PHORWATER
Integral Management Model for Phosphorus recovery and reuse from Urban Wastewater
LIFE12 ENV/ES/000441
Implementation of the phosphorus recycling installation at the Calahorra WWTP

Workshop
P-recovery as struvite
Regulation constraints for its use as a fertilizer

Lyon-Villeurbanne, le 12 Mai 2016
Integral management of WWTP for P recovery

Design, construction and start-up of the crystallization process

Implementation of the P recovery demonstration plant

Validation of the struvite
El Cidacos WWTP
- El Cidacos WWTP, Calahorra, Spain
- 23,000 m$^3$/d
- EBPR (A2O Configuration)
- Anaerobic digestion for primary and secondary sludge
El Cidacos WWTP
Characterization of the water and sludge lines

- 5 analytical campaigns (November 2013 to February 2014):
  - To determine the P removal efficiency in the water line.
  - To assess the precipitation processes in the sludge line.
Assessment of P recovery feasibility

Average P removal in water line = 80%

SIDESTREAM RETURNS

Primary Sludge Thickening

Mixing Chamber

Secondary Sludge Thickening

SIDESTREAM RETURNS

Sludge Dewatering

Secondary Anaerobic Digestion

Anaerobic Digestion

S

DAM

Universitat de València

Cal Água

Université Claude Bernard Lyon 1

LAGEP
Assessment of P recovery feasibility
Assessment of P recovery feasibility
P, Mg, K and Ca mass balances

  - Considering the P, Mg, K release by PAOs in anaerobic conditions

<table>
<thead>
<tr>
<th>Phosphorus loss (gP/kg sludge):</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Precipitation in the digester</td>
<td></td>
</tr>
<tr>
<td>Precipitation in the mixing chamber</td>
<td>3.8</td>
</tr>
<tr>
<td>Dewatered sludge</td>
<td>0.2</td>
</tr>
<tr>
<td>Total P lost</td>
<td>13.5</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Phosphorus available (gP/kg sludge):</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Primary sludge overflow</td>
<td>0.4</td>
</tr>
<tr>
<td>WAS liquor</td>
<td>0.1</td>
</tr>
<tr>
<td>Dewatering centrate</td>
<td>1.7</td>
</tr>
<tr>
<td>Total P available</td>
<td></td>
</tr>
</tbody>
</table>

The main phosphorus loss point in the plant was the anaerobic digester

14% P entering the sludge line is available for its recovery

Results based on the average mass flowrate entering the sludge line (4057 kgTS/d)
Optimal WWTP operation to maximize P recovery

- El Cidacos WWTP was simulated with a software tool (DESASS©) using the experimental data obtained.

- Once the current WWTP operational configuration was validated in DESASS, different strategies were proposed:
  - To reduce the high P precipitation observed in the digester.
  - To obtain an overflow stream with a high phosphate concentration ready to be used in a crystallization step.

- Optimal configuration:

  ELUTRIATION OF THE MIXED SLUDGE IN THE GRAVITY THICKENER
Optimal WWTP operation to maximize P recovery

- The proposed sludge line configuration was exhaustively simulated to determine the optimal operating conditions that:
  - Reduce the P precipitation during the anaerobic digestion.
  - Increase the P concentration in the effluent of the primary thickener for further P recovery.

- Parameters evaluated:
  - Elutriation flow
  - Digestion flow
  - Sludge blanket height
Optimal WWTP operation to maximize P recovery

The higher elutriation flow and the lower digestion flow the higher P concentration in the P recovery stream, increasing the potential P recovery

This elutriation flow is limited by the sludge blanket height
Validation of the new WWTP configuration
Characterization of the water and sludge lines

Water line sampling points

Sludge line sampling points

Elutriation flow

Digestion flow
Validation of the new WWTP configuration

Average P removal in water line = 92%
Validation of the new WWTP configuration
Validation of the new WWTP configuration
P, Mg, K and Ca mass balances

- Following the methodology developed by Martí et al. (2008) Chem. Eng. J. 141, 67-74:
  - Considering the P, Mg, K release by PAOs in anaerobic conditions

<table>
<thead>
<tr>
<th>Phosphorus loss (gP/kg sludge):</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Precipitation in the digester</td>
<td>5.5</td>
</tr>
<tr>
<td>Precipitation in the mixing chamber</td>
<td>4.0</td>
</tr>
<tr>
<td>Dewatered sludge</td>
<td>0.4</td>
</tr>
<tr>
<td>Total P lost</td>
<td>9.9</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Phosphorus available (gP/kg sludge):</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Primary sludge overflow</td>
<td>1.5</td>
</tr>
<tr>
<td>Dewatering centrate</td>
<td>2.4</td>
</tr>
<tr>
<td>Total P available</td>
<td>3.9</td>
</tr>
</tbody>
</table>

