P-Recovery from waste water: Implementation of an industrial demonstrator and study of the struvite valorization as fertilizer

PHORWater Workshop

12 May 2016, Lyon
The project
Implementation of an industrial demonstrator

Design
Industrial Project

Construction
Full-scale struvite installation

Validation of struvite as fertilizer

Pilot testing/Development Design...

Implementation of the process *
Production and optimisation

Characterization Regulation Constraint

* Operation carried out with financial support from the Water Agency Adour -Garonne  (www.eau-adour-garonne)
Wastewater treatment plant of Castres

Characteristics:
- 130,000 PE
- Biological phosphorus removal
- Anaerobic digestion

P discharge consents:
- From 2017: < 1 mg P/L
- Effective P discharge before 2015: [P] effluent > 2.5 mg/L

Influent 90 kg P/d

Pre-treatment → Primary Settling → Biological treatment → Clarification → Sludge thickening → Anaerobic digestion → Sludge dewatering → Recycling sludge → Struvite recovery plant
Objective of the project:

1) A waste water treatment solutions
   • Treatment of phosphorus
   • Improve biological phosphorus removal performance
   • Ensure compliance with phosphorus discharge consents
   • Alternative to avoid the use of metal salts (iron chloride)

2) Recycling phosphorus as a fertilizer
   • Renewable phosphorus source
The Precipitation process

- **Industrial property**: Naskeo french patent in June 2010

- **Fluidized bed process**
  - Precipitation controlled by addition of the magnesium reactant
  - Continuous process
  - Internal recirculation loop
  - Extraction of struvite: controlled and periodic

- **MgO : Magnesium Oxyde**
  - By-product of magnesium industry
  - Third reactant
  - pH increase
The Precipitation process
**Exploitation and Performances**

- **Design, building and exploitation:**
  Industrial demonstrator: V = 2.5 m$^3$ (up to 5 m$^3$/h effluent)
  WWTP of Castres in 2015

- **Performances achieved in 2015:**
  Recovery of 90% of phosphorus from treated wastewater
  Production of a fertilizer NP+Mg: 5-25-0 +17%MgO
  Reduction of the phosphorus flow of the treated water (output of the station)

- **Expected balance sheet for nominal operation**

  Flow = 90 m$^3$/d  
  [P-$\text{PO}_4$] = 160 mg/L  
  [N-$\text{NH}_4$] = 1500 mg/L

  Recovery of 4.2 t P/year
  Use of 14 t Mg reactant / year
  Production of 35 t struvite/year
Analysis and evaluation of the impact of the process

Phosphorus balance of the WWTP

Impact on the treated water

P flow recovered as struvite => Decrease of the P flow in WWTP treated effluent

*% of liquid treated in the struvite process
(100% = 90 m3/d)
Wastewater treatment plant

Flow sheet before

Pre-treatment → Primary Settling → Biological treatment → Clarification

90 kg P/d → 30 kg P/d (33%)

14 kg P/d → 58 kg P/d (64%)

Sludge thickening → Anaerobic digestion → Sludge dewatering → Recycling sludge

30 kg P/d

58 kg P/d
Wastewater treatment plant

Flow sheet after

Pre-treatment

Primary Settling

Biological treatment

Clarification

90 kg P / day

Struvite recovery plant

+ 11.5 kg P/d
13 %

30 kg P/d - 11.5 = 18 kg P/d
20 %

58 kg P/d
64 %

Sludge thickening

Anaerobic digestion

Sludge dewatering

Recycling sludge
Agronomic quality of produced struvite

- Production stability (analytical characteristics)
- Agronomic efficiency as Phosphorus fertilizer
- Ecotoxicological risks evaluation
Production stability

Main chemical characteristics:
- Dry matter content: 60,3%
- Total nitrogen: 4,5% N
- Total phosphorus: 24,9% P$_2$O$_5$
- Total magnesium: 17,4% MgO
- Organic matter: 10,2%

Nutrient content is homogeneous between batches and allows to consider struvite with denomination **NP+Mg fertilizer (5-25-0 + 17%MgO)**.
Agronomic quality of produced struvite

Agronomic efficiency

**Ray-grass assays:** Phosphorus fertilization compared to different mineral fertilizers (TSP: triple superphosphate, SSP: simple superphosphate & Pnat: natural phosphates).

