Phosphate removal from secondary effluent of wastewater treatment: characterization and potential re-use as fertilizer of recovered precipitates

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ISWM - TINOS 2015

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PhoReSE

Outline

Theoretical background

Phosphate precipitates

Analysis
Characterization

Phosphorus bioavailability

Diffusion into soil?
Available to plants?

Phosphorus - P

- **Essential**
- **Limited**
- **Non-renewable**
- **Non-substitutable**

Phosphorus excess → problem! → **eutrophication**

<u>Desire:</u> **Phosphorus recovery**

<u>Source</u>
wastewater

Precipitates production

wastewater treatment plant of “AINEIA”
(Conventional treatment plant) → Wastewater samples

1 Batch precipitation tests – ferric phosphate precipitate

1 L sample of secondary effluent + $FeClSO_4$ Jar tests

2 “Rapid Small Scale Column Tests” (RSSCTs) – calcium & magnesium salts

Adsorbent: iron oxy-hydroxides (FeOOH)

residual concentration 1 mg $P\text{-}PO_4^{3-}$ L^{-1} → Regeneration (NaOH) → Effluent + $CaCl_2$ or $MgCl_2$ solution

Aim of the study

Phosphate precipitates

Phosphorus content? ⇉ Analysis
Characterization

- **High enough to use as phosphorus recovery source?**

Bioavailability

Phosphorus available to soils? → Chemical soil tests

- **Potential re-use as fertilizer?**

Composition of the precipitates

wt.% content	Ferric phosphate precipitate	Calcium phosphate precipitate	Magnesium phosphate precipitate
P-PO_4^{3-}	**9.5**	**17.0**	**6.4**
Fe^{3+}	28.5	4.1	0.7
Ca^{2+}	0.3	12.7	0.05
Mg^{2+}	0.4	0.9	24.0

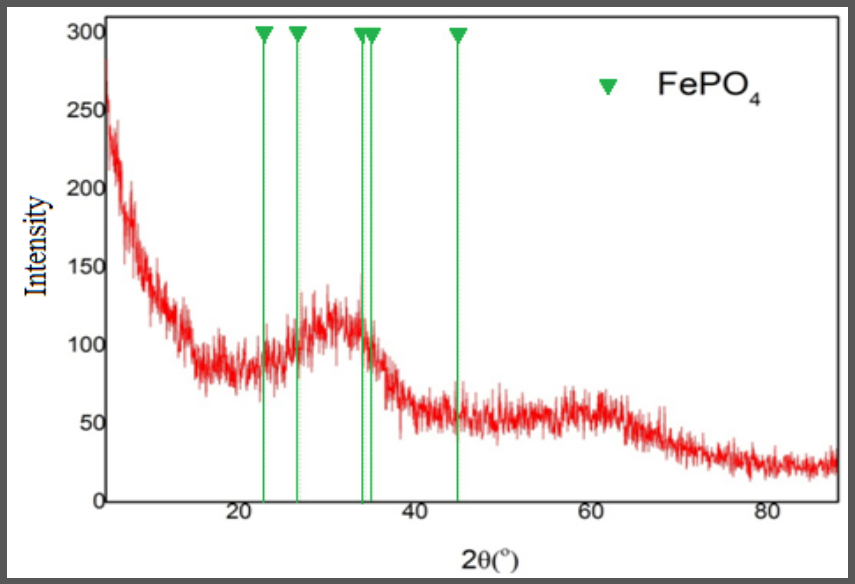
- precipitates' phosphorus content is within the commercial fertilizers' range (4-30%)
- **Carbon percentage**