The phosphorus loss in the anaerobic digester was reduced

28% P entering the sludge line is available for its recovery

Results based on the average mass flowrate entering the sludge line (3136 kgTS/d)
Validation of the new WWTP configuration

- **Without elutriation**

<table>
<thead>
<tr>
<th>Phosphorus loss (gP/kg sludge):</th>
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</thead>
<tbody>
<tr>
<td>Precipitation in the digester</td>
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</tr>
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<tr>
<td>Dewatered sludge</td>
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<tr>
<td>Total P lost</td>
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<td>Dewatering centrate</td>
<td>1.7</td>
</tr>
<tr>
<td>Total P available</td>
<td>2.1</td>
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- **With elutriation**

<table>
<thead>
<tr>
<th>Phosphorus loss (gP/kg sludge):</th>
<th>5.5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Precipitation in the digester</td>
<td>5.5</td>
</tr>
<tr>
<td>Precipitation in the mixing chamber</td>
<td>4.0</td>
</tr>
<tr>
<td>Dewatered sludge</td>
<td>0.4</td>
</tr>
<tr>
<td>Total P lost</td>
<td>9.9</td>
</tr>
</tbody>
</table>

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<tr>
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<tbody>
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<tr>
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<td>2.4</td>
</tr>
<tr>
<td>Total P available</td>
<td>3.9</td>
</tr>
</tbody>
</table>

The phosphorus loss in the anaerobic digester was reduced a 43%
Validation of the new WWTP configuration

### Without elutriation

<table>
<thead>
<tr>
<th>Conventional configuration</th>
<th>Q (m³/d)</th>
<th>Pt (mg/l)</th>
<th>kgP/d</th>
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</thead>
<tbody>
<tr>
<td>WWTP Influent</td>
<td>13310</td>
<td>7.0</td>
<td>93.5</td>
</tr>
<tr>
<td>WWTP Effluent</td>
<td>13281</td>
<td>1.4</td>
<td>18.3</td>
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<tr>
<td>P in the sludge line</td>
<td></td>
<td></td>
<td>75.2</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>P availability</th>
<th>Q (m³/d)</th>
<th>P-PO4 (mg/l)</th>
<th>kgP/d</th>
</tr>
</thead>
<tbody>
<tr>
<td>Primary sludge overflow</td>
<td>42.2</td>
<td>37.8</td>
<td>1.6</td>
</tr>
<tr>
<td>Dewatering centrate</td>
<td>79.8</td>
<td>84.6</td>
<td>6.8</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td></td>
<td>8.4</td>
</tr>
</tbody>
</table>

- %P available regarding total P entering the sludge line: **11**
- %P available regarding total P entering the WWTP: **9**

### With elutriation

<table>
<thead>
<tr>
<th>New configuration</th>
<th>Q (m³/d)</th>
<th>Pt (mg/l)</th>
<th>kgP/d</th>
</tr>
</thead>
<tbody>
<tr>
<td>WWTP Influent</td>
<td>10000</td>
<td>7.1</td>
<td>71.0</td>
</tr>
<tr>
<td>WWTP Effluent</td>
<td>9537</td>
<td>0.6</td>
<td>5.7</td>
</tr>
<tr>
<td>P in the sludge line</td>
<td></td>
<td></td>
<td>65.3</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>P availability</th>
<th>Q (m³/d)</th>
<th>P-PO4 (mg/l)</th>
<th>kgP/d</th>
</tr>
</thead>
<tbody>
<tr>
<td>Primary sludge overflow</td>
<td>61.0</td>
<td>75.7</td>
<td>4.6</td>
</tr>
<tr>
<td>Dewatering centrate</td>
<td>92.7</td>
<td>81.5</td>
<td>7.6</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td></td>
<td>12.2</td>
</tr>
</tbody>
</table>

- %P available regarding total P entering the sludge line: **19**
- %P available regarding total P entering the WWTP: **17**
Validation of the new WWTP configuration