**Petunia assay:** evaluate the use of struvite in horticulture, with a peat substrate and a floral plant (*Petunia* sp.)
Agronomic efficiency

- **Phosphorus bioavailability**

- The P exports of struvite modalities are **similar** to those of the TSP & SSP modalities, and **significantly superior** to P$_{nat}$ fertilized modality exports.
- The P soil solution of struvite modalities are **equivalent** to the **reference modalities** (TSP & SSP).
Even at the maximum apply dose of 4.8T struvite per hectare, none of the MTE quantity brought to the field reaches the **authorized thresholds for the fertilizing matters in France**.

<table>
<thead>
<tr>
<th>MTE content (average value of batches)</th>
<th>Dose ($t_{\text{RawMat.}}$/ha) &amp; MTE flow (g/ha)</th>
<th>Max. acceptable annual flows</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.4$t_{\text{RM}}$/ha  1.2$t_{\text{RM}}$/ha  2.4$t_{\text{RM}}$/ha  4.8$t_{\text{RM}}$/ha</td>
<td>Annual average value on 10 years (g/ha/year)</td>
</tr>
<tr>
<td>Arsenic  mg/kg$_{\text{RM}}$</td>
<td>7,450</td>
<td>2,980  8,940  17,880  35,760</td>
</tr>
<tr>
<td>Cadmium  mg/kg$_{\text{RM}}$</td>
<td>&lt; 0,210</td>
<td>0,084  0,252  0,504  1,008</td>
</tr>
<tr>
<td>Chromium mg/kg$_{\text{RM}}$</td>
<td>4,880</td>
<td>1,952  5,856  11,712  23,424</td>
</tr>
<tr>
<td>Mercury  mg/kg$_{\text{RM}}$</td>
<td>&lt; 0,100</td>
<td>0,040  0,120  0,240  0,480</td>
</tr>
<tr>
<td>Nickel   mg/kg$_{\text{RM}}$</td>
<td>19,150</td>
<td>7,660  22,980  45,960  91,920</td>
</tr>
<tr>
<td>Lead     mg/kg$_{\text{RM}}$</td>
<td>&lt; 5,100</td>
<td>2,040  6,120  12,240  24,480</td>
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<tr>
<td>Selenium mg/kg$_{\text{RM}}$</td>
<td>&lt; 0,490</td>
<td>0,196  0,588  1,176  2,352</td>
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<tr>
<td>Copper   mg/kg$_{\text{RM}}$</td>
<td>&lt; 9,500</td>
<td>3,800  11,400  22,800  45,600</td>
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<tr>
<td>Zinc     mg/kg$_{\text{RM}}$</td>
<td>&lt; 16,600</td>
<td>6,640  19,920  39,840  79,680</td>
</tr>
</tbody>
</table>
Ecotoxicological risks evaluation

- **Environmental risk evaluation**
- 8 ecotoxicological tests have been performed
- On terrestrial and aquatic compartments
- Indicators usually studied in registration files

<table>
<thead>
<tr>
<th>Compartment</th>
<th>Indicators</th>
<th>Criteria studied</th>
<th>Threshold of biological significant effect</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Terrestrial</strong></td>
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<tr>
<td>Plants</td>
<td>Barley &amp; cress</td>
<td>Germination</td>
<td>-</td>
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<tr>
<td></td>
<td></td>
<td>Vegetative growth</td>
<td>25%</td>
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<tr>
<td>Microorganisms</td>
<td>Nitrifying bacteria</td>
<td>Activity</td>
<td>25%</td>
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<tr>
<td></td>
<td>Mycorrhizal fungi</td>
<td>Germination</td>
<td>20%</td>
</tr>
<tr>
<td>Macroorganisms</td>
<td>Earthworms</td>
<td>Mortality</td>
<td>-</td>
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<tr>
<td><strong>Aquatic</strong></td>
<td></td>
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<tr>
<td>Plants</td>
<td>Duckweed</td>
<td>Growth</td>
<td>-</td>
</tr>
<tr>
<td>Macroorganisms</td>
<td>Microcrustacean</td>
<td>Mobility</td>
<td>20%</td>
</tr>
<tr>
<td>Microorganisms</td>
<td>Unicellular algae</td>
<td>Growth</td>
<td>15%</td>
</tr>
</tbody>
</table>
Ecotoxicological risks evaluation