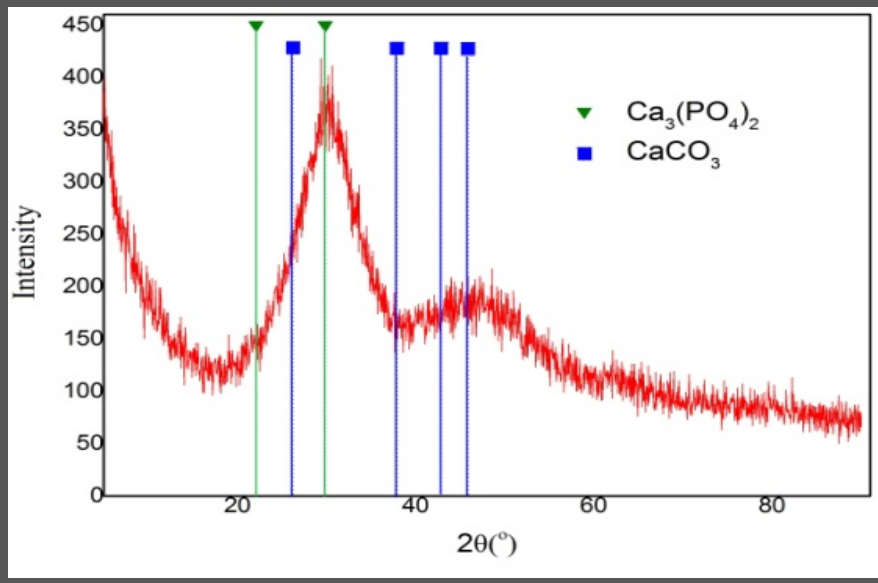
  Ferric phosphate precipitate: 3 wt.%

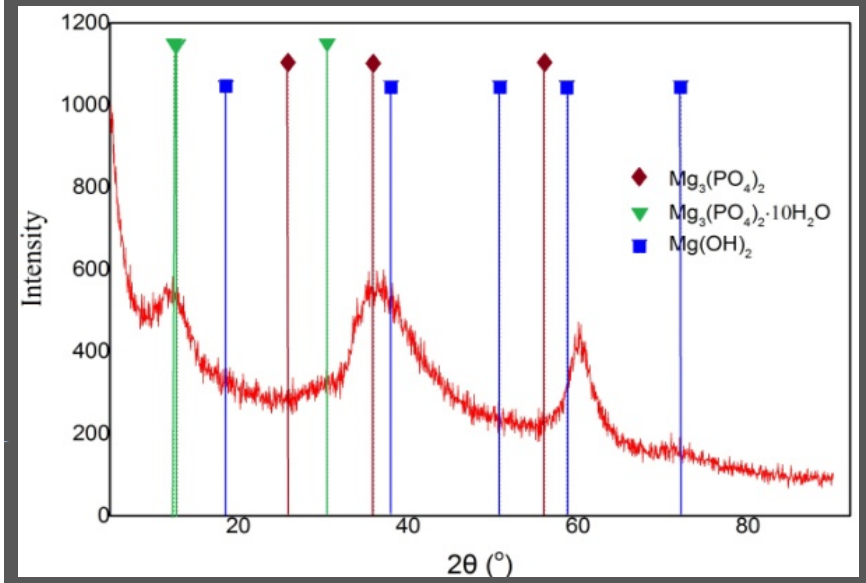
  Calcium & magnesium phosphate precipitates: 1 wt.%
- **Organic compounds**