- The operation of the sludge line under the new operating conditions shows:
  - P concentrations in the thickener supernatant up to 100-132 mg PO4-P/L (Average elutriation flow rate: 70 – 80 m³/d)
  - P availability in the thickener supernatant: 1.5g P/kg sludge (increased from 0.4)
  - P availability in the digester (IN + TOTrel) = 263 mg/L (with the former configuration 535 mg/L).
Background

Integral management of WWTP for P recovery

Design, construction and start-up of the crystallization process

Implementation of the P recovery demonstration plant

Validation of the struvite
Design, construction and start-up of the crystallization process

- In order to support the industrial crystallizer design task, lab-scale assays from this real gravity thickener supernatant were carried out:
  - Lab-scale experiments were carried out in a 20.6 L continuous crystallization reactor.
Design, construction and start-up of the crystallization process

Lab-scale crystallization assays

Crystallizing process results for the three experiments

<table>
<thead>
<tr>
<th></th>
<th>Exp. 1</th>
<th>Exp. 2</th>
<th>Exp. 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>HRT (h)</td>
<td>4.35</td>
<td>2.05</td>
<td>1.05</td>
</tr>
<tr>
<td>pH</td>
<td>8.7±0.1</td>
<td>8.7±0.1</td>
<td>8.7±0.1</td>
</tr>
<tr>
<td>Molar ratio Mg/P</td>
<td>1.5±0.3</td>
<td>1.6±0.1</td>
<td>1.6±0.1</td>
</tr>
<tr>
<td>Molar ratio N/P</td>
<td>2.3±0.2</td>
<td>2.6±0.1</td>
<td>2.4±0.2</td>
</tr>
<tr>
<td>PO₄-P_influent</td>
<td>150±26</td>
<td>134±6</td>
<td>132±9</td>
</tr>
<tr>
<td>Total P_effluent</td>
<td>13.8±5.4</td>
<td>24.1±2.3</td>
<td>35.9±11.2</td>
</tr>
<tr>
<td>PO₄-P_effluent</td>
<td>5.9±0.8</td>
<td>4.7±0.5</td>
<td>5.5±0.9</td>
</tr>
<tr>
<td>Precipitation Efficiency (%)</td>
<td>95.8±1.3</td>
<td>96.4±0.3</td>
<td>95.8±0.9</td>
</tr>
<tr>
<td>Recovery Efficiency (%)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Struvite production (g struvite/L supernatant treated)</td>
<td>1.1±0.3</td>
<td>1.00±0.04</td>
<td>0.96±0.08</td>
</tr>
<tr>
<td>Average particle size (µm)</td>
<td>183±59</td>
<td>207±8</td>
<td>213±19</td>
</tr>
</tbody>
</table>
Design, construction and start-up of the crystallization process

Lab-scale crystallization assays

Characteristics of the crystals obtained

- Particles average sizes: >180μm
- X-ray diffractogram and energy-dispersive X-ray spectroscopy (SEM) confirms struvite as the main product:
  - 12.6% P, 5.0% N, 9.5% Mg and 1.3% Ca
Design, construction and start-up of the crystallization process

- Designed to treat 20 m³/d (HRT = 2.5 h).
- The reactor is composed of:
  - A stirred mixing zone in which precipitation takes place.
  - A settling zone to keep the solid particles inside of the reactor.
- The reactor is operated in continuous mode with the liquid phase and batchwise with the solid particles.
Background

Integral management of WWTP for P recovery

Design, construction and start-up of the crystallization process

Implementation of the P recovery demonstration plant

Validation of the struvite
Implementation of the P recovery demonstration plant

Demonstration crystallization plant

- Operated from May-2015 uninterruptedly
- Efficiencies ≈ 90%
- Struvite production: 7.6 kg/d – 0.5 kg/m³
Background

Integral management of WWTP for P recovery

Design, construction and start-up of the crystallization process

Implementation of the P recovery demonstration plant

Validation of the struvite
Validation of the struvite
Characteristics of the obtained crystals

- Particles average sizes: >200μm
Validation of the struvite
Characteristics of the obtained crystals

- X-ray diffraction analysis also confirms struvite as the main product
Validation of the struvite

Characteristics of the obtained crystals

Proposed struvite requirements (ESPP):
- P: 10.0-13.9%
- MgO: 13.1-18.1%
- N: 4.6-6.3%
- TOC < 2%

- Optical and electronic microscopy (SEM) show struvite as the main product
- Total Organic Carbon (TOC) < 0.9%

11.8% P
6.0% N
9.5% Mg
5.1% Ca

Product struvite purity ≈ 81%
Validation of the struvite
Characteristics of the obtained crystals