- Environmental risk evaluation - SYNTHESIS

At the maximum agronomic apply dose of 4,8T struvite per hectare, none of the terrestrial indicators is significantly impacted.

<table>
<thead>
<tr>
<th>Dose (t/ha)</th>
<th>0,4</th>
<th>0,8</th>
<th>1,2</th>
<th>1,7</th>
<th>2</th>
<th>2,4</th>
<th>3,3</th>
<th>4</th>
<th>6</th>
<th>8,3</th>
<th>12</th>
<th>16,6</th>
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<tbody>
<tr>
<td>Earthworms</td>
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<tr>
<td>No impact on earthworms</td>
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<td>Mycorrhizal fungi</td>
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<tr>
<td>No impact on germination</td>
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<tr>
<td>Nitrifying bacteria</td>
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<tr>
<td>No impact on nitrifying activity</td>
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<td>Higher plants</td>
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<tr>
<td>No phytotoxicity on emergence or growth</td>
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</tr>
</tbody>
</table>
Agronomic quality of produced struvite

Ecotoxicological risks evaluation

- Environmental risk evaluation - SYNTHESIS

At the maximum agronomic apply dose of **4,8T struvite per hectare**, none of the aquatic indicators is significantly impacted.

<table>
<thead>
<tr>
<th>PEC&lt;sub&gt;water&lt;/sub&gt; (g/L)</th>
<th>0,1</th>
<th>0,699</th>
<th>1</th>
<th>4</th>
<th>5,533</th>
<th>11,25</th>
<th>29,9</th>
<th>36,4</th>
<th>37</th>
<th>50,7</th>
<th>57,1</th>
<th>68,6</th>
</tr>
</thead>
<tbody>
<tr>
<td>Duckweed (number)</td>
<td>NOEC</td>
<td>7j</td>
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<tr>
<td>Duckweed (fronds area)</td>
<td>NOEC</td>
<td>CE20</td>
<td>7j</td>
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<tr>
<td>Microcrustacean</td>
<td>NOEC</td>
<td>48h</td>
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</tr>
<tr>
<td>Unicellular algae</td>
<td>NOEC</td>
<td>72h</td>
<td>CE10</td>
<td>CE20</td>
<td>CE50</td>
<td>48h</td>
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<tr>
<td>Apply dose (t/ha)</td>
<td>0,3</td>
<td>2,097</td>
<td>3</td>
<td>12</td>
<td>16,6</td>
<td>33,75</td>
<td>89,7</td>
<td>109,2</td>
<td>111</td>
<td>152,1</td>
<td>171,3</td>
<td>205,8</td>
</tr>
</tbody>
</table>

*PEC = Previsible environment concentration*
**CONCLUSIONS**

- Nutrient content is stable and corresponds to a 5-25-0, 17%MgO fertilizer.
- Fertilizing effect is similar to reference fertilizers (TSP & SSP) and better than natural phosphates.
- Possible use in growing media, complemented with N & K.

- MTE & OTC content are close to quantification thresholds.
- MTE & OTC flows are considerably lower than authorized thresholds.

- The use of struvite at agronomic apply doses presents:
  - No negative effect on terrestrial compartment (higher plants, soil micro and macro fauna).
  - No negative effect on *aquatic indicators* (algae, microcrustacean, plants).
THANK YOU FOR YOUR ATTENTION

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