21
Al (mM)	16	7
Ca (mM)	22	12
Mg (mM)	13	9

* Both WWTP1 and WWTP2 use biological P removal combined with Fe_3Cl precipitation

irstea

ECSM 5th

Results

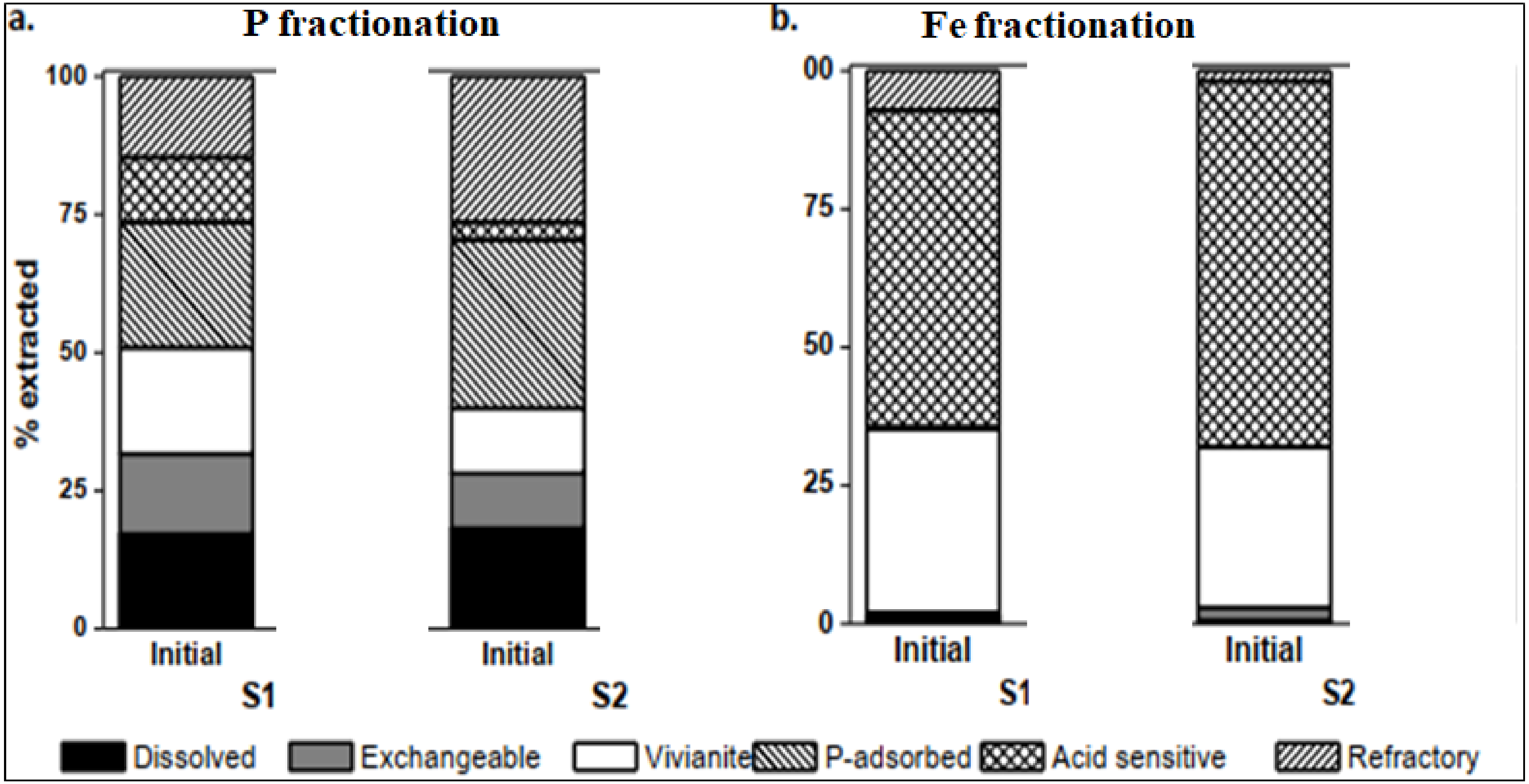
Bioacidification conditions:

- Co-substrate concentration: 0,5gCOD.gVS^{-1}
- Incubation at 38°C under anaerobic conditions for 24h

WWTP	***Raw sludge***			***After bioacidification (24h)***				
	pH $_{initial}$	[P] $_{initial}$ (mM)	[Fe] $_{initial}$ (mM)	pH $_{final}$	$[P]_{final}$ (mM)	[Fe] $_{final}$ (mM)	% of P_{diss}	% of Fe_{diss}
1	6.7	3.3	0.1	4.1	23.6	12.4	**48**	**57**
2	6.1	10.1	0.1	3.9	20.0	14.7	**53**	**70**

