WIRE

Waste biorefinery technologies for accelerating sustainable energy processes

Livestock waste – from problem to opportunity

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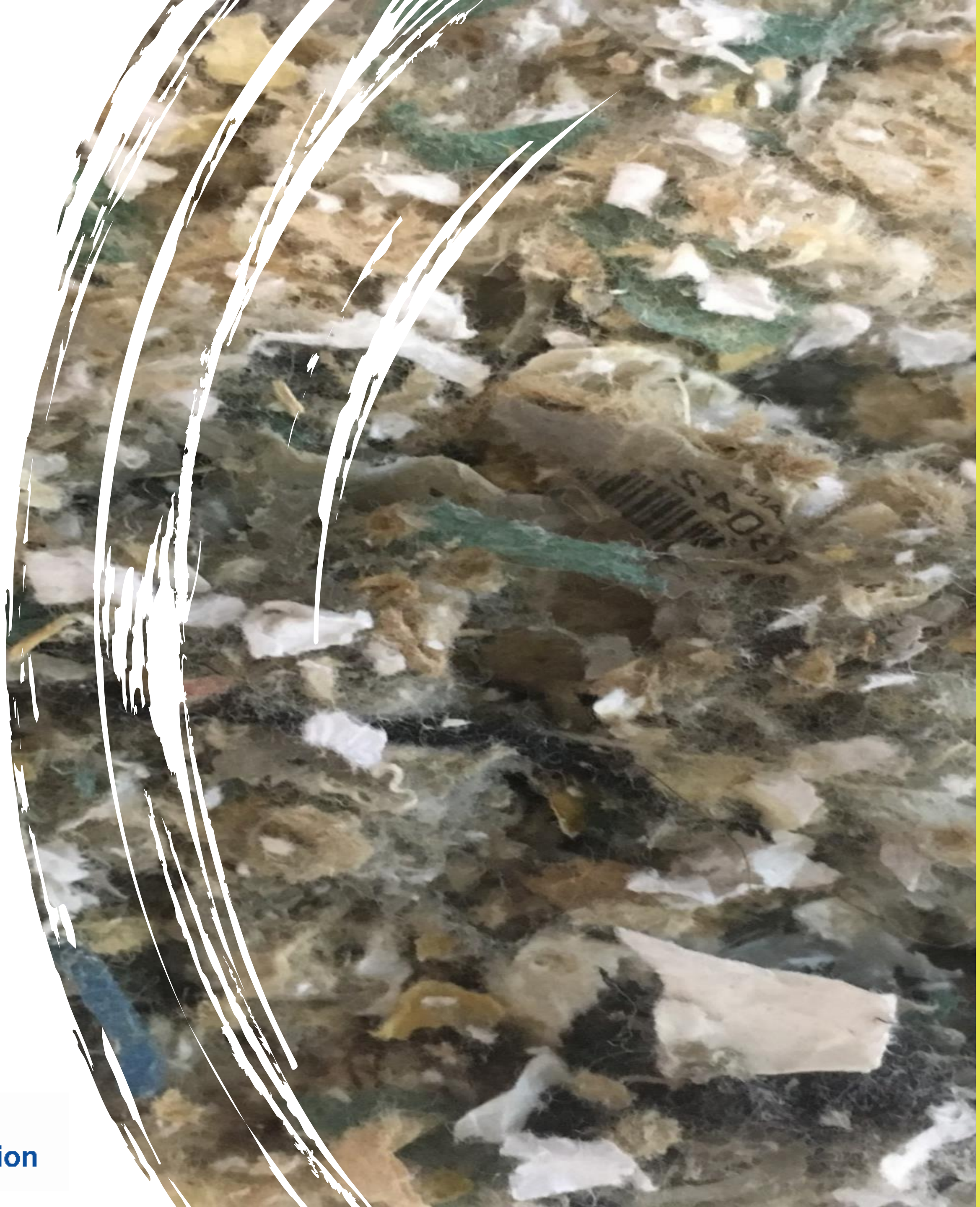


COST EUROPEAN COOPERATION IN SCIENCE & TECHNOLOGY

11/5/2022

Funded by the European Union

Improving innovation capacities of private and public actors for sustainable and profitable REcycling of LIVEstock WASTE

- **Funding scheme:** Interreg Med Programme
- **Priority Axis 1:** Promoting Mediterranean Innovation capacities to develop smart and sustainable growth
- **Theme:** Green Growth, in particular Waste management
- **Modular project**: Testing module (pilot activities)
- **Budget:** 2,285,087.50 € (ERDF + IPA)
- **Duration:** 1 February 2018 - 30 April 2021
- **Participating countries:** Italy (PI), Cyprus, Spain, Bosnia and Herzegovina

Overall objective: to improve innovation capacities of public and private actors involved in the management of waste from intensive livestock farming, through stronger cooperation among the 4-helix actors (science, policy, industry, and society).