  widely used products which are not toxic

XRD - diagrams



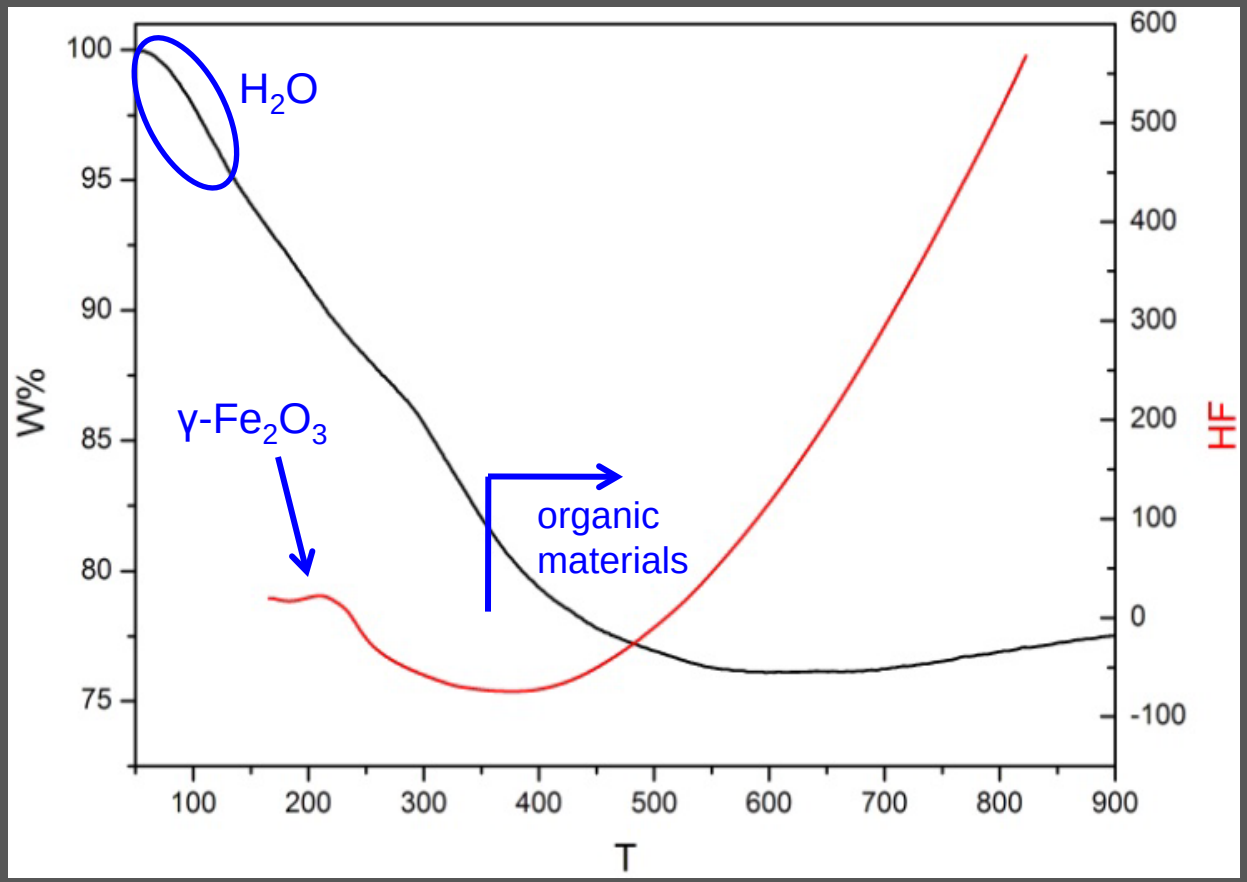




XRD diagrams of the ferric phosphate precipitate, the calcium phosphate precipitate and the magnesium phosphate precipitate