- Atomic absorption spectroscopy analysis:

<table>
<thead>
<tr>
<th>Element</th>
<th>Sludge from WWTP 1</th>
<th>Sludge from WWTP 2</th>
<th>Struvite from Calahorra WWTP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn</td>
<td>16.77</td>
<td>11.0</td>
<td>LOQ-241</td>
</tr>
<tr>
<td>Cd</td>
<td>2.2</td>
<td>2.87</td>
<td>&lt;3</td>
</tr>
<tr>
<td>Cr</td>
<td>11.6</td>
<td>17.0</td>
<td>&lt;3</td>
</tr>
<tr>
<td>Cu</td>
<td>288</td>
<td>318</td>
<td>&lt;3</td>
</tr>
<tr>
<td>Ni</td>
<td>67.2</td>
<td>59.0</td>
<td>&lt;3</td>
</tr>
<tr>
<td>Pb</td>
<td>51.5</td>
<td>72.4</td>
<td>&lt;2</td>
</tr>
<tr>
<td>Ca</td>
<td>55571</td>
<td>59214</td>
<td>255-40000</td>
</tr>
<tr>
<td>Mg</td>
<td>5306</td>
<td>5426</td>
<td>16500-81871</td>
</tr>
<tr>
<td>K</td>
<td>913</td>
<td>705</td>
<td>1260-1558</td>
</tr>
</tbody>
</table>

All measurements in mg/kg of dry matter

Proposed struvite requirements (ESPP):
- Inorganic contaminants (limits):
  - Cd: 60 mgCd/kgP2O5
  - Cr(VI): 2 mg/kg dry matter
  - Hg: 2 mg/kg dry matter
  - Ni: 120 mg/kg dry matter
  - Pb: 150 mg/kg dry matter
  - As: 60 mg/kg dry matter
Validation of the struvite Characteristics of the obtained crystals

### Priority substances analysis

<table>
<thead>
<tr>
<th>Micropollutant</th>
<th>Unit (µg/kg)</th>
<th>Micropollutant</th>
<th>Unit (µg/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Octylphenol</td>
<td>&lt;3</td>
<td>Hexachlorobenzene</td>
<td>&lt;10.0</td>
</tr>
<tr>
<td>t-Nonylphenol</td>
<td>&lt;0.1</td>
<td>Hexachlorobutadiene</td>
<td>&lt;0.0</td>
</tr>
<tr>
<td>4-Nonylphenol</td>
<td>&lt;0.1</td>
<td>Pentachlorocyclohexene</td>
<td>&lt;0.0</td>
</tr>
<tr>
<td>Alachlor</td>
<td>&lt;0.1</td>
<td>Trifluoracarbon</td>
<td>&lt;0.0</td>
</tr>
<tr>
<td>Chlorfenvinphos</td>
<td>&lt;0.1</td>
<td>1,1,1-Trichloroethane</td>
<td>&lt;0.0</td>
</tr>
<tr>
<td>Aldrin</td>
<td>&lt;0.1</td>
<td>1,1,2-Trichlorobenzene</td>
<td>&lt;0.0</td>
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<tr>
<td>Dieldrin</td>
<td>&lt;0.1</td>
<td>1,1,3-Trichlorobenzene</td>
<td>&lt;0.0</td>
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<tr>
<td>Isodrin</td>
<td>&lt;0.1</td>
<td>Quinoline</td>
<td>&lt;0.0</td>
</tr>
<tr>
<td>Endrin</td>
<td>&lt;0.1</td>
<td>Aconifine</td>
<td>&lt;0.0</td>
</tr>
<tr>
<td>Endosulfan 1</td>
<td>&lt;0.1</td>
<td>Irgarol</td>
<td>&lt;0.0</td>
</tr>
<tr>
<td>Brominated diphenylethers</td>
<td>&lt;10</td>
<td>Terbutryn</td>
<td>&lt;0.0</td>
</tr>
<tr>
<td>Chloroalkanes</td>
<td>&lt;60</td>
<td>Di(2-ethylhexyl)phthalate</td>
<td>&lt;1.0</td>
</tr>
<tr>
<td>Anthracene</td>
<td>&lt;30</td>
<td>Naphthalene</td>
<td>&lt;1.0</td>
</tr>
<tr>
<td>Benzo(a)pyrene</td>
<td>&lt;30</td>
<td>Fluoranthene</td>
<td>&lt;1.0</td>
</tr>
<tr>
<td>Benzo(b)fluoranthene</td>
<td>&lt;30</td>
<td>3-Methylcholanthrene</td>
<td>&lt;1.0</td>
</tr>
<tr>
<td>Benzo(k)fluoranthene</td>
<td>&lt;30</td>
<td>Indeno(1,2,3-cd)pyrene</td>
<td>&lt;1.0</td>
</tr>
</tbody>
</table>