COMMON PROBLEMS OF INVOLVED REGIONS

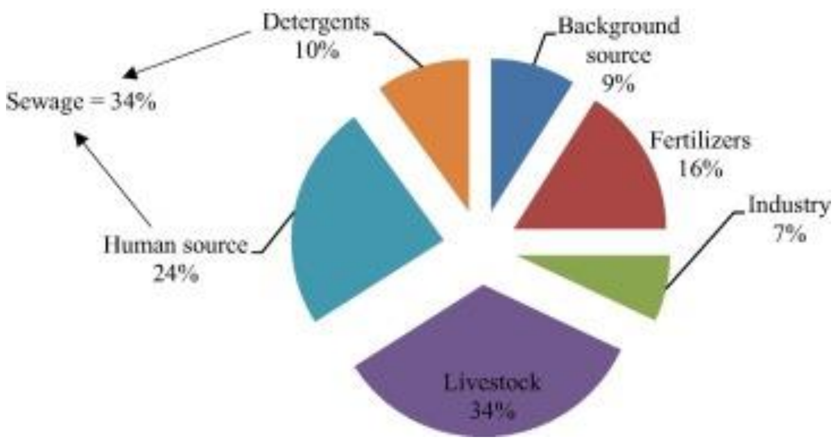
- Intensive cattle and pig livestock farming, producing large amounts of **waste** that represent:
  I. A major source of pollution (soil, water, GHG)
  II. An economic problem for farms.
  III. All pilots are located on Nitrogen Vulnerable Zones (NVZ)

- RE-LIVE WASTE tests **innovative solutions** to convert livestock waste into resource (principle of the circular economy).

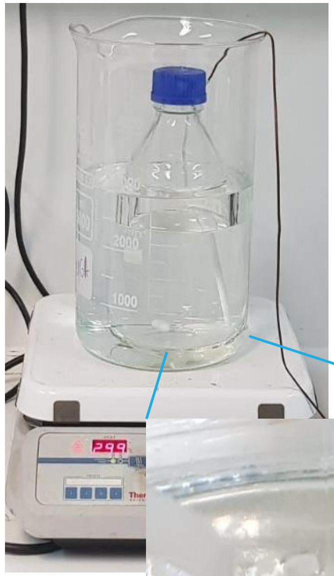
- Project pilot actions will transform livestock waste into organic **high-value commercial fertilizers (struvite).**

Struvite

- Crystalline mineral salt with equal molar concentrations of magnesium (Mg), ammonium (NH_4^+), and phosphates (PO_4^{3-}).
  - **$MgNH_4PO_4 \cdot 6H_2O$**
- High value (bio)-fertilizer because:
  - Releases minerals (K, N, P) slowly
  - Insect repellant.
  - Not easily washed-out by rain
- Produced by a number of wastewater streams (urban, livestock, dairy, agro-industrial, and industrial waste)
  - Color depends on the constituents used during production
- Precipitation reaction at alkaline conditions:
  - **$Mg^{2+} + NH_4^+ + PO_4^{3-} + 6H_2O \rightarrow MgNH_4PO_4 \cdot 6H_2O \downarrow$**
- Addition of a Magnesium source is needed to optimize the struvite crystallization process



Sources of P in the wastewaters



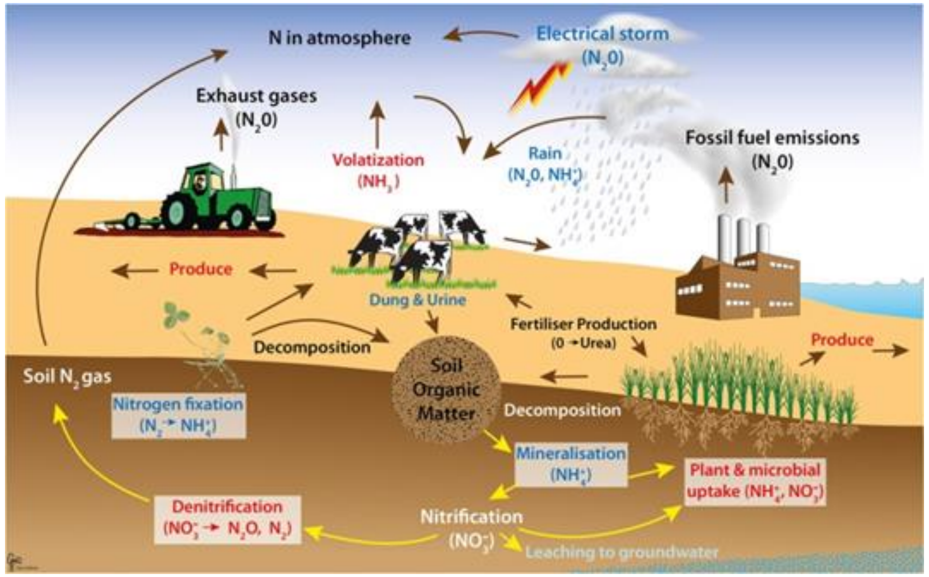
Bottom of the bottle with synthetic struvite

AQUA

Advantages and disadvantages of struvite production

ADVANTAGES:

- Struvite production from livestock waste is a sustainable solution for nutrient recovery.
  - Synthetic mineral fertilizers are produced from phosphates rocks, which are depleting.
- Compliance with **Nitrates Directive 91/676/EEC**.
- Struvite, in the granular from, is a slow-release fertilizer
  - Slow release of nitrogen (N) and phosphorus (P) enhance the plants' growth at different stages.
- Struvite produced from wastewater streams contributes to the reduction of greenhouse gases emissions, pollution of surface (eutrophication), and groundwater, and soil fertility problems.
  - ***EU's "Towards a zero pollution ambition for air, water and soil".***