TG-DTA - diagrams

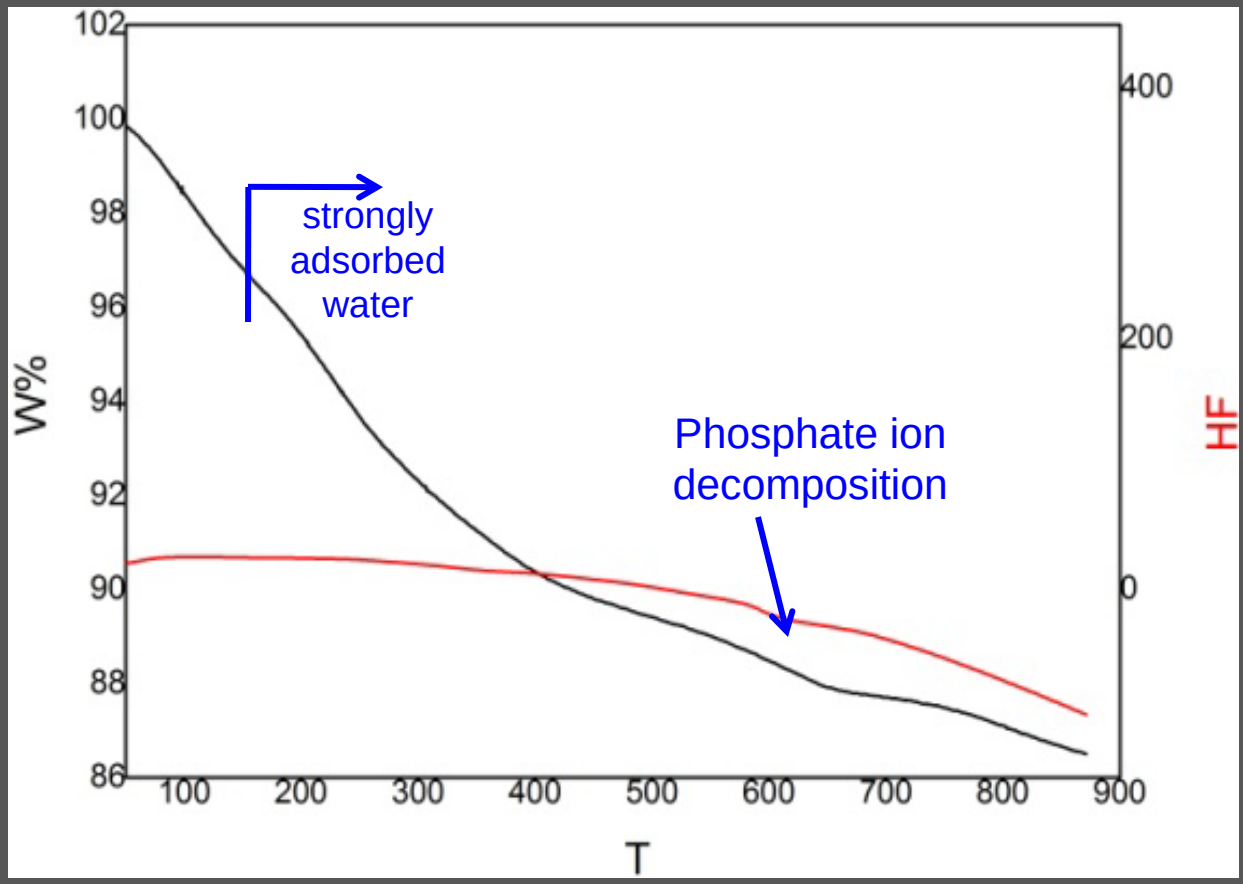
Ferric phosphate precipitate



TG-DTA diagram of the ferric phosphate precipitate

TG-DTA - diagrams

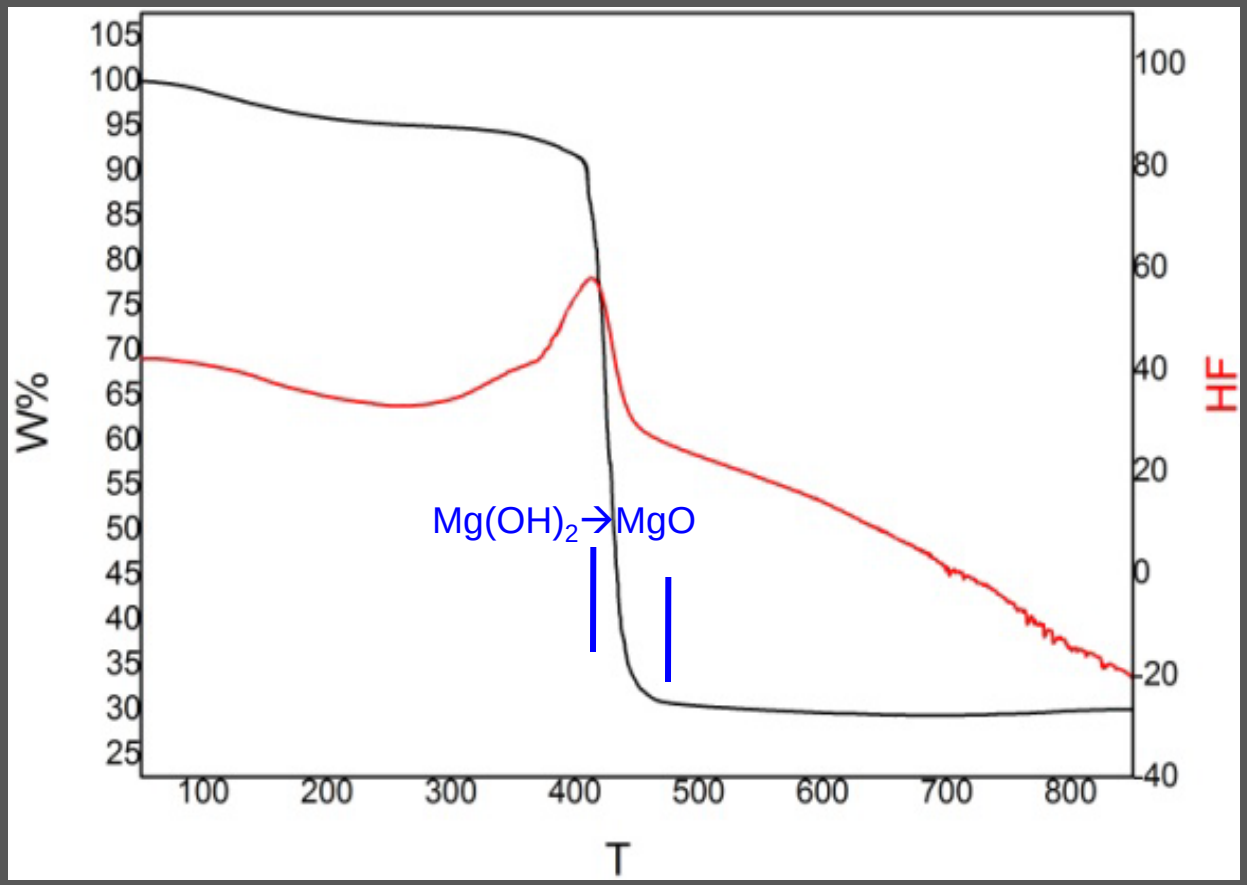
Calcium phosphate precipitate



TG-DTA diagram of the calcium phosphate precipitate

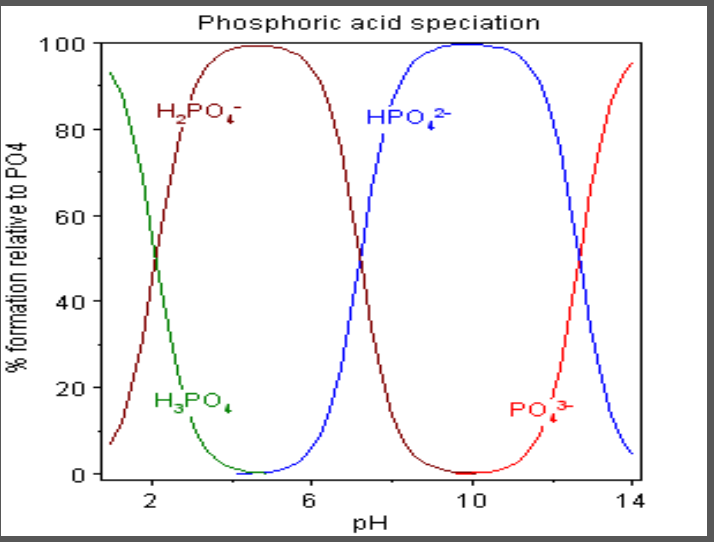
TG-DTA - diagrams

Magnesium phosphate precipitate



TG-DTA diagram of the magnesium phosphate precipitate

Phosphorus and soil



Roots absorb: orthophosphate ions

$H_2PO_4^-$ HPO_4^{2-}

Soil

Acidic
Neutral
Basic

→ Optimum pH range: 6.5 - 7

microorganisms Ca^{2+}, Al^{3+}, Fe^{3+}

Organic P ⇌ $H_2PO_4^-$ HPO_4^{2-} ⇌ **Insoluble compounds**

mineralization

Soluble phosphates

Soil preparation

Soil samples: air dried, ground and sieved (> 2mm)