Results

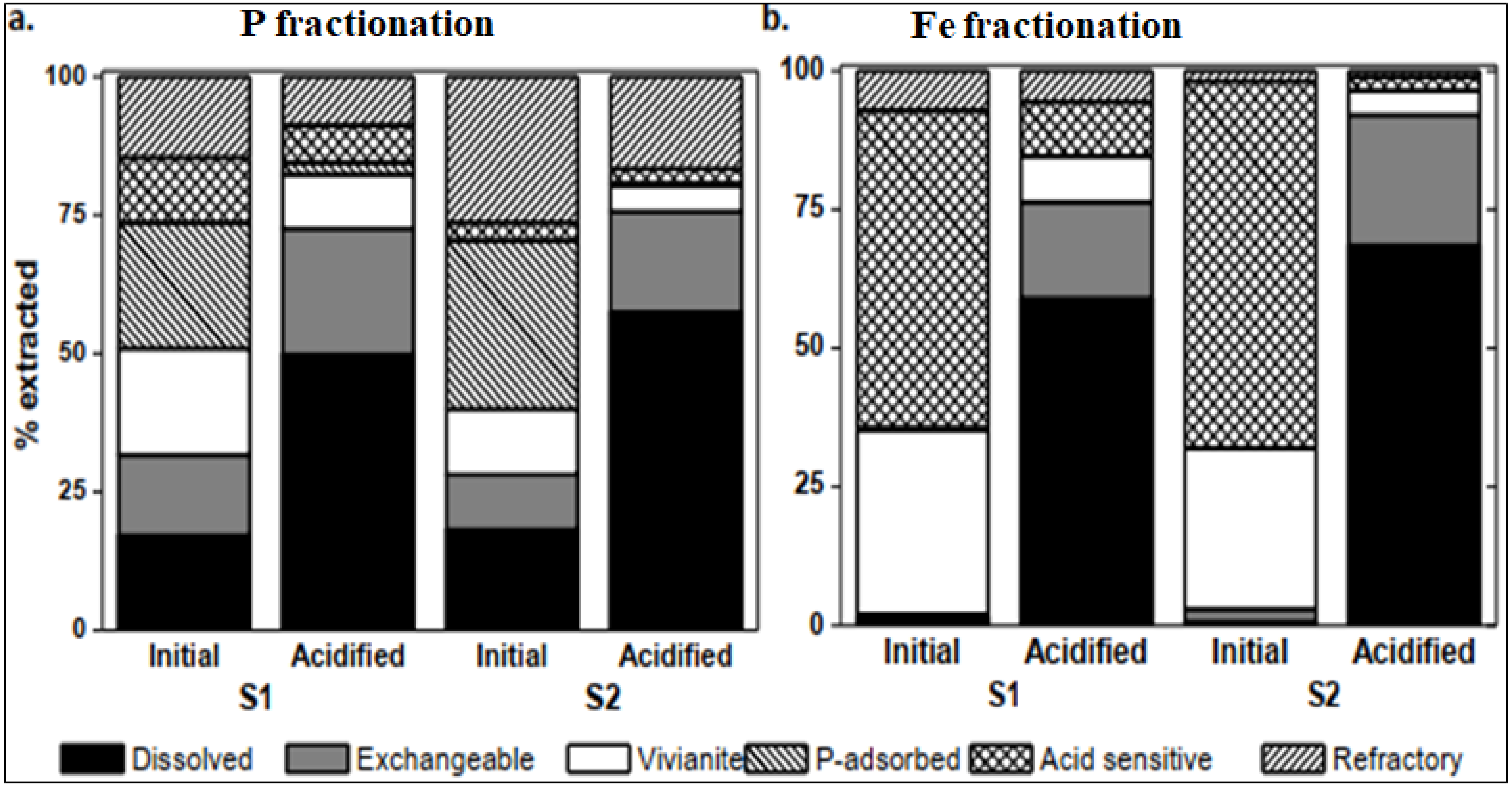
- Sequential Extraction before Bioacidification:



The extraction was carried on duplicate, Standard deviation in each fraction were below 2%)

Results

- Sequential Extraction **After** Bioacidification:



Conclusion

- It's not just an Acidification.
    - Several mechanisms are responsible of the P dissolution (Iron reduction, pH, ions exchange, desorption,…)
- Source control:
    - P removal configuration has a significant impact on the sludge quality regarding bioacidification efficiency.
- Simple characterisation (Fe/P ratio, TS, ….) is not enough to evaluate sludge quality,
- Sequential extraction with Fe(II) extraction step could help better understand the Fe-P interactions in sludge.

Perspectives

- Evaluate several sludge from multiple WWTP with different treatment configurations (In progress)
- Replace NaOH extraction with a reduction agent to differentiate P-Ca and P-Fe(III) precipitate,
- Sludge characterization with direct methods such as XRD
- Optimization of bioacidification by ethier:

Thank you for your attention