Phosphate rock


Soil acidification

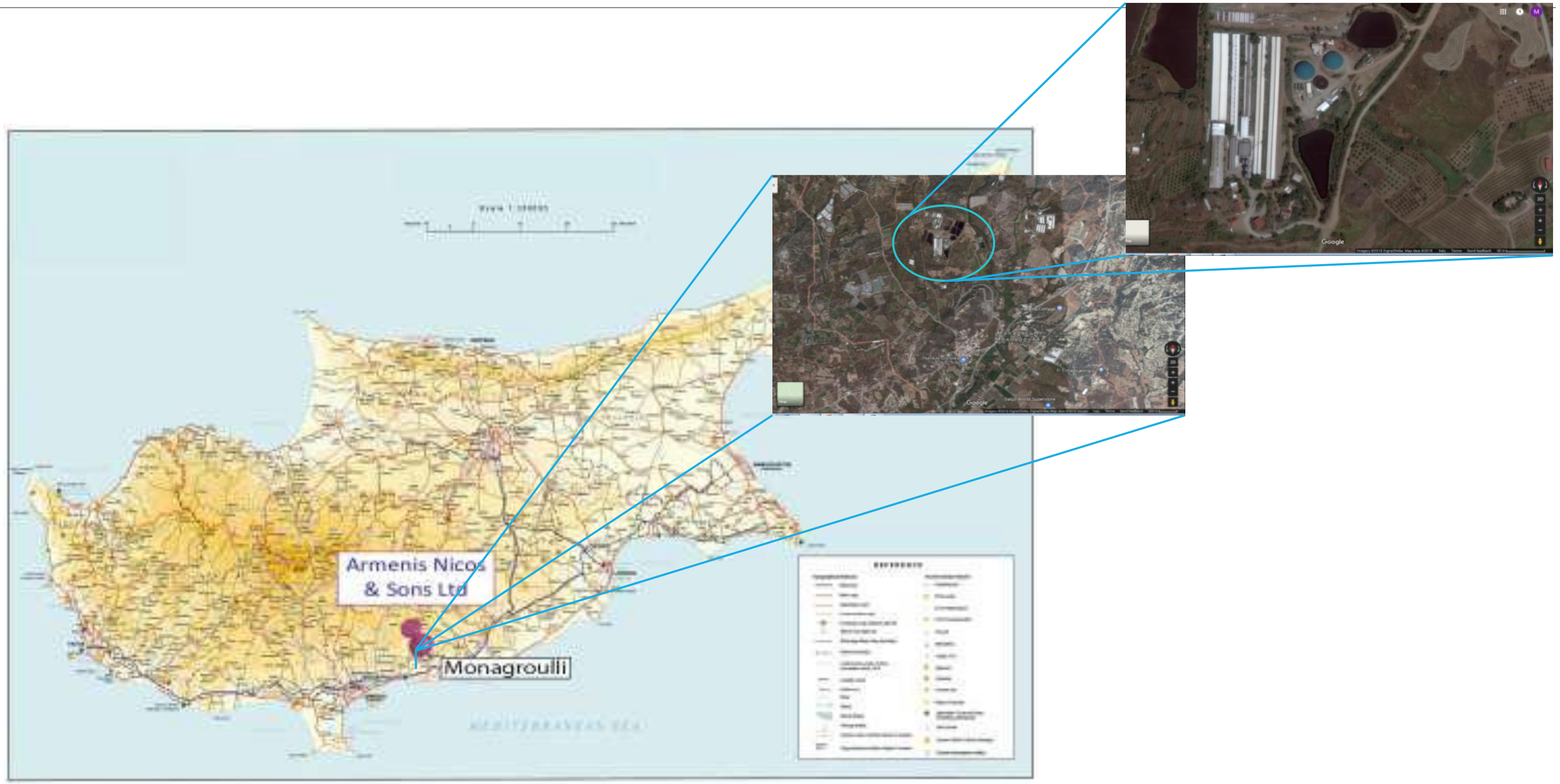

Eutrophication

DISADVANTAGES:

- Struvite produced from wastewater streams may contain heavy metals, PCBs, PAHs, hormones, pesticides.
  - Pretreatment of the wastewater stream used for its production is of great significance.

Location of CUT Pilot

- Location: Armenis Nicos & Sons Ltd, Monagroulli, Lemesos
- Livestock farming activities: 35,000 pigs/yr
- Biogas plant



AQUA

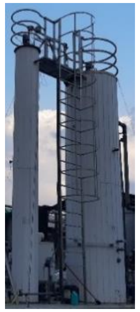
The CUT Pilot

Compost Unit

Bio-trickling filter

Biofilter

Mixing and Homogenization Tank



Dark Fermentation (DF) and
Anaerobic Digestion (AD)

Struvite Crystallization Reactor (SCR)

Filter Bags

UF Ceramic Membrane

short cut Sequencing Batch Reactor (scSBR)

Goals of upgrade:

- Recovery of Nitrogen and Phosphorus as Struvite
- **N-abatement in the mixed wastewater**
  - High ammonium concentrations in swine and cheese whey wastewater)
- Increase struvite production and quality

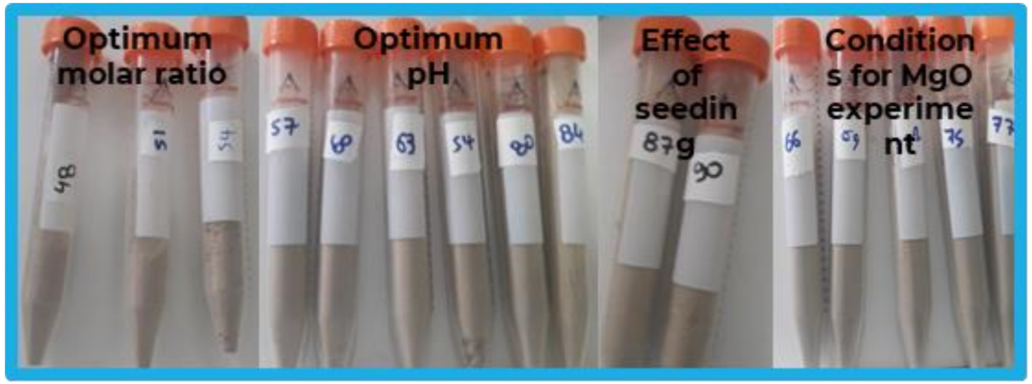
A. Lab precipitation experiments- UF permeate