- **Acidic, pH = 4.5, 40 mg P/kg$_{soil}$**
- **Basic, pH = 7.8, 5 mg P/kg$_{soil}$**

Desired phosphorus content: **~45 mg P/kg$_{soil}$**

Desired moisture: **10 – 20 wt.%**

Soil samples	Incubation time	Extractable P measurements
1 kg	30 days	Every 5 days

Soil extraction

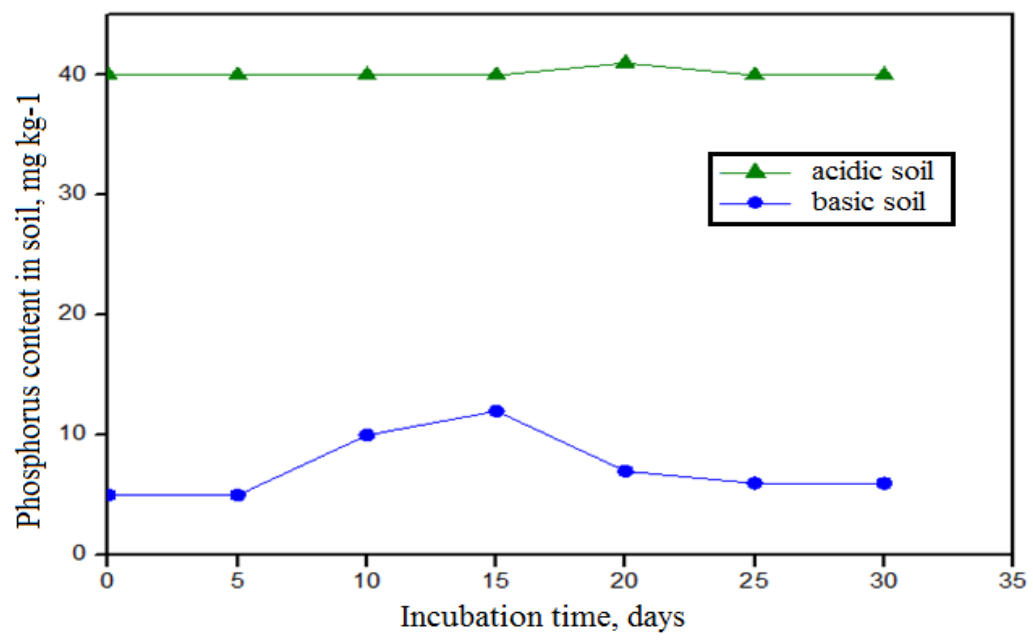
	Acidic soil	Basic soil
Method	Extraction	Extraction
Chemical Extractant	Mehlich 3 *(CH_3COOH 0.2 M, HNO_3 0.013 M, NH_4F 0.015 M, NH_4NO_3 0.25 M και EDTA 0.001 M)*	Olsen *($NaHCO_3$ 0.5 M)*