- Values much lower than those found in digested anaerobic sludge

**Proposed struvite requirements (ESPP):**

- Organic contaminants (limits):
  - PAHs: 6 mg/kg dry matter
  - Salmonella spp: 0 in 25g
  - E. coli: 1000 CFU/g
  - Enteroococcos: 1000 CFU/g
Validation of the struvite
Agriculture application assays

- Application assay of struvite for potato and wheat

### Potato assays

<table>
<thead>
<tr>
<th>Trt. No</th>
<th>Treatment Name</th>
<th>Form Conc.</th>
<th>Form Unit</th>
<th>Form type</th>
<th>Rate</th>
<th>Rate Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>SOLUCROS = K2O [51]</td>
<td>11.0</td>
<td>%</td>
<td>L</td>
<td></td>
<td>kg/ha</td>
</tr>
<tr>
<td></td>
<td></td>
<td>46.0</td>
<td>%</td>
<td>GR</td>
<td></td>
<td>kg/ha</td>
</tr>
<tr>
<td></td>
<td></td>
<td>32.0</td>
<td>%</td>
<td>SL</td>
<td></td>
<td>kg/ha</td>
</tr>
</tbody>
</table>

### Wheat assays

<table>
<thead>
<tr>
<th>Trt. No</th>
<th>Treatment Name</th>
<th>Form Conc.</th>
<th>Form Unit</th>
<th>Form type</th>
<th>Rate</th>
<th>Rate Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>STRUVITE</td>
<td>12.6</td>
<td>%</td>
<td>GR</td>
<td></td>
<td>kg/ha</td>
</tr>
<tr>
<td>2</td>
<td>UREA</td>
<td>12.6</td>
<td>%</td>
<td>GR</td>
<td>631.6</td>
<td>kg/ha</td>
</tr>
<tr>
<td></td>
<td>LIKI-K</td>
<td>32.0</td>
<td>%</td>
<td>SL</td>
<td>2</td>
<td>kg/ha</td>
</tr>
<tr>
<td>3</td>
<td>HEROGRA ABOSOL</td>
<td>11.0</td>
<td>%</td>
<td>L</td>
<td>300</td>
<td>kg/ha</td>
</tr>
<tr>
<td></td>
<td>UREA</td>
<td>46.0</td>
<td>%</td>
<td>GR</td>
<td>150</td>
<td>kg/ha</td>
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<tr>
<td></td>
<td>LIKI-K</td>
<td>32.0</td>
<td>%</td>
<td>SL</td>
<td>2</td>
<td>kg/ha</td>
</tr>
</tbody>
</table>

**Formulas**
- STRUVITE
- SOLUCROS = K2O [51]
- UREA = urea [46]
- LIKI-K = Ntotal+K2O [3+32]
- HEROGRA ABOSOL = Ntotal+P2O5+K2O+CaO+MgO[11+11+11+0+0]
Validation of the struvite
Agriculture application assays

- Application assay of struvite for potato and wheat

Struvite application
Validation of the struvite
Agriculture application assays

- Application assay of struvite for potato and wheat

Potato and wheat sowing
Validation of the struvite
Agriculture application assays

- Application assay of struvite for potato and wheat

Assessment of crops growth
Validation of the struvite 
Agriculture application assays

- Application assay of struvite for potato and wheat

Assessment of crops growth
Conclusions

- The elutriation in the gravity thickener of the mixed sludge contained in the mixing chamber:
  - Reduces the P load to the anaerobic digestion minimising precipitation problems.
  - Increases P availability in the thickener supernatant from 0.4 to 1.5 g P/kg sludge.

- The crystallization of the thickener supernatant:
  - Shows good P precipitation and recovery efficiencies.
  - Good characteristics of the product obtained → marketable???
Next steps!!!

- Operation of the crystallization plant using:
  - Elutriated gravity thickener supernatant + Dewatering centrate.

- Validation of the product obtained as a fertiliser (agriculture application assays).

- Economic feasibility study.
THANK YOU FOR YOUR ATTENTION!