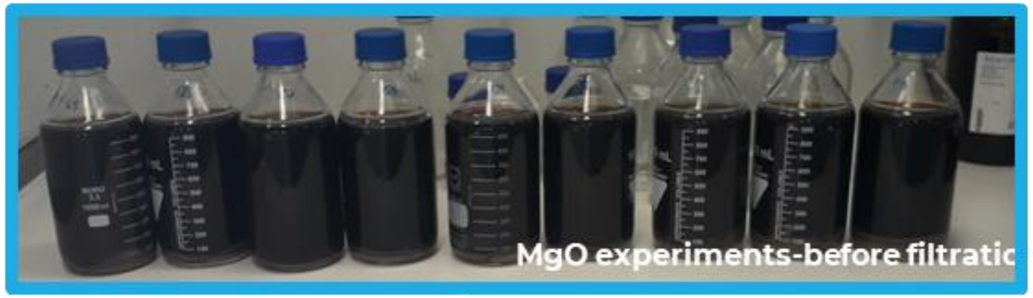
Goal: Process optimization:

- Optimum molar ratio Mg: NH_4^+: PO_4^{-3}
- Optimum pH
- Temperature
- Magnesium source
- Solids retention time (SRT)

Evaluation:

- XRD (CUT, University of Sassari)
- XRF analysis with a Handheld XRF Elvatech analyzer in CUT.
- TN, TP, Mg, Ca, Organic Matter





A. Lab precipitation experiments- UF permeate

- Optimum Ratio: $Mg:NH_4^+:PO_4^{3-}$ **1.5:1.0:1.0**
- Oxidant addition: Acid, Mg-source, and then pH adjustment with NaOH
- Optimum pH= **8.7**
- Optimum contact time: **4 days**

→ Technical Protocol and excel sheet with calculations

→ **Reproducible results** (8 runs overall)

Interreg Mediterranean
RE-LIVE WASTE

Project co-financed by the European Regional Development Fund

Methodological Protocol for struvite production from the Pilot Plant of Cyprus University of Technology

1. Struvite production from anaerobically treated mixed influent, which was filtered through filter-bags and ultra-filtration (UF) ceramic membranes. The mixed influent was comprised of 50% pig slurry, 25% chicken manure, 25% cheese whey and rarely organic fruit waste and barley.
2. A day prior to struvite production, the UF permeate is analyzed for its ammonia nitrogen ($N\text{-}NH_3$), magnesium (Mg^{2+}) and phosphates (PO_4^{3-}). This will give us the initial molar concentrations.
3. The analytical methods used are depicted in the table below:

Parameters	Method
Ammonia Nitrogen,$N\text{-}NH_3$	4500-NH_3 B, 4500-NH_3 C. (The distillation and titration procedure is used especially for NH_3-N concentrations greater than 5 mg/L).
Magnesium, Mg^{2+}	Magnesium Cell Test Method: photometric 5.0 - 75.0 mg/L Mg Spectroquant® Mg In neutral solution magnesium ions react with phthalein purple to form a violet dye, that is determined photometrically.
Phosphates, PO_4^{3-}	Phosphate Cell Test: (o-phosphate and total phosphorous) Method: photometric, PMB 0.5 - 25.0 mg/l PO_4-P 1.5 - 76.7 mg/l PO_4^{3-} 1.1 - 57.3 mg/l P_2O_5 Spectroquant® . Please see Instructions for use- Procedure. Orthophosphates are determined without digestion. The method is analogous to EPA 365.2+3, APHA 4500-P E and DIN EN ISO 6878.

	A	B	C	D	E	F	G	H
1	Sampling date							
2	Analysis date							
3	Influent- UF permeate	average (mg/L)	Molarity (mM)	Molarity (M)				
4	pH	8,65						
5	Mg^{2+} (mg/L)	164	**6,749**	0,006749				
6	PO_4^{3-} (mg/L)	35	**0,368**	0,000368				
7	NH_4^+ (mg/L)	1288	**71,556**	0,071556				
8								
9								
10	For the molar ratio 1.5:1:1		You have (M)	You need to add to have mole in 1L final volume	Quantity of chemicals needed in the 250L crystallization reactor		pH	T= °C
11	NH_4^+	0,0716	0,071556	0,0000			1st day	8,7
12	PO_4^{3-}	0,0716	0,000368	0,0712	**1,217290262**		2nd day	
13	Mg^{2+}	0,1073	0,006749	0,1006	**1466,512456**		3rd day	
14							4th day	
15								
16	Molarity of Phosphoric acid 85% w/w in M (Stock solution PO_4^{3-})	14,62						
17	Molecular weight of magnesium hydroxide $Mg(OH)_2$ (g/mol)	58,3197						
18	Calculations for 16 L							
19	For 15 L of solution I should add (in gr)		1467					
20	For 16 L of solution how many grams **x?**		**1564**					
21	gr for extra 1L		**98**					
22								

Nomiki I. Kallikazarou:
Mixing strength of the agitator is 50 s^{-1}.The order for the addition of chemicals is always the same.Firstly the phosphoric acid and then magnesium hydroxide as a suspension.After the harvesting, precipitate is air-dried for 2-3 days.

Nomiki I. Kallikazarou:
Quantity of phosphoric

Nomiki I. Kallikazarou:
Quantity of magnesium hydroxide in gr suspended in 15 L of water.The prepared solution is 16 L, but 15 L are pumped in the reactor.