- 2 g (acidic) ή 1 g (basic) soil

- 20 mL extractant
- Shaking 250 rpm 10 min
- Filter Whatman No. 42

- Phosphate spectrophotometrical determination: stannous chloride method

Ferric phosphate precipitate

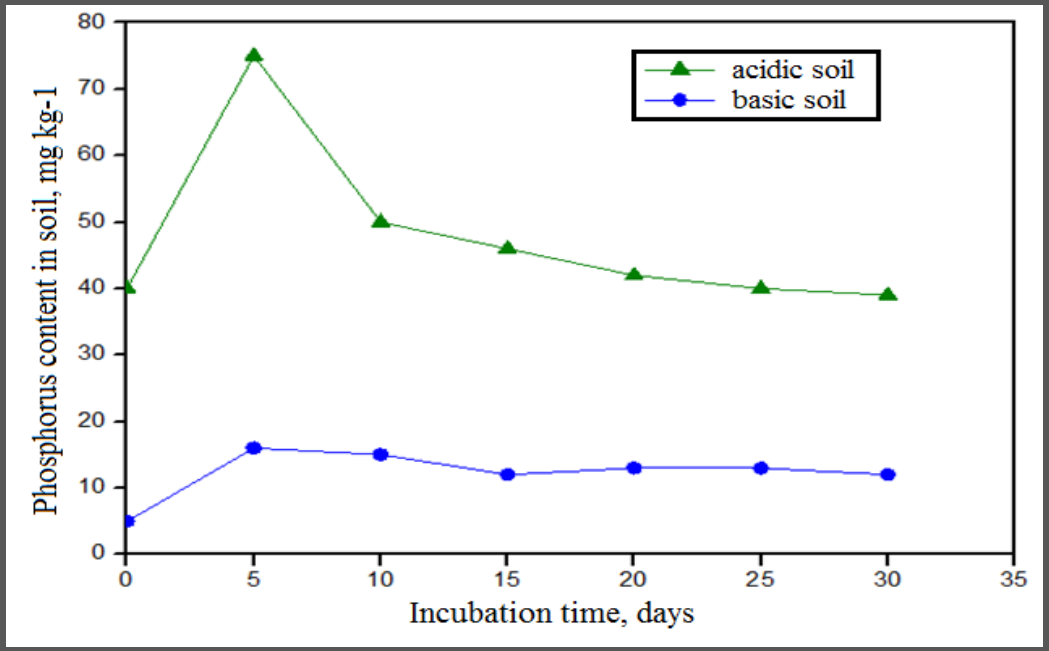


Phosphorus content variation in soil versus incubation time, after the addition of the ferric phosphate precipitate

- Acidic soil: complexes between the little amount of the diffused phosphates and the Fe^{3+} and Al^{3+} of the soil
- Organic matter: might affect beneficially phosphorus release

	Acidic soil	Basic soil
Initial P content	40 mg P/kg_{soil}	5 mg P/kg_{soil}
Max P content	40 mg P/kg_{soil}	12 mg P/kg_{soil}
Increment	-	**7 mg P/kg_{soil}**
Time for max P content	-	15 d

Calcium phosphate precipitate

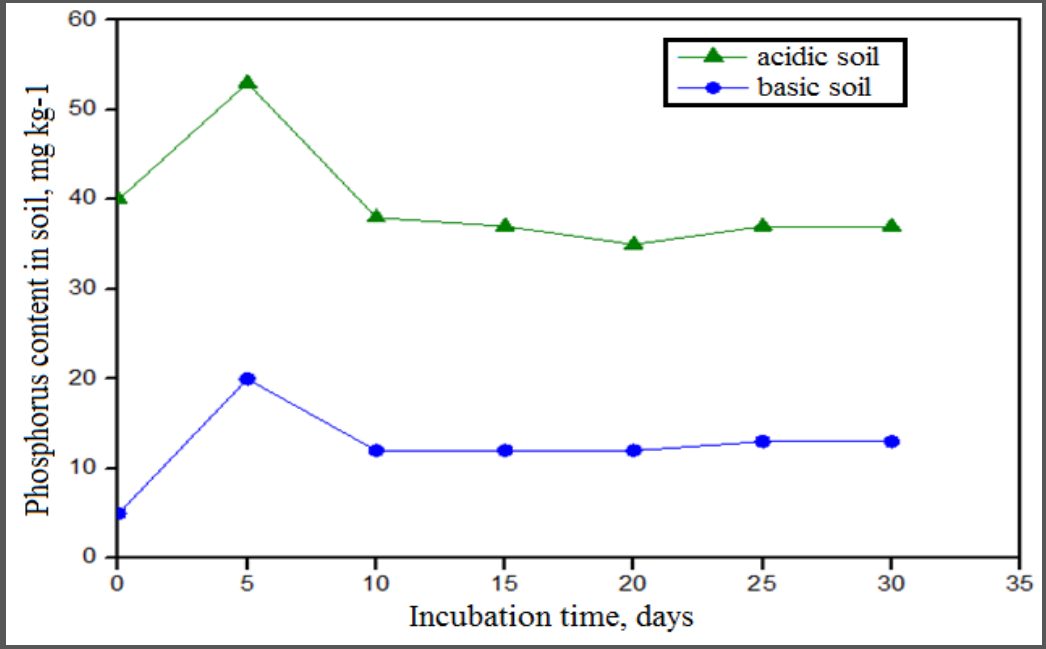


Phosphorus content variation in soil versus incubation time, after the addition of the calcium phosphate precipitate