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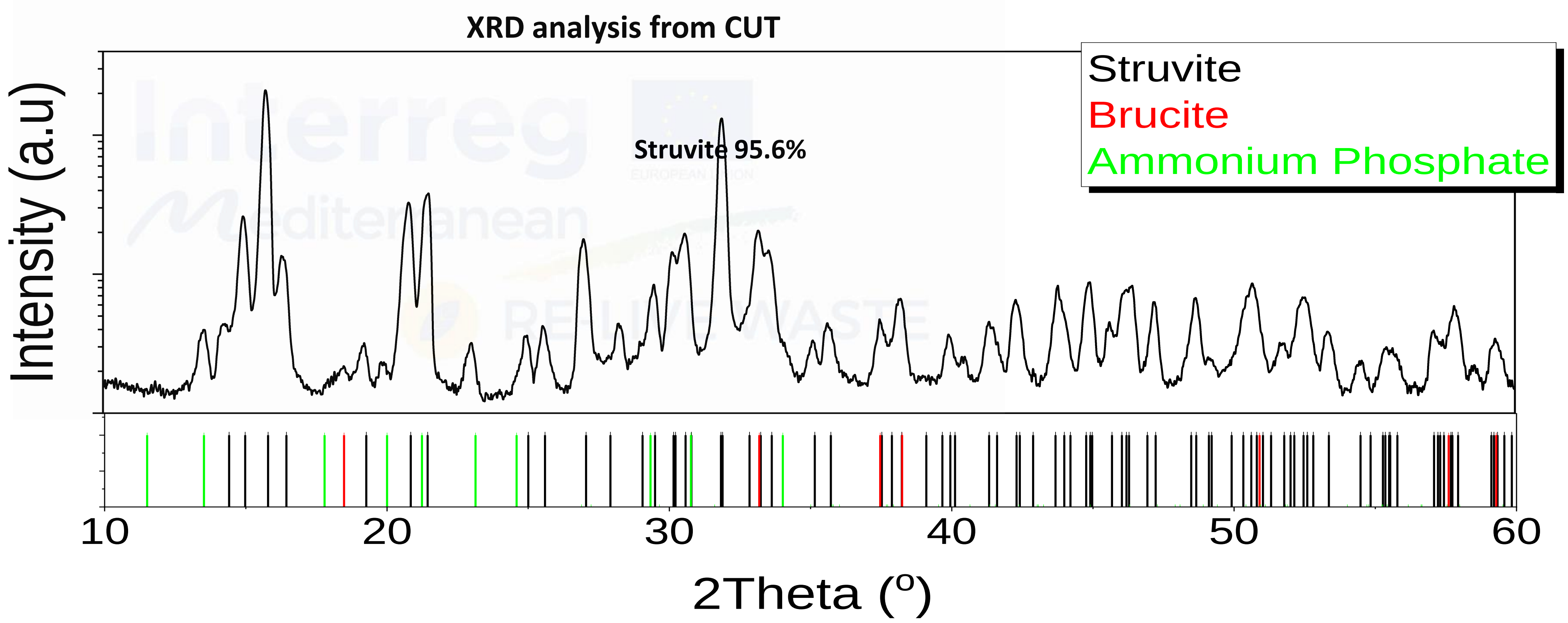
B. Struvite precipitation at the pilot

Precipitation experiment at the pilot

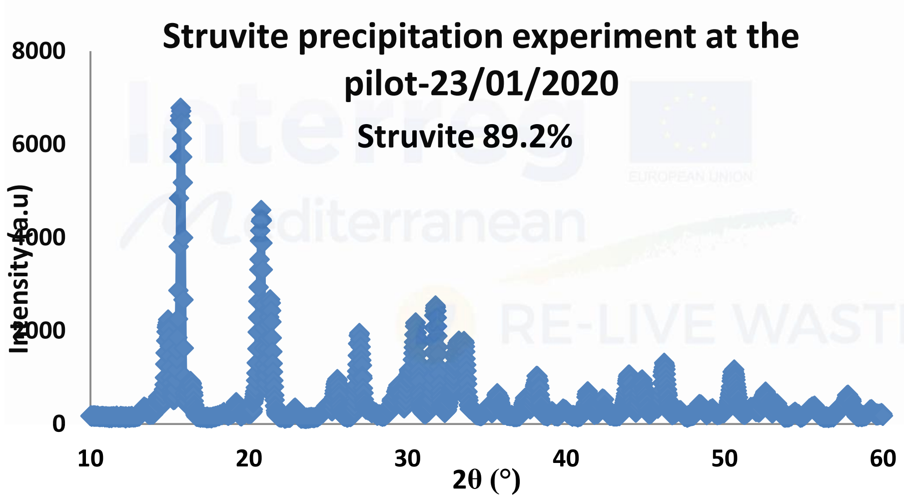


Quantitative results were obtained by using RIR reference values from PDF-2 database from PDXL software.

Lu X. et al., Water Resources, 90,(2016), pp. 9–14.

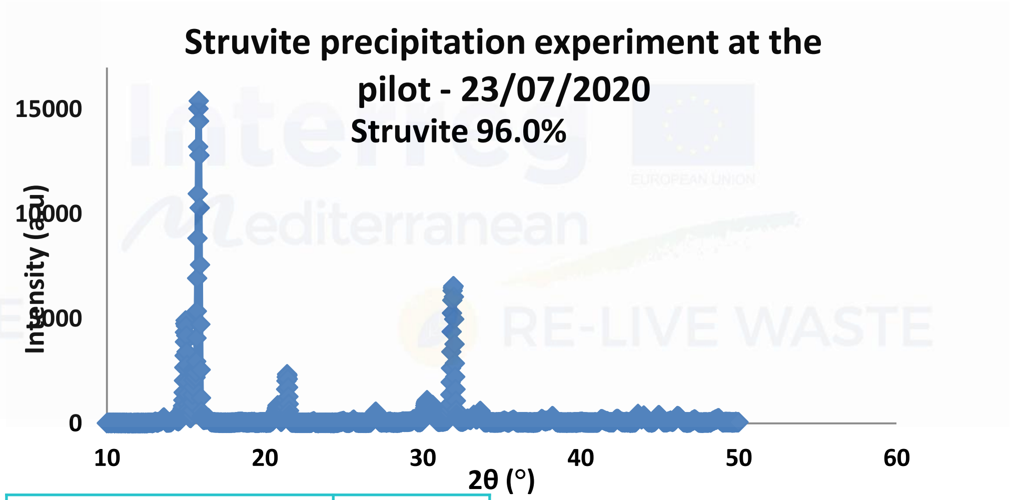
Temperature effect on struvite production at the pilot

Batch 23/01/20 T_{air}=8-11.5 °C



Parameters	Result (%)
Magnesium (Mg^{2+})	11.04
Phosphorus ($P\text{-}PO_4^{3-}$)	4.45
Ammonium (NH_4^+)	4.94
Calcium (Ca^{2+})	0.86
Potassium (K^+)	0.55

Batch 23/07/20 T_{air}=30-33 °C



Parameters	Result (%)
Magnesium (Mg^{2+})	10.68
Phosphorus ($P\text{-}PO_4^{3-}$)	4.55
Ammonium (NH_4^+)	5.1
Calcium (Ca^{2+})	1.5
Potassium (K^+)	0.59

Temperature increase benefited struvite purity!

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Struvite characterization

Struvite (batch 23/01/2020)

Parameters	Result(%)
Ammonium (NH_4)	4.94
Total Nitrogen (TN)	**4.96**
Phosphates phosphorus (P-PO_4^{3-})	4.45
Phosphorus pentoxide (P_2O_5)	**10.21**
Magnesium (Mg)	11.04
Magnesium oxide (MgO)	18.31
Potassium (K)	0.55
Potassium oxide (K_2O)	**0.66**
Calcium (Ca)	0.86
Calcium Oxide (CaO)	1.2
Water Content	12.1

Page 42 of EU Regulation 2009/2019/EC

1. **A solid organo-mineral fertiliser** shall contain **at least one** of the following declared primary nutrients:
   - nitrogen (N)
   - phosphorus pentoxide (P_2O_5) or
   - potassium oxide (K_2O).
2. Where a solid organo-mineral fertiliser contains only one declared primary nutrient, that nutrient content shall be at least the following:

(a) 2,5 % by mass of total nitrogen (N), out of which 1 % by mass shall be organic nitrogen (N org),

(b) 2 % by mass of total phosphorus pentoxide (P_2O_5 or

(c) 2 % by mass of total potassium oxide (K_2O).

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Struvite characterization

Struvite (batch 23/01/2020)

Parameters	Result
Cadmium (Cd)	ND*
Chromium (Cr)	ND*
Mercury (Hg)	ND*
Nickel (Ni)	19 ± 3 ppm
Lead (Pb)	ND*
Inorganic arsenic (As)	ND*
Zinc (Zn)	13.3 ± 2.4 ppm
Copper (Cu)	8 ± 3 ppm
Iron (Fe)	126 ± 8 ppm
Zirconium (Zr)	69 ± 4 ppm
Manganese (Mn)	34± 11 ppm

Page 41-42 of EU Regulation 2009/2019/EC

Contaminants in an organo-mineral fertiliser must not exceed the following limit values:

(a) (ii) cadmium (Cd): 60 mg/kg phosphorus pentoxide (P_2O_5);

(b)hexavalent chromium (Cr_{VI}): 2 mg/kg dry matter;

(c) Mercury (Hg): 1 mg/kg dry matter;

(d) Nickel (Ni): 50 mg/kg dry matter;

(e) Lead (Pb): 120 mg/kg dry matter;

(f) inorganic arsenic (As): 40 mg/kg dry matter;

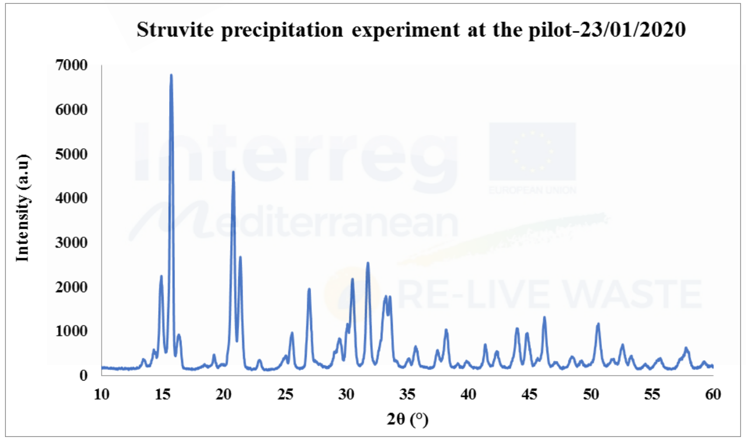
The copper (Cu) content in an organo-mineral fertiliser must not exceed 600 mg/kg dry matter, and the zinc (Zn) content in an organo-mineral fertiliser must not exceed 1500 mg/kg dry matter.

ND* Not detected in XRF analyzer

Struvite characterization

Struvite (batch 23/01/2020)

Parameters	Result
Salmonella spp.	**absence in 25 g struvite**
Escherichia coli or Enterococcaceae	**< 5 cfu/g**
Organic Matter	48.9
Organic Carbon (Corg)	**27.4**



Struvite produced at the unit had a purity ranging between 89,2% -99,0 %

Page 42 of EU Regulation 2009/2019/EC

Pathogens in an organo-mineral fertiliser must not exceed the limits set out below:

For Salmonella spp. the limit is absence in 25 g and for *Escherichia coli or Enterococcaceae the limit is* 1000 in 1 g.

No pathogens detected in our struvite!

Page 43 of EU Regulation 2009/2019/EC

Organic carbon (Corg) content in a solid organo-mineral fertilizer shall be at least 7,5 % by mass.

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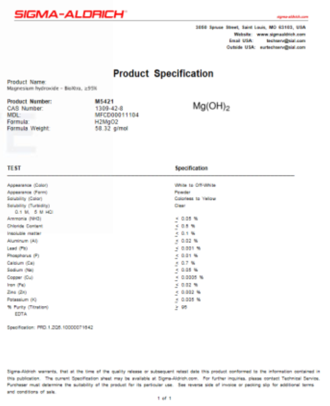
Struvite composition for different Mg sources

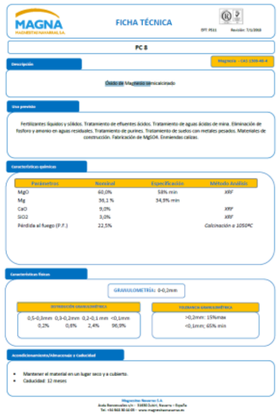
- $Mg(OH)_2$ Magnesium hydroxide BioXtra, ≥95% (**188,02 €/kg**)
- MgO (58%) (from semi-calcination of magnesite) (**0,102 €/kg**)

Heavy metals (mg/kg dry matter)		$Mg^{2+}:NH_4^+:PO_4^{3-}$ 1,2 MgO:1,0:1,0 Struvite 95%, Magnesite 3.4%, Dolomite 1.6%	$Mg^{2+}:NH_4^+:PO_4^{3-}$ 0,9 $Mg(OH)_2$:1,0:1,0 Struvite 94.1%, brucite 5.9%	Limit values from Regulation (EU) 2019/1009 (mg/kg dry matter)
Fe	Average values (SD<1.5%)	5486 ± 18	201±7	5000* or 200**
Mn		357 ± 19	<LOQ	1000* or 100**
Zn		144 ± 4	68±3	1500
Ni		45 ± 5	19±4	50
Cu		32 ± 3	<LOQ	600
Pb		ND	ND	120
Cr		<LOQ	ND	Cr(VI): 2

* for use on crops or grassland
** for horticultural use
ND: not detected in XRF analyser;
LOQ: level of quantification of XRF analyzer

- Cd, Hg and As were not detected in any of the samples.
- The determination of Cr (VI) is pending.
- Nitric acid reduced metals, except for Ni and Pb.
- It is obvious that increasing MgO, metals are increased in struvite.


SIGMA-ALDRICH
Product Specification
$Mg(OH)_2$


MAGNA
FICHA TÉCNICA
PC 8

AQUA

Agronomic Evaluation

- For the evaluation of struvite as a potential fertilizer additive, two experiments, one for baby leaf lettuce (*Lactuca sativa*) and one for radish (*Raphanus sativus*) were conducted.
- The obtained results support that the physical chemical characteristics of the crops were substantially enhances (i.e., water retention).
- The post-harvesting behavior of the crops was similar to those produced with the commercial fertilizers.
- Struvite could substitute conventionally produced fertilizers.

- T1: Peat without fertilizers
- T2: Peat + Fertilizer (1)
- T3: Peat + Fertilizer (2)
- T4: Peat + Struvite (1)
- T5: Peat + Struvite (2)

Interreg Mediterranean RE-LIVE WASTE

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Conclusions:

- Struvite of **high purity (89-99%)** was produced in the CUT pilot from anaerobically treated livestock waste.
- Struvite was **free** of pathogens, transition metals, and carcinogens.
- Proven to be as **efficient** as commercially available fertilizers.
- An environmentally friendly approach for **nutrient recovery.**
  - **Ammonium Removal= 32.05%**
  - **Phosphates Removal =77.42%**
- A **sustainable solution** for mitigating of soil acidification, greenhouse gases emissions, and pollution of surface and groundwater.
- Opening **new market** opportunities in Cyprus and EU on biofertilizers.
- Supports **circular economy**

Interreg Mediterranean
RE-LIVE WASTE
Project co-financed by the European Regional Development Fund

WTL-AQUA Team

Team Leader: Dr. Maria G. Antoniou

PhD Students:

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Cyano-HABs monitoring and treatment

Nomiki Kallikazarou
Nutrient recovery-struvite
Livestock waste management

Funding

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European Regional Development Fund

Republic of Cyprus

Structural Funds of the European Union in Cyprus

RESEARCH & INNOVATION FOUNDATION

cyprusseeds FOR TECHNOLOGICAL INNOVATION

Cyprus University of Technology

Interreg Mediterranean RE-LIVE WASTE

CYANOCOST
COST ES 1105 Action

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Funded by:

RESEARCH & INNOVATION FOUNDATION

Republic of Cyprus

Co-funded by the European Union

AQUA

A sustainable and innovative management system for toxic cyanobacteria blooming of surface waters with combined energy production, sustainable agriculture, and food safety