- Phosphorus – calcium complexes have high solubility in low pH
- basic soil: expected low availability due to reaction of phosphate ions with Ca^{2+} of the soil

	Acidic soil	Basic soil
Initial P content	40 mg P/kg_{soil}	5 mg P/kg_{soil}
Max P content	75 mg P/kg_{soil}	16 mg P/kg_{soil}
Increment	**35 mg P/kg_{soil}**	**11 mg P/kg_{soil}**
Time for max P content	5 d	5 d

Magnesium phosphate precipitate



Phosphorus content variation in soil versus incubation time, after the addition of the magnesium phosphate precipitate

- slightly higher solubility of phosphorus – magnesium complexes in alkaline pH
- basic soil: expected low availability due to reaction of phosphate ions with Ca^{2+} of the soil

	Acidic soil	Basic soil
Initial P content	40 mg P/kg_{soil}	5 mg P/kg_{soil}
Max P content	53 mg P/kg_{soil}	21 mg P/kg_{soil}
Increment	**13 mg P/kg_{soil}**	**16 mg P/kg_{soil}**
Time for max P content	5 d	5 d

Conclusions

Precipitates: **amorphous, presence of H_2O and phosphate ions** **significant amounts** of phosphorus →potentially phosphorus recovery source

+Fe^{3+}: 95 mg P/g, **+Ca^{2+}:** 170 mg P/g, **+Mg^{2+}:** 64 mg P/g

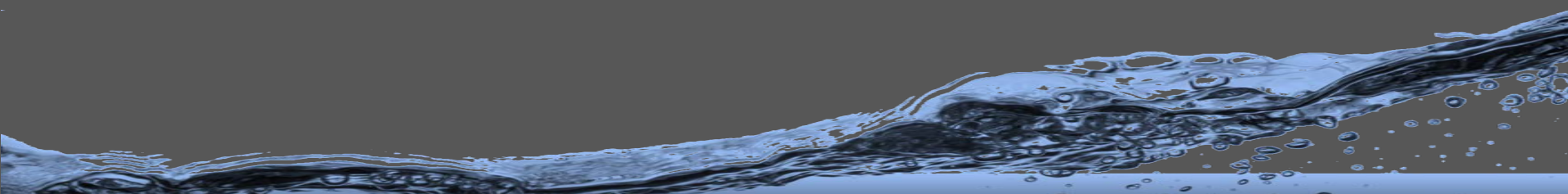
phosphorus content within commercial fertilizer range (4-30 wt.%)

Bioavailable phosphorus: release from precipitates to soil

Calcium and magnesium phosphate precipitates: noteworthy phosphorus release

same pattern: max content in 5 d and equilibrium after 10 d

Ferric phosphate precipitate: low phosphorus diffusion only in basic soil



Acknowledgements

The financial support through the co-financed by the European Union and the Greek State Program PAVET, Project (PhoReSE) - “Recovery of Phosphorus from the Secondary Effluent of Municipal Wastewater Treatment”, is gratefully appreciated.

This research project was supported by the approval of EYATh's S.A.-Department of Plants' Operation, Maintenance & Environmental Monitoring, which is gratefully appreciated.

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EUROPEAN UNION EUROPEAN REGIONAL DEVELOPMENT FUND

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NSRF 2007-2013 EUROPEAN SOCIAL FUND

Ministry of Education and Religious Affairs, Sport and Culture, GGET - EYDE-ETAK

OPC II, ROP Macedonia–Thrace, ROP Crete and the Aegean Islands, ROP Thessaly–Central Greece–Epirus, ROP Attica, Co-financed by Greece and the European Union

Thank you very much for your attention!!!