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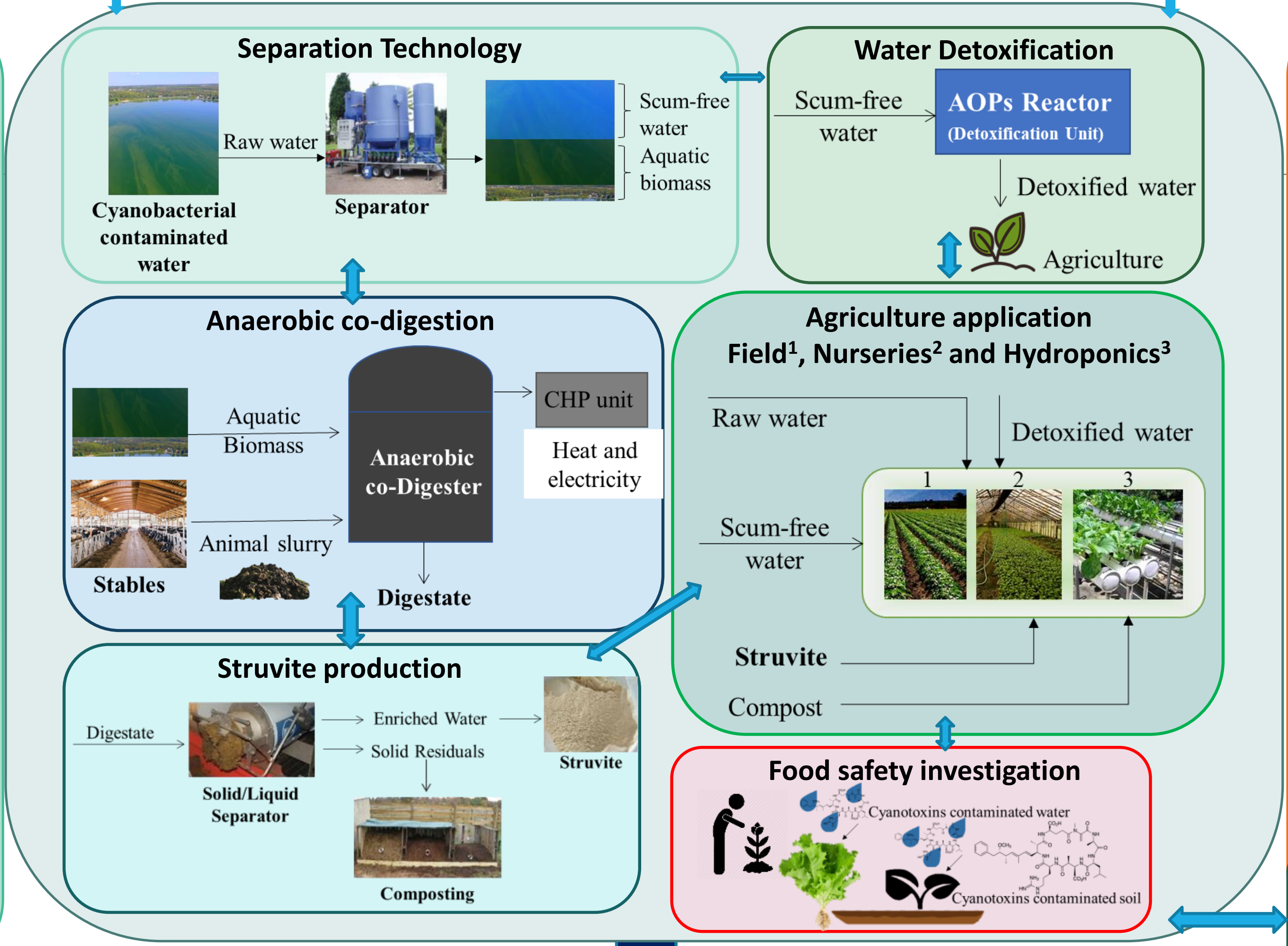
The Project EXCELLENCE/0421/0212 is co-financed by the European Union and the Republic of Cyprus through the Research and Innovation Foundation

ACTION PLAN FOR A CYANOBACTERIAL CONTAMINATED SITE

Challenge Analysis

- High nutrient (P,N) load into waterbodies/ Eutrophication.
- Depletion of surface water quality and availability worldwide.
- Livestock waste management and treatment costs.
- Greenhouse gas emissions from manure waste treatment (open lagoons).
- Chemical fertilizers used in agriculture.
- Legislate biofertilizers application
- Need for validated methods for treating toxic cyanobacteria and cyanotoxins
- Nutrients (P,N) recovery.
- Soilless cultivation and alternative food production.
- Food safety and public health.



CYANO-TECH approach:

- **Nutrient** (N,P) **recovery** from aquatic biomass and manure
- Scum-free water harvesting and **detoxification** to reuse for irrigation.
- **Upgrade of surface water quality** and available **quantity** as source for potable water
- Production of **struvite** (biofertilizer) from **co-digestion of livestock** waste with aquatic **biomass**
- Utilization of co-digestion by-products (e.g. methane) for **energy** (heat & electricity) **production**.
- Biofertilizer application in **agriculture** and **soilless cultivation**.
- **Food safety** verification

- Reach **Policy** makers & **stakeholders**

Legal Framework

Aiming for a circular economy business model
Involvement of citizens, farmers & stakeholders

CYanoTech System

LCA

DST-Decision Support Tool

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www.cyanotechproject.wordpress.com

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Cyprus University of Technology

- Founded by law in December 2003
- One of 7 universities in Cyprus
- One of 3 state universities in Cyprus
- Welcomed its first students in September 2007
- Became autonomous in March 2012
- 6 Faculties
- 13 Departments
- 1 Institute
- 1 Language